

Reduction of reaction mechanisms on the basis of the repro-modelling approach

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1. Reducing chemical kinetics - the repro-modelling approach

Modern experimental techniques of chemical kinetics provide more and more information about elementary reactions. Information about the stoichiometry of reactions (product channels and branching ratios), temperature and pressure dependence of reaction rates are stored in published data evaluations and computational databases. Also, modern theoretical methods allow the prediction of rate expressions for many experimentally inaccessible reactions. Consequently, modellers can easily construct reaction mechanisms of several hundred or thousand reaction steps. The expected developments in this field include the production of increasingly large and complex reaction mechanisms.

However, chemical kinetic modelling has many practical applications and reaction mechanisms are expected to be used in laminar and turbulent computational fluid dynamic (CFD) calculations. Many techniques have been invented to transform detailed chemical mechanisms to computationally more efficient forms. A short description of all these methods is given in a recent review [1], which includes 248 references to other papers.

Detection and elimination of all redundant species and reactions [2] is very important for the chemical interpretation of reaction processes, but may increase the simulation speed only up to a factor of ten. The most effective methods for reducing computational effort are all based on time-scale separation in chemical kinetic systems. Loosely speaking, time-scale separation means that some reactions in the mechanism are much faster than others and consequently the concentration of some species can always be expressed as an algebraic function of the concentration of the others. This phenomenon has long been known in chemical kinetics as the quasi-steady-state approximation (QSSA) [3] and partial equilibrium assumption. The classical utilization of time-scales was based on the assumption that some species were in quasi-steady-state and some reactions in partial equilibrium. A reduced model was generated and the assumptions were checked by comparing the simulation results using the full and reduced mechanisms.

The computational singular perturbation (CSP) method [4] can directly detect the QSSA species and fast equilibria via an analysis of the Jacobian matrix of the kinetic ODEs. The intrinsic low dimensional manifold (ILDM) approach [5] allows the detection and parameterization of the manifolds in composition space. This manifold theory is a generalization of the QSSA and the manifolds can be used in tabulated or fitted form in CFD calculations. Here we should like to present an alternative approach, called repro-modelling, that is also based on the time-scale separation in chemical kinetic systems.

The repro-modelling technique (the version we use) consists of the following steps:

- (i) Several hundred or thousand chemical kinetic simulations are carried out using a detailed reaction mechanism. The conditions and parameters of the simulations are selected in such a way that they cover the parameter region of the later CFD calculations. Results of the calculations are recorded in a database.
- (ii) Results in the database are fitted with simple algebraic functions (e.g. polynomials). The requirement is fitting several ten thousand data points within an accuracy of about 1%.
- (iii) During the CFD calculations these algebraic functions are used for the evaluation of the chemical source term, which is several thousand times faster than the solution of the kinetic ODEs during the CFD calculations.

Repro-modelling can be applied for any system where the number of variables of the ODEs is identical to the number of variables of the fitted explicit functions. However, for systems with significant time-scale separation, the real dimension of the system is quickly reduced and the system can be fully characterized by a few variables only. Fitting the functions to slightly relaxed systems (*i.e.* after the induction period has expired) allows the parameterization of big mechanisms with only few-variable algebraic functions.

Repro-modelling (maybe under different names) has been used in many fields where dynamical systems with very different time-scales are simulated. In chemistry, repro-modelling has been applied in atmospheric chemistry [6], [7], [8], and for the simulation of the Belousov-Zhabotinsky reaction [9], CO ignition [10], and turbulent $H_2/CO_2/O_2$ flames [11]. Here we are going to illustrate the method on two other examples, the simulation of the spread of shock waves in hydrogen-oxygen mixtures, and the ignition of alkane-air mixtures due to compression.

2. Simulation of shock-induced hydrogen combustion

Shock induced combustion of H_2/O_2 mixtures was simulated by Clifford et al. [12]. The model described the spread of shock waves in stoichiometric hydrogen-oxygen mixtures diluted by argon. When a shock wave reaches a combustible mixture, for a while very little energy is released (induction period), followed by a shorter period when most of the chemical energy is released and the system variables change rapidly. The induction parameter models (IPM) parameterize the induction time as a function of initial temperature and pressure. Clifford et al. constructed an induction parameter model that incorporated a repro-model for the description of the energy release phase. This is a useful matching of two techniques, because a few-parameter repro-model alone would not be able to describe the induction period. Note, that since induction times were also parameterized on the basis of homogeneous calculations, the IPM can also be considered to be a special repro-model.

In the model of Clifford et al., the actual state of the mixture at any point during the energy release phase was described by three variables: temperature T , density ρ , and reaction progress variable β . The latter was defined as the ratio of the energy released up to a particular point in time, and the total energy that can be released by a complete reaction. As a first step, a homogeneous mixture was simulated at many different conditions. The combustion reaction was described by a validated detailed mechanism of 9 species and 46 reactions. The initial pressure was varied from 0.5 atm to 10 atm and the initial temperature from 1100 K to 3000 K, relevant to the ranges of shock-induced combustion. Over 4000 initial conditions were used and the generation of the database took 4 hours on a desktop workstation using the program SENKIN. Each line of the database included the present state of the system in terms of the above three

variables and the state of the system after 5×10^{-8} s, which was the chosen time-step of the simulations.

The database for the behaviour of homogeneous mixtures was fitted by orthonormal polynomials. This method [7] is based on the fact that using Gram-Schmidt orthonormalization, a set of linearly independent functions (like monomials of a general m -variable polynomial) can be transformed to a series of functions that are orthonormal on the set of input data. The following definition of scalar product is used:

$$(\varphi_j, \varphi_k) = \sum_{i=1}^n w_i \varphi_j(\mathbf{x}^i) \varphi_k(\mathbf{x}^i)$$

where \mathbf{x}^i , $i=1, \dots, n$ denote the set of data, n is the number of data, φ_j and φ_k are two $R^m \rightarrow R$ functions and w_i is the weighting.

On the basis of the generated orthonormal functions, the input data can be approximated by a generalized Fourier series:

$$F \approx \sum_{j=1}^l (F, \varphi_j) \varphi_j$$

At the generation of the Fourier series only the efficient members are used, that is members that improve considerably the agreement between the input data and the approximation. In most cases this procedure gave a good approximation [2, 3] using a series with only few members. Finally, the orthonormal polynomials were converted to 'usual' polynomials, which can be efficiently evaluated using a generalized Horner arrangement.

The fitted polynomials constitute a set of difference equations and its solution can be directly compared to the solution of kinetic ODEs. In Figure 1, the solid lines show the SENKIN solution of the detailed mechanism and the dashed line represents the repro-model solution. A similar good agreement was found for all other initial conditions checked and the solution of the repro-model was 1500 times faster than that of the detailed mechanism. This ratio would be even higher if a larger molecule fuel was used instead of hydrogen, the chemically simplest fuel.

A series of one-dimensional reflected shock simulations were carried out for a variety of Mach numbers and in each case the results were similar for the detailed chemical mechanism and the repro-model. The transition to detonation and the propagation of the detonation wave was also well reproduced by the repro-model.

Finally, two-dimensional simulations of shock interactions with a rectangular obstacle were also carried out. The geometry chosen allowed a direct comparison with available experimental data. Results of the simulation with the repro-model is given in Figure 2.

There is a very good qualitative agreement between the simulated temperature contours and the experimental Schlieren photographs. This 2D modelling study was also carried out using the detailed chemical mechanism. The results are almost identical to that of the repro-model, but the simulation with the detailed mechanism required about 80 times more CPU time.

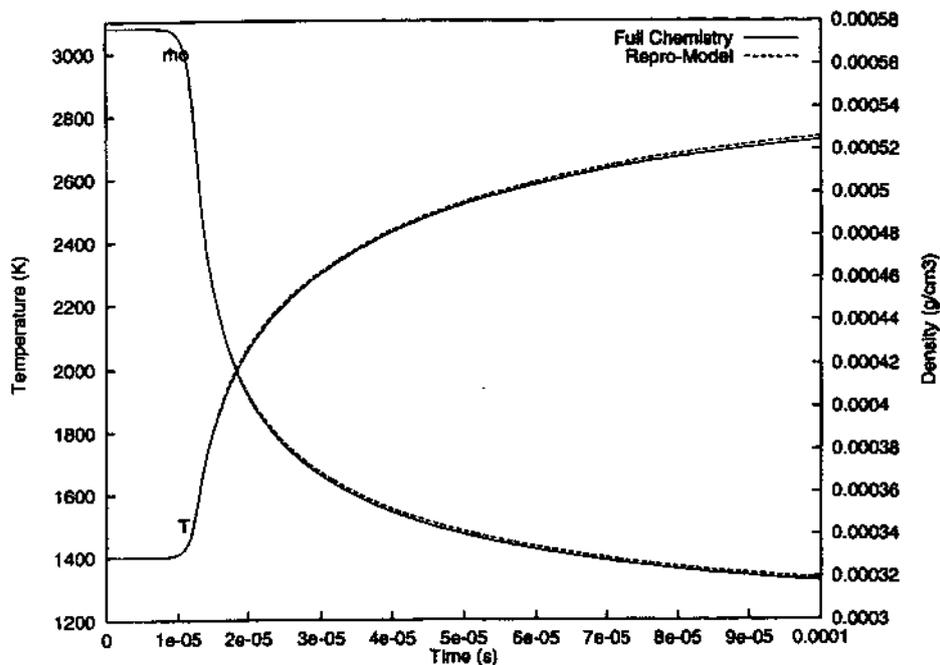


Figure 1. Evolution of temperature and density in time in a spatially homogeneous hydrogen explosion, simulated using the full chemical mechanism and the repro-model. In this case the initial pressure was 2.1 atm and the initial temperature was 1400 K.

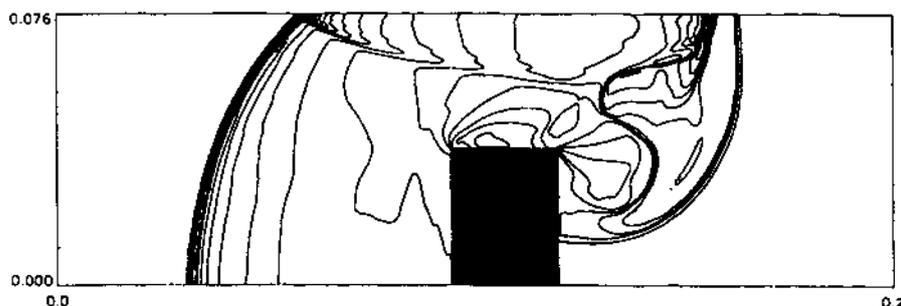


Figure 2. Simulated temperature contours in the 2D system after 80 μ s simulation time. The speed of the shock wave is 2.49 Mach. All chemical changes in the system were described by the repro-model.

3. Simulation of heat release in compressed alkane-air bubbles

During the manufacture of propellants, high pressure is used to move the propellant dough through the preparation system. The dough usually incorporates small voids, which are filled with lean alkane-air mixtures. The compression heat raises the temperature of the gas bubbles and the starting oxidation of the alkane produces extra heat. In fortunate cases, cooling of the gas through the wall of the bubble keeps the temperature low. However, there is a hazard potential in that the compression heat may initiate fast combustion of the alkane and the resultant high temperature may ignite the propellant itself.

Braithwaite et al. [13] have analyzed the problem using a detailed numerical description. In their model each bubble is effectively isolated and therefore it is sufficient to consider a single bubble. The bubble is always spherical during the compression. In a typical situation, pressure reaches 50 atm in 7 seconds. In their 1D model the temperature of the gas is calculated as a function of time and distance from the centre. In the basic model, heat is generated by compression only and it is conducted through the gas layers and finally through the wall of the bubble. In the second model of Braithwaite et al. [13], a one-step $\text{RH} + \text{O}_2 \rightarrow \text{products}$ chemical reaction is assumed. The rate of the reaction is described by a single Arrhenius expression. In both cases the gas is the hottest in the centre and its temperature is close to that of the bulk near the wall.

Büki et al. [14] developed further the above model by applying realistic chemistry on the basis of the repro-modelling approach. First, many heat release-pressure curves were calculated using a detailed mechanism within a spatially homogeneous model, assuming various fuel-to-air ratios ϕ_0 and heat loss coefficients α during the compression. These data cover all possible situations that are present in any part of a bubble during the compression. A database was formed which was used in all subsequent calculations.

The oxidation of alkane was simulated using the chemical kinetic model of 37 species and 108 reactions by Griffiths et al. [15] for combustion of normal heptane. The reactions are explicit for the smaller species (up to C_3) and are lumped for the other organic molecules and radicals. The rapid compression machine program of John Griffiths and Kevin Hughes was used for the simulation of the time history of compressed spatially homogeneous bubbles. The program was modified in such a way that heat loss occurred during the slow compression and the compression lasted till the end of simulation.

The simulations demonstrated that the temperature increases in two steps. Figure 3 shows the temperature-time history of a compressed bubble (fuel-to-air ratio is 0.2, adiabatic case) and the concentration-time curves of the major species. During the oxidation process, only heptane (RH), CO, C_2H_4 , C_3H_6 , and H_2O_2 have a higher mole fraction than 0.001. There is very little change until about 5 s, while the compression heat continuously increases the temperature of the mixture. Then, there is a sudden temperature jump near 570 K, which corresponds to the oxidative pyrolysis of the alkane ('cool flame'). The alkane content of the mixture is totally consumed very rapidly at that temperature, and CO, C_2H_4 , C_3H_6 , and H_2O_2 appear. There is a second temperature jump near 860 K, caused by the oxidation of olefins. In Figure 4, the chemical heat release is plotted against time. The two sharp heat release peaks are associated with the two-stage ignition process. There is also some heat release after each main peak due to the oxidation of CO. A rate-of-production analysis was also carried out to explore the chemical processes in the system.

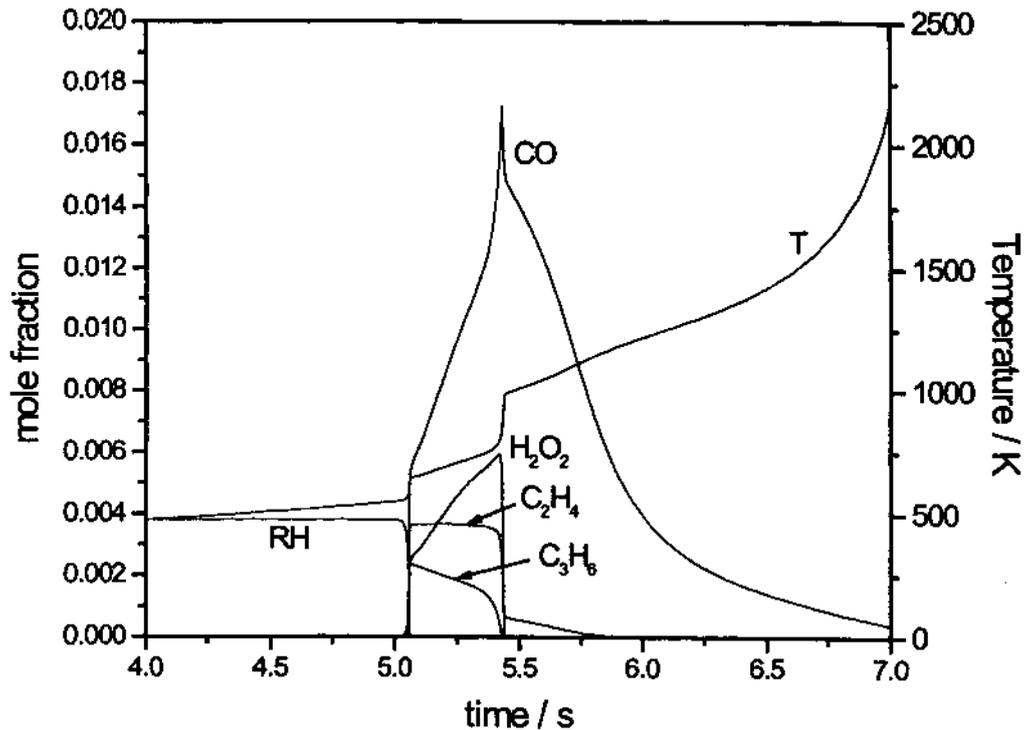


Figure 3. Concentration-time profiles of the major species during the compression of a lean heptane-air mixture.

The 1D model on the heat distribution in compressed bubbles required the following three types of information from the chemical submodel: (i) Amount of chemical heat release at any point of the bubble during compression. (ii) Change of the number of moles of the gas mixture during compression. (iii) Heat effect of the fuel diffusion towards the hot region.

(i) Repro-model for the chemical heat release

The basic database contained the rate of chemical heat release dq/dt as a function of pressure p , temperature T , and initial heptane content ϕ_0 . The known compression rate means that pressure is a known function of time. First, dq/dt was fitted as a function of p , T , and ϕ_0 , but the later integration of dq/dt was found to magnify the errors of fitting. Therefore an alternative route was applied, when the chemical heat release rate was integrated first. This chemical heat release and the compression heat together account for the total heat generation in the bubble. An expression was fitted to describe the integrated chemical heat as a function of p , T , and ϕ_0 . Figure 5 compares the chemical heat release calculated from the detailed mechanism and the repro-model approximation. A similar good agreement was found for a wide range of conditions.

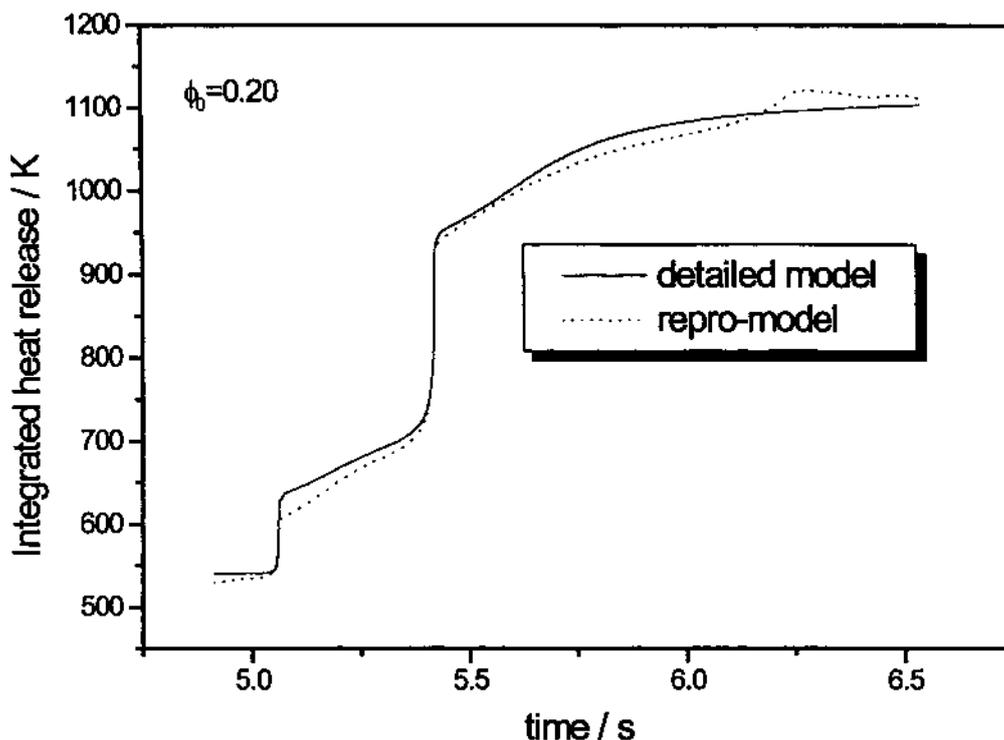


Figure 5. Integrated temperature curves on the basis of ODE solution and using fitted model

(iii) *Repro-model for the heat effect of fuel diffusion*

The rate of chemical heat release depends on the actual temperature and the concentration of the fuel. In a fresh mixture the fuel concentration is determined by the alkane content, but in the aged mixture the fuel consists of mainly olefins and carbon-monoxide. The bubble always has a higher temperature than its surroundings, therefore the direction of heat flux is always outwards, and the temperature in the middle of the bubble is always higher than at the boundary. No similar simple rule can be provided for fuel diffusion. The increase in pressure may induce a condensation of hydrocarbon on the wall of the void at low temperatures ($T < 570\text{K}$). At higher temperatures ($T > 570\text{K}$) the alkane has been converted to high boiling point species, like C_2H_4 , C_3H_6 , and CO ; and these species cannot condense on the near room temperature wall. As the temperature of the gas increases, alkane may evaporate from the wall and diffuse inwards. Therefore, the inward diffusion of the fuel is more likely than the opposite. Also, it can be shown that only the inward diffusion of the fuel contributes to the chemical heat release. Let us suppose that some partially burned fuel from the centre of the bubble gets closer to the boundary by diffusion. It is obvious that this change will not lead to any heat effects, because the decomposed material arrives at a lower temperature region where no further decomposition or other chemical change can occur. On the other hand, if fuel diffuses into the centre, it arrives at a high temperature region and it will burn, causing additional heat release.

Chemical heat release can be easily calculated during homogeneous simulations. It could be assumed that a diffusion related effect would need the application of a reaction-diffusion model. However, a postprocessing of the basic database can provide an estimation on extra heat release

caused by the inward fuel diffusion. From now on, φ denotes the fuel content of the gas at a given location as alkane equivalent, disregarding the actual chemical composition of the fuel.

The heat effect of diffusion can be approximated from the partial derivative of the heat release function with respect to the mole fraction of the fuel. In order to determine this partial derivative, we have used a local linear approximation using the points of the basic database. Let us denote a given point of the database by $(T^0, P^0, \phi^0, \alpha^0)$, where T denotes temperature, p pressure, ϕ fuel mole fraction, and α heat loss coefficient. The surrounding points close enough to it can be approximated by a hyperplane passing through this point:

$$T - T^0 = d_p(P - P^0) + d_\phi(\phi - \phi^0) + d_\alpha(\alpha - \alpha^0)$$

In this equation the coefficients denoted by letters d are approximations of the partial derivatives, from which only d_ϕ is important in this case. In order to determine them, deviations of surrounding points from the hyperplane were calculated, and the sum of these deviations was minimised by fitting coefficients d_i . In this way the tangent plane of a curved hypersurface is determined. If points too far from the nominal points are considered, nonlinearity may distort the calculation of the hyperplane. If the nearest points are considered only, numerical problems may arise. To overcome this problem, reciprocal distances from the central point were used as weights. This way points apart from the centre will play less role in the fitting of the plane, than closer ones.

The calculated coefficients, attached to each line of the basic database, formed a secondary database. A fitted expression was derived, that describes coefficient d_ϕ as a function of T , p , and ϕ . During the 1D bubble calculations, the heat effect of fuel diffusion can be calculated as a product of d_ϕ and the inward flux of the fuel at any local value of T , p , and ϕ .

In all the above three cases the MARS algorithm [16] was used for the generation of the approximating function. The MARS algorithm is a new multivariate fitting method, a successor of the recursive partitioning method. The latter is based on dividing the multidimensional database into smaller subregions in which it can be approximated by simple functions. As a first step of fitting, MARS does the same: finds the points at every axes, where the most significant (most abrupt) changes take place in the dependent variable, and places 'knots' at these points. There can be more than one point on a given axis, and the subregions bordered by them can be nested into each other. Parallel with the generation of knots, MARS produces a set a basis functions by multiplying truncated power basis functions centred around the knots. When a new knot is found on an axis, MARS generates the proper truncated power function around it, and multiplies it with each basis function that contains the given variable. At the same time, the parent basis functions also remain in the set, the size of which is determined by the maximal number of knots allowed. In the last step, MARS determines coefficients for all basis functions by a least squares method, discards the least significant ones, and in the remaining basis functions replaces truncated power functions by piecewise cubic functions. This latter step must be performed in order for the fitted function to be smooth, that is its first derivative be continuous. The results of the MARS fitting can be easily inserted to any FORTRAN simulation program.

Simulations of heat distribution using the 1D bubble model with the repro-modelling description of chemistry are in progress.

4. Conclusions

Detailed chemical mechanisms incorporate a huge amount of chemical knowledge, but practical simulations use only a fraction of this information. It is therefore possible to construct small mathematical models, that include all information necessary for CFD calculations. All methods that offer a significant reduction in computer time are based on the time-scale separation in chemical kinetic systems. These methods include the direct application of QSSA, the CSP and ILDM methods. Repro-modelling is another technique based on this time-scale separation, that can be used for the production of compact reduced models and provides accurate agreement with the original detailed chemical model.

Creation of a repro-model includes several thousand spatially homogeneous simulations of the detailed chemical mechanism at the conditions of the future use of the reduced model. The simulation results are stored in a database and are fitted with empirical functions. These empirical functions can be used in the CFD model for modelling the chemical source term. Several chemical systems have been parameterized in this way and usually simulation of homogeneous systems is about 1000 times faster. This leads to about one hundred times calculation speed increase in the application of the CFD code. The agreement between the simulation results using the detailed chemical mechanism and that of the repro-model was within a few percent in all cases.

The method is illustrated here by two recent applications. A series of 1D and 2D simulations of shock-induced hydrogen combustion [12] were carried out using a detailed chemical mechanism and a repro-model. In this case the original system of kinetic ODEs was transformed to a three-variable system of difference equations. Very good agreement was found between the experimental results and the simulations with either detailed chemistry or the repro-model. However, a comprehensive numerical study of the 2D model is feasible only using the repro-model version. Studying an industrial safety problem, local chemical heat generation was described [14] by a repro-model in compressed bubbles containing lean alkane-air mixtures. The repro-model captured with high accuracy the complex two-stage ignition phenomenon and provided all information required for a 1D model of heat and fuel diffusion.

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