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Technical Notes

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Genetic-Algorithm Optimization of a Chemistry Mechanism for Oxidation of Liquid Hydrocarbons

A. S. Wade,* A. G. Kyne,† N. S. Mera,‡
M. Pourkashanian,§ D. B. Ingham,¶ and S. Whittaker**
University of Leeds,
Leeds, England LS2 9JT, United Kingdom

I. Introduction

JET fuel is used as the primary coolant in aircraft before it enters the combustor. As the fuel heats up, trace species react with dissolved oxygen resulting in the thermal-oxidative stressing of the fuel and the subsequent formation of surface deposits. The autoxidation process involves a complex series of free-radical chain reactions. Unfortunately, subsequent reactions lead to the production of solids and gums, which can go on to foul engine components. Such reaction products have been implicated in observed reductions in the efficiency of heat exchangers and can ultimately lead to blocked fuel system filters and other undesirable disturbances within the fuel flow.[1]

In this study the genetic-algorithm (GA) optimization process is used optimize a pseudodetailed hydrocarbon oxidation mechanism over a wide range of conditions and compare the results to those of Kuprowicz et al.[2] to illustrate the benefits of using such a technique over traditional manual calibration methods.

The simple chemical kinetics modeling package "Acuchem" of Braun et al.[3] can be run using a kinetic scheme defined by decoding data encoded into GA individual's genetic information, that is, the Arrhenius parameters. 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 superior solutions are discovered.

In the future, such an approach promises the ability to predict the rate and location of deposit accumulation in fuel system components is becoming of paramount importance to the aviation industry in the 21st century.

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*Ph.D. Student, Energy and Resources Research Institute; che9asw@leeds.ac.uk.
†Research Fellow, Energy and Resources Research Institute; fueagk@leeds.ac.uk.
‡Research Fellow, Energy and Resources Research Institute; fuensm@sun.leeds.ac.uk.
§Professor, Energy and Resources Research Institute; fue6mtz@leeds.ac.uk.
¶Professor, Department of Applied Mathematics; amt6dbi@amsta.leeds.ac.uk.
**Ph.D. Student, Department of Applied Mathematics; che9sw@leeds.ac.uk.

II. Model Description

A. Reaction-Rate Parameters

In chemically reacting processes, the net chemical production or destruction rate of each species results from a competition between all of the chemical reactions involving those species. In this study it is assumed that each reaction proceeds according to the law of mass action and the forward rate coefficients are in the two-parameter functional Arrhenius form, namely,

$$k_i = A_i \exp\left(-E_{a_i} \big/ RT\right) \tag{1}$$

for $i = 1, \ldots, N_R$, where R is the universal gas constant and there are N_R competing reactions occurring simultaneously. The rate equations (1) contain the two parameters A_i and E_{a_i} for the ith reaction. It is the possibility of the automated calibration of these parameters for each reaction by using a GA, based on experimentally measured autoxidation data, that is investigated in this paper. For the calculations we have implemented the Acuchem code of Braun et al.[3] along with the reaction mechanism of Kuprowicz et al.,[2] which are described in the following sections.

B. Acuchem Calculations

Acuchem is a relatively simple code that integrates the set of multiple differential equations which result from a chemical kinetic mechanism and yield the species concentration profiles vs time.

The pseudodetailed kinetic model of Kuprowicz et al.,[2] shown in Table 1, has shown some success in the prediction of autoxidation characteristics in heater sections for the paraffin blend Exxsol D-80 over a range of temperature and initial oxygen concentrations.[2]

If the flow is considered completely isothermal, then, for a given set of reaction rates, the profiles of oxygen consumption as a function of stress time are calculated. If Acuchem calculations are performed for N_C different sets of operating conditions, that is, fuel chemistry, temperatures, etc., then the output data of the code, which is used by the GA in the matching process, consist of a set of $N_C \times N_P$ oxygen concentration values ($[\mathrm{O}_2]_{j,k}(t)$, $j = 1, \ldots, N_P$), where $[\mathrm{O}_2]_j(t)$ represents the value of the oxygen concentration at the jth time interval along the oxygen profile at the kth set of conditions. It is the purpose of this paper to determine the reaction-rate coefficients, that is, the A and E_a in Eq. (1), and the unknown reactant concentration for the initiator species $[I]_0$, needed to predict experimentally measured autoxidation behavior.

The values of $[\mathrm{O}_2]_0$ used for the simulations in this work in moles per liter (M) are 0.8, 1.68, 2.84, 4.05, 6.01, and 8.04 mM, corresponding to 10, 21, 35, 50, 75, and 100% oxygen saturation as measured by Pickard and Jones.[4] For consistency with earlier pseudodetailed modeling studies performed by Zabarnick[5] and Kuprowicz et al.,[2] an initial concentration of 4.4 M for the fuel species (RH) is used for all cases. Unless otherwise specified, all other initial species concentrations are set to zero.

The inversion process aims to determine the unknown reaction-rate parameters $[(A_i, E_{a_i}), i = 1, \ldots, N_R]$ that provide the best fit to a set of given data. This can be achieved by looking for the maximum of the following function:

$$f\left[\left(A_i, E_{a_i}\right)_{i=1,N_R}\right] = \left\{\varepsilon + \frac{1}{N_P N_C} \sum_{j=1}^{N_P} \sum_{k=1}^{N_C} \left(\left|[\mathrm{O}_2]_{j,k}^{calc} - [\mathrm{O}_2]_{j,k}^{exp}\right|\right)\right\}^{-1} \tag{2}$$

Table 1 Pseudodetailed chemical kinetic oxidation mechanism of a) Kuprowicz et al.[2] and b) the current GA investigation

Reaction number	Reaction	a) Original mechanism		b) GA optimized mechanism	
		A, mol, L, S	E_a, kcal/mol	A, mol, L, S	E_a, kcal/mol
1	$I \rightarrow R^{\bullet}$	1.0×10^{-3}	0.0	1.59×10^{-3}	0.00
2	$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$	3.0×10^{9}	0.0	2.97×10^{9}	0.00
3	$RO_2^{\bullet} + RH \rightarrow RO_2H + R^{\bullet}$	3.0×10^{9}	12.0	1.70×10^{9}	13.39
4	$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow$ termination	3.0×10^{9}	0.0	1.31×10^{9}	0.00
5	$RO_2^{\bullet} + AH \rightarrow RO_2H + A^{\bullet}$	3.0×10^{9}	5.0	3.00×10^{9}	5.00
6	$AO_2^{\bullet} + RH \rightarrow AO_2H + R^{\bullet}$	3.0×10^{5}	10.0	3.00×10^{5}	10.0
7	$A^{\bullet} + O_2 \rightarrow AO_2^{\bullet}$	3.0×10^{9}	0.0	3.00×10^{9}	0.00
8	$AO_2^{\bullet} + AH \rightarrow AO_2H + A^{\bullet}$	3.0×10^{9}	6.0	3.00×10^{9}	6.00
9	$AO_2^{\bullet} + AO_2^{\bullet} \rightarrow$ products	3.0×10^{9}	0.0	3.00×10^{9}	0.00
10	$R^{\bullet} + R^{\bullet} \rightarrow R_2$	3.0×10^{9}	0.0	1.11×10^{6}	0.00
11	$RO_2H \rightarrow RO^{\bullet} + {}^{\bullet}OH$	1.0×10^{15}	39.0	7.90×10^{15}	37.25
12	$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$	3.0×10^{9}	10.0	2.44×10^{9}	12.35
13	$RO^{\bullet} \rightarrow R_{prime}^{\bullet} +$ carbonyl	1.0×10^{16}	15.0	5.65×10^{15}	20.82
14	${}^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet}$	3.0×10^{9}	10.0	2.11×10^{9}	10.27
15	$RO^{\bullet} + RO^{\bullet} \rightarrow$ termination	3.0×10^{9}	0.0	3.19×10^{9}	0.00
16	$R_{prime}^{\bullet} + RH \rightarrow$ alkane $+ R^{\bullet}$	3.0×10^{9}	10.0	3.09×10^{9}	10.96
17	$RO_2H + SH \rightarrow$ SH products	3.0×10^{9}	0.0	3.00×10^{9}	0.00
18	$RO_2^{\bullet} \rightarrow R^{\bullet} + O_2$	1.0×10^{16}	19.0	5.43×10^{15}	17.30
19	$RO_2^{\bullet} + R^{\bullet} \rightarrow$ termination	3.0×10^{9}	0.0	2.04×10^{9}	0.00

where $[O_2]_{j,k}^{calc}$ represents the oxygen concentration at the jth point along the profile at the kth set of conditions, calculated by using the set of reaction rate parameters $[(A_i, E_{a_i}), i = 1, \ldots, N_R]$; $[O_2]_{j,k}^{exp}$ are the corresponding original values that were taken from curve fits to experimental measurements; and ε is a constant added to the fitness function to avoid numerical overflow. We note that the maximum value of these objective functions is $1/\varepsilon$, which indicates a perfect fit to the data. A small value, namely, $\varepsilon = 10^{-8}$, was used to increase the selective pressure applied by the GA. However, similar results are obtained with various other values of ε.

III. Genetic-Algorithm Inversion Technique

A complete description of genetic-algorithm techniques has been provided by several authors (for example, see Michalewicz[6]). The concept of a GA has been discussed in more detail previously.[7]

Currently there are a wide variety of genetic algorithms that can be used for optimization problems, and their efficiency depends on the particular problem being solved. A GA for a particular problem must have the following components: 1) a genetic representation for potential solutions to the problem; 2) a method for creating an initial population of potential solutions; 3) an evaluation function that plays the role of the environment, rating solutions in terms of their "fitness"; 4) genetic operators that alter the composition of children of a population of individuals; and 5) values of various parameters that the GA uses, that is, population size, probabilities of applying genetic operators, etc.

The GA operators and techniques used here are identical to those used in the work of Wade et al.[8]

The near-isothermal flowing test rig experimental measurements of Pickard and Jones[4] are used in this study to tune and hence improve upon the Arrhenius parameters used in the pseudodetailed autoxidation reaction mechanism of Kuprowicz et al.[2]

The new sets of rate constants generated at every generation of the GA are constrained to lie between predefined boundaries. In this case these boundaries have been chosen, where possible, to reflect the range of values found in the literature for analogous reactions. For a list of parameter ranges used and an explanation of their values, see Wade et al.[8]

IV. Results and Discussion

The experimental results of Pickard and Jones[4] utilized in this investigation are given in Figs. 1 and 2. Oxygen depletion vs time plots are shown in Fig. 1 for air-saturated Exxsol D-80 over a temperature range 408–438 K. Figure 2 shows O_2 depletion for Exxsol D-80 over a wide range of initial O_2 concentrations at 413 K. O_2 depletion data expressed as $\%[O_2]_0$ were converted to units of moles per liter by Pickard and Jones[4] from the fuel density within the specified temperature range.

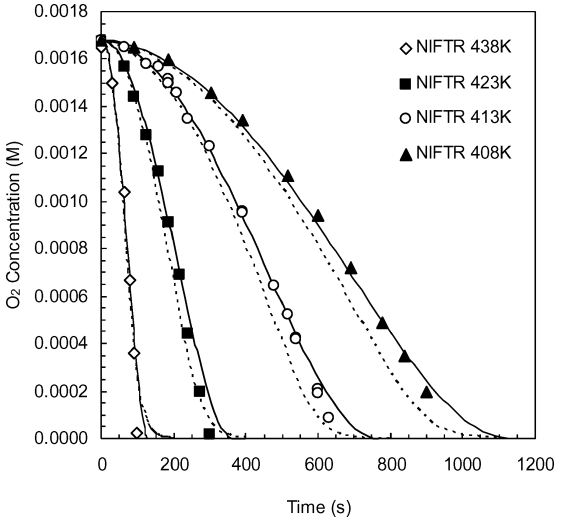


Fig. 1 Influence of temperature on O_2 depletion for air-saturated Exxsol D-80 from 418 to 463 K: ◇, ■, ○, ▲, NIFTR measurements; - - - -, simulations of Kuprowicz et al.[2]; and ——, GA-optimized mechanism simulations.

The data to be utilized in the GA inversion process were chosen as three O_2 depletion profiles over the entire temperature range of Fig. 1 and three over the entire range of O_2 saturation given in Fig. 2. Namely, the optimization data were for air-saturated Exxsol D-80 at 408, 423, and 438 K along with 21, 50, and 100% O_2 saturated Exxsol D-80 at 413 K. In arriving at these GA solutions, a Pentium 4, 2.6-GHz workstation took about 6.5 h for the computations.

Predictions given by the GA-optimized mechanism are presented in Figs. 1 and 2 for the oxidation data involved in the optimization process along with the predictions of the original mechanism of Kuprowicz et al.,[2] which was calibrated by hand to fit this specific data. It can be seen from Fig. 1 that at low temperatures both mechanisms perform well, giving very good predictions of oxygen consumption at early times. However, the GA-optimized mechanism produces trends that more closely correlate with experimental data

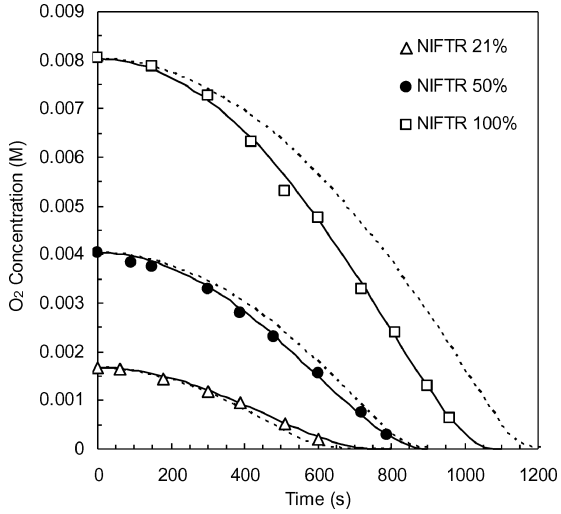
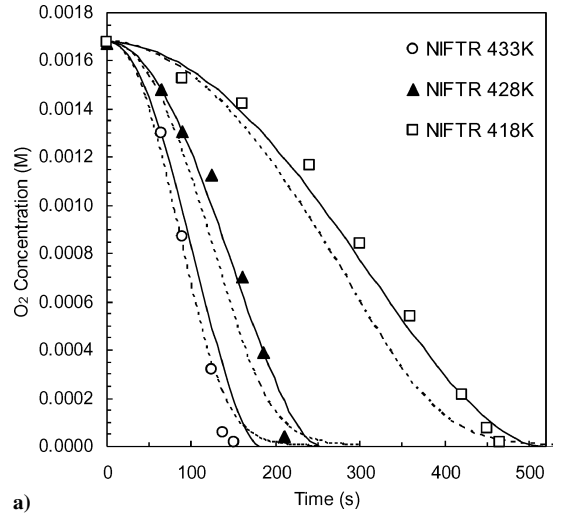


Fig. 2 Influence of dilution on O_2 depletion for Exxsol D-80 at 413 K. Percentages represent O_2 saturation, and 21% is representative of air-saturated Exxsol D-80: △, ●, □, NIFTR measurements; - - - -, simulations of Kuprowicz et al.[2]; and ——, GA-optimized mechanism simulations.



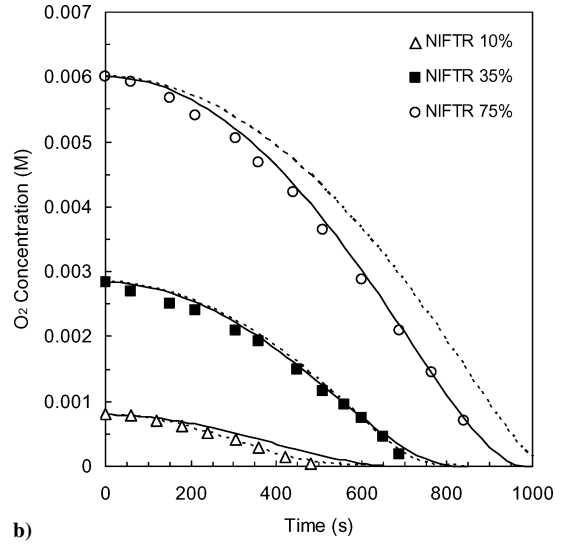


Fig. 3 Comparisons between NIFTR measurements (○, ▲, □, △, ■), the predictions of the original mechanism of Kuprowicz et al.[2] (– – –), and the GA-optimized mechanism (——) of O_2 depletion for a) air-saturated Exxsol D-80 over the range of temperatures and b) Exxsol D-80 at 413 K over the range of initial O_2 concentrations not used in the GA optimization process.

when oxygen concentration has been depleted to very low levels. It is observed from Fig. 1 that as the temperature decreases, the deviation between the predictions of Kuprowicz et al.[2] and the experimental data becomes greater, whereas the GA-optimized mechanism still predicts oxidation behavior very well. Similarly, as the initial oxygen concentration is increased above air saturation, shown in Fig. 2, the predictions of the original mechanism are seen to differ more and more markedly from experimental measurements, whereas the GA-optimized mechanism is seen to accurately predict oxygen depletion curves for all initial oxygen conditions.

Figure 3 compares the predictions of the original model of Kuprowicz et al.[2] with those of the GA-optimized mechanism for all of the data from Figs. 1 and 2, which was not involved in the GA optimization process. It can be seen in Fig. 3 that the GA inversion process has recovered parameters that offer significant improvements upon the original model of Kuprowicz et al.[2] both for conditions other than those implemented in the optimization process.

The optimized reaction mechanism is listed in Table 1, and large differences in the Arrhenius parameters compared to the original mechanism possibly indicate greater or lesser influences of certain reactions than previously expected. It is thought that the use of very large data sets will produce parameters that are more accurately descriptive of the underlying chemistry.

V. Conclusions

The GA optimization procedure has been shown to be a highly effective tool in the optimization of pseudodetailed models and also as a method of characterizing fuels according to optimized species classes that have not at present been accurately identified or measured experimentally. The GA optimization investigation has shown that a large, diverse data set is required to produce a truly robust reaction mechanism, which describes the underlying chemistry of hydrocarbon oxidation. In future, a more detailed model for oxidation would benefit from automated GA optimization utilizing a very large data set covering a wide range of hydrocarbons, over a large range of conditions.

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H. Chelliah
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