

APPLICATION OF REPRO-MODELING FOR THE REDUCTION OF COMBUSTION MECHANISMS

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The basic problem of mechanism reduction methods is to find functional relationships between selected state variables (e.g., some concentrations and temperature) and their rates. However, this information is present during the simulations with the full chemical model.

As a new application of the repro-modeling approach, information for rates is extracted from detailed chemical calculations and stored in the form of high-order multivariate polynomials. For an efficient utilization of the polynomials, a computer program was written that rearranges them to the form of multivariate Horner equations. The repro-modeling method is an alternative to the application of the quasi-steady-state approximation (QSSA) and of the low-dimensional manifold method. Pros and cons of these three methods are discussed in detail considering the preparations required, the accuracy attainable, the yield in computer time, and the limitations of the techniques.

Simulations of the combustion of wet CO using two-variable and three-variable repro-models were 24,000 and 11,700 times faster, respectively, than the SENKIN calculation using the full model. These calculations represent the first use of repro-modeling for combustion mechanism reduction.

Introduction

Due to rapid progress in the research of elementary gas reactions, more and more information has become available for the rate coefficients and stoichiometry of reaction steps. When these data are incorporated into detailed models, the mechanisms obtained reproduce the ignition times and species profiles of flames with fair accuracy for most practically important fuels. These mechanisms typically contain 20–50 species and 70–200 reactions. Applying detailed chemistry, the calculation of spatially homogeneous systems and one-dimensional flames is straightforward using generally available hardware and software, while calculation of two-dimensional laminar flames requires several hundred hours of supercomputer time and the simulation of three-dimensional deflagrations is not possible. Also, it is still impossible to do turbulent flame calculations with detailed chemistry.

The elimination of redundant species and redundant reactions from detailed mechanisms may speed up the calculations by a factor of 10 [1], but it is still not enough in most cases.

Fortunately, in chemical kinetic systems, the chemical changes span very diverse timescales. Starting with arbitrary initial conditions in composition space, the concentration of fast variables (i.e., QSSA species) is determined soon by the concentration of slow variables (non-QSSA species). Although this behavior of chemical systems was observed very early

[2], the basis of this phenomenon was frequently misinterpreted (see Ref. 3 for a brief history of QSSA).

Three methods are available for the identification of fast variables. According to a “chemical” rule, a QSSA species has a low net production rate compared to its production and consumption reaction rates [4]. The “mathematical” methods are based on the eigenvalue analysis of the Jacobian of the kinetic ordinary differential equations (ODEs). The method of computational singular perturbation (CSP) [5,6] provides a list of fast variables (called CSP radicals). Recently, a method was published [3] for the identification of QSSA species and for the calculation of QSSA errors. According to this article, the error of a QSSA species is equal to the product of its lifetime and net production rate.

After a transition time, concentration changes in a chemical system are determined by $n = n_t - n_f - n_c$ variables, where n_t is the total number of state variables (e.g., concentrations and temperature), n_f is the number of fast variables, and n_c is the number of conservation equations such as atomic conservation relations.

Having selected this minimal number of variables, the next step is to correlate their values to their rates, allowing the simulation of a system containing only n variables. Two basically different methods have been proposed for the calculation of such relations:

1. Quasi-steady-state approximation: In each step of the simulation, the concentrations of QSSA species are calculated from the concentrations of

- non-QSSA species, and the production rates of non-QSSA species are calculated using the original system of kinetic ODEs.
- The intrinsic low-dimensional manifold method [7,8]: n variables are selected, and the values of other variables are determined on the basis of the Jacobian. Production rates for the n variables are calculated using the original system of kinetic ODEs in each point of an n -dimensional grid and tabulated. In each step of the solution of kinetic ODEs, the nearest values in the table are looked up, and the production rates are estimated using multilinear regression.

In this paper, a third method is described for the generation of reduced models, which is also based on the existence of diverse timescales in chemical kinetic models:

- Repro-modeling: Several hundred simulations of the original mechanism are carried out, and the values of n variables and the rate information corresponding to these variables are collected. The data are fitted using high-order multivariate polynomials. Then, in each step of the simulation, these polynomials are evaluated.

The Repro-Modeling Approach

Very frequently, complex computational models have CPU time-consuming submodels, which may be used several million times during a single simulation. The input of such submodels usually covers a well-defined region. Based on several thousand simulations with typical input data, the input-output relations of the submodel can be approximated by explicit empirical equations. This approach is called repro-modeling [9] and was successfully applied to, for example, the modeling of freeway control. As the evaluation of explicit equations is much faster than the simulation of the submodel, the simulation of the original model can be sped up significantly.

Models of reactive flows have a similar structure, as the calculation of chemical rates is a very time-consuming submodel of the transport model. The spread of air pollution is one of the applications of reactive flow models, and repro-modeling has been applied to atmospheric chemical problems [10–12]. Repro-modeling has also been applied to a liquid-phase chemical reaction [13]. A similar approach was used for the modeling of electronic circuits [14].

The approximating empirical function has to be simple for a fast evaluation and flexible to mimic well the submodel. Continuous piecewise linear functions [9], second order polynomials [10,11], and high-order polynomials, evaluated in Horner form, [12,13] have been successfully used.

Application of Repro-modeling for Combustion Simulations

Reactive flow problems can be characterized by the following system of partial differential equations deduced from the conservation equations:

$$d\mathbf{U}/dt = A(\mathbf{U}) + B(\mathbf{U}) \quad (1)$$

where \mathbf{U} is the vector of state variables (e.g., species mass fractions, temperature, density, and velocity field), A is the rate of state variables due to transport (advection and diffusion), and B is the rate of state variables due to chemical reaction. Inputs of function B are the temperature and the species concentrations and the output is their rates.

While Eq. (1) has a simple form, it is difficult in most cases to solve it numerically. In the case of two- and three-dimensional systems, the method of operator splitting is common for the solution of Eq. (1). Using this method, the changes of state variables during time interval Δt are calculated from

$$\mathbf{U}(t + \Delta t) - \mathbf{U}(t) = T(\mathbf{U}, \Delta t)C(\mathbf{U}, \Delta t) \quad (2)$$

where T is the operator of changes of state variables due to transport and C is the operator of changes of concentrations and temperature due to chemical reaction. The inputs of operator C are the concentrations and temperature at time t and the outputs are the same variables time Δt later. It has been shown that the method of operator splitting is well applicable for the calculation of deflagrations (see Ref. 15 and citations therein). Operator C is also well applicable in turbulent flame calculations using the probability density function (PDF) approach (see e.g., Ref. 16).

The concentrations of all those species have to be calculated by Eq. (1), which are interesting for the purposes of the simulation. The chemical term B usually determines other species, which have an influence on the concentration of important species (and temperature) and which have to be calculated as well. The fewer chemical substances considered, the faster the calculation of transport. The chemical term is also the source of another problem. The chemical equations are usually very stiff, and therefore, a small time step has to be used for the solution of Eq. (1), even if the accuracy and stability of transport equation allowed a longer time step. This problem is eliminated when the operator-splitting method is used, but evaluation of operator C is time-consuming due to the stiffness of the kinetic equations.

The repro-modeling technique can be used for the calculation of both chemical rates B and operator C . The repro-model uses the minimal number of state variables, which influence the selected state variables. Creation of the repro-model starts with the

creation of a big table, which consists of some selected state variables and information about their rates. The procedure can be summarized by the following steps.

Tabulation of Variable Value-Rate Relationships

Due to the existence of diverse timescales and conservation relations, chemical changes in a longer timescale have much less degree of freedom than the number of species. As a first guess, $n = n_t - n_f - n_c$, slow variables have to be selected from the state variables. Since some of the slow variables may be redundant in the original chemical mechanism, the final repro-model may contain even less variables. A good fit can be obtained if the repro-model has equal to or more variables than the degree of freedom of the mechanism. This provides a suggestion for the degree of freedom in an indirect way. However, a repro-model with less variables is not senseless since the error induced by the inadequate number of variables is minimized as a consequence of the least-squares fit.

Proper preparation of the table is the crucial step of repro-modelling. Values of the selected n state variables (e.g., temperature and some concentrations) have to cover the whole region where the mechanism is intended to be used. In the case of a working reactive flow model, a possible solution is to use the model with several representative input data and record the input and output of chemical kinetic calculations, i.e., the values and rates of selected variables. If the construction of the final model is impossible, then probing the chemical mechanism with similar concentrations and temperatures can be carried out using spatially homogeneous or one-dimensional calculations. It is important that the recorded rates must belong to relaxed values of fast variables, and therefore, the rates obtained, for example, from spatially homogeneous calculations, have to be recorded only after some initial induction time.

The rate information collected may be either the time derivative of the variables or the changes of variables during time Δt . In the first case, the repro-model can be used for the calculation of chemical rates B in Eq. (1). In the second case, the repro-model is applied as chemical operator C in Eq. (2). In this case, the table has to contain the values of state variables at time t and their values Δt time later. Time interval Δt has to be chosen according to the stability and accuracy requirements of the transport calculations and to keep the error induced by the operator splitting low.

The table obtained resembles the table that is the final result of the intrinsic low-dimensional manifold method. The main difference is that the input variables do not form a grid, and therefore, a fast search

in the table is impossible. If the table is prepared carefully, it contains rate information for all regions where the repro-model is intended to be used. The table of the low-dimensional manifold method also contains information for nonrealistic combinations of state variables.

Fitting a Polynomial to the Data of the Table

If the physical model suggests some special functions, then these functions have to be used for fitting the table. In our case, there are no such "natural" functions, and any function is good, which is simple and flexible. Our choice is the application of high-order multivariate polynomials. As a general tenth-order five-variable polynomial has 3003 coefficients, application of such polynomials is only feasible if most of the parameters are set to zero, and there are at most a few dozen nonzero parameters. The fitting procedure has to be suitable for fitting a polynomial to tens of thousands of data points, determining the noneffective parameters of the polynomial and fitting the remaining parameters using the method of least squares. An algorithm, which meets these requirements, was described in detail in a recent article [13]. A series of polynomials, having a discrete orthonormal property on the input data set, is constructed and used for the least-squares approximation. Orthonormal polynomials, which do not decrease the root-mean-square error more than a predefined limit, are rejected, and only the effective orthonormal polynomials are used for the construction of the approximating polynomial. In the final step, the sum of orthonormal polynomials is converted into a single multivariate polynomial.

It is well known that the evaluation of polynomials can be made faster using appropriate factorization. In the case of a single variable, the generation of a Horner equation is straightforward. An algorithm was given in Ref. 13 for the construction of multivariate Horner equations, and a FORTRAN program was provided, which produced a FORTRAN function including the multivariate Horner equation. Evaluation of such functions is very effective on computers with scalar processors. However, this function is not easy to parallelize, and therefore, a new variant for the construction of FORTRAN functions is also used here. In this version, the powers of variables are calculated sequentially and these values are used during the calculation of monomials. While this version is less effective on scalar computers, the calculation of monomials is independent here, and therefore, it is expected to be faster on multiprocessor computers.

The set of FORTRAN functions obtained represents the reduced mechanism.

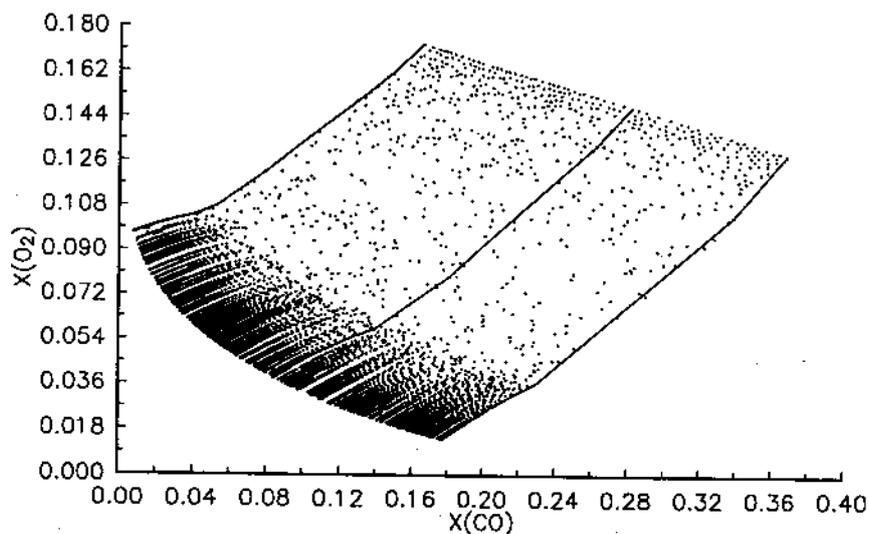


FIG. 1. Carbon monoxide-oxygen phase plane. The solid lines give the trajectories corresponding to a starting temperature of 1000 K and fuel-to-air ratios 0.5, 1.0, 1.5, respectively, until simulation time 0.01 s. The upper ends of the lines belong to the initial unburned mixture. In the case of the simulations applied for the preparation of the table, the initial composition of the mixture was uniformly distributed between $\phi = 0.5$ and 1.5. Dots represent the dependent variables CO and O₂ used in the table. Only a part of 30,000 data points are plotted on the figure for clarity.

Example: Ignition of a Wet Carbon Monoxide-Air Mixture

To promote a direct comparison with the results described in the papers by Maas and Pope [7,8], the mechanism used in those papers is used here without modification. In accordance with Ref. 7, the repro-modeled process is the ignition of a carbon monoxide-hydrogen air mixture at 1-atm constant pressure with a hydrogen-to-carbon atom mole ratio of 1:10.

Our aim was to create a repro-model that describes the combustion of wet CO at ambient temperatures between 990 and 1010 K and fuel-to-oxygen ratios from 0.5 to 1.5. The choice of these limits is arbitrary. Wider limits can also be chosen or different repro-models can be used for different regions of ambient temperature and concentrations. As Maas and Pope have successfully used tables with one and two chemical species concentrations, as a first step, two species concentrations and temperature were selected as variables of the repro-model.

All in all, 300 initial conditions, uniformly distributed within the above limits, were selected by a random number generator and used in spatially homogeneous simulations. The calculations were carried out by program SENKIN [17]. Temperature and mole fractions of CO and O₂, together with their rate information, were recorded at every 10⁻⁴ s until the final simulation time of 0.01 s. The distribution of the input variables of the table is illustrated in Fig. 1. The rate information was the values of these three variables one time step (10⁻⁴ s) later. The table contained 300 × 100 = 30,000 entries, but the rate information belonging to the initial induction time, when the concentrations of QSSA species have not reached their quasi-stationary value, was not used. Therefore, data with a temperature above 1100 K were used only, and these approximately 20,000 data were fitted by the polynomial.

Fitting fourth-order polynomials to the data took

```
function h31(y)
implicit real*8(a-h,o-z)
dimension y(*), a(22)
data a/
1.25887E+04, -9.64505E+00, -4.77828E+04, 6.51249E+01,
*-1.27202E+01, -1.73475E+04, -2.09878E+04, -8.07198E+04, 1.70698E-06,
*-2.62401E-02, 1.73978E-02, 2.16878E+01, 1.51500E+04, -1.13259E+06,
*-3.28281E-10, 3.28475E-06, -4.65053E-06, 1.36031E-03, 3.39181E+02,
* 7.03503E+04, 1.88323E+06, 3.01338E+06/
h31 = a(1)+y(3)*y(3)*a(8)+y(2)*a(3)+y(3)*a(7)+y(3)*a(14)+y(3)*
*a(22))+y(2)*a(6)+y(3)*y(3)*a(21)+y(2)*a(13)+y(3)*a(20)))+y(1)*
*a(2)+y(3)*a(5)+y(3)*a(12))+y(2)*a(4)+y(3)*y(3)*a(19))+y(1)*y(3)
*a(11)+y(2)*a(10)+y(2)*a(18))+y(1)*a(9)+y(3)*a(17)+y(2)*a(18)+
*(1)*a(15)))
return
end
```

FIG. 2. An example for a computer-generated multivariate Horner equation. The repro-model obtained consists of a set of such FORTRAN functions. This function calculates the temperature 10⁻⁴ s later, given the temperature and mole fractions of CO and O₂.

about 25 s on an IBM RISC 6000/340 workstation. For the rates of the three variables, polynomials with 22-25 nonzero parameters were fitted. The average deviations between the tabulated rates and the fitted values were below 0.26%.

The fitting program provided the powers of variables in each monomial and the corresponding coefficients. These data were converted to a FORTRAN function by the appropriate program that created multivariate Horner equations. An example for the obtained function is given in Fig. 2. Another program produced alternative FORTRAN functions. In these functions, the powers of variables are calculated sequentially and then applied for the independent calculation of monomials.

Recursive calculation of the values of variables resulted in temperature-time and concentration-time curves. A sample result for such a calculation is given in Fig. 3. The repro-model was randomly checked using other initial conditions within the limits applied in the preparation of the repro-model, using initial temperatures greater than 1100 K only. In a series of such calculations, similarly good agreement was obtained to the SENKIN solution.

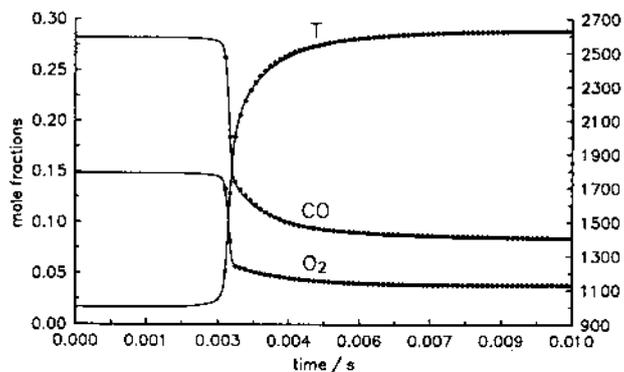


FIG. 3. Concentration-time and temperature-time curves for 1000 K initial temperature and a stoichiometric mixture. Solid lines represent the SENKIN solution, and dots were calculated using a three-variable repro-model. Calculation of the curves with the repro-model was 11,700 times faster.

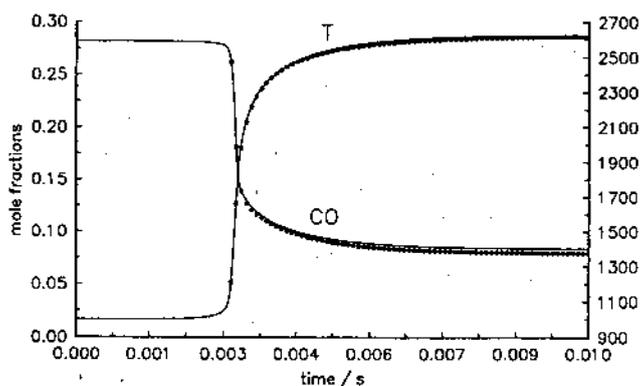


FIG. 4. Concentration-time and temperature-time curves for the same initial concentrations as in Fig. 3. Solid lines represent the SENKIN solution, and dots were calculated by a two-variable repro-model. Calculation of the curves with the repro-model was 24,000 times faster.

When the polynomials were calculated without any factorization, the repro-model calculation was 68 times faster than the SENKIN simulation. Applying independently calculated monomials, the repro-model was already 2220 times faster. Using the multivariate Horner equations, calculation of time curves with the repro-model was 11,700 times faster than the simulations with the full mechanism using program SENKIN.

In a similar way, a two-variable repro-model was also prepared. The two variables selected were temperature and mole fraction of CO. In this case, fifth-order polynomials gave a better fit to the tabulated data. The temperature-time and CO concentration-time curves obtained are given in Fig. 4. Now, the agreement is not as perfect as in the previous case, but it is still good. In this case, the repro-model calculation was 162, 5300, and 24,000 times faster than the SENKIN simulation, using the direct calculation of polynomials, the independently calculated mono-

mials, and the multivariate Horner equations, respectively.

Comparison of the Features of the Three Methods

QSSA:

Preparations

Setting the left-hand side of the kinetic ODEs for the QSSA species to zero always provides algebraic equations for the concentrations of QSSA species. The numerical solution of these equations is very time-consuming [3], and therefore, in practical applications, explicit expressions have to be derived for the calculation of the concentration of QSSA species. Since the conversion of a system of algebraic equations to explicit expressions is not always possible even using algebraic manipulation programs [3], in most cases, the algebraic equations have to be truncated [18]. Note that the CSP can provide hints for such a truncation. Explicit expressions can be supplemented by inner iteration for some QSSA species [19]. Anyhow, the generation of a reduced model containing explicit QSSA expressions always requires significant human effort. On the other hand, identification of QSSA variables provides a physical insight into the model.

Accuracy

It is well known that the QSSA is a first-order approximation only [20]. In principle, much more accurate higher-order QSSAs can be derived as well [21], but generation of such approximations is only possible in the case of small systems.

Further errors are induced when the algebraic equations are truncated. Application of partial equilibrium for some species can also be considered as a truncated QSSA equation.

Yield in computer time

Although the calculation of rates requires the previous calculation of the concentration of QSSA species, the evaluation of the rate equations is very fast. Unfortunately, there are no data for computer time yield for this system, but in the case of mechanisms of similar size, application of QSSA usually results in 20–50 times increase in calculation speed.

Limitations

As in the case of the other two methods, the QSSA is not applicable until the radical concentrations have approached their QSSA values, i.e., a short time interval after the ignition. It has been demonstrated in several cases that the same QSSA equations are applicable for a wide range of conditions.

*The Intrinsic Low-Dimensional Manifold Method:***Preparations**

Generation of the tables has not been automated and requires considerable human effort. The rates are calculated by a special program that has not been published.

Accuracy

The calculated rates correspond to a high-order QSSA and, therefore, can be more accurate than the rates calculated by the QSSA. This feature becomes apparent at low temperatures. Using adaptive gridding in the preparation of the table, the interpolated values can also be accurate, but at the expense of significantly increased size of the tables.

Yield in computer time

Finding the nearest entries in the big table is very time-consuming, and therefore, the calculation of the rates is much slower than by the QSSA. Note that this drawback of the method could have been eliminated if the information of the table were stored in multivariate polynomials. For the wet CO ignition example, this method was 16 times faster than the simulation of the full mechanism [8].

Limitations

The table contains information for every combination of species concentrations, provided that they remain within predefined limits. The table becomes too big if the number of variables is more than five. In case of reaction diffusion systems, this limit seems to be too tight. Application of polynomials, instead of tables would also solve this problem. Note that application of polynomials instead of look-up tables is a good alternative in the case of turbulent-flame calculations as well.

*Repro-Modeling:***Preparations**

The original simulation program with minor modifications can be used for the generation of the table. The table has to contain data for all realistic combinations of the state variables, and preparation of such a table requires attention. Fitting of the polynomials and conversion of the polynomials to a Horner form requires small programs, which are available from the author.

Accuracy

The table contains not approximated rates but the "real" rates of variables. The polynomials approximate the tabulated values with an accuracy well below 1%.

Yield in computer time

When the repro-model provides the rates of state variables, these rates are calculated from the values of variables in one step and not in two stages like in the case of QSSA calculations. Calculation of QSSA concentrations might involve time-consuming calculation of square roots, while the equations of the repro-model are always polynomials, which can be evaluated very quickly using their Horner form. Therefore, application of repro-models allows faster calculations of rates than using the quasi-steady-state approximation. Then, the calculated rates are used in the usual simulation models.

When the repro-model provides the changes of state variables over time Δt due to chemical reactions, the solution of stiff kinetic equations is replaced by the evaluation of polynomials. This version allows a several thousand time increase in the speed of the calculation of chemical changes.

Limitations

The repro-model contains information only for the conditions of the simulations used for the generation of the tables. However, these conditions can be very wide, and also, different sets of polynomials can be used for different conditions.

There is very little experience on the maximum applicable number of variables in a repro-model. Repro-models with 13 and 15 variables have been reported (see Refs. 12 and 11, respectively). This limit seems to be rather high, which might allow the application of repro-modeling in reaction-diffusion calculations for most of the fuels.

Conclusions

This paper represents the first application of repro-modeling to combustion simulations. Several other variants of this technique have been used in other areas of computer modeling, especially in air quality simulations. Repro-modeling seems to be competitive to previous mechanism reduction procedures, considering the human effort needed and the accuracy compared to the full mechanism. Furthermore, repro-models allow about two orders of magnitude faster calculation of chemical changes than the reduced mechanisms obtained in the usual way.

Further work is needed for a detailed assessment of the possibilities of repro-modeling in combustion. A series of repro-models has to be produced for the combustion of other fuels and for other reaction conditions. In each case, the relation of efficiency and accuracy to the number of variables and parameters of the repro-model has to be investigated. Potentially, the most important field of application of repro-modeling is the simulation two- and three-di-

mensional deflagrations and of turbulent flames. Insertion of repro-models into laminar and turbulent flame codes also requires further work. These planned calculations will reveal the scope and limitations of repro-modeling in combustion science.

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