

A Polynomial Repro-Model Applied to Propane Cracking

R.B. Brad^a, M. Fairweather^{a*}, A.S. Tomlin^a and J.F. Griffiths^b

^aSchool of Process, Environmental and Materials Engineering

^bSchool of Chemistry

University of Leeds, Leeds LS2 9JT, UK

Abstract

The application of a repro-modelling approach for the representation of chemical kinetic changes is described. The repro-model is constructed from fitted orthonormal polynomial equations describing the change in concentration of selected key species over a chemical time-step within the model. The number of key species required is established by a linear perturbation method. Application to a propane cracking kinetic scheme demonstrates that lack of mass conservation within the repro-model can pose a threat to accuracy at long reaction times, due to the accumulation of small local errors leading to large global errors. Within many previous applications of repro-modelling, the control of global errors has relied upon the accuracy of the fitting/tabulation method used for the key variables, i.e. the local fitting error. In the current approach the reconstruction of all model species is achieved and enables the conservation of predicted mass across the chemical time-step. The accuracy of the resulting repro-model is shown to be better maintained throughout the simulation when this mass conservation method is used. However, only values of the key repro-model variables must be operated on by any model of the non-chemical kinetic changes, e.g. flow, making the method applicable for use in, for example, computational fluid dynamics codes.

Keywords: chemical kinetics, repro-modelling, mass-conservation, propane cracking.

1. Introduction

Attempts at incorporating detailed chemical kinetic descriptions into complex flow calculations to accurately model processes, such as the thermal cracking of propane, often necessitate the retention of excessive numbers of model variables. Repro-modelling offers the possibility of removing a large number of these variables from the flow calculations whilst maintaining accurate representations of the chemical kinetic behaviour. This is done by replacing the ordinary differential equation (ODE) system describing chemical kinetic changes over a time-step with some functional fit or tabulation method for a subset of the species present in the scheme. Examples of methods that fall into this category are fitted polynomial difference equations (Turanyi, 1994; Tonse et al., 1999), trained neural networks (Blasco et al., 1998) and in situ adaptive tabulation (ISAT) (Pope, 1997). The two main drawbacks of repro-modelling

* Author to whom correspondence should be addressed: m.fairweather@leeds.ac.uk

with a subset of species from a skeletal scheme are the lack of guaranteed mass conservation that would be inherent using a system of differential equations incorporating kinetic terms including an Arrhenius temperature dependence, and the loss of information on the species not chosen as key variables. Both of these can be overcome by fitting polynomials that can at any time, given the concentrations of the key variables, predict the concentrations of all other species, enabling a mass correction step to be applied. This approach is demonstrated here by its application to a propane cracking scheme, within a simple model designed to simulate plug flow type conditions.

2. Preliminaries

The kinetic scheme chosen for demonstrating this approach is the skeletal scheme of Tomlin et al. (1995), featuring 51 reactions of 19 chemical species, developed from the comprehensive scheme of Dente and Ranzi (1983) of 422 reactions of 28 species. As such, an impressive reduction is already displayed, although further reduction in the number of species is clearly required. The previous study showed that 12 of the remaining species could be represented by the quasi-steady state approximation (QSSA) due to their rapid local equilibration with respect to the slow species within the scheme. This demonstrates the potential for exploiting time-scale based methods for the further reduction of species. However, the application of the QSSA required the solution of complex algebraic expressions that limited its usefulness for highly coupled QSSA species. In the present study, a dimensional analysis of the skeletal scheme was performed by a linear perturbation analysis, following the approach of Lowe and Tomlin (2000). This approach considers the eigenvalues of the system Jacobian, allowing the presence of slow, intermediate and rapidly equilibrating variables to be determined. The distance of reaction trajectories from potential underlying low-dimensional or slow manifolds are calculated (Tomlin et al. 2001; Maas and Pope, 1992). If a variable is found to be close to the manifold it can be considered as no longer contributing to the long term dynamics of system since it has locally equilibrated with respect to the slow variables within the manifold. Further, if a variable is found to be a slow mode, identified by the existence of near zero eigenvalues, this mode can be considered redundant as it does not contribute to the immediate behaviour of the system. Using this approach, all but five modes were found to collapse onto a lower dimensional manifold or have near zero eigenvalues, and hence the total number of variables required to represent the long term dynamics of the system was five.

The model used was that of a simple closed vessel reactor, with perfect mixing. The time variable of this model can be directly correlated to the distance down a plug flow reactor tube by the residence time. Heat transfer from the vessel wall was evaluated using a simple analytical solution. Operator splitting methods were employed to solve the chemical kinetic and flow and heat transfer steps alternately, with a sufficiently small time-step producing a solution to the combined perturbation of the two. The use of operator splitting facilitates the replacement of the ordinary differential equations describing the chemical time-step with the repro-model.

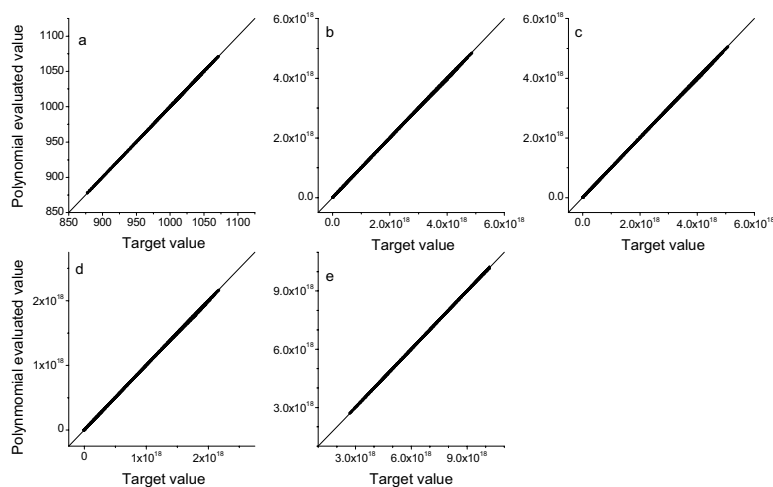


Figure 1. Results of the polynomial fits for the time stepping variables, where *a* is temperature, *b*: CH_4 , *c*: C_2H_4 , *d*: C_3H_6 , *e*: C_3H_8 , and where the scale is temperature (K) for *a*, and concentration (molecules) for all others.

3. Constructing the Repro-Model

The construction of a repro-model consisted of performing a number of example calculations in order to generate data describing the behaviour of the system. A functional fit or tabulation is then created from these data that can be used to describe chemical change over a time-step. The functional fit or interpolated solution is used in place of a usually stiff system of differential equations to obtain the state of the system at a small time Δt later considerably more efficiently. In this instance, each variable in the model is defined by a polynomial of between second and fifth order, with 5 input variables producing a concentration at $t + \Delta t$ with fewer than 25 terms.

To generate the fit, a data set is required containing concentrations of each of the time stepping variables, separated by a small time Δt . This should represent changes due to the chemical effects within the system only. Calculations were performed at a variety of operating conditions and at each time point the current values of the repro-model variables were compared with those already present in the data set by means of a Euclidean distance. Data 'further away' from existing data, as defined by a distance greater than a user defined tolerance, were added to the fitting data. This data set was then used to construct a polynomial for each variable in the skeletal scheme. For the time stepping repro-model variables, each polynomial will, given the concentration of the five input variables at any time t , evaluate a new concentration for this variable at a time Δt later. For the remaining variables, polynomials were developed that, given the concentration at any time of the time stepping variables, evaluate the concentration of each of the remaining variables at this time. Although the selection of the five key repro-modelling variables is relatively arbitrary, some choices are better than others in terms of the success of the fits. Obvious choices are those of the main reactants and products. In this example the five time-stepping variables were the reactant, C_3H_8 , and

the main products; C_2H_4 , C_3H_6 and CH_4 , plus the gas temperature. The concentrations of all other variables were reconstructed from these five variables as described above.

The polynomials were constructed as orthonormal monomials using a least squares fitting technique and then converted into Horner polynomial form for ease of storage and computation, as described by Turanyi (1994). The maximum order imposed was six, although polynomials of maximum 2nd order, with fewer than 10 terms, were required to generate fits for the time stepping variables with local errors of less than 0.2 percent over all times and compositions considered. Examples of the fitting results can be seen in Figure 1. For the mass reconstruction variables, polynomials of up to 5th order were used with fewer than 25 terms with comparable errors.

In order to use these polynomials in place of the kinetic equations the following procedure was applied, as demonstrated in the flow chart provided (Figure 2). The initial total mass was computed by summing the species concentrations multiplied by their corresponding molar masses. This quantity was then stored for use in the mass correction step. Any non-chemical kinetic perturbations were then applied to the system; such as the change in temperature caused by heat exchange between the gas and the reactor wall. The repro-model polynomials were then evaluated, which produced the uncorrected new species concentrations for the time stepping variables, and in this case temperature. From these values the mass reconstruction polynomials were evaluated providing concentrations for all species in the system, and the new total mass was then easily computed and compared to the initial total mass. A scaling correction was subsequently applied to all species in order equalise total mass with the initial total mass. Although this correction was often very small, typically within 0.2%, the results show that this can contribute significantly to the overall performance of the model.

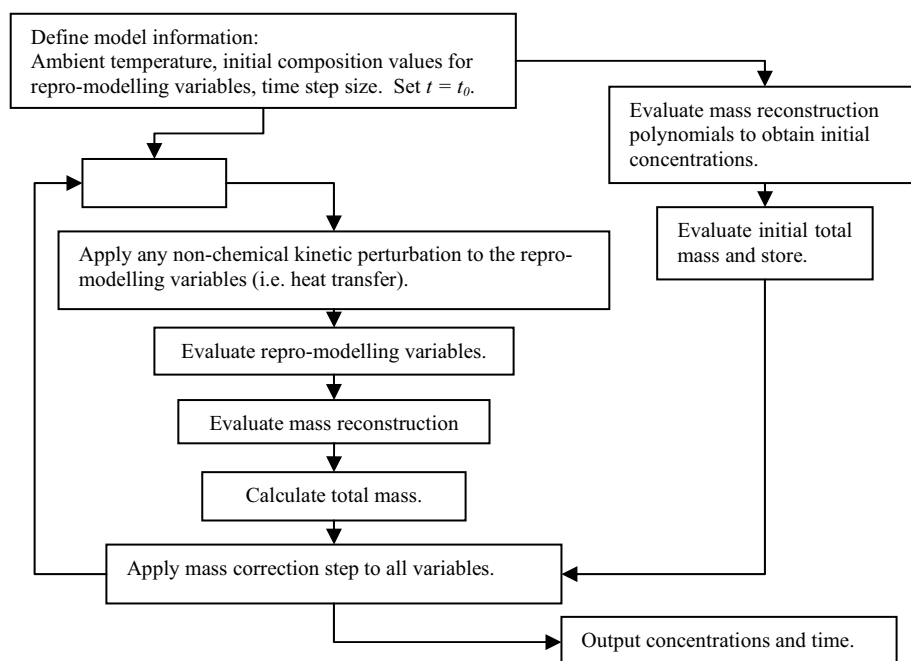


Figure 2. Flow chart showing the implementation of the mass correction procedure.

4. Results and Discussion

Application of this approach without the mass correction step demonstrates its importance. Figure 1 shows the performance of the polynomial fitting, displaying the impressive local accuracy of these low order polynomials in this application. However, without the conservation of mass, as the simulation proceeds, these small local errors build up and lead to spurious global results (Figure 3). Initially there is an unrealistic production of propane, and as the simulation progresses the errors lead to the system suddenly ‘blowing up’. The implementation of the mass correction step brings these results in line with those of the differential equation solution (Figure 4). Preliminary studies suggest that where the accuracy of the polynomial fits increased, either through increasing the order of, or the number of terms in the polynomials, or by partitioning the fitting data, trajectories could be computed without the divergent effects seen here. However, the use of mass reconstruction polynomials reduces the need to explore such complex options, whilst simultaneously conserving estimated total mass and providing concentration information for all species at all times.

The second purpose of the mass reconstruction polynomials is to provide the ‘lost’ information on the concentrations of the non-time stepping variables. Figure 4 shows the impressive ability of this approach to reproduce the concentrations of non-time stepping species in the system, whilst only actually advancing in time with five variables. This would make the incorporation of a more realistic model for the non-chemical kinetics considerably computationally more efficient. In fact, the time taken to compute a typical run for the simplified model described using this method is approximately 140 times faster than solving the corresponding differential equation system with the SPRINT (Berzins and Fuzland, 1985) integration package.

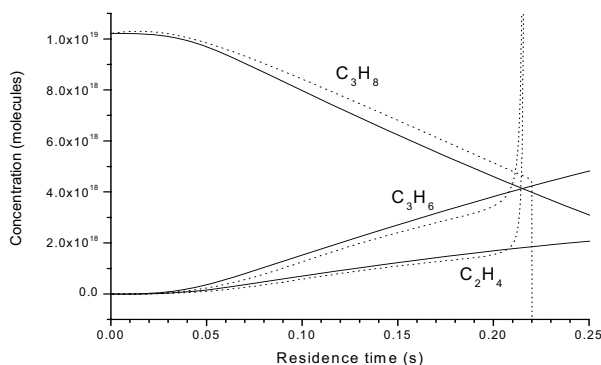


Figure 3. Propane cracking at 1450K, 1 atm. Solid lines: ODE solution of skeletal scheme, dotted lines: polynomial repro-model without mass correction.

4. Conclusions and Future Work

This paper has demonstrated the advantage of maintaining mass conservation within the repro-modelling approach. The unchecked progress of the system without monitoring

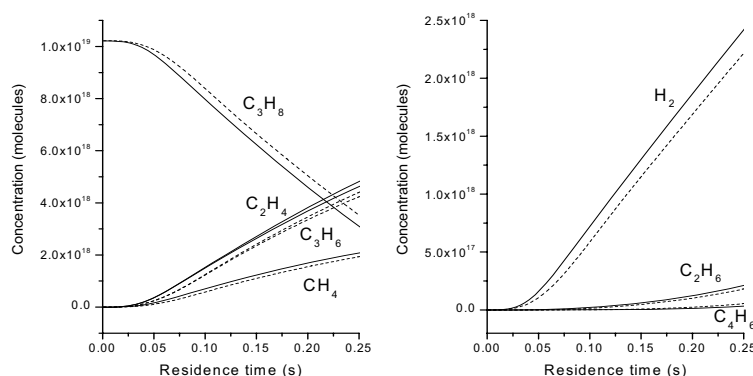


Figure 4. Propane cracking at 1450K, 1 atm. Solid lines: ODE solution of skeletal scheme, dash lines: polynomial re-pro-model. Left hand side time stepping variables, right hand side selection of mass reconstruction variables.

and correcting for any small gains or losses in total mass can lead to the growth of global errors which, despite small local fitting errors, can in some cases lead to unrealistic and unacceptable predictions. The development of species reconstruction polynomials that can estimate the concentration of all remaining species in the system from the key re-pro-model variables has allowed two actions. Firstly, the user is now able to describe the progress of all variables in the system, whilst only having to carry the re-pro-modelling variables over any non-chemical kinetic time steps within an operator splitting environment. Secondly, using these reconstructed concentrations the application of a small correction scaling enables the present total mass to be brought in line with an initial control mass. This correction, whilst small, improves the behaviour of the model considerably and prevents spurious and unrealistic results.

Further use of this method in complex fluid dynamic calculations is warranted. The polynomials and mass correction approach described have already been used to model a plug flow reactor, simulated as a series of continuously stirred tank reactors, with encouraging results, thereby demonstrating the robustness of the approach.

References

- Berzins, M. and R.M. Furzland, 1985, Shell Research Ltd., TNER 85058.
 Blasco, J.A., N. Fueyo, C. Dopazo and C. Ballester, 1998, *Combust. Flame* 113, 387.
 Dente, M.E. and E.M. Ranzi, 1983, in *Pyrolysis: Theory and Industrial Practice*, Academic Press, New York (Eds. Albright, L.F., B.L. Crynes and W.H. Corcoran).
 Lowe, R.M. and A.S. Tomlin, 2000, *Environ. Modelling and Software* 15, 611.
 Maas, U. and S.B. Pope, 1992, *Combust. Flame* 88, 239.
 Pope, S.B., 1997, *Combust. Theory Modelling* 1, 14.
 Tomlin, A.S., M.J. Pilling, J.H. Merkin, N. Burgess and A. Gough, 1995, *Ind. Eng. Chem. Res.* 34, 3749.
 Tomlin, A.S., L. Whitehouse, R. Lowe and M.J. Pilling, 2001, *Faraday Discuss.*, 118.
 Tonse, S.R., N.W. Moriarty, N.J. Brown and M. Frenklach, 1999, *Israel J. Chemistry* 39, 97.
 Turanyi, T., 1994, *Computers Chem.* 18, 45.

Acknowledgements

The authors wish to thank the EPSRC for their financial support of the work described.