The Treatment of Non-Integer Exponents in Reaction Rate Expressions

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Abstract

The modelling of chemical reactions relies upon expressions being supplied which give the rate of reaction as a function of local temperature and local concentrations. When power law rate expressions are used with concentrations to integer powers the analysis and numerical solution of these equations is made easier. In this note the numerical difficulties that arise when the order is non-integer are described and one method is proposed which overcomes them in a differential-algebraic equation model of a catalytic monolith reactor.

1 Introduction

In the modelling of chemical reactions power law rate expressions of the form

$$r = k\, C_A^{\alpha}\, C_B^{\beta}\, \ldots,$$

are sometimes used where C_A, C_B represent concentrations. In cases where the exponents α, $\beta, \ldots$ have integer values the analysis of the equations is easier and their numerical solution often simpler. In this note the use of non-integer exponents is considered within a model of a catalytic combustor. As an example, the catalytic combustion of methane is considered where, with excess oxygen present, the rate of reaction is represented by

$$r = k\, C_{CH_4}^{0.75}.$$

This produces a set of differential-algebraic equations, see [2, 3, 5]. The non-integer order reaction terms occur in the *algebraic* equations, and these terms produce numerical difficulties in the codes when fuel concentration tends to zero. This is what occurs in the model discussed here. To be precise, the reaction rate depends exponentially on temperature and so when the wall temperature in the axial direction

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increases, the fuel concentration at the wall falls rapidly towards zero. The point of this note is to illustrate the use of a substitution procedure which overcomes these difficulties.
The plan of the note is as follows. Details of the model and difficulties present are discussed in Section 2 where an example of the failure of some standard software is given. In Section 3 a description of the technique used to overcome the problem and supporting numerical evidence are given. Section 4 contains some final remarks.

2 Catalytic Combustor Model

The mathematical modelling of catalytic combustion is the motivation for this work and the system of equations given here is a simple model for the adiabatic steady state catalytic combustion of methane in a single circular channel where the inside wall has been coated with a catalyst. The system is a modified form of the equations described in [5] where a first order catalytic reaction was assumed with respect to fuel concentration. The model in this note is made more complicated by changing the reaction to non first order (the order chosen is 0.75 — a value of 0.8 is reported by [1] for the oxidation of methane on a palladium catalyst system), but is made simpler by ignoring axial conduction, and assuming adiabatic operation (i.e. setting $T_S(x) \equiv T_W(x),\ 0 < x < L$). The nondimensional equations are,

$$\begin{aligned}
\frac{\mathrm{d}x_1}{\mathrm{d}\xi} &= J_D\,[\alpha_W(\xi) - x_1(\xi)], && (1)\\
\frac{\mathrm{d}x_2}{\mathrm{d}\xi} &= J_H\,[w(\xi) - x_2(\xi)], && (2)\\
0 &= J_H\,[x_2(\xi) - w(\xi)] - \Gamma D_c \exp\{\gamma_c(w(\xi)-1)/w(\xi)\}\alpha_W^{0.75}, && (3)\\
0 &= J_D\,[\alpha_W(\xi) - x_1(\xi)] + D_c \exp\{\gamma_c(w(\xi)-1)/w(\xi)\}\alpha_W^{0.75}, && (4)
\end{aligned}$$

where $x_1(\xi)$ is the gas mole fraction of fuel, $x_2(\xi)$ is the nondimensional gas temperature, $w(\xi)$ is the nondimensional wall temperature, and $\alpha_W(\xi)$ is the mole fraction of fuel at the wall for $0 < \xi < 1$ (see the derivation using mass and energy balances in [5]).
The parameters are chosen (see Table 1) so that complete conversion occurs. This should present no problem in theory as the reaction stops when $\alpha_W = 0$ and α_W holds this value throughout the remainder of the combustor.

J_D	J_H	Γ	D_c	γ_c
38.16	35.58	-0.1959	23.41	1.928

Table 1: Parameters for the catalytic combustor model

In practice however, the equations are integrated numerically, usually by a predictor-corrector scheme, in this case the routine DASSL, see [4]. These algorithms use information about the past solution values to 'predict' an initial guess for the solution at a new spatial position, and then 'correct' by solving a system of nonlinear equations to obtain the solution at the new point. The difficulties in this numerical procedure caused by the non-integer order term are:

- the value of α_W can become negative at the predictor stage or at the corrector stage, either of which gives immediate numerical collapse in the evaluation of the right hand side of (3) and (4),
- the Jacobian matrix used in the nonlinear solver of the corrector stage is unbounded as $\alpha_W \to 0$.

To illustrate this, the equations (1)–(4) were solved using DASSL, with relative and absolute tolerances set to 0.5×10^{-5}. The integration failed after 27 steps, at $\xi_{\text{end}} = 0.645$, with $\alpha_W(\xi_{\text{end}}) = 1.297 \times 10^{-6}$. DASSL contains an option to constrain solutions above 0. These results were obtained with this option switched on.

3 Overcoming the Difficulties

The idea is to remove the non-integer exponent by substitution. To be specific, the variable α_W in (1)–(4) is replaced by the variable $u(x)$ defined by the substitution

$$\begin{aligned} \alpha_W(x) &= \exp\{-k\,u(x)\} \\ &\text{or} \\ u(x) &= -\frac{1}{k}\ln \alpha_W(x). \end{aligned} \tag{5}$$

The new system of equations written for u becomes:

$$\begin{aligned} \frac{\mathrm{d}x_1}{\mathrm{d}\xi} &= J_D\,[\exp\{-k\,u(\xi)\} - x_1(\xi)], \\ \frac{\mathrm{d}x_2}{\mathrm{d}\xi} &= J_H\,[w(\xi) - x_2(\xi)], \\ 0 &= J_H\,[x_2(\xi) - w(\xi)] - \Gamma D_c \exp\{\gamma_c(w(\xi)-1)/w(\xi)\}\exp\{-0.75k\,u(\xi)\}, \\ 0 &= J_D\,[\exp\{-k\,u(\xi)\} - x_1(\xi)] + \\ &\quad D_c \exp\{\gamma_c(w(\xi)-1)/w(\xi)\}\exp\{-0.75k\,u(\xi)\}. \end{aligned}$$

There are many advantages here,

- the exponential form has the properties expected of a concentration,
- the exponential is always positive,
- $u \to \infty$ as $\alpha_W \to 0$,
- $\alpha_W^{0.75} = \exp\{-0.75k\,u\}$, and so the need for non-integer powers is removed.

This exponential substitution worked well in the case considered, the integration is complete in each case. The results obtained using DASSL for $k = 1$ and $k = 1000$ are given in Table 2. The number of steps taken when $k = 1000$ is less than for $k = 1$ since the substitution variable, $u(x)$, has a less steep profile to integrate in this case.

k	$\alpha_W(1)$	# steps
1	1.382×10^{-11}	191
1000	2.081×10^{-11}	82

Table 2: Results for exponential approximation of $\alpha_W^{0.75}$

4 Conclusion

The difficulties of numerical integration of equations with non-integer reaction rate order as concentrations reach zero have been considered and a technique of exponential substitution proposed to overcome these difficulties. The technique was tested on a simple model of a single channel catalyst coated reactor where complete conversion was achieved and was shown to work well. It is envisaged that this substitution will work in the same way for more general power law reaction rate expressions or Langmuir type expressions.

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