



The optimisation of reaction rate parameters for chemical kinetic modelling of combustion using genetic algorithms

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Received 5 March 1999; received in revised form 15 September 1999

Abstract

A general inversion procedure for determining the optimum rate coefficients for chemical kinetic schemes based upon limited net species production data is presented. The objective of the optimisation process is to derive rate parameters such that the given net species production rates at various conditions are simultaneously achieved by searching the parameter space of the rate coefficients in the generalised Arrhenius form of the reaction rate mechanisms. Thus, the goal is to both match the given net species production rates and subsequently ensure the accurate prediction of net species production rates over a wide range of conditions. We have retrieved the reaction rate data using an inversion technique whose minimisation process is based on the Darwinian principle of survival of the fittest which has inspired a class of algorithms known as genetic algorithms. The excellent results presented here from our initial study are based upon the recovery of reaction rate coefficients for hydrogen/nitrogen/oxygen flames. The successful identification of the reaction rate parameters which correspond to product species measurement data from a sequence of such experiments clearly suggests that the progression onto other chemical kinetic schemes and the optimisation of higher-order hydrocarbon schemes can now be realised. The results of this study therefore demonstrate that the genetic algorithm inversion process promises the ability to assess combustion behaviour for fuels where the reaction rate coefficients are not known with any confidence and, subsequently, accurately predict emission characteristics, stable species concentrations and flame characterisation. Such predictive capabilities are of paramount importance in a wide variety of industries. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Optimisation; Reaction rate parameters; Chemical kinetics; Combustion; Genetic algorithms

1. Introduction

The chemistry of combustion may be modelled using a system of chemical reactions for which the rates of each reaction are known. Databases which give measurements of reaction rate parameters for various reactions are commercially available. These give data for the logarithm of the reaction rate as a function of $1/T$ but a large variation in the reaction rates at all temperatures is generally observed. Furthermore, the effect of temperature increases can be seen to either increase or decrease the reaction rate, depending on which set of data is taken to be the most accurate. Since there is so much uncertainty in the rate data, problems occur when calculating species concentration for the products of combustion.

Recently the Gas Research Institute initiated an extensive research programme for the optimisation of the chemical scheme for natural gas. Precise details of the optimisation scheme considered in that programme are discussed in detail in [3]. Combustion of simple fuels, such as hydrogen, can be calculated using

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a simple eight-step reaction mechanism, for which the reaction rate data is known with confidence. However, complex fuels, such as kerosene, require more than 500 reaction steps with over 100 species. Since not all the reaction rate data are well known there is a high degree of uncertainty in the results obtained.

We attempt to optimise the reaction rate data using a process based upon an abstraction of the Darwinian principle of survival of the fittest which has inspired a class of algorithms known as genetic algorithms. Genetic algorithms attempt to find the best solution to a problem by imitating the process of evolution in nature. Thus, a typical algorithm will repeatedly “breed” populations of individuals which represent possible solutions to a particular problem. The reaction rate parameters are each encoded into “genes” which are then concatenated to form the “chromosomes” of the individuals of a population of possible solutions to the problem. CHEMKIN’s Perfect Stirred Reactor (PSR) computer library (see [10,13]) can be run using a kinetic scheme defined by decoding the genetic data within each individual chromosome and the resulting net species concentration outputs compared to known data. The fittest individuals within a population are identified according to an objective function and subsequently used to provide offspring for the next generation. As this process is repeated, increasingly better solutions are discovered.

The genetic algorithm approach has recently been applied to a related chemical kinetics problem by Polifke et al. [17], wherein a method for the rapid extraction of the chemical kinetics rate coefficients for a simplified combustion mechanism from a given set of (detailed) chemical data is proposed. They developed a method that allows one to quickly find rate coefficients for particular operating conditions by matching the heat release and species production rates of the simplified mechanism to those of an underlying detailed chemical mechanism.

In this initial study, genetic algorithms are used to predict the reaction rate parameters for hydrogen/oxygen/nitrogen flames to enable confidence in the technique to be generated before the possible progression onto higher-order hydrocarbon scheme optimisations. An inverse solution procedure is set up in an attempt to recover a certain number of unknown reaction rate parameters based upon a given set of net species concentrations. The PSR code is used to determine the net species concentrations of each of the nine products based upon different reactor conditions, namely different inlet temperatures, residence times and fuel/air equivalence ratios, for a given estimate to the set of reaction rate coefficients. Thus, the inversion process aims to determine the unknown reaction rate parameters which both match the given net product species concentrations at different reactor conditions and will, furthermore, correctly predict the net product species concentrations at other reactor conditions which have not previously been applied.

After a detailed investigation of the inversion process for two and three reaction rate parameters in the first or second reaction equations only, with the remaining reaction rate parameters specified, it is concluded that the original values of these reaction rate parameters cannot always be recovered. In fact, based on imposed net species concentrations at a limited number of reactor conditions we have been able to provide slightly different sets of the reaction rate parameters which both match all the net product species concentrations at the given reactor conditions and the net product species concentrations based upon simulations of further reactor conditions to a sufficient degree of accuracy. Thus, within the solution space of the unknown reaction rate parameters, there are a set of optimum values which, although not necessarily the mathematical global optimum parameters in the sense that they provide a perfect match to the net species concentration data, suffice when experimental measurement error is accounted for.

In the extension to the inverse formulation for the recovery of all 57 reaction rate parameters as unknowns, the results indicate that different sets of reaction rate parameters can be determined which define net product species concentrations matching the imposed data over a wide range of reactor conditions to a degree of accuracy which is far beyond that which could be detected experimentally.

The ability to assess the combustion behaviour of all fuels and accurately predict flame characterisation, stable species concentration and emission characteristics is becoming of paramount importance to a wide variety of industries. The study presented here therefore offers the following substantial benefits:

- (i) The research has the potential to generate an automated procedure for optimising chemical kinetic schemes and to reduce the number of reaction steps required for complex hydrocarbon fuel.
- (ii) Improved kinetic data will help improve the predictive capability of computational fluid dynamics in combustion.
- (iii) To allow the prediction of emissions from gas turbine combustors.

2. The Perfect Stirred Reactor (PSR) code

2.1. Introduction

PSR is a FORTRAN computer program that predicts the steady-state temperature and species composition in a perfectly stirred reactor, see [10]. These reactors are characterised by a reactor volume, residence time or mass flow rate, heat loss or temperature and the incoming temperature and mixture composition. The PSR code is not a stand-alone program; it is designed to be run in conjunction with the CHEMKIN library, see [13], which handles the chemical reaction mechanism and the thermodynamic properties.

The stirred reactor consists of a small, thermally insulated chamber that has inlet and outlet ducts. A steady flow of fuel and oxidiser are introduced in such a way that high-intensity turbulent mixing causes the contents of the reactor to be nearly spatially uniform. This means that the rate of conversion from reactants to products is controlled by chemical reaction rates and not by mixing processes. Thus, a well-stirred reactor can be modelled as a micromixed perfectly stirred reactor, where the mixing rates are assumed to be infinitely fast. A mathematical description of the process occurring within the perfectly stirred reactor is obtained by relating the conservation of mass and energy to the net generation of chemical species within the reactor volume.

2.2. Reactor and reaction rate parameters

In general, we use Y_k to denote the mass fraction of the k th species, where $k = 1, \dots, K$ and K represents the total number of species. The mass fractions of the k th species at the inlet are denoted by Y_k^* , for $k = 1, \dots, K$, and the inlet temperature by T^* , whilst the temperature and composition which exit the reactor are assumed to be the same as those in the reactor since the mixing in the reactor chamber is intense.

The net chemical production rate of each species results from a competition between all the chemical reactions involving that species. It is assumed that each reaction proceeds according to the law of mass action and the forward rate coefficients are in modified Arrhenius form

$$\text{rate, } k_{f_i} = A_i T^{\beta_i} \exp\left(-\frac{E_i}{RT}\right) \quad (2.1)$$

for $i = 1, \dots, N_R$, where T is the temperature, $R = 1.9860 \text{ cal mol}^{-1} \text{ K}^{-1}$ is the universal gas constant and there are N_R competing reactions occurring simultaneously. The rate equations (2.1) contain the three parameters A_i , β_i and E_i for the i th reaction. It is the possibility of the determination of these parameters for each reaction, based upon outlet species mass fractions alone, which is investigated in this paper.

The flow through the reactor is characterised by a nominal residence time, τ , which is related to the reactor volume, V , the constant mass flow rate, \dot{m} , and the mass density, ρ , by the expression

$$\tau = \frac{\rho V}{\dot{m}}. \quad (2.2)$$

The residence time is used as a characteristic parameter of the reactor so that the mass flow rate is computed from Eq. (2.2).

2.3. Implementation of the PSR code

As well as the nominal residence time in the reactor, τ (s), and the inlet temperature, T^* (K), there are several other parameters which must be specified for the reactor. The pressure in the reactor, p (atmospheres), the volume of the reactor, V (cm^3), and the heat loss of the reactor, Q (cal/s), are three such parameters which are assumed to be fixed in all the simulations which we have performed. Also, the fuel mole fraction composition and the oxidiser mole fraction composition remain unchanged in all cases. Given the value of the fuel/air equivalence ratio, ϕ , and the product species then the inlet composition can be determined.

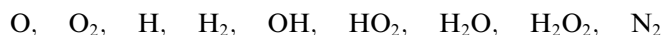
2.4. Sensitivity and rate of production analyses

The sensitivity and rate of production analyses provided by the PSR code can be used to indicate how much every reaction contributes to the total production of each species and which reactions could be neglected if we were developing a reduced system. In the inversion process applied to the full system these analyses also reveal any sets of reaction rate coefficients, from the Arrhenius expressions (2.1) for the reaction rates, that we would not expect to recover with any precision due to the relative insensitivity of the corresponding total species product concentrations to changes in their values. We consider a slightly different formulation of the sensitivity analysis in Section 4, where we calculate the sensitivity coefficients and their ratios for the individual coefficients A_i , β_i and E_i in the Arrhenius form (2.1) of the reaction rate, and use the results obtained to develop our inversion process.

2.5. Combustion of the hydrogen/nitrogen/oxygen mixture

The example we consider is the combustion of a hydrogen/nitrogen/oxygen mixture in a stirred reactor at a constant atmospheric pressure, $p = 1$ atm. The reactor has a volume $V = 67.4$ cm³ and the nominal residence time is the variable parameter τ . The inlet composition is defined by a specified fuel/air equivalence ratio ϕ . The fuel is 80% H₂ and 20% N₂ and the oxidiser is air, i.e. 79% N₂ and 21% O₂. In order to use the equivalence ratio input we specify the products for complete combustion, namely H₂O and N₂. We must also impose an inlet temperature T^* and, for no heat loss from the reactor, we take $Q = 0$.

As there is no mechanism within the chemical scheme to consider NO_x species, these have been excluded from the procedure. Thus, we consider only the following nine major species competing within the reactor:



and the reaction rates which determine their production and consumption are governed by Arrhenius kinetics according to expression (2.1). The three parameters A_i , β_i and E_i for each of the $N_R = 19$ reactions simultaneously occurring are well-known and have been presented in Table 1, see [10]. The efficiencies of the third bodies for three body reactions are included within this table. However, in this study the efficiencies of the third bodies were kept constant and not included within the unknown parameter sets for the optimisation procedure.

2.6. Validation of results using ignition delay time and flame speed

To provide additional validation of the results obtained by the optimisation process presented in this paper, the predicted ignition delay times and flame speed will be computed using both the original and the calculated reaction rate parameters. The laminar premixed one-dimensional flame structure calculations (PREMIX) and the SENKIN library will be used to predict the flame speed and the ignition delay time, respectively, at a variety of initial conditions.

2.6.1. PREMIX

The laminar premixed flame structure calculations were performed using the PREMIX code (see [14]) for burner stabilised flames with a known mass flow rate. Species concentrations and flame velocity as a function of the distance from the burner surface are computed by solving the energy equation. The PREMIX code accounts for finite rate chemical kinetics and molecular transport.

2.6.2. SENKIN

The SENKIN code (see [15]) predicts the time-dependent chemical kinetic behaviour of a homogeneous gas mixture in a closed system. In addition to predicting the species and temperature histories, the program can also compute the first-order sensitivities with respect to the elementary reaction rate parameters. For the purpose of this paper, the system is considered to be adiabatic under conditions of constant volume and spontaneous ignition temperature has been obtained.

Table 1

Reaction rate parameters for the hydrogen/nitrogen/oxygen mixture in a stirred reactor

Reaction number, i	Chemical reaction	Arrhenius rate parameters		
		A_i	β_i	E_i
1	$\text{H} + \text{O}_2 = \text{O} + \text{OH}$	5.1×10^{16}	−0.82	16510
2	$\text{H}_2 + \text{O} = \text{H} + \text{OH}$	1.8×10^{10}	1.0	8830
3	$\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$	1.2×10^9	1.3	3630
4	$\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$	6.0×10^8	1.3	0
5	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$ $\text{H}_2\text{O} / 20.0 /$	7.5×10^{23}	−2.6	0
6	$\text{O}_2 + \text{M} = \text{O} + \text{O} + \text{M}$	1.9×10^{11}	0.5	95 560
7	$\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$ $\text{H}_2\text{O} / 6.0 /$ $\text{H} / 2.0 /$ $\text{H}_2 / 3.0 /$	2.2×10^{12}	0.5	92 600
8	$\text{H}_2 + \text{O}_2 = \text{OH} + \text{OH}$	1.7×10^{13}	0.0	47 780
9	$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ $\text{H}_2\text{O} / 21.0 /$ $\text{H}_2 / 3.3 /$ $\text{O}_2 / 0.0 /$ $\text{N}_2 / 0.0 /$	2.1×10^{18}	−1.0	0
10	$\text{H} + \text{O}_2 + \text{O}_2 = \text{HO}_2 + \text{O}_2$	6.7×10^{19}	−1.42	0
11	$\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$	6.7×10^{19}	−1.42	0
12	$\text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2$	2.5×10^{13}	0.0	700
13	$\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$	2.5×10^{14}	0.0	1900
14	$\text{HO}_2 + \text{O} = \text{OH} + \text{O}_2$	4.8×10^{13}	0.0	1000
15	$\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$	5.0×10^{13}	0.0	1000
16	$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	2.0×10^{12}	0.0	0
17	$\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$	1.2×10^{17}	0.0	45 500
18	$\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$	1.7×10^{12}	0.0	3750
19	$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	1.0×10^{13}	0.0	1800

3. The genetic algorithm inversion technique

3.1. Introduction

The attempt to imitate the principles of biological evolution in the construction of optimisation strategies has led to the development of the powerful and efficient process of *genetic algorithms*, also known as *evolution strategies*. By utilising a vocabulary with genetic foundations, we see in this section that the critical ingredients of typical genetic algorithms are a *population* of *individuals*, each described or parameterised by a set of *genes*. The individuals undergo a process of *selection* such that only the *chromosomes* of the *fittest* individuals of every *generation* survive and become *children* within the next generation. In the process of constructing the next generation's individuals from the *gene pool* composing the *parents* chromosomes, genetic information is exchanged by the processes of *recombination* to form children and some random *mutations* occur.

Genetic algorithms have been successfully applied to nonlinear optimisation problems in many dimensions, where more traditional methods are often found to fail. Also, deterministic, gradient-based optimisation methods do not search the parameter space and can tend to converge towards local extrema of the fitness function, which is clearly unsatisfactory for problems where the fitness varies non-monotonously with the parameters. On the other hand, genetic algorithms are able to depart from local optima due to the variability of the parameters within the “gene pool” and the element of randomness inherent within the methods. Furthermore, genetic algorithms do not require knowledge of the gradient of the fitness functions, which makes them particularly suited to optimisation problems for which an analytical expression for the

fitness function is not known. A complete description of genetic algorithm techniques has been provided by several authors, see for example [9,16].

3.2. The concept of a genetic algorithm

There is a large class of interesting problems for which no reasonably fast algorithms have been developed. Many of these problems are optimisation problems that arise frequently in applications. For small search spaces classical methods usually suffice, but for larger spaces special artificial intelligence techniques must be employed. Genetic algorithms are among such techniques; they are stochastic algorithms whose search tools model some natural phenomena, namely genetic inheritance and the strive for survival.

Genetic algorithms use a vocabulary borrowed from natural genetics. We may talk about *individuals* (or *genotypes*, *structures*) in a population and often refer to these individuals as *strings* of *chromosomes*. Each genotype represents a potential solution to a problem and the meaning of a particular chromosome is defined externally by some user supplied encoding. An evolution process run on a population of chromosomes corresponds to a search through a space of potential solutions.

A genetic algorithm performs a multi-directional search. It starts with a randomly initialised population of candidate solutions and implements a probabilistic, parallel search in the solution space using domain-independent “genetic operators” to form a new population of candidate solutions. The population undergoes a simulated evolution process. At each generation the relatively “good” solutions reproduce, while the relatively “bad” solutions die. To distinguish between different solutions we use an objective (evaluation) function which plays the role of an environment. There are unary transformations m_i (mutation type) which create new individuals by small changes in single individuals and higher-order transformations c_j (crossover type) which create new individuals by combining parts from several (two or more) individuals. Crossover and mutation produce new areas of the solution space to explore.

The central theme of research on genetic algorithms has been *robustness*, the balance between efficiency and efficacy necessary for survival in many different environments. Genetic algorithms are a class of general purpose search methods which strike a remarkable balance between exploration and exploitation of the search space. They have been successfully applied to many optimisation problems, such as wire routing, scheduling, adaptive control, game playing, cognitive modelling, transportation problems, travelling salesman problems and optimal control problems, see for example [1,2,5–9,11,12,18].

The theoretical foundations of genetic algorithms rely on a binary string representation of solutions and on the notion of *schemata*, templates allowing exploration of similarities among chromosomes. Based upon the schema representation, a growth equation can be derived to verify improvement with evolution and this result is interpreted as the Schema theorem, see, for example, [16].

3.3. Implementation of a genetic algorithm approach

In a simple genetic algorithm, the process of *evaluation* assigns each candidate solution in a population, usually encoded as a binary string, with an associated fitness value measuring the candidate’s survivability. Subsequently, the genetic algorithm must evolve this population of individual candidates into a new population using the three operations of *selection*, *crossover* and *mutation*. A genetic algorithm does its search through an iterative process. Selection probabilistically chooses better candidates for a new generation, whilst crossover and mutation manipulate candidate solutions to generate new individuals for the selection procedure to process again. After a certain number of generations, when no further improvement is observed, the best chromosome represents an optimal (possibly global) solution. Often we stop the algorithm after a fixed number of iterations depending on the time of iteration from one generation to the next and computational resource criteria.

3.3.1. Initialisation of a population

To initialise a population, we can simply set a number N of chromosomes randomly in bitwise fashion. However, if we do have some knowledge about the distribution of potential optima, we may use such information in arranging the set of initial (potential) solutions.

In the problem that we are addressing in this paper, we randomly construct an initial population characterising estimates to the solution of the problem through their separate genes. The genes represent encodings of all the unknown reaction rate parameters over some specified ranges.

3.3.2. Selection operators and sampling mechanisms

Selection is a process in which individual strings are copied according to their objective function values or *fitness*. The higher the fitness, the more likely an individual is to be selected.

There are two important issues in the evolution process of a genetic search, namely *population diversity* and *selective pressure*. These factors are closely related since an increase in the selective pressure decreases the diversity, and vice versa. Strong selective pressure “supports” the premature convergence of the technique whilst weak selective pressure can make the search ineffective. Sampling mechanisms aim to strike a balance between these factors.

The method which we shall employ here for the selection of the parents of the next generation is *k-tournament selection*, which utilises the idea of ranking. This method (in a single iteration) selects some number k individuals and, from this pool of individuals, one member is selected as a parent for the next generation. The selection of one member from the pool begins by ranking the individuals according to the fitness function which measures the accuracy of the net product species concentrations at some set of reactor conditions against some known (simulated or experimental) measurements. As each individual is composed of sets of reaction rate parameters drawn from specified ranges, it is clear that, primarily in the initial stages of the optimisation procedure, unrealistic sets of reaction rate parameters may be chosen. In such cases the PSR code may fail and be unable to determine the products and therefore such individuals will be assigned a nominal low fitness value of, say, 10^{-8} in order to attempt to avoid their propagation into the next generation. The highest ranking individual is then selected with a probability p_T . If the fittest individual is not selected, for which the probability is $(1 - p_T)$, the second ranking individual is selected with probability $(1 - p_T)p_T$. This process is repeated until an individual is selected, or until we reach the k th and final, lowest ranking individual which then becomes a parent with probability $(1 - p_T)^{k-1}$. A typical value for many applications is $k = 2$, where the parameter k is called the *tournament size*.

3.3.3. Crossover operators

Crossover is the mating process allowing information exchange. One of the parameters of a genetic system is p_c , which defines the probability that a particular pair of chromosomes are selected for crossover. If selected, we have chosen to employ the method of *two-point crossover* which chooses two random cross sites and swaps the inner parts of the parent chromosomes between these cross sites to obtain a pair of offspring. If crossover does not occur the chromosomes of the parents are duplicated to produce the chromosomes of the children. If the crossover probability is too high then highly fit individuals are discarded faster than selection can produce improvements. On the other hand, if the crossover rate is too low, the search might stagnate for lack of exploration. Usually p_c lies between 0.5 and 1.0.

3.3.4. Mutation operators

The next operator, mutation, is performed on a bit-by-bit basis, with a probability of mutation p_m . Every bit (in all the chromosomes and in the whole population) has an equal chance to undergo mutation, i.e. change from 0 to 1 or vice versa.

By repeating the steps of parent selection, crossover and mutation we can generate a pool of offspring of size M , where $M > N$ is even, and merge these children with the parent population of N chromosomes. De Jong [4] considered several variations of simple selection for the derivation of the next generation from the parents and children of the previous generation. The first variation, named the *Elitist Model*, preserves the best chromosome out of the old population and transfers it directly into the new population. We employ a form of the Elitist Model in which the n_e best chromosomes from the old population are retained along with the fittest $(N - n_e)$ child chromosomes. The rest of the evolution process is just a cyclic repetition of the above steps and can be repeated for a specified number of generations or until a match to the imposed data is achieved to within a desired tolerance.

4. Inversion procedure

4.1. The sensitivity coefficients and sensitivity ratios

The inverse formulated problem requires the recovery of a certain number of the reaction rate parameters A_i , β_i , E_i , $i = 1, \dots, 19$, which are the coefficients in the Arrhenius form of the reaction rate equations (2.1), only from measurements of the net product species concentrations and the final reactor temperature.

Prior to performing the inverse analysis for the identification of the required reaction rate parameters, it is useful to calculate the sensitivity coefficients as a function of some variable defining the conditions within the reactor chamber, namely the reactor inlet temperature, T^* , the nominal residence time, τ , or the fuel/air equivalence ratio ϕ . Sensitivity coefficients are the first derivatives of the measured quantities, i.e. the net product species concentrations, with respect to the unknown parameters, i.e. the reaction rate coefficients, and they provide indicators of the suitability of the design of the experiment. In general, the sensitivity coefficients are desired to be uncorrelated, i.e. linearly independent. A sense of the magnitude of the sensitivity coefficients is gained through normalising them with respect to their corresponding unknown differentiation variable, so that the resulting units for the normalised sensitivity coefficients are the same as for the original measured quantity. The deviation of the ratios of these sensitivity coefficients from a constant function then provides an illustration of the degree of uncorrelation. Based upon these criteria we can determine the optimal data measurements to be imposed or recorded in order to reduce the ill-posedness of the inverse formulated problem. Therefore, a study of the sensitivity coefficients, prior to performing experiments, can lead to better experimental designs.

The (normalised) sensitivity coefficients as a function of the parameter γ governing the conditions within the reactor, where $\gamma \in \{T^*, \tau, \phi\}$, are defined according to the formula

$$\text{Sens}(P(\gamma); \alpha_i^j) = \alpha_i^j \frac{\partial P}{\partial \alpha_i^j} \quad (4.1)$$

for $i = 1, \dots, 19$ and $j = 1, 2, 3$, where α_i^j is a reaction rate parameter from the i th reaction rate equation (2.1) and $j = 1, 2$ and 3 indicate the use of the parameter A_i , β_i and E_i , respectively. The measurement P can denote either one of the nine net product species concentrations O, O₂, H, H₂, OH, HO₂, H₂O, H₂O₂, N₂ or the final reactor temperature, T_R . In the remainder of this paper we utilise measurements of product species concentrations alone and hence refer to P as a 'product' of the reaction.

The measured value of each of the products P , based upon specified values of the inlet temperature, T^* , the nominal residence time, τ , and the fuel/air equivalence ratio, ϕ , is controlled only by the reaction rate parameters A_i , β_i and E_i , for $i = 1, \dots, 19$. As these reaction rate parameters are introduced only through the Arrhenius form (2.1) of the rate equations we can write the sensitivity coefficients (4.1) as

$$\text{Sens}(P(\gamma); \alpha_i^j) = \alpha_i^j \frac{\partial P}{\partial k_{f_i}} \frac{\partial k_{f_i}}{\partial \alpha_i^j}. \quad (4.2)$$

The precise dependence of the reaction rate k_{f_i} on the parameters α_i^j , through the Arrhenius expression (2.1), can now be introduced to give

$$\text{Sens}(P(\gamma); \alpha_i^1) = \text{Sens}(P(\gamma); A_i) = \frac{\partial P}{\partial k_{f_i}} k_{f_i}, \quad (4.3)$$

$$\text{Sens}(P(\gamma); \alpha_i^2) = \text{Sens}(P(\gamma); \beta_i) = \frac{\partial P}{\partial k_{f_i}} (\beta_i \ln T_R) k_{f_i}, \quad (4.4)$$

$$\text{Sens}(P(\gamma); \alpha_i^3) = \text{Sens}(P(\gamma); E_i) = \frac{\partial P}{\partial k_{f_i}} \left(-\frac{E_i}{RT_R} \right) k_{f_i} \quad (4.5)$$

since $T = T_R$, the final reactor temperature, at the measurement of the product P .

A much enhanced characterisation of the degree of correlation of the sensitivity coefficients can be viewed by calculating their ratios in the form

$$R(P(\gamma); \alpha_{i_1}^{j_1}, \alpha_{i_2}^{j_2}) = \frac{\text{Sens}(P(\gamma); \alpha_{i_1}^{j_1})}{\text{Sens}(P(\gamma); \alpha_{i_2}^{j_2})} \quad (4.6)$$

for any pair of different reaction rate parameters $\alpha_{i_1}^{j_1}$ and $\alpha_{i_2}^{j_2}$. All the sensitivity ratios (4.6) can now be calculated by introducing the definition (4.1) and approximating the partial derivatives $\partial P / \partial \alpha_i^j$ by using forward finite differences.

In the cases where the sensitivity coefficients are for reaction rate parameters from the same reaction rate equation, so that $i_1 = i_2 = i$, the alternative forms (4.3)–(4.5) of the sensitivity coefficients can be introduced to give

$$R(P(\gamma); A_i, \beta_i) = \frac{1}{\beta_i \ln T_R}, \quad (4.7)$$

$$R(P(\gamma); \beta_i, E_i) = -\frac{\beta_i R}{E_i} T_R \ln T_R, \quad (4.8)$$

$$R(P(\gamma); E_i, A_i) = -\frac{E_i}{RT_R} \quad (4.9)$$

in which the dependence on the product measurement through the expressions $\partial P / \partial k_f$ has been eliminated by taking the sensitivity ratios. Thus, the sensitivity ratios in Eqs. (4.7)–(4.9) as functions of one of the parameters γ defining the reactor conditions, depend only upon the final reactor temperature, $T_R = T_R(\gamma)$. If the relationship between the final reactor temperature and γ is known then the sensitivity ratios immediately follow from Eqs. (4.7)–(4.9) when the parameters are from the same reaction equation.

4.2. Sensitivity ratios as a function of inlet temperature, T^*

In Section 4.1 we established expressions for the ratios of the sensitivity coefficients for any pair of reaction rate parameters and showed that for the case of two parameters from the same reaction equation these ratios could be written as a simple function of the final reactor temperature, T_R . The sensitivity ratios in this special case as a function of the reactor parameter $\gamma \in \{T^*, \tau, \phi\}$ then follow, when the dependence of T_R on γ is known, and are independent of the product being measured.

For given values of ϕ and τ , the PSR code can be used to describe the variation in the final reactor temperature T_R over a large range of inlet temperatures, T^* , for the reaction rate parameters defined in Table 1. The associated function $T_R(T^*)$ then immediately allows us to construct the sensitivity ratios (4.7)–(4.9) for two reaction rate parameters from the i th reaction equation.

Figs. 1(a) and (b) show the sensitivity ratios for the first two reaction equations when $\phi = 1.0$ and $\tau = 3 \times 10^{-5}$. In both these cases we see that, for any measured product P , the pairs of sensitivity coefficients composing the ratios $R(P(T^*); \beta_i, E_i)$ and $R(P(T^*); E_i, A_i)$ are uncorrelated as functions of the inlet temperature whilst the pair of sensitivity coefficients composing the ratio $R(P(T^*); A_i, \beta_i)$ are almost correlated. It follows in general, from Eqs. (4.7)–(4.9), that if we are attempting to invert for any pair of reaction rate parameters from a single rate equation then we would expect that measurements of one product at two different inlet temperatures would provide sufficient data for the inversion process but that the convergence towards the solution would be much more rapid if we seek the pair β_i, E_i or E_i, A_i compared to the pair A_i, β_i . Furthermore, the values of the sensitivity coefficients themselves provide an indication of the inlet temperature values at which the product measurements exhibit the most sensitivity to variations in the reaction rate parameters. It is observed that the magnitudes of the values of the sensitivity coefficients as functions of the inlet temperature depend upon the species concentrations being measured and which reaction rate parameter the sensitivity is taken with respect to.

There exists a total of 15 sensitivity ratios for pairs of reaction rate parameters from the first two reaction equations, of which six correspond to pairs from the same rate equation and are displayed in Fig. 1. The remaining nine sensitivity ratios, as functions of the inlet temperature, must be calculated using a finite-difference formulation and are dependent upon the product which is being measured. The sensitivity ratios for the same pairs of reaction rate parameters have been observed to differ greatly between the measured

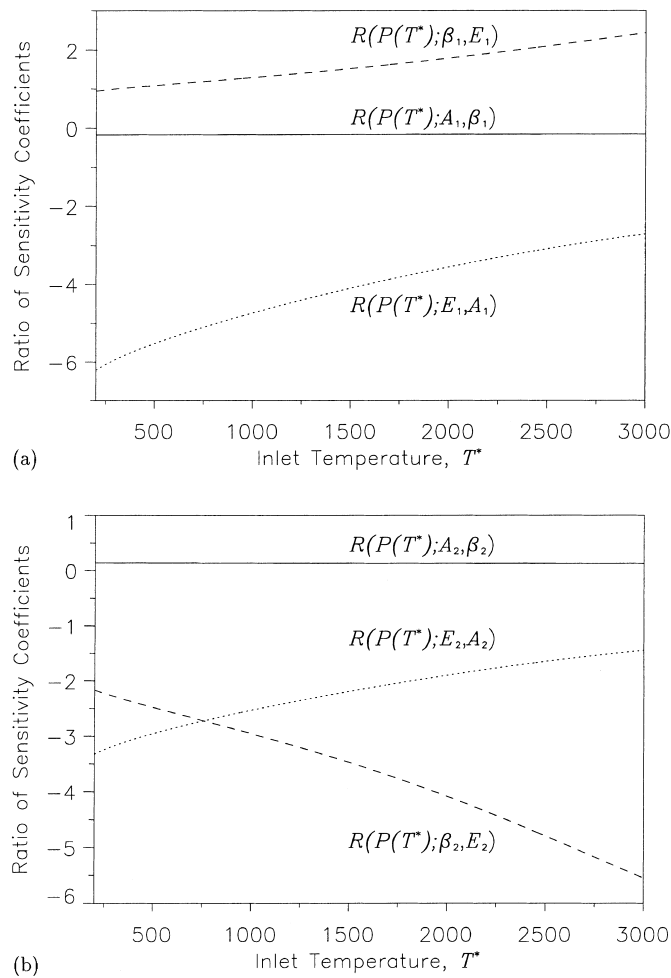


Fig. 1. The sensitivity ratios for the Arrhenius rate coefficients in (a) the first, and (b) the second, reaction equation as a function of the inlet temperature, T^* , for any product measurement P .

products and, for each product, the pairs of sensitivity coefficients composing each of the nine ratios are uncorrelated.

4.3. Sensitivity ratios as a function of nominal residence time, τ

The nominal residence time, τ , defines the duration of the reaction process and therefore measurements of the products at different residence times can be used to construct data values representing the evolution of net species concentrations from a small residence time towards a time at which these concentrations approach an equilibrium state. Thus, we expect that measurements of product species concentrations at small residence times, when these values are changing rapidly and can differ greatly from the equilibrium concentrations, may provide important information to be utilised in the inversion process.

For given values of ϕ and T^* , the PSR code can be used to describe the variation in the final reactor temperature, T_R , over a range of nominal residence times, τ . The resulting function $T_R(\tau)$ again allows us to construct the sensitivity ratios (4.7)–(4.9) for two reaction rate parameters from the i th reaction equation.

In a similar way to that described for Fig. 1, the sensitivity ratios demonstrate that the sensitivity coefficients for β_i , E_i or E_i , A_i are uncorrelated but that the sensitivity coefficients for A_i , β_i are almost linearly dependent. Again, if we are attempting to invert for any pair of reaction rate parameters from a single rate equation we would expect that measurements of one product at two different residence times would provide

sufficient data for the inversion process but that the convergence towards the solution would be much slower for the latter pair of parameters.

Sensitivity ratios for pairs of reaction rate parameters from two distinct reaction equations must again be calculated using a finite-difference formulation for each sensitivity coefficient and are dependent upon the product which is being measured.

4.4. Sensitivity ratios as a function of fuel/air equivalence ratio, ϕ

The equivalence ratio, ϕ , specifies the ratio of the initial fuel to air concentrations within the reactor. Thus, there exists a limited range of values of ϕ , for a given set of reactor conditions and reaction rate parameters, at which combustion takes place. Specifying values for T^* and τ , we can use the PSR code to determine the final reactor temperature, T_R , as a function of the fuel/air equivalence ratio within the valid ϕ range. Again, the resulting sensitivity coefficients for β_i , E_i or E_i , A_i are uncorrelated but the sensitivity coefficients for A_i , β_i are almost linearly dependent.

Although the sensitivity analysis provides extremely useful information, as has been demonstrated for a small number of parameters in this section, it becomes difficult to interpret or even accomplish for a large number of parameters, such as those required for a complete inversion of all the unknown reaction rate coefficients A_i , β_i and E_i , for $i = 1, \dots, 19$.

5. Results

With the aim of building up gradually to the problem of the identification of all the reaction rate parameters A_i , β_i and E_i , for $i = 1, \dots, 19$, in Section 5.5, we begin by discussing the application of the genetic algorithm technique to the inversion process for the first and second reaction equations and incorporate the observations from the sensitivity analysis of Section 4.

5.1. Inversion for two reaction rate parameters in the first reaction

In this section we assume that the reaction rate parameters A_i , β_i and E_i are all known for $2 \leq i \leq 19$ and attempt to retrieve the reaction rate parameters $\beta_1 = -0.82$ and $E_1 = 16510$, given the value of A_1 . The sensitivity analysis of Section 4 suggests that the ratio of the sensitivity coefficients for β_1 and E_1 varies with the temperature at the inlet, T^* , but is independent of the product P being measured. Therefore, based upon two values of any species concentration at different values of T^* we should be able to solve the inverse problem and determine the two unknown reaction rate parameters β_1 and E_1 . Having established that β_1 and E_1 can be estimated independently, we refer to the raw sensitivity coefficient values to ascertain the values of T^* for which the product measurement changes most rapidly with β_1 and E_1 and which therefore ensure the most rapid convergence of the inversion technique towards the optimal solution. Based upon imposing measurements of the net O_2 production, the two inlet temperature values $T^* = 300$ K and $T^* = 1000$ K were used to define the data for the inversion process. The nominal residence time and the equivalence ratio were set at the constant values $\tau = 3 \times 10^{-5}$ and $\phi = 1.0$, respectively.

We require a “fitness” function whose value becomes large as the calculated data, based upon estimates of the unknown reaction rate parameters β_1 and E_1 , for the net O_2 concentration approaches the corresponding data for the known values of β_1 and E_1 . Thus, we define the fitness function

$$\text{fitness} = \left\{ 10^{-8} + \sum_{J=1}^2 \left[\frac{O_{2,J}^{\text{calc}} - O_{2,J}^{\text{orig}}}{O_{2,J}^{\text{orig}}} \right]^2 \right\}^{-1}, \quad (5.1)$$

so that a maximum fitness of 10^8 indicates a perfect match to the specified data. In the definition of the fitness function (5.1), the notation $O_{2,J}^{\text{calc}}$ and $O_{2,J}^{\text{orig}}$ represents the calculated and original measurements, respectively, for the net O_2 concentration at the end of the simulation, where $J = 1$ and $J = 2$ indicate values corresponding to $T^* = 300$ K and $T^* = 1000$ K, respectively.

To begin the inversion process, an initial search region must be specified within the (β_1, E_1) parameter space. We choose the parameter ranges $\beta_1 \in [-1.0, 0.2]$, $E_1 \in [1.2, 2.0] \times 10^4$ and the discretisation of the parameter space is defined by employing 10 digit binary representations for each of β_1 and E_1 within the genetic algorithm approach. Each individual of the population is therefore represented by a 20 digit binary chromosome composed of two 10 digit genes which represent encodings of β_1 and E_1 . We can consider this representation to define a gridding of the parameter space composed of $2^{10} - 1$ increments in each direction and allowing maximum errors of 0.00059 for β_1 and 3.91 for E_1 .

The parameters governing selection, crossover and mutation within the genetic algorithm procedure, as discussed in Section 3, were specified as shown in Table 2.

Within 100 generations the genetic algorithm inversion procedure had produced a pair of values for β_1 and E_1 which remained unaltered with further evolution. In this example, the reaction rate parameter values:

$$\beta_1 = -0.82053, \quad E_1 = 16496.58 \quad (5.2)$$

were retrieved and the net product species concentrations achieved by using these parameters compared to those obtained using the original parameter values $\beta_1 = -0.82$ and $E_1 = 16510$ are presented in Table 3. The tabulated values have been specified to a high degree of accuracy to highlight the excellent agreement between the calculated and original net product species concentrations and the final reactor temperatures, particularly at the higher inlet temperature. It should be emphasised that the agreement between the calculated and the original measurements has been demonstrated for all the products based only upon the O_2 measurements, as guaranteed by the sensitivity analysis.

Table 2

Parameters governing selection, crossover and mutation within the genetic algorithm procedure

Parameter name	Value
Population size, N	50
Number of children, M	60
Probability of mutation, p_m	0.008
Probability of crossover, p_c	0.65
Tournament pool size, k	2
Tournament probability, p_T	0.8
Elitism Model parameter, n_e	2

Table 3

A comparison of the net product species concentrations and the final reactor temperature using the original parameters with those determined using the calculated values for the reaction rate parameters β_1 and E_1

Data type	Net O_2 concentration			
	At $T^* = 300$ K		At $T^* = 1000$ K	
	Original	Calculated	Original	Calculated
O	0.0079661	0.0079634	0.0165826	0.0165828
O_2	0.0391081	0.0391141	0.0342107	0.0342104
H	0.0503937	0.0503910	0.0693313	0.0693313
H_2	0.0640676	0.0640775	0.0582291	0.0582288
OH	0.0060578	0.0060563	0.0157191	0.0157192
HO_2	0.0000184	0.0000184	0.0000082	0.0000082
H_2O	0.2030104	0.2030022	0.1888078	0.1888081
H_2O_2	0.0000256	0.0000256	0.0000189	0.0000189
N_2	0.6293523	0.6293515	0.6170923	0.6170923
T_R	1400.487	1400.469	1756.124	1756.124

5.2. Inversion for two reaction rate parameters in the second reaction

The sensitivity analysis of Section 4 again suggests that the sensitivity coefficients for each of the net product species and the final reactor temperature as functions of the temperature at the inlet, T^* , are uncorrelated for β_2 and E_2 or A_2 and E_2 , but they are almost linearly dependent for A_2 and β_2 . Thus, we expect to be able to rapidly invert for pairs of the reaction rate parameters, given data corresponding to two different inlet temperature values, in the first two of these cases but to encounter problems with convergence to the optimal solution in the final case.

5.2.1. The two reaction rate parameters β_2 and E_2

Following the corresponding example for the first reaction equation, as detailed in Section 5.1, we set $A_2 = 1.8 \times 10^{10}$ and attempt to recover values for the parameters β_2 and E_2 , by imposing net product species concentration data corresponding to $\beta_2 = 1.0$ and $E_2 = 8830$.

The initial search region of the (β_2, E_2) parameter space is defined by the ranges $\beta_2 \in [0.5, 1.7]$, $E_2 \in [0.4, 1.2] \times 10^4$ and we attempt to retrieve values for β_2 and E_2 which provide a match to net O_2 concentration data at the two inlet temperature values $T^* = 300$ K and $T^* = 1000$ K.

In this example the inversion technique converged rapidly towards the following solution for the two reaction rate parameter values:

$$\beta_2 = 0.99501, \quad E_2 = 8731.18. \quad (5.3)$$

The solution (5.3) was reached after only seven generations and remained unchanged after a large number of subsequent generations.

The reaction rate parameter values (5.3) are approaching the original parameter values $\beta_2 = 1.0$ and $E_2 = 8830$ but, based upon the maximum accuracy achievable using 10 digit binary representations, the results are a significant number of grid points in error in both the β_2 and E_2 directions of the parameter space. It can be verified that the fitness of the reaction rate parameter values (5.3) is higher than some points in the parameter space which are much closer to the known solution. The optimal value at $\beta_2 = 1.0$, $E_2 = 8830$ appears to be an extremely sharp maximum of the fitness and either there exists another solution to the problem near to $\beta_2 = 0.99501$, $E_2 = 8731.18$ or this calculated solution is simply a non-global, *local* maximum of the fitness function. In either case, it is clear that there exists a region of the parameter space near to the optimal solution for which a match to the given product measurements can be achieved to an accuracy well within that which could be usually guaranteed by experimental data values. The coarseness of the gridding of the parameter space, combined with the sharpness of the fitness function at the optimal solution, means that we are unlikely to locate any points in the grid around the optimum which have a higher fitness than the result attained in Eq. (5.3).

We now attempt to move away from the non-global optimal values of the reaction rate parameters presented in Eq. (5.3) and obtain a solution which is close to the known values $\beta_2 = 1.0$ and $E_2 = 8830$ by employing a refined grid over a reduced search region of the parameter space. The chosen intervals $\beta_2 \in [0.92, 1.08]$, $E_2 \in [8.45, 9.05] \times 10^3$ encompass both the estimate (5.3) and the known solution $\beta_2 = 1.0$, $E_2 = 8830$ and the use of a 12 digit binary representation for both β_2 and E_2 enables accuracies of 0.00002 for β_2 and 0.07 for E_2 in the discretisation of the domain.

The genetic algorithm was terminated after 132 generations as no further progress had been made beyond the 35th generation at which the reaction rate parameters

$$\beta_2 = 1.00014, \quad E_2 = 8832.71 \quad (5.4)$$

had been recovered.

Again, further reductions of the search region would probably allow a successful inversion towards the exact parameter values for β_2 and E_2 . However, as the inversion procedure is intended to be applied to experimental data measurements, either of the results shown in Eqs. (5.3) or (5.4) would be valid parameter values based upon the expected errors in the supplied data.

5.2.2. The two reaction rate parameters A_2 and β_2

In exactly the same manner as presented in Section 5.2.1, we now seek the first two reaction rate parameter values in the second reaction equation, namely $A_2 = 1.8 \times 10^8$ and $\beta_2 = 1.0$. We define the initial search region of the (A_2, β_2) parameter space by the ranges $A_2 \in [1, 2] \times 10^{10}$, $\beta_2 \in [0.0, 1.4]$ and specify the net O_2 concentration at the two inlet temperature values $T^* = 200$ K and $T^* = 1000$ K to define the measurement data for the inversion process.

After a large number of generations, the genetic algorithm was terminated with the best current individual being defined by the pairing $A_2 = 1.822 \times 10^{10}$ and $\beta = 0.99829$, which was first achieved at the 141st generation.

As discussed previously in Section 4.2, the sensitivity coefficients for any product measurement as a function of the temperature at the inlet, T^* , are almost correlated for A_2 and β_2 . This observation has the effect of increasing the likely number of generations required to approach the optimal solution and thus the inversion process may be much more computationally intensive than, for example, the inversion for the parameters β_2 and E_2 . A direct comparison of the number of generations required for this example with those required in Section 5.2.1 confirms this to be true.

5.3. Inversion for three reaction rate parameters in the first reaction

The approach presented in Sections 5.1 and 5.2 for the retrieval of two unknown reaction rate parameters can be extended to search for three parameters by the inclusion of an additional product measurement value. The sensitivity analysis of Section 4 again suggests that the use of net product concentration data for one species only, say O_2 , is required since the sensitivity ratios for all the other products are identical. However, the sensitivity coefficients for the reaction rate coefficients A_1 and β_1 as a function of any one of the reactor condition parameters T^* , τ and ϕ were also shown to be almost correlated over the ranges considered. Therefore, we expect that the use of the net product concentration data at three different reactor conditions may not enable the retrieval of the original three reaction rate parameters. In this example, we attempt to recover the reaction rate coefficients A_1 , β_1 and E_1 using a genetic algorithm inversion process based upon the net product O_2 concentration data at two different inlet temperature values combined with a third data measurement at a different residence time and inlet temperature.

The initial search region of the (A_1, β_1, E_1) parameter space is defined by the ranges $A_1 \in [2, 8] \times 10^{16}$, $\beta_1 \in [-1.0, 0.2]$, $E_1 \in [1.2, 2.0] \times 10^4$ and 12 digit binary representations are employed for each of the three unknown parameters. We define the fitness function

$$\text{fitness} = \left\{ 10^{-8} + \sum_{j=1}^3 \left| \frac{O_{2,j}^{\text{calc}} - O_{2,j}^{\text{orig}}}{10^{-1}} \right| \right\}^{-1}, \quad (5.5)$$

where the subscripts $J = 1, 2, 3$, respectively, denote net O_2 concentration data at the three different sets of reactor conditions (i) $T^* = 300$ K, $\tau = 3 \times 10^{-5}$ s, $\phi = 1.0$; (ii) $T^* = 1000$ K, $\tau = 3 \times 10^{-5}$ s, $\phi = 1.0$; and (iii) $T^* = 1500$ K, $\tau = 1 \times 10^{-6}$ s, $\phi = 1.0$.

After a large number of generations the genetic algorithm was terminated with the best current individual being defined by

$$A_1 = 2.064 \times 10^{16}, \quad \beta_1 = -0.71223, \quad E_1 = 16165.08. \quad (5.6)$$

Expanding the original ranges to $A_1 \in [1, 12] \times 10^{16}$, $\beta_1 \in [-2.0, 2.0]$, $E_1 \in [1.0, 2.0] \times 10^4$ and employing a 15 digit binary representation for each of the three unknown parameters, the genetic algorithm was terminated after a large number of generations with the best individual being defined by the three reaction rate parameter values

$$A_1 = 5.136 \times 10^{16}, \quad \beta_1 = -0.82076, \quad E_1 = 16513.87. \quad (5.7)$$

A direct comparison of the net O_2 species concentration values for the two sets (5.6) and (5.7) of reaction rate parameter values and the results from a further two inversion calculations against the original data is given in Table 4. The match between the calculated O_2 production and the imposed O_2 production is

Table 4

Net O₂ concentration for different calculated triples of A_1 , β_1 and E_1 in the parameter space in comparison to the imposed concentrations

A_1	β_1	E_1	Net O ₂ concentration		
			$T^* = 300 \text{ K},$ $\tau = 3 \times 10^{-5} \text{ s}, \phi = 1.0$	$T^* = 1000 \text{ K},$ $\tau = 3 \times 10^{-5} \text{ s}, \phi = 1.0$	$T^* = 1500 \text{ K},$ $\tau = 1 \times 10^{-6} \text{ s}, \phi = 1.0$
5.1×10^{16}	−0.82	16510.0	0.0391141	0.0342104	0.1377015
2.064×10^{16}	−0.71223	16165.08	0.0391135	0.0342118	0.1377015
5.136×10^{16}	−0.82076	16513.87	0.0391133	0.0342098	0.1377015
2.378×10^{16}	−0.72848	16231.88	0.0391142	0.0342094	0.1377015
3.302×10^{16}	−0.76814	16345.49	0.0391134	0.0342107	0.1377015

observed to be very good, with the largest deviation of 1.4×10^{-6} corresponding to approximately a 0.004% error in the measured data value and representing an error which is insignificant in comparison to expected experimental measurement errors. Moreover, the net product concentrations for all other species obtained by using the calculated reaction rate parameters in Table 4 can be verified to accurately match the corresponding species concentrations at the original parameter values. This observation has been demonstrated earlier in Table 3 and is guaranteed by the sensitivity analysis.

5.4. Reducing the accuracy of the imposed data measurements

All the calculations of the net species concentration values used so far have been made to a high degree of accuracy, both for the data taken as experimental measurement values and the data produced from estimates to the unknown parameters. Clearly, whilst mathematically significant in the development of the genetic algorithm inversion procedure, the formulation of such an accurate approach is unrealistic in an experimental data inversion process. Thus, in this section we investigate how the use of the genetic algorithm technique allows us to recover reaction rate parameter values when the experimentally measured net species concentration data are specified to a smaller number of decimal places.

5.4.1. Inversion for three reaction rate parameters in the first reaction

To recover the three reaction rate parameters A_1 , β_1 and E_1 from the first reaction we follow the formulation of Section 5.3, except that the net O₂ concentration data are specified to five places of decimals only, as shown in Table 5.

The results presented in Table 6 have been achieved by employing an accuracy of seven significant figures in the calculation of the net O₂ concentration data, for a given set of estimates to the reaction rate parameters A_1 , β_1 and E_1 . The tabulated sets of net O₂ concentration values at the three sets of reactor conditions almost match perfectly to the specified data shown in Table 5 when comparing the first five places of decimals.

Table 5

The imposed net O₂ concentration values rounded to five decimal places for three different reactor conditions

Reactor condition number, J	Reactor condition parameters			Net O ₂ concentration
	$T^* \text{ (K)}$	$\tau \text{ (s)}$	ϕ	
1	300	3×10^{-5}	1.0	0.03911
2	1000	3×10^{-5}	1.0	0.03421
3	1500	1×10^{-6}	1.0	0.13770

Table 6

Results from three inversion calculations for A_1 , β_1 and E_1 using a fitness function in which the calculated net O_2 concentration values are rounded to seven significant figures for each of the three different reactor conditions

Reaction rate parameters			Net O_2 concentration		
A_1	β_1	E_1	1	2	3
3.019×10^{16}	-0.76083	16242.26	0.039111	0.034223	0.137701
7.075×10^{16}	-0.85989	16614.90	0.039110	0.034212	0.137701
10.981×10^{16}	-0.91189	16789.81	0.039110	0.034210	0.137701

5.4.2. Inversion for three reaction rate parameters in the second reaction

In this section we apply the inversion process discussed in Section 5.4.1 to the problem of recovering the three reaction rate parameters A_2 , β_2 and E_2 , based upon the net O_2 concentrations at the three reactor conditions specified in Table 5 and the initial search region of the (A_2, β_2, E_2) parameter space defined by the ranges $A_2 \in [1, 8] \times 10^{10}$, $\beta_2 \in [-2, 2]$, $E_2 \in [0.3, 1.3] \times 10^4$. The values of A_2 , β_2 and E_2 retrieved from two inversion calculations are presented in Table 7 and the net O_2 concentration values at the three sets of reactor condition match perfectly to the specified data shown in Table 5 when the first five places of decimals are compared.

Using the second set of reaction rate parameters presented in Table 7, namely

$$A_2 = 7.037 \times 10^{10}, \quad \beta_2 = 0.83688, \quad E_2 = 9331.93 \quad (5.8)$$

the net species concentrations for all the products were compared against the corresponding net product species concentrations achieved using the original parameters $A_2 = 1.8 \times 10^{10}$, $\beta_2 = 1.0$ and $E_2 = 8830$. The comparison was carried out over wide ranges of reactor conditions specified through the reactor parameters T^* , the inlet temperature, τ , the nominal residence time, and ϕ , the fuel/air equivalence ratio. A sample of the original and calculated sets of net species production data for some different sets of reactor conditions is presented in Table 8. Good agreement has been observed to exist between the original and the calculated data measurements with the magnitudes of all the errors lying below approximately 0.1%. It should be emphasised that we have been able to retrieve reaction rate parameters which not only match the given net product O_2 concentrations but also accurately estimate the net product concentrations of the other eight species at the given reactor conditions and ensure an accurate estimate to all product species measurements at other reactor conditions.

5.5. Retrieval of all 57 reaction rate parameters

The aim of this study is to recover all the 57 reaction rate parameters for the combustion of a hydrogen/nitrogen/oxygen mixture presented in Table 1. In this section we use the genetic algorithm inversion process, whose application to the recovery of a small number of these reaction rate parameters has been considered in Sections 5.1–5.4, to identify the reaction rate parameters A_i , β_i and E_i , for $i = 1, \dots, 19$, using specified net species production data.

Table 7

Results from three inversion calculations for A_2 , β_2 and E_2 using a fitness function in which the calculated net O_2 concentration values are rounded to seven significant figures for each of the three different reactor conditions

Reaction rate parameters			Net O_2 concentration		
A_2	β_2	E_2	1	2	3
2.844×10^{10}	0.94520	8994.29	0.039110	0.034210	0.137701
7.037×10^{10}	0.83688	9331.93	0.039110	0.034210	0.137701

Table 8

The predicted net species concentration values for the original reaction rate parameters A_2 , β_2 and E_2 and the calculated parameters (5.8) over a wide range of reactor conditions

Reactor condition parameters		O	O ₂	H	H ₂	OH
$T^* = 300, \phi = 1.0$ $\tau = 3 \times 10^{-5}$	Original	0.007963	0.039114	0.050391	0.064077	0.006056
	Calculated	0.007963	0.039110	0.050395	0.064067	0.006058
$T^* = 1500, \phi = 1.0$ $\tau = 3 \times 10^{-5}$	Original	0.022656	0.033060	0.076971	0.062444	0.024272
	Calculated	0.022657	0.033061	0.076970	0.062446	0.024271
$T^* = 2500, \phi = 1.0$ $\tau = 3 \times 10^{-5}$	Original	0.032479	0.029561	0.083105	0.072075	0.044036
	Calculated	0.032481	0.029563	0.083102	0.072080	0.044034
$T^* = 1500, \phi = 1.0$ $\tau = 1 \times 10^{-6}$	Original	0.000001	0.137701	0.000005	0.275402	0.000000
	Calculated	0.000001	0.137701	0.000005	0.275402	0.000000
$T^* = 2500, \phi = 1.0$ $\tau = 1 \times 10^{-6}$	Original	0.017969	0.069279	0.077022	0.129511	0.022973
	Calculated	0.017997	0.069330	0.076912	0.129674	0.022926
$T^* = 1500, \phi = 0.9$ $\tau = 1 \times 10^{-5}$	Original	0.024691	0.048844	0.083475	0.061086	0.018594
	Calculated	0.024691	0.048844	0.083476	0.061086	0.018594
$T^* = 1500, \phi = 1.1$ $\tau = 1 \times 10^{-5}$	Original	0.021284	0.035870	0.098413	0.080504	0.018582
	Calculated	0.021284	0.035870	0.098413	0.080504	0.018582
		HO ₂	H ₂ O	H ₂ O ₂	N ₂	
$T^* = 300, \phi = 1.0$ $\tau = 3 \times 10^{-5}$	Original	0.000018	0.203002	0.000026	0.629351	
	Calculated	0.000018	0.203010	0.000026	0.629353	
$T^* = 1500, \phi = 1.0$ $\tau = 3 \times 10^{-5}$	Original	0.000005	0.172351	0.000009	0.608232	
	Calculated	0.000005	0.172350	0.000009	0.608232	
$T^* = 2500, \phi = 1.0$ $\tau = 3 \times 10^{-5}$	Original	0.000005	0.143622	0.000001	0.595115	
	Calculated	0.000005	0.143620	0.000001	0.595115	
$T^* = 1500, \phi = 1.0$ $\tau = 1 \times 10^{-6}$	Original	0.000000	0.000005	0.000000	0.586885	
	Calculated	0.000000	0.000005	0.000000	0.586885	
$T^* = 2500, \phi = 1.0$ $\tau = 1 \times 10^{-6}$	Original	0.000006	0.096043	0.000001	0.587196	
	Calculated	0.000006	0.095959	0.000001	0.587195	
$T^* = 1500, \phi = 0.9$ $\tau = 1 \times 10^{-5}$	Original	0.000009	0.147804	0.000017	0.615480	
	Calculated	0.000009	0.147804	0.000017	0.615480	
$T^* = 1500, \phi = 1.1$ $\tau = 1 \times 10^{-5}$	Original	0.000007	0.162063	0.000014	0.583264	
	Calculated	0.000007	0.162062	0.000014	0.583264	

The initial search region of the parameter space is defined by specifying different ranges for each of the reaction rate parameters A_i , β_i and E_i , for $i = 1, \dots, 19$. We define the fitness function

$$\text{fitness} = \left\{ 10^{-8} + \frac{1}{N_p} \sum_{J=1}^{57} \sum_{j=1}^{N_{p,J}} \left| P_{j,J}^{\text{calc}} - P_{j,J}^{\text{orig}} \right| \right\}^{-1}, \quad (5.9)$$

where the subscripts $J = 1, 2, \dots, 57$ denote net product concentration data at the J th set of reactor conditions, $N_{p,J}$ denotes the number of net product species concentrations measured at the J th reactor condition, $N_p = \sum_{J=1}^{57} N_{p,J}$ denotes the total number of product measurements taken and $P_{j,J}$, for $j = 1, 2, \dots, N_{p,J}$, denotes the j th product measured at the J th reactor condition. The imposed data used in the matching process are given to five places of decimals whilst all the net species production data, based upon estimates to the unknown reaction rate parameters, are calculated to seven significant figures. The parameters governing the application of the genetic algorithm inversion procedure are as defined in Table 2 with the modification that $p_m = 0.02$.

We now present the results of three separate calculations to retrieve all the 57 unknown reaction rate parameters A_i , β_i and E_i , for $i = 1, \dots, 19$, in which the initial parameter space bounds are as shown in Table 9, 8 digit binary representations are employed for each parameter over their specified domains and the same initial population of potential solutions is taken. It should be noted that these apparently small ranges for each reaction rate parameter actually enable a large variation in possible predicted net species concentrations for a given set of reactor conditions. The imposed data measurements upon which the recovery of the reaction rate parameters is based are derived from 57 sets of reactor condition parameters T^* , τ and ϕ (see Table 10 for a representative subset of the reactor conditions taken) and the values of the imposed net species are obtained by rounding the exact calculated data to five decimal places. In the first two calculations only the net O_2 production data were used whilst for the third calculation all the nine net species production measurements were included at each set of reactor conditions. These calculations were terminated when the fitness value for the fittest individual had stabilised and no further significant improvements were anticipated.

The evolution of the fitness of the best individual at each generation is represented graphically in Fig. 2 for each of the three inversion calculations, although the form of the fitness function (5.9) means that the

Table 9

The ranges for the reaction rate parameters A_i , β_i and E_i in the i th reaction for the retrieval of all 57 reaction rate parameters

Reaction number i	Parameter ranges		
	A_i	β_i	E_i
1	5.0×10^{16} to 6.0×10^{16}	–1.0 to –0.5	16000 to 18000
2	1.0×10^{10} to 2.0×10^{10}	0.75 to 1.25	8000 to 9000
3	1.0×10^9 to 2.0×10^9	1.0 to 1.5	3000 to 4000
4	5.5×10^8 to 6.5×10^8	1.0 to 1.5	–500 to 500
5	7.0×10^{23} to 8.0×10^{23}	–3.0 to –2.5	–500 to 500
6	1.0×10^{11} to 2.0×10^{11}	0.25 to 0.75	94000 to 96000
7	2.0×10^{12} to 3.0×10^{12}	0.25 to 0.75	91000 to 93000
8	1.0×10^{13} to 2.0×10^{13}	–0.25 to 0.25	46000 to 48000
9	2.0×10^{18} to 3.0×10^{18}	–1.25 to –0.75	–500 to 500
10	6.0×10^{19} to 7.0×10^{19}	–1.5 to –1.0	–500 to 500
11	6.0×10^{19} to 7.0×10^{19}	–1.5 to –1.0	–500 to 500
12	2.0×10^{13} to 3.0×10^{13}	–0.25 to 0.25	0 to 1000
13	2.0×10^{14} to 3.0×10^{14}	–0.25 to 0.25	1000 to 2000
14	4.0×10^{13} to 5.0×10^{13}	–0.25 to 0.25	500 to 1500
15	4.5×10^{13} to 5.5×10^{13}	–0.25 to 0.25	500 to 1500
16	1.5×10^{12} to 2.5×10^{12}	–0.25 to 0.25	–500 to 500
17	1.0×10^{17} to 2.0×10^{17}	–0.25 to 0.25	44000 to 46000
18	1.0×10^{12} to 2.0×10^{12}	–0.25 to 0.25	3000 to 4000
19	0.5×10^{13} to 1.5×10^{13}	–0.25 to 0.25	1000 to 2000

Table 10

A reduced set of the reactor condition parameters upon which the comparison between the calculated and imposed data measurements is based

Reactor condition number, J	Inlet temperature, T^* (K)	Residence time, τ (s)	Equivalence ratio, ϕ
1	300	3×10^{-5}	1.0
2	700	3×10^{-5}	1.0
3	1200	3×10^{-5}	1.0
4	1800	3×10^{-5}	1.0
5	2400	3×10^{-5}	1.0
6	3200	3×10^{-5}	1.0
7	3300	1×10^{-6}	1.0
8	3300	1×10^{-6}	0.4
9	3300	1×10^{-6}	1.6

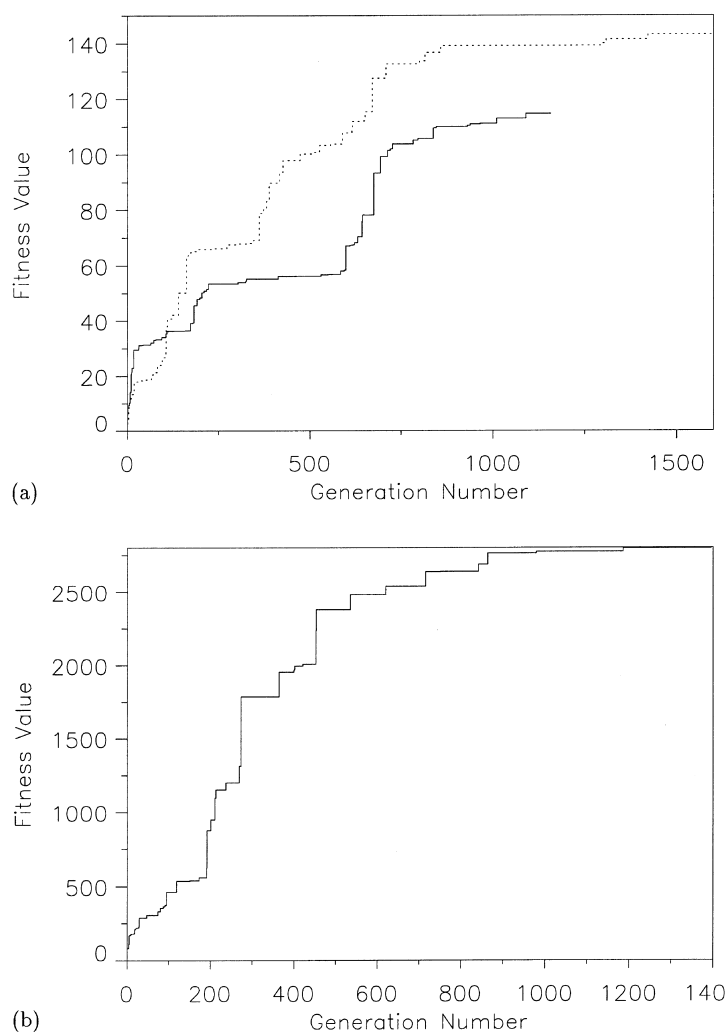


Fig. 2. The evolution of the fitness of the best individual with generation number (a) for the first (full line) and second (broken line) inversion calculations based upon imposing net O₂ measurements only; (b) for the third inversion calculation based upon imposing measurement data for all net product species.

magnitude of the fitness value when all nine products are measured cannot be directly compared with the case when only net O₂ measurements are taken. At the termination of the inversion process each of these evolution functions is displaying only a slight improvement with generation number and we will see that, in each case, the match to the specified data is within a tolerance comparable to typical experimental data measurement errors.

The reaction rate parameters recovered for the first and third inversion calculations are presented in Tables 11 and 12. Based upon the specified ranges displayed in Table 9 for each unknown reaction rate parameter, it appears that variations in some parameters have a minimal influence upon the match to the imposed data measurements and so such parameters cannot be recovered to any degree of accuracy. Other parameters, in particular most of the β_i reaction rate coefficients, appear to be close to the original values upon which the imposed data measurements are based. Furthermore, there appears to be little difference in the degree of accuracy of the retrieved parameters for the first calculation, based only upon O₂ measurements, in comparison to the retrieved parameters for the third calculation, based upon all product species measurements. However, although the first two inversion calculations involve matching against imposed net O₂ production data in a similar way to the methods described in Sections 5.1–5.4, the sensitivity analysis of Section 4 suggests they will not guarantee that subsequent predictions of net production data for the

Table 11

A comparison of the 57 original reaction rate parameters against the corresponding calculated reaction rate parameters for the first inversion calculation

Reaction number, <i>i</i>	A_i		β_i		E_i	
	Original	Calculated	Original	Calculated	Original	Calculated
1	5.1×10^{16}	5.757×10^{16}	-0.82	-0.8275	16510.0	16807.8
2	1.8×10^{10}	1.651×10^{10}	1.0	1.0814	8830.0	8639.2
3	1.2×10^9	1.918×10^9	1.3	1.1784	3630.0	3309.8
4	6.0×10^8	6.422×10^8	1.3	1.2510	0.0	-472.5
5	7.5×10^{23}	7.863×10^{23}	-2.6	-2.7608	0.0	272.5
6	1.9×10^{11}	1.780×10^{11}	0.5	0.5441	95560.0	94925.5
7	2.2×10^{12}	2.376×10^{12}	0.5	0.3794	92600.0	91423.5
8	1.7×10^{13}	1.039×10^{13}	0.0	0.0657	47780.0	46956.9
9	2.1×10^{18}	2.745×10^{18}	-1.0	-1.0853	0.0	209.8
10	6.7×10^{19}	6.027×10^{19}	-1.42	-1.3804	0.0	245.1
11	6.7×10^{19}	6.188×10^{19}	-1.42	-1.1000	0.0	354.9
12	2.5×10^{13}	2.412×10^{13}	0.0	0.0775	700.0	231.4
13	2.5×10^{14}	2.004×10^{14}	0.0	-0.2343	1900.0	1258.8
14	4.8×10^{13}	4.325×10^{13}	0.0	-0.1951	1000.0	1303.9
15	5.0×10^{13}	4.982×10^{13}	0.0	-0.0402	1000.0	1252.9
16	2.0×10^{12}	1.916×10^{12}	0.0	-0.0245	0.0	-100.0
17	1.2×10^{17}	1.373×10^{17}	0.0	-0.1873	45500.0	44172.5
18	1.7×10^{12}	1.565×10^{12}	0.0	0.2167	3750.0	3505.9
19	1.0×10^{13}	1.280×10^{13}	0.0	-0.0441	1800.0	1270.6

Table 12

A comparison of the 57 original reaction rate parameters against the corresponding calculated reaction rate parameters for the third inversion calculation

Reaction number, <i>i</i>	A_i		β_i		E_i	
	Original	Calculated	Original	Calculated	Original	Calculated
1	5.1×10^{16}	5.804×10^{16}	-0.82	-0.8392	16510.0	16564.7
2	1.8×10^{10}	1.541×10^{10}	1.0	0.9657	8830.0	8580.4
3	1.2×10^9	1.247×10^9	1.3	1.3020	3630.0	3545.1
4	6.0×10^8	6.167×10^8	1.3	1.5000	0.0	-60.8
5	7.5×10^{23}	7.063×10^{23}	-2.6	-2.5961	0.0	-41.2
6	1.9×10^{11}	1.251×10^{11}	0.5	0.3912	95560.0	95223.5
7	2.2×10^{12}	2.980×10^{12}	0.5	0.4324	92600.0	92913.7
8	1.7×10^{13}	1.557×10^{13}	0.0	0.0951	47780.0	47537.3
9	2.1×10^{18}	2.008×10^{18}	-1.0	-0.9598	0.0	225.5
10	6.7×10^{19}	6.682×10^{19}	-1.42	-1.4765	0.0	-311.8
11	6.7×10^{19}	6.184×10^{19}	-1.42	-1.4255	0.0	460.8
12	2.5×10^{13}	2.643×10^{13}	0.0	-0.0814	700.0	337.3
13	2.5×10^{14}	2.090×10^{14}	0.0	0.0265	1900.0	1670.6
14	4.8×10^{13}	4.584×10^{13}	0.0	0.0245	1000.0	1421.6
15	5.0×10^{13}	4.559×10^{13}	0.0	0.1461	1000.0	570.6
16	2.0×10^{12}	2.484×10^{12}	0.0	-0.0363	0.0	-41.2
17	1.2×10^{17}	1.212×10^{17}	0.0	0.2010	45500.0	45082.4
18	1.7×10^{12}	1.616×10^{12}	0.0	0.1167	3750.0	3396.1
19	1.0×10^{13}	0.531×10^{13}	0.0	-0.0480	1800.0	1309.8

other eight species are accurate. Using the 57 reaction condition parameters at which product measurements are imposed, a direct comparison of predicted product species concentrations was performed for the reaction rate parameters retrieved from each of the three inversion calculations. In the first and second

inversion calculations the match to the imposed net O_2 production data is excellent for typical reactor conditions, with a maximum relative error of approximately 0.44% and 3.2%, respectively, for the most extreme conditions considered. However, the subsequent prediction of the production of the remaining species was found to be poor and, for example, relative errors of up to 25% were achieved for predictions of H concentration at typical reactor conditions. A comparison of the predicted and original O_2 and H concentrations at the representative subset of reactor conditions shown in Table 10 is presented in Table 13 for the reaction rate parameters recovered from the first inversion calculation, where the predicted H concentrations were found to exhibit the worst match to the original data. The failure to achieve a successful recovery of all 57 reaction rate parameters from the first two inversion calculations is further demonstrated in Fig. 3, where the evolution of the absolute error in the predicted net product concentrations associated with the fittest individual at each generation for some of the species involved are presented. The evolution of the absolute error in the species concentrations is presented at the reactor conditions $T^* = 400$ K, $\tau = 3 \times 10^{-5}$ s, $\phi = 1.0$ and we observe that only the net O_2 concentration value appears to converge satisfactorily, whilst the other species make little significant improvement with generation number.

In the third inversion calculation, we base the recovery of the reaction rate parameters on the imposition of net product concentrations of every species at each of the same 57 reactor conditions, so that the inversion process is over-specified. Thus, if the process converges towards an individual with a high enough fitness we will expect to have retrieved a set of reaction rate parameters which both satisfy the given constraints and accurately predict the species concentrations at other reactor conditions. Using the retrieved reaction rate parameters presented in Table 12 and the original reaction rate parameters, a direct comparison between the observed O_2 and H species concentrations at the subset of reactor conditions, shown in Table 10, is presented in Table 14. The agreement between the two sets of predicted species concentration data is observed to be good over all the reactor conditions imposed and for all product species, with the maximum relative errors in concentration being around 1%, or less, for the majority of measurements taken and therefore within the error expected from experimental data measurements. Furthermore, we are able to provide a good estimate to the net species production data at other reactor conditions using the set of reaction rate parameters displayed in Table 12. Fig. 4 displays the evolution of the absolute error in the predicted net product concentrations associated with the fittest individual at each generation for some of the species at two different reactor conditions, namely $T^* = 400$ K and $T^* = 2000$ K, when $\tau = 3 \times 10^{-5}$ s, $\phi = 1.0$. The absolute error in every species concentration is observed to decay with an increase in the generations so that, at the termination of the process, a good match to the imposed species production data has been achieved.

To further validate the results obtained by the optimisation process presented in this paper, the predicted ignition delay times and flame speed have been computed using both the retrieved reaction rate parameters presented in Table 12 and the original reaction rate parameters shown in Table 1. The SENKIN library and

Table 13

A comparison of the net O_2 and H species concentration values obtained using the original and the calculated reaction rate parameters for the first inversion calculation

<i>J</i>	O ₂ species concentration			H species concentration		
	Imposed value	Calculated value	Error ($\times 10^{-5}$)	Imposed value	Calculated value	Error ($\times 10^{-5}$)
1	0.03911	0.03917	6	0.05039	0.04604	435
2	0.03516	0.03515	1	0.06300	0.06033	267
3	0.03376	0.03376	0	0.07278	0.07145	133
4	0.03220	0.03225	5	0.08000	0.07974	26
5	0.02997	0.03008	11	0.08291	0.08347	56
6	0.02713	0.02715	2	0.08642	0.08656	14
7	0.05931	0.05929	2	0.07804	0.07769	35
8	0.10928	0.10914	14	0.03202	0.03216	14
9	0.04177	0.04164	13	0.09862	0.09831	31

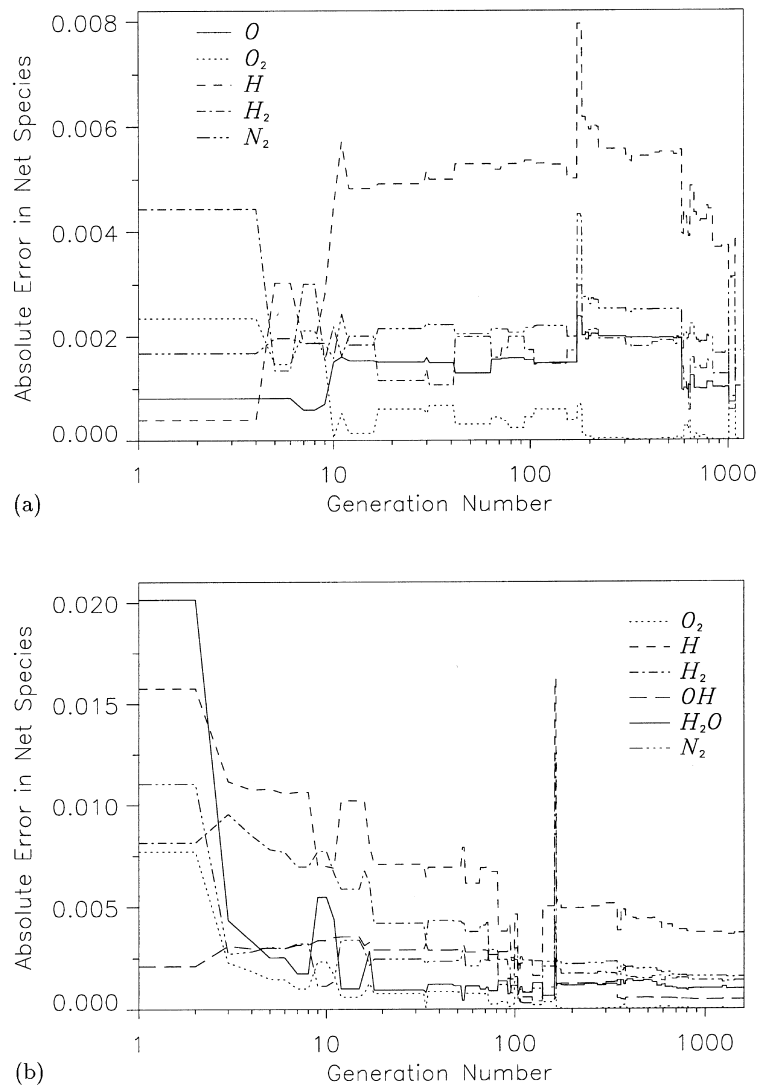


Fig. 3. The evolution of the absolute error in the net measurements of particular product species for the reactor conditions $T^* = 400$ K, $\tau = 3 \times 10^{-5}$ s, $\phi = 1.0$ associated with the best individual at each generation (a) for the first inversion calculation, and (b) for the second inversion calculation, based upon imposing net O_2 measurements only.

Table 14
A comparison of the net O_2 and H species concentration values obtained using the original and the calculated reaction rate parameters for the third inversion calculation

J	O_2 species concentration			H species concentration		
	Imposed value	Calculated value	Error ($\times 10^{-5}$)	Imposed value	Calculated value	Error ($\times 10^{-5}$)
1	0.03911	0.03903	8	0.05039	0.05052	13
2	0.03516	0.03517	1	0.06300	0.06294	6
3	0.03376	0.03380	4	0.07278	0.07268	10
4	0.03220	0.03223	3	0.08000	0.07986	14
5	0.02997	0.03000	3	0.08291	0.08279	12
6	0.02713	0.02717	4	0.08642	0.08640	2
7	0.05931	0.06009	78	0.07804	0.07779	25
8	0.10928	0.11023	95	0.03202	0.03176	26
9	0.04177	0.04239	62	0.09862	0.09845	17

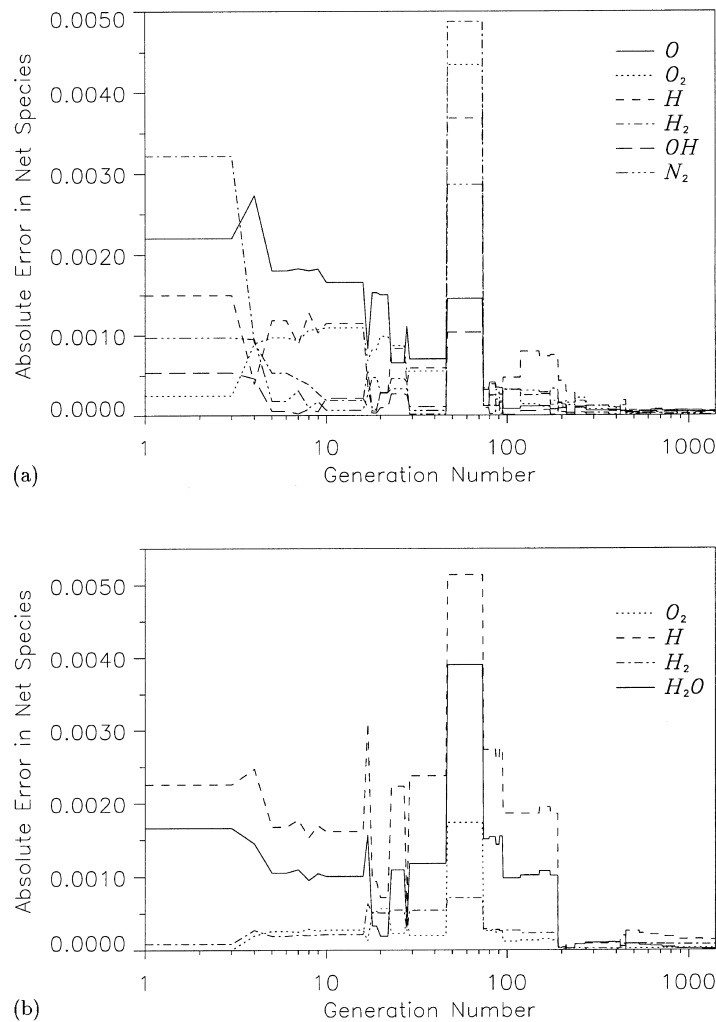


Fig. 4. The evolution of the absolute error in the net measurements of particular product species for the third inversion calculation at the reactor conditions (a) $T^* = 400 \text{ K}$, $\tau = 3 \times 10^{-5} \text{ s}$, $\phi = 1.0$, and (b) $T^* = 2000 \text{ K}$, $\tau = 3 \times 10^{-5} \text{ s}$, $\phi = 1.0$, based upon imposing measurement data for all net product species.

the laminar premixed flame structure calculations (PREMIX), described in Section 2.6, have been used to predict the ignition delay time and the flame speed, respectively, for a variety of initial conditions and the results are compared in Tables 15 and 16, respectively. In addition, the transient behaviour of three selected species concentrations have been presented in Table 15 for both the original and calculated reaction rate parameters. The predicted flame speeds at different initial mole fractions and different distances from the inlet are also shown to differ from the flame speeds calculated using the original parameters by a relative error of at most 0.5%. Although the relative error between the predicted ignition delay times for the original and calculated reaction rate parameters is larger, the absolute error in time is small. Furthermore, the transient behaviour of the three selected species concentrations are observed to be similar when the results from the original and calculated reaction rate parameters are compared. It is possible that the inclusion of the results obtained from the SENKIN library within the optimisation procedure may lead to better predictions of the reaction rate parameters and this will form part of a future investigation.

At present, the genetic algorithm optimisation process described in this paper is fairly computationally intensive, due to the requirement to calculate the predicted species concentrations for every individual of the population at a wide variety of reactor conditions. Typically, for a population requiring the fitness evaluation of 60 children at each generation and each individual consisting of 57 unknown reaction rate

Table 15

A comparison of the ignition delay time and transient species concentrations predicted using original and calculated reaction rate parameters at different initial temperatures when the initial mole fractions for O₂, N₂ and H₂ are in the proportions 1:4:1

Initial temperature (K)	Ignition delay time (μ s)		Selected species concentrations				
	Original	Calculated		Original		Calculated	
				10 ms	20 ms	10 ms	20 ms
1500	39.0	50.6	O ₂	0.083	0.084	0.083	0.084
			N ₂	0.706	0.714	0.701	0.712
			H ₂	0.012	0.008	0.014	0.009
2100	58.8	69.7	O ₂	0.079	0.079	0.078	0.079
			N ₂	0.694	0.702	0.690	0.699
			H ₂	0.017	0.014	0.019	0.015

Table 16

A comparison of the flame speed predicted using original and calculated reaction rate parameters at various initial conditions

Initial mole fractions			Distance from inlet (cm)	Flame speed (cm s ⁻¹)	
				Original	Calculated
O ₂	0.19	1		520.1	521.5
N ₂	0.53	10		741.7	745.6
H ₂	0.28				
O ₂	0.20	1		480.6	481.8
N ₂	0.60	10		695.6	697.4
H ₂	0.20				

parameters, thereby requiring 57 different reactor conditions in the PSR code, the advancement from one generation to the next required 1288 s of CPU time on a Sun Ultra 1 (140 MHz processor). It is hoped that, based upon the excellent results demonstrated by this initial study, the present genetic algorithm can be refined to improve convergence rates. Clearly, the CPU time required to recover reaction rate parameters in a given situation should be balanced with the accuracy required and the experimental errors present within the imposed data. For the optimisation calculation presented in Fig. 4(a) the absolute error in the predicted species concentration has fallen below 0.001 at around generation 30 for all the species displayed and the additional calculation time needed to halve the error for all these species, corresponding to approximately a further 170 generations, may not be justified.

6. Further work

In a further study it is important to investigate the following extensions to the genetic algorithm inversion techniques that we have developed here:

1. The application to problems in which some of the reaction rate parameters are known with a high confidence whilst others are allowed to vary within larger ranges. The bounds for each parameter should then be based upon commercially available databases of experimental data measurements.
2. The inclusion of some simulated errors in the net species concentration measurements is the intermediate step towards the full inversion of reaction rate coefficients based upon experimental data.
3. Using experimental net species concentration data, the best estimate to the net product species concentrations at each generation can be monitored. The inversion process becomes invalid and should be terminated when the deviations fall below tolerances determined by the expected experimental error.

4. It is expected that simplifications to the problem discussed here may arise by the consideration of a reduced kinetic scheme containing only the most significant reactions. Insensitive reaction rate coefficients can be highlighted by employing sensitivity and rate of production analyses from the PSR code and we clearly cannot expect to recover their values with any precision. Alternatively, it is possible that some of the reaction rate coefficients will be known with sufficient confidence and can therefore be specified. A novel method for automating these processes is required which will produce a robust mechanism applicable to any combustion process.
5. The excellent results presented here suggest that the progression onto other chemical kinetic schemes and the optimisation of higher-order hydrocarbon schemes can now be realised.
6. The genetic algorithm inversion process provides the potential to generate an automated procedure for the optimisation of chemical kinetic schemes and the reduction of the number of reaction steps required for complex hydrocarbon fuels.

7. Conclusions

In this study we have presented a general inversion procedure for the recovery of optimum rate coefficients for chemical kinetic schemes, based upon limited net species production data from a sequence of simulations at different reactor conditions.

The reaction rate coefficients are introduced through the generalised Arrhenius form of the reaction rate mechanisms and these parameters control the creation and destruction of each species through the reaction, which we have modelled according to the PSR code. We have shown that it is possible to derive rate coefficients such that the given net species production rates, defined at various conditions, are simultaneously achieved by searching the corresponding multi-dimensional parameter space. The use of genetic algorithms in the inversion process has enabled a guided exploration over this complex parameter space of up to 57 dimensions using a process, based on the Darwinian principle of survival of the fittest, in which candidate solutions evolve through a series of generations. Moreover, the optimisation techniques have been shown to recover reaction rate parameters which both match the given net species production rates and subsequently ensure the accurate prediction of net species production rates over a wide range of conditions. The excellent results of this initial study have been based upon the recovery of reaction rate coefficients for hydrogen/nitrogen/oxygen flames. These results indicate that a successful identification of the reaction rate parameters based only upon measurements from a sequence of such experiments is achievable. Moreover, the methods presented here provide foundations for the progression onto other chemical kinetic schemes and the optimisation of higher-order hydrocarbon schemes. The genetic algorithm inversion process therefore promises the ability to assess combustion behaviour for fuels where the reaction rate coefficients are not known with any confidence and, subsequently, accurately predict emission characteristics, stable species concentrations and flame characterisation. Such predictive capabilities are of paramount importance to a wide variety of industries.

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