

Chemical Kinetics Mechanism Reduction Based on Principal Component Analysis: Development and Testing of Some New Implementations

by Michael J. McQuaid

ARL-TR-6449

May 2013

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ARL-TR-6449

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Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) May 2013		2. REPORT TYPE Final		3. DATES COVERED (From - To) January 2012–December 2012	
4. TITLE AND SUBTITLE Chemical Kinetics Mechanism Reduction Based on Principal Component Analysis: Development and Testing of Some New Implementations			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Michael J. McQuaid			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-WML-D Aberdeen Proving Ground, MD 21005-5066			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-6449		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Principal component analysis of local sensitivity (PCAS) coefficients was investigated as a means for producing finite-rate chemistry submodels for computational fluid dynamics models. A programmable approach for reducing chemical kinetics mechanisms, PCAS appeared to have some potential advantages over the trial mechanism method (TMM) the U.S. Army Research Laboratory has been employing for mechanism reduction. However, it was found that published PCAS approaches were unable to produce viable mechanisms as small as those produced by the TMM. Therefore, some PCAS variations were implemented and tested. To compare the effectiveness of the variations to published PCAS and TMM implementations, results for two test cases were obtained. One, which involved a relatively small H ₂ -O ₂ mechanism, demonstrated the variations' implementation and potential benefit. The other, which involved a moderately complex mechanism for monomethylhydrazine-red fuming nitric acid (MMH-RFNA), better tested the variations' potential for applications of interest. In the MMH-RFNA test case, none of the implemented variations produced viable mechanisms with sizes as small as those produced by the TMM. However, the results suggest that a PCAS-based approach, employed as a means for understanding the role specific reactions play in sets produced by the TMM, could prove useful. In addition, because PCAS approaches have the potential to be less computationally demanding than the TMM, there may be applications for which it would be beneficial to employ a PCAS-based reduction approach prior to employing the TMM.					
15. SUBJECT TERMS propulsion, combustion, propellants, computational chemistry					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Michael J. McQuaid
Unclassified	Unclassified	Unclassified	UU	38	19b. TELEPHONE NUMBER (Include area code) 410-278-6185

Contents

List of Figures	iv
List of Tables	v
Acknowledgments	vi
1. Introduction	1
2. Bases for Creating Reduced Mechanisms and Criteria for Screening Their Merit	4
3. Computational Methods	7
4. Results and Discussion	14
4.1 Results Based on Full Mechanisms and TMM-Produced Reduced Mechanisms.....	14
4.1.1 H ₂ -O ₂	14
4.1.2 MMH-RFNA	15
4.2 Vajda et al.'s (1985) PCAS Approach	17
4.2.1 H ₂ -O ₂	17
4.2.2 MMH-RFNA	19
4.3 Alternative Eigenvalue and Eigenelement Cutoffs	20
4.3.1 H ₂ -O ₂	20
4.3.2 MMH-RFNA	20
4.4 PCAS for Rate of Heat Release.....	21
4.4.1 H ₂ -O ₂	21
4.4.2 MMH-RFNA	22
4.5 Two-Step PCAS Approach	23
4.5.1 H ₂ -O ₂	23
4.5.2 MMH-RFNA	24
5. Summary	25
6. References	26
Distribution List	29

List of Figures

Figure 1. The H ₂ -O ₂ homogeneous reactor test case: comparison of solutions generated by the full mechanism and a TMM-generated reduced mechanism.	14
Figure 2. The MMH-RFNA homogeneous reactor test case: comparison of solutions generated by the full mechanism and a TMM-generated reduced mechanism.	16
Figure 3. The MMH-RFNA homogeneous reactor test case: comparison of solutions generated by the full mechanism and the reduced mechanism produced by Vajda et al.'s (1985) PCAS approach.	19
Figure 4. Plots of results relevant to identifying the importance of N ₂ O ₄ ↔ 2 NO ₂ in the MMH-RFNA mechanism.	21
Figure 5. The MMH-RFNA homogeneous reactor test case: comparison of solutions generated by the full mechanism and a reduced mechanism produced by a PCAS approach based on sensitivity coefficients for rate of heat release.	22
Figure 6. The MMH-RFNA homogeneous reactor test case: comparison of solutions generated by (1) the full mechanism, (2) a mechanism (PCA-M04) supplied to the second step of the two-step PCAS approach, and (3) a reduced mechanism (PCA-M05) derived by expanding PCA-M04 based on species-specific $q(A)$ s.	24

List of Tables

Table 1. The full H ₂ -O ₂ mechanism.....	9
Table 2. Reduced H ₂ -O ₂ mechanisms.....	15
Table 3. Reduced MMH-RFNA mechanisms.....	17
Table 4. H ₂ -O ₂ test case: eigenvalue and eigenelement values for $\lambda_{jmax} \geq 0.49$	18

Acknowledgments

I am indebted to Dr. A. Kotlar, U.S. Army Research Laboratory (ARL), for sharing his insights into mechanism reduction and the application of thermodynamic principles for the prediction of propulsion system performance. In addition, programs employed in this study for screening the merit of reduced mechanisms were derived from programs developed by Dr. Kotlar for the trial mechanism method. The homogeneous reactor model employed in this study was derived from a program developed and maintained by Dr. W. Anderson (ARL, emeritus) and some of his former summer students. Dr. Kotlar also made contributions to this model. Dr. J. Ianni (Lockheed-Martin/ARL DSRC [Department of Defense Supercomputing Resource Center]) introduced me to the principal component analysis of local sensitivity coefficients approach to mechanism reduction; Dr. Ianni's implementation of Vajda et al.'s¹ approach (Atropos-Kintecus) was employed in some preliminary investigations of the method. Computer time was provided at the U.S. Air Force Research Laboratory (AFRL)-DSRC, Wright-Patterson Air Force Base, OH.

¹Vajda, S.; Valko, P.; Turanyi, T. Principal Component Analysis of Kinetic Models. *International Journal of Chemical Kinetics* **1985**, *17*, 55–81.

1. Introduction

The U.S. Army is developing novel rocket motor concepts with the potential to increase the performance and/or reduce the vulnerability of tactical missiles. To accelerate these efforts, the U.S. Army Research Laboratory (ARL) is developing and utilizing computational fluid dynamics (CFD) models to obtain insight into these concepts' performance as a function of various design parameters (Nusca and Michaels, 2004; Nusca and Michaels, 2005; Nusca et al., 2008; Nusca et al., 2011). The development of system-specific gas-phase finite-rate chemical kinetics mechanisms is a significant part of these efforts (Anderson et al., 2010; Chen and McQuaid, 2007; Chen and McQuaid, 2011; Chen and McQuaid, 2012; Kotlar, 2010; McQuaid et al., 2011; McQuaid et al., 2012). Built on a foundation laid by prior ARL efforts to model the ignition and combustion of gun propellants (see Anderson et al. [2011] and references therein), the Army's support for mechanism development has been based on the demonstrated ability of such mechanisms to improve the predictive power of the CFD models.

Support for mechanism development is also predicated on the results being timely and practical. Specifically, the mechanisms need to be developed concurrent with the CFD models and motor development programs they are intended to benefit, and the numbers of species and reaction rate expressions included in a mechanism need to be small enough for the CFD simulations to be computationally tractable. These objectives have been met via a three-step process. The first step involves exploiting computationally based methods to develop rate expressions for elementary reaction steps for the decomposition of propellant ingredients for which little or no relevant kinetic data exists. The second step involves creating a "detailed" mechanism by combining the rate expressions for the decomposition steps with a set of rate expressions for small molecule reactions that have been developed and employed to model other combustion systems. The final step involves producing a "reduced" (or skeletal) mechanism from the detailed/full one.

This report summarizes an investigation into a programmed approach to mechanism reduction that appeared to offer some advantages over the one ARL has been developing and using since 2004. The latter approach is called the trial mechanism method (TMM). The initial impetus for the development of the TMM was a need for a finite-rate chemical kinetics mechanism that could be used in a CFD model of a hypergolic propulsion system concept being developed at the U.S. Army Aviation and Missile Research, Development, and Engineering Center (AMRDEC). Referred to as the impinging stream vortex engine (ISVE), the concept was fueled at the time with monomethylhydrazine (MMH) and inhibited red fuming nitric acid (IRFNA). Even though MMH and IRFNA (individually) were well-known rocket propellants, a usable chemical kinetics mechanism for the combination could not be identified. When a single-step mechanism with an adjustable rate constant that was developed for the application proved to be inadequate (Nusca

and Michaels, 2004), a detailed MMH-RFNA mechanism was assembled. (It was assumed that chemistry associated with the inhibitor [HF] could be ignored. Therefore, reactions associated with fluorine were not included in the mechanism.) However, its (initial) formulation included 489 reactions and 72 species, making it too large to be practical as a CFD submodel. (When its development was discontinued, the mechanism involved 513 reactions and 81 species [Anderson et al., 2010]. Reductions of that mechanism are presented here.) More specifically, the complete inclusion of the initially constructed mechanism would have required that 71 partial differential equations (PDEs) be added to the 5 (Navier-Stokes) PDEs required to model mass, momentum, and energy transport. (The total number of additional PDEs required to include a chemical kinetics mechanism in a CFD model equals the mechanism's total number of species minus one.) Because the rate expressions in a mechanism represent PDE source terms, the computational burden a mechanism imposes on a CFD model scales with their number as well.

Given the millions of grid points needed to adequately discretize the internal volumes of an ISVE's components (including injectors, combustion chamber, and nozzle) and the millions of time steps needed to adequately resolve temporal transients occurring during a motor firing, even with the considerable computing resources available to ARL through the Department of Defense Shared Resource Center (DSRC), the time needed to perform simulations with more than about 50 PDEs would have made the calculations impractical. Therefore, ARL sought to reduce the full mechanism's reaction set to a subset with less than 45 species (and less than 70 reactions) that retained the full one's ability to represent MMH-RFNA reaction chemistry under conditions of interest.

Although a number of established mechanism reduction methods were potential candidates for the application, the TMM was devised and developed by Kotlar (2010). Briefly, it involves producing subsets of rate expressions for elementary reactions in a detailed mechanism by

- ordering (usually randomly, but deterministically if desired) the full set's rate expressions,
- creating trial mechanisms by sequentially eliminating individual expressions from the set on a temporary basis,
- employing the trial mechanism as a basis for simulating the temporal evolution of a homogeneous reacting gas mixture in a closed system (such simulations being referred to hereafter as homogeneous reactor simulations), and
- permanently eliminating any reaction whose deletion does not change (beyond specified tolerances) selected results of the solution produced with the full mechanism.

When all reactions having a given species are eliminated, that species is eliminated.

Targeting the production of mechanisms with less than 45 species and 70 (reversible) reactions, Kotlar (2010) developed a TMM implementation that had no difficulty in achieving that goal. More importantly, CFD simulations with these mechanisms as submodels well-reproduced ISVE

test stand data without any adjustable kinetic parameters (Nusca and Michaels, 2005). Moreover, the TMM has successfully reduced (to practical size) every detailed mechanism to which it has since been applied. Those mechanisms include TMEDA-RFNA, DMAZ-RFNA, TMEDA-DMAZ-RFNA, HTPB-RFNA, and ethyl nitrate (McQuaid et al., 2011; Nusca, 2012). There are, however, issues in applying the TMM that make it a less than ideal method for mechanism reduction. For one, for mechanisms as large as TMEDA-DMAZ-RFNA, which currently includes 2153 reactions and involves 481 species, the TMM begins to approach the limit of computational practicality (as currently programmed). Also, until recently it was not clear how effective it might be in producing reduced mechanisms that would be valid for a wide range of initial/operating conditions. Finally, the method by itself offers little insight into why reactions in a given mechanism are important or not. (Kotlar [2010] notes that statistically based analyses of a multitude of mechanisms generated by the technique should yield insight into the relative importance of individual reactions, but this approach remains to be more fully developed and exploited.) Therefore, there was interest in identifying alternatives that might address these issues.

Of the many published reduction methods that were reviewed, principal component analysis of local sensitivity (PCAS) coefficients for kinetic parameters was considered particularly intriguing. First developed and demonstrated by Vajda et al. (1985), the technique involves computing a “response function” from normalized first-order sensitivity coefficients for a “target function” (such as species concentrations) calculated in the course of obtaining a solution to a “canonical” combustion problem (such as a homogeneous reactor simulation). (Mathematical details of the approach are presented in the Computational Methods section.) Transformed into eigenvalue-eigenvector form, the response function establishes bases for selecting the reactions to include in a reduced set. Bases include (1) an eigenvalue cutoff that establishes which principal components/eigenvectors are important, and (2) an eigenelement cutoff that identifies reactions whose contribution to the important principal components can be ignored. Besides having its roots in a traditional approach to mechanism reduction—i.e., a chemical kineticist proposing reduced reaction sets on the basis of his/her experience and plots of sensitivity coefficients—the PCAS-based method was available in a commercially available package (Ianni, 2006).

Expectations notwithstanding, mechanisms produced by Vajda et al.’s (1985) approach proved disappointing for the case of MMH-RFNA. Based on a response function built from sensitivity coefficients for species concentrations and temperature, the smallest mechanisms that could reasonably reproduce the (standard) solution produced with the full mechanism were significantly larger than those generated by the TMM. Indeed, to produce mechanisms with less than 120 reactions that were capable of passing established screening criteria, it was necessary to add one invariably eliminated (but obviously important) reaction to sets produced with this approach. (This case is discussed in detail in the Results section.) Another surprising result was the inclusion of reactions in the reduced sets in which both a reactant and product were not found

in any other reaction in the set. As such, these reactions were not connected to the rest of the mechanism and thus had no function. Such results indicated that this approach was not identifying important “feeder” reactions, prompting a search for means to overcome the shortcoming.

One of the PCAS variations that was investigated was based on allowing the eigenvalue and eigenelement cutoffs to be varied such that mechanisms with a targeted number of reactions were produced. When that proved of little benefit, the sensitivity coefficients for mass-specific rate of heat release rather than species concentrations and temperature were employed to create the response function. That approach proved to have some significant advantages over Vajda et al.’s (1985) approach. However, from the standpoint of producing compact mechanisms, it still fell short of the TMM. That led to the investigation of a two-step approach in which reactions identified as important for heat release formed the kernel of a reduced mechanism, and response functions whose target functions were the concentrations of individual species found in the kernel were employed as a basis for expanding it. In the implementation of this approach, an issue was raised concerning the basis for selecting the temporal solutions to include in building response functions. This issue is discussed.

Results obtained from the PCAS variations are presented for two test cases. Both involve creating reduced mechanisms that can reasonably reproduce a homogeneous reactor problem solution that is produced with a full mechanism. One case involves a 20 reaction-9 species H_2 - O_2 mechanism, the results for which demonstrate (in principle) the potential benefits of the PCAS variations that were proposed. The other involves the aforementioned MMH-RFNA mechanism. Representing a more realistic challenge, this case provides a better basis for comparing the potential of the PCAS variations relative to the TMM for applications of interest to ARL.

2. Bases for Creating Reduced Mechanisms and Criteria for Screening Their Merit

As a prelude to a discussion of specific details of the PCAS approaches developed and tested in this study, this section outlines the bases for creating reduced mechanisms and the criteria employed to screen a mechanism’s merit. The bases and criteria employed in this study were established in the development and application of the TMM (Kotlar, 2010; McQuaid et al., 2011). The bases are homogeneous reactor simulations, and the results from them that are compared include the magnitudes of (local) maxima for volumetric and mass-specific rates of heat release, the times at which those maxima occur, and the final (adiabatic) temperature. The final temperature depends on the temporal duration selected for the simulation. Durations are selected such that all possible major heat release events occur and the temperature plateaus,

reaching to within about 1 K of its (adiabatic) equilibrium value. These selections have their roots in ARL's history in developing models to predict the performance of guns, and that background bears mentioning.

The overall problem addressed by interior ballistic (IB) models for (classic) guns concerns converting chemical energy stored in a propellant into kinetic energy. Given the high pressures and temperatures occurring during a gun IB cycle, an assumption about the conversion can be made; namely, that propellant combustion instantaneously goes to completion, reaching an equilibrium (thermochemical) state (Mayer and Hart, 1945). Therefore, one does not need a finite-rate chemical kinetics mechanism to obtain reasonable limit-of-performance predictions for guns. They can be obtained by knowing thermochemical properties of the propellant, the rate at which the propellant burns, and various intrinsic global properties of the gas (or working fluid) produced by the propellant's combustion.

The working fluid's properties that are needed as input for basic gun IB models include (mean) molecular weight and heat capacities at constant pressure and constant volume. Estimates for these properties are traditionally derived from a thermodynamics code's predictions for the equilibrium chemical composition that will be produced in a constant volume system with a loading density of 0.2 g/cm^3 (Freedman, 1988; Kotlar, 1992). Based on species-specific thermochemical parameters, predictions for the mole fractions of every species included in a product database are produced by codes such as BLAKE (Freedman, 1982). However, the chemical composition comprising those fractions is not used directly in the IB model; only global or mean properties computed on the basis of the composition are used.

As is the case for guns, reasonable limit-of-performance predictions for a rocket motor-propellant combination can be obtained from equilibrium thermochemical codes. However, unlike the pressures produced during gun IB cycles, the pressures in rocket motor combustion chambers are (typically) not high enough to assume that the products of combustion instantaneously go to completion. Therefore, to obtain insights into the performance of a specific motor design with a CFD model, a chemical kinetics mechanism is needed to convert chemically stored energy into kinetic energy at appropriate rates. In addition, because it replaces the equilibrium code, the mechanism is expected to produce (in an appropriate time frame) a fluid whose molecular weight and heat capacities at constant volume and constant pressure are similar to those of the fluid produced by an equilibrium code.

Assuming that a given detailed mechanism can adequately perform these functions, to determine whether a reduced mechanism will perform similarly, one needs to identify a relevant canonical combustion "problem" with a temporally dependent solution that can serve as a basis for comparison. Insofar as a homogeneous reactor simulation is the simplest problem that approximates the finite-rate chemical dynamics that will occur in a rocket motor's combustion chamber, it is an obvious first choice to investigate as a basis for mechanism reduction.

Selecting the criteria to rank the solutions to the problem produced by reduced mechanisms, however, is another matter.

To ensure that a reduced mechanism is capable of producing a reasonable working fluid, the homogeneous reactor simulation needs to be of sufficient duration for the combustion process to approach completion (as would be expected of a well-designed rocket motor), and the properties of the fluid have to compare well with the fluid produced by the detailed mechanism. While one could ensure the latter by requiring that the temperature and the concentrations of all product species fall within certain bounds, it was assumed in the development of the TMM that if the final temperature of the solution produced by the reduced mechanism was reasonably close to that of the standard, the other global thermodynamic properties of the gas would be reasonably well estimated as well.

The requirement that only the final temperature of a homogeneous reactor simulation need fall within certain bounds contrasts with requirements employed by others in applying PCAS-based approaches. In the PCAS approach published by Vajda et al. (1985), eigenvalue and eigenelement cutoffs were established such that the full mechanism-based predictions for the concentrations of all (important) species would be reproduced to within 4% over the entire course of the simulation. Clearly, if one is trying to predict the yield of a certain chemical species, this is an appropriate requirement. But if, as in ARL's case, one is only interested in producing a working fluid with certain global properties, less demanding agreement between the results for the concentrations of many (if not all) species may be acceptable. However, to specify relaxed tolerances for individual species concentrations, one must determine all the species concentration permutations that would produce a fluid with reasonable values for molecular weight and heat capacities at constant volume and constant pressure. Thus, taking advantage of this latitude would likely be very difficult to implement in practice. Moreover, tolerances established for ensuring that a reasonable working fluid will be produced may be at odds with those needed to ensure that the rate of heat release is reasonably reproduced.

At the other extreme is a PCAS approach employed by Esposito and Chelliah (2011) in which the only basis for the reduction was the time-to-ignition produced in a homogeneous reactor problem; no regard was given to the reduced mechanism's ability to reproduce the thermodynamic end state predicted by the full mechanism. In developing reduced mechanisms for CFD applications, ARL has found that the TMM can generate mechanisms that well-reproduce time-to-ignition values but do not yield good final temperatures. Given the reasonable limit-of-performance predictions produced by equilibrium codes, the imposition of a criterion for the end state produced by a reduced mechanism was considered prudent.

With respect to ranking a reduced mechanism's ability to model the rate of heat release, there are also several criteria that could be/have been employed for screening a reduced mechanism's merit. In the implementation of the TMM that has been used to date, the magnitudes of (local) heat release maxima and the time at which those maxima occur have been employed (Kotlar,

2010; McQuaid et al., 2011). Again, this approach contrasts with Vajda et al.'s (1985) imposition of eigenvalue and eigenvalue cutoffs that lead to the concentrations of important species being reproduced to within 4% over the entire course of a simulation. As will be shown, although Vajda et al.'s approach works, it is overly restrictive for ARL's current purposes.

At the other extreme is the aforementioned approach investigated by Esposito and Chelliah (2011) in which candidates were derived on the basis of just one aspect of heat release—namely, its first sharp rise as indicated (indirectly) via the inflection point observed in the temperature vs. time profile. In the application of the TMM at ARL, reduced mechanisms were found that yielded solutions in which the ignition delay predicted by a full mechanism was well reproduced but the magnitude of the rate of heat release was not. Thus, standards of agreement are considered necessary for both of these parameters.

Esposito and Chelliah (2011) also discuss PCAS reductions based on premixed or non-premixed (counterflow) flame simulations. Until recently, ARL's efforts in mechanism reduction have involved mechanisms for hypergolic bipropellants. Since hypergolic bipropellants react spontaneously upon mixing at low pressures and temperatures, one encounters issues when trying to simulate premixed scenarios involving them. It is assumed that counterflow flames could be modeled. However, such a basis would impose extra computational burden without providing any obvious benefit. Therefore, ARL has not attempted to implement a reduction method on such a basis.

3. Computational Methods

The equations governing the time evolution of a homogeneous reacting gas mixture in a closed system are summarized by Lutz et al. (1988). The set of differential algebraic equations (DAEs) describing such systems has the general form

$$\frac{d\mathbf{Z}}{dt} = \mathbf{F}(\mathbf{Z}, t; \mathbf{A}), \quad (1)$$

where t is time, $\mathbf{Z}$ is a vector of temperature and concentrations for m species ($T, Y_1, Y_2, \dots, Y_i, \dots, Y_m$), and $\mathbf{A}$ is a vector of pre-exponential constants ($A_1, A_2, \dots, A_j, \dots, A_p$) for a mechanism's p Arrhenius (forward) rate expressions ($\mathbf{k}_f$),

$$\mathbf{k}_f = \mathbf{A}T^\beta \exp\left(-\frac{E}{RT}\right). \quad (2)$$

In equation 2, E is a vector of activation energies, β is a vector of temperature exponents, and R is the ideal gas constant. The rates of reverse reactions are computed based on microscopic reversibility.

Differentiating equation 1 with respect to the A_j yields

$$\frac{dw_{i,j}}{dt} = \frac{dF}{dZ} * w_{i,j} + \frac{dF_i}{dA_j}, \quad (3)$$

where

$$w_{i,j} = \frac{dZ_i}{dA_j} \quad (4)$$

are elements of the first-order sensitivity coefficient matrix. (Equations 3 and 4 are from Lutz et al. [1988], but to be consistent with the indices employed in the equations describing the PCAS method, here the index i is associated with $\mathbf{Z}$ and the index j is associated with $\mathbf{A}$.) For constructing the response functions that are the bases of the PCAS approaches, values at each analysis time point (k) in the solution were normalized per

$$\hat{w}_{i,j,k} = \frac{A_j}{Z_{i,k}} \frac{dZ_{i,k}}{dA_j}. \quad (5)$$

The homogeneous reactor model that performed the simulations employed the CHEMKIN-II subroutine library (Kee et al., 1989). Solutions for the model's DAEs were obtained with DASPK (Li and Petzold, 2000).

The homogenous reactor simulations that are considered in this report include (1) a constant pressure process involving a mixture of H_2 , O_2 , and N_2 whose reaction chemistry is modeled with a H_2 - O_2 mechanism that was employed for a simulation that was provided as an example of the application of CHEMKIN-II (Kee et al., 1989) and (2) a constant volume process involving a mixture of MMH and RFNA whose reaction chemistry is modeled with the aforementioned detailed MMH-RFNA mechanism (Anderson et al., 2010). TMM-based reductions of the MMH-RFNA mechanism have been produced on the basis of a constant pressure process simulation (with the same initial conditions), but they were found to be more computationally expensive. There being no obvious difference in the results produced by the two bases, constant volume processes have been employed for all the applications-related reductions that have since been conducted with the TMM.

The H_2 - O_2 mechanism is provided in table 1. For simulations produced with full and reduced versions of this mechanism, the DASPK default for outputting intermediate solutions established the frequency with which analysis points became available. For simulations produced with full and reduced versions of the MMH-RFNA mechanism, intermediate solutions were output based on the formula

$$\Delta t_{n+1} = \Delta t_n \left(\frac{T_c}{\text{abs}(\Delta T_n) + 0.001} \right), \quad (6)$$

where T_c is a specified constant, and the index n is associated with the most recently computed time interval (Δt) and temperature change (ΔT). In both test cases, the relative and absolute tolerances for the solutions for the dependent variables were 1×10^{-5} and 1×10^{-12} , respectively. The tolerances for solutions for the sensitivity coefficients were the DASPK default (1×10^{-5}).

Table 1. The full H₂-O₂ mechanism.^a

No.	Reaction	A (s ⁻¹)	β	E (cal/mol)
1	H+O ₂ +M=HO ₂ +M	3.61E + 17	-0.72	0
	H ₂ O Enhanced by 1.86			
	H ₂ Enhanced by 2.86			
2	H+H+M=H ₂ +M	1.00E + 18	-1.00	0
3	H+H+H ₂ =H ₂ +H ₂	9.20E + 16	-0.60	0
4	H+H+H ₂ O=H ₂ +H ₂ O	6.00E + 19	-1.25	0
5	H+OH+M=H ₂ O+M	1.60E + 22	-2.00	0
	H ₂ O Enhanced by 5.00			
6	H+O+M=OH+M	6.20E + 16	-0.60	0
	H ₂ O Enhanced by 5.00			
7	O+O+M=O ₂ +M	1.89E + 13	0.00	-1788
8	H ₂ O ₂ +M=OH+OH+M	1.30E + 17	0.00	45500
9	H ₂ +O ₂ =2OH	1.70E + 13	0.00	47780
10	OH+H ₂ =H ₂ O+H	1.17E + 09	1.30	3626
11	O+OH=O ₂ +H	3.61E + 14	-0.50	0
12	O+H ₂ =OH+H	5.06E + 04	2.67	6290
13	OH+HO ₂ =H ₂ O+O ₂	7.50E + 12	0.00	0
14	H+HO ₂ =2OH	1.40E + 14	0.00	1073
15	O+HO ₂ =O ₂ +OH	1.40E + 13	0.00	1073
16	2OH=O+H ₂ O	6.00E + 08	1.30	0
17	H+HO ₂ =H ₂ +O ₂	1.25E + 13	0.00	0
18	HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	2.00E + 12	0.00	0
19	H ₂ O ₂ +H=HO ₂ +H ₂	1.60E + 12	0.00	3800
20	H ₂ O ₂ +OH=H ₂ O+HO ₂	1.00E + 13	0.00	1800

^a From Lutz et al. (1988). Species include H₂, H, O₂, O, OH, HO₂, H₂O₂, H₂O. A ninth species (N₂) is not explicitly included in any of the mechanism's reactions. However, it is an initial reactant in the test case presented and is therefore included implicitly via M.

Formally, the response function $[Q(\mathbf{A})]$ for a PCAS approach is given by

$$Q(\mathbf{A}) = \sum_{k=1}^l \sum_{i=1}^m \left[\frac{f_i(\mathbf{x}_k, \mathbf{A}) - f_i(\mathbf{x}_k, \mathbf{A}^0)}{f_i(\mathbf{x}_k, \mathbf{A}^0)} \right], \quad (7)$$

where $\mathbf{A}^0$ and $\mathbf{A}$ are, respectively, unperturbed and perturbed normalized pre-exponential factors, $\mathbf{x}$ is a collection of (l) analysis time points, and $\mathbf{f}$ is the set of (m) target functions. In this study, target functions included T , species concentrations (Y_i , collectively and individually), and the mass-specific rate of heat release (r').

Vajda et al. (1985) show that response functions can be approximated by a Taylor series expansion about $\mathbf{A}^0$, giving

$$Q(\mathbf{A}) \approx q(\mathbf{A}) = (\Delta \mathbf{A})^T \mathbf{S}^T \mathbf{S} (\Delta \mathbf{A}), \quad (8)$$

where $\Delta \mathbf{A} = \mathbf{A} - \mathbf{A}^0$ and $\mathbf{S}$ is an $l^*m \times p$ matrix constructed by concatenating (column-wise) the normalized sensitivity coefficient matrices for temporal analysis points (k),

$$S_k = \begin{bmatrix} \hat{w}_{1,1,k} & \hat{w}_{1,2,k} & \hat{w}_{1,p,k} \\ \hat{w}_{2,1,k} & \hat{w}_{2,2,k} & \hat{w}_{2,p,k} \\ \vdots & \vdots & \vdots \\ \hat{w}_{m,1,k} & \hat{w}_{m,2,k} & \hat{w}_{m,p,k} \end{bmatrix}, \quad (9)$$

to form

$$S = \begin{bmatrix} S_1 \\ S_2 \\ \vdots \\ S_l \end{bmatrix}. \quad (10)$$

Diagonalization of the matrix $S^T S$ yields

$$S^T S = U \lambda U^T, \quad (11)$$

where λ is a diagonal matrix of eigenvalues, and U is a matrix of normalized eigenvectors ($u_1, u_2, \dots, u_p$). Performed in this study with a program based on the Householder method (Press et al., 1992), the decomposition produces a set of eigenvectors (Ψ),

$$\Psi = U^T A, \quad (12)$$

called principal components. Related to $q(A)$ per

$$q(A) = \sum_{j=1}^p \lambda_j \|\Psi_j\|^2 \quad (13)$$

since the eigenvectors are normalized, the relative magnitudes of the eigenvalues correspond to the relative contributions their associated principal components make to $q(A)$. As such, the eigenvalues are a metric that can be employed to distinguish important eigenvectors from nonimportant eigenvectors. This is done by setting an eigenvalue cutoff (λ_{jmax}). Similarly, the magnitudes of eigenelements of the important eigenvectors correspond to the importance of their corresponding reaction within the eigenvector and thus represent a metric that can be employed to distinguish important reactions from nonimportant ones. This is done by setting an eigenelement cutoff (u').

Based on a numerical analysis, Vajda et al. (1985) show that eliminating reactions that are dominant elements of eigenvectors (j) corresponding to eigenvalues (λ_j) less than $m * l \times 10^{-4}$, i.e.,

$$\lambda_j < m * l \times 10^{-4} \leq \lambda_{jmax}, \quad (14)$$

will make less than a 1% change in the target functions composing the response function. They further suggest that eliminating all reactions associated with eigenelements in the remaining eigenvectors with magnitudes less than $u' = 0.2$ will produce less than a 4% error in those functions.

Given these basics, there are four main parameters/variables that determine a PCAS approach's output (mechanism). The first is the target function (or functions) employed as the basis for the

response function. In the first published implementation of the method, the target functions were collective sets of species concentrations (only). Temperature was included later (Zsely and Turanyi, 2003). Esposito and Chelliah (2011) have since investigated the utility of performing PCASs based on sensitivity coefficients for derived (or global) functions. Results were presented for time-to-ignition values produced in homogeneous reactor simulations, the spatial profile for the rate of heat release produced in one-dimensional (premixed) flame simulations, and the extinction conditions predicted for non-premixed counterflow flame simulations.

Three different target functions are considered in this report. They include

- a collective function that includes temperature and the concentrations of all species, which was within the purview of Vajda et al. (1985) and employed by Zsely et al. (2003),
- the rate of heat release, and
- the concentrations of single species.

Esposito and Chelliah derive an analytical expression for computing sensitivity coefficients for the rate of heat release, but it was not employed in this study. Rather, they were determined numerically via DASPK using its auxiliary routine DSENSD.

The second two selectable parameters with a strong influence on the results achieved with a PCAS-based approach are λ_{jmax} and u' . Vajda et al. recommendations for their specification notwithstanding, the selection of these parameters depends ultimately on the degree of fidelity one is willing to accept for the solution produced by a reduced mechanism. Esposito and Chelliah (2011) published results that show the importance of the number of eigenvalues retained for various homogeneous reactor problems, but these results do not appear to justify their statement that “it is important to establish a priori the number of eigenvectors to retain.” Indeed, if the primary purpose for implementing the method is to produce a reduced mechanism with the minimum number of reactions and species necessary for a given application, there is no (obvious) reason to determine and impose such a constraint. Rather, when the mechanisms produced with the λ_{jmax} and u' values imposed on the basis of Vajda et al. analysis proved to be significantly larger than those obtained with the TMM, the cutoffs were adjusted in a systematic manner to produce skeletal mechanisms with targeted numbers of reactions. That was accomplished by choosing a u' value that identified as important a prespecified minimum number of reactions from eigenvectors associated with the largest eigenvalues. A mechanism would be constructed from the set, and its ability to reproduce the full mechanism’s solution screened. The specified number of significant eigenvectors would then be increased (by a unit increment), and the u' value increased such that the same number of reactions was selected. The screening procedure would then be performed again. This process was repeated for the targeted number of reactions until the number of eigenvectors whose modes were screened equaled the number of targeted reactions. The targeted number of reactions was then increased by one, and

the process repeated. Subsequent repetitions were performed until mechanisms with a prespecified maximum number of reactions were obtained.

For the case involving the MMH-RFNA mechanism, the minimum number of reactions to include in a mechanism was set by requiring the sum of the eigenvalues for the retained eigenvectors to exceed 99.9% of the total for all the eigenvalues and making the minimum number of targeted reactions equal to the number of eigenvectors in that set. The maximum number of reactions to include in a mechanism was set at 120. This value was based on the current upper limit considered practical for a CFD model of the ISVE. In the MMH-RFNA test case, these bounds led to the generation of over 7000 reaction sets. Even though not all of the sets were unique, to facilitate the screening of this overwhelming amount of data, the method employed (to date) by the TMM for identifying potentially viable candidates was utilized.

The last important consideration in the implementation of a PCAS approach concerns the selection of $\mathbf{S}_k$ samples for inclusion in $\mathbf{S}$. In the two cases to which the method was applied in Vajda et al.'s 1985 paper, several $\mathbf{S}_k$'s corresponding to relatively short time steps were selected during the first 1/10th of the systems' evolutions; then a larger number of $\mathbf{S}_k$'s corresponding to longer, equally spaced time steps was selected. Unfortunately, the basis for these selections is not discussed, belying the importance of the matter. As noted by Esposito and Chelliah (2011), one must be careful when selecting the $\mathbf{S}_k$, because if results for similar conditions are included, they could introduce bias into the response function. Indeed, for generating a reduced mechanism that could accurately reproduce a full mechanism's prediction for the ignition delay of a homogeneous reactor problem, these researchers used the sensitivity coefficients computed for a *single* time point: either the temperature inflection point or the minimum chemical time of the species. (Unfortunately, they do not give a specific definition for either of these parameters.)

By the nature of the DAE solver time-step selection algorithm and equation 6, the frequency of analysis points in the homogeneous reactor simulations of interest to ARL tends to be very high at the beginning of the simulation and near the ignition event, and low everywhere else. While one might guess that sampling should concentrate near the ignition event, that approach effectively adds weight to the importance of reactions whose importance is already indicated by the magnitude of sensitivity coefficients associated with them. A selection technique that produces more uniform sampling has potential drawbacks as well. In the case of the MMH-RFNA simulation considered here, which is pretty typical of those produced for systems involving hypergolic bipropellants, conditions are highly transient during the first 10^{-9} s, level out until about 10^{-6} s, are highly transient for the next 10^{-7} s, then settle down but do not get close to equilibrium until about 1 s. Thus, it would take on the order of 10^7 points to uniformly sample the temporal domain of the simulation and ensure sampling occurs during major heat release events. And if the timescale of species concentration transients was the determining factor, it would take on the order of 10^{10} points. In such cases, the response function would be overwhelmingly biased by $\mathbf{S}_k$ associated with unimportant times. In addition, since the dimensions of $\mathbf{S}$ are $l^*m \times p$, and there is a compiler-based maximum for the number of elements

that an array can have of 2.56×10^8 , with $m = 81$, and $p = 513$, it is not possible (in a straightforward manner) to construct $\mathbf{S}$ with more than about 6000 $\mathbf{S}_k$. And for mechanisms with sizes that approach 2000 reaction and 500 species (such as TMEDA-DMAZ-RFNA), that number drops to <300. Therefore, even if it made sense, implementing such a strategy could prove problematic.

For the initial implementations of the PCAS approaches that were investigated in this study, the times at which the $\mathbf{S}_k$'s were sampled were based on a criterion that was already employed by the homogeneous reactor model for outputting data. That is, the program did not select the set for the first analysis point until the temperature had increased or decreased some specified amount with respect to the starting temperature, and this specified amount had to be exceeded again before adding the $\mathbf{S}_k$ for another point. When the results achieved with this approach fell short of those obtained with the TMM, other criteria were employed. The first alternative to be developed and tested was based on increments of heat release. That is, the program calculated (via numerical integration) the total heat generated in the course of a simulation, then reran the simulation and selected an $\mathbf{S}_k$ each time a specified fraction of the total had accumulated. Perhaps not surprisingly, given the close relationship between the rate of heat release and temperature change, the sampling intervals did not vary much between the two cases. In the case of the two-step approach to be discussed, the program determined the minimum and maximum concentrations each (individual) species reached in the course of the simulation. Response functions whose target functions were the concentration of individual species were then constructed by rerunning the simulation for each individual and selecting the $\mathbf{S}_k$ based on changes in the individual's concentration.

One other approach that was investigated involved sampling at a frequency consistent with the intermediate time steps reported by the DAE solver. This approach was examined based on an intuition that the sampling needed to be biased toward earlier times in the simulation, and the intermediate solutions reported by the solver exhibited this bias naturally. The approach was implemented in conjunction with a PCAS based on sensitivity coefficients for rate of heat release. That case was chosen for investigation because the relatively small array size of the target function allowed every solution output by the DAE solver to be employed for the construction of $\mathbf{S}$.

To screen the merit of a solution produced by a reduced mechanism, the automated screening method utilized in conjunction with previous applications of the TMM was employed. That is, the magnitudes of local maxima of heat release features, the times at which those maxima occur, and the final temperature of a simulation produced with a reduced mechanism were established and compared to those of the (standard) solution produced by the full mechanism. To facilitate comparisons, the same standards of agreement that have been used to guide the selection of mechanisms for CFD models were applied. That is, results for the rate of heat release parameters could not vary from those of the standard by more than 10%, and the final temperature could not be more than 100 K different (Kotlar, 2010; McQuaid et al., 2011). These requirements are

referred to in the discussion that follows as the 10%–100 K agreement criteria. In addition, because the screening method has the potential to be fooled, for mechanisms for which results are reported, agreement was verified by visually inspecting in their entirety their associated rate of heat release and temperature vs. time plots.

4. Results and Discussion

4.1 Results Based on Full Mechanisms and TMM-Produced Reduced Mechanisms

4.1.1 H₂-O₂

Figure 1 presents plots of the rate of heat release and temperature vs. time that were produced by the homogeneous reactor model with the full H₂-O₂ mechanism. The results are for a constant (1 atm) pressure process. The initial reactants were H₂, O₂, and N₂, and their starting mole fractions were 0.286, 0.143, and 0.571, respectively. The mixture's initial temperature was 1000 K. Representing the standard for this case and comprising solutions for 1178 time points, the plot exhibits a single heat release feature. The maximum rate of heat release is 4.6155×10^3 cal/cm³-s, and that value occurs at 0.17765 ms. The temperature at the end of the (2.0000 ms) simulation is 2667.90 K. This value is 0.82 K lower than the system's equilibrium value.

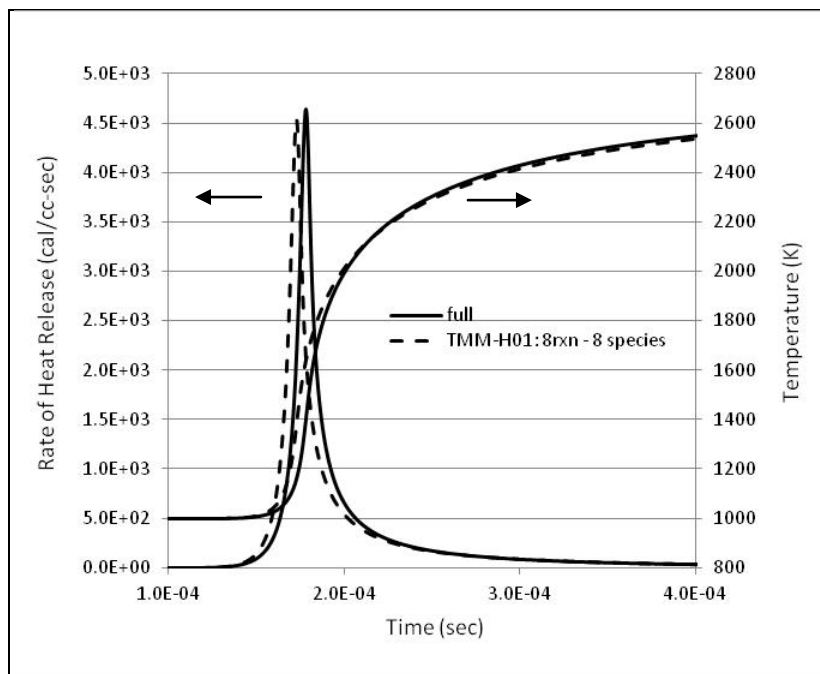


Figure 1. The H₂-O₂ homogeneous reactor test case: comparison of solutions generated by the full mechanism and a TMM-generated reduced mechanism.

Figure 1 also shows a solution produced for the process by an 8 reaction-8 species mechanism (TMM-H01) generated by the TMM. The values of its rate of heat release parameters are within 4% of those in the standard, and the final temperature is within 0.02 K. The species that was eliminated was H_2O_2 . In addition, the TMM generated a 9 reaction-8 species mechanism (TMM-H02) and a 10 reaction-8 species mechanism (TMM-H03) that produced solutions in even better agreement (table 2). These results represent standards of reduction to which results from the PCAS approaches will be compared.

Table 2. Reduced $\text{H}_2\text{-O}_2$ mechanisms.

Mechanism	No. of Species	No. of Reactions	Specific Reactions	Max Error ^a (%)	ΔT_{final}^b (K)
TMM-H01	8	8	1 4 5 9 10 11 12 14	3.9	0.02
TMM-H02	8	9	TMM-H01 + 17	2.9	<0.01
TMM-H03	8	10	TMM-H02 + 2	-1.1	<0.01
PCA-H01	9	14	TMM-H03 + 3 18 19 20	-0.8	<0.01
PCA-H02	9	12	TMM-H01 + 8 18 19 20	-3.6	0.01
PCA-H03	9	10	1 5 8 9 10 11 12 14 17 18	-11.9	0.03
PCA-H04	8	6	1 9 10 11 12 14	-19.3	9.38
PCA-H05	8	9	TMM-H01 + 2	-2.9	<0.01
PCA-H06	8	10	PCA-H05 + 6	-2.9	<0.01
PCA-H07	8	11	PCA-H06 + 17	-0.3	<0.01
PCA-H08	8	12	PCA-H07 + 13	-0.2	<0.01
PCA-H09	8	8	PCA-H04 + 5 + 17	-12.0	0.03
PCA-H10	8	10	TMM-H03/PCA-H09 + 2 4	-1.1	<0.01

^a Maximum error in the rate of heat release parameters.

^b ΔT_{final} values are magnitudes.

4.1.2 MMH-RFNA

Figure 2 presents plots of the rate of heat release and temperature vs. time produced by the homogeneous reactor model with the full MMH-RFNA mechanism. The solution is for a constant volume process. The chemical composition of RFNA, which when loaded in a rocket motor can contain from 5 to 20 weight-percent (wt-%) $\text{N}_2\text{O}_4\text{-NO}_2$, was specified to be 84 wt-% HNO_3 , 14 wt-% N_2O_4 , and 2 wt-% H_2O . Coupled with a desire to produce results for an oxidizer-to-fuel (O/F) ratio whose products balanced to CO_2 , H_2O , and N_2 , this choice led to the specification of starting mole fractions for MMH, HNO_3 , N_2O_4 , and H_2O that were 0.3506, 0.5418, 0.0622, and 0.0454, respectively. The initial pressure of the mixture was 75 atm, and the initial temperature was 800 K.

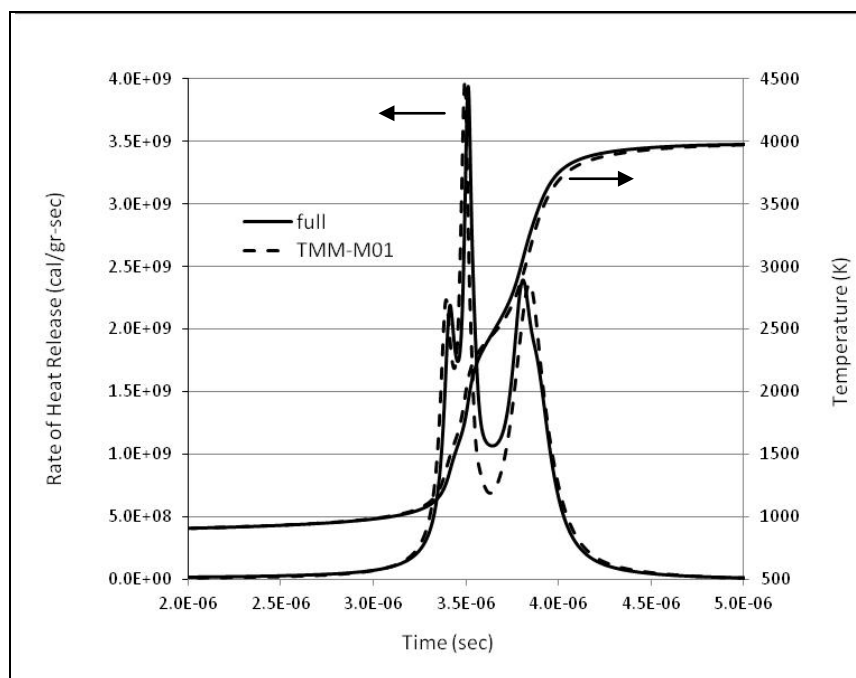


Figure 2. The MMH-RFNA homogeneous reactor test case: comparison of solutions generated by the full mechanism and a TMM-generated reduced mechanism (Kotlar, 2010).

Comprising solutions for 1618 time points, the rate of heat release plot has three main features. The peak of the largest feature occurs at $3.5128 \mu\text{s}$ and has a value of $2.5458 \times 10^8 \text{ cal/cm}^3\text{-s}$. A shoulder on the left side of this feature peaks at $1.42 \times 10^8 \text{ cal/cm}^3\text{-s}$, and this maximum occurs at $3.413 \mu\text{s}$. The third feature peaks at $1.551 \times 10^8 \text{ cal/cm}^3\text{-s}$, and that value occurs at $3.8065 \mu\text{s}$. The temperature at the end of the (2.0000 s) simulation is 3987.10 K. This value is 0.03 K higher than the equilibrium value that was calculated for the system.

In isolation, N_2O_4 and NO_2 will exist in equilibrium, establishing at 75 atm and 800 K (based on the thermochemical parameters employed for them in the MMH-RFNA mechanism) a mixture dominated by NO_2 . Thus, specifying the initial mixture to be 100% N_2O_4 , which was done when the MMH-RFNA mechanism was being reduced for the ISVE application, may seem ill-advised. However, this specification, which was identified as an issue in the first attempts to reduce the MMH-RFNA mechanism with a PCAS-based approach, exposes a weakness of the PCAS. Therefore, it was purposely left unchanged. (Because the enthalpy of formation $[\Delta H_f]$ of two NO_2 molecules is slightly higher than the ΔH_f of N_2O_4 , at a given temperature and pressure, the enthalpy of a mixture in which NO_2 is dominant is slightly higher, and the system exhibits a slightly shorter ignition delay. Otherwise, the dynamics produced by the two composition extremes are very similar.)

Figure 2 also shows a plot of the rate of heat release vs. time that was produced by a 36 reaction-31 species mechanism (TMM-M01) generated by the TMM (Kotlar, 2010). All its time

and magnitude of peak heat release values are within 1.6% of their corresponding value in the standard, and the final temperature is within 0.67 K (table 3). These results represent standards of reduction to which results from the PCAS approaches will be compared.

Table 3. Reduced MMH-RFNA mechanisms.

Mechanism	No. of Species	No. of Reactions	Max Error ^a (%)	ΔT_{final} ^b (K)
TMM-M01 ^c	31	36	1.6	0.67
PCA-M01	77	187	2.9	<0.01
PCA-M02	43	55	-9.3	0.51
PCA-M03	50	87	-4.6	0.27
PCA-M04	36	33	-63.8	0.46
PCA-M05	44	54	-75.1	2.38

^a Maximum error in the rate of heat release parameters.

^b ΔT_{final} values are magnitudes.

^c From Kotlar (2010).

4.2 Vajda et al.'s (1985) PCAS Approach

4.2.1 H₂-O₂

The construction of $\mathcal{S}$ for this case was based on selecting the $\mathcal{S}_k$ produced after every 2+ K change in temperature. In all, 599 $\mathcal{S}_k$'s were included, i.e., about half of the 1178 that were available. Based on equation 14, λ_{jmax} became 0.49. Table 4 shows the eigenvectors associated with the ($jmax = 11$) eigenvalues that exceed 0.49. Coupled with $u' = 0.2$, this approach produced a 14 reaction-9 species mechanism (PCA-H01). The plot of the rate of heat release vs. time produced with PCA-H01 is essentially indistinguishable from the standard and therefore is not presented. Its peak value (4.639×10^3 cal/cm³-s) and the time at which that value occurs (0.17810 ms) differ from the standard by less than 1%. (See table 2.) Also, the difference in the final temperatures of the solutions produced with this mechanism and the full one is <0.01 K. As such, PCA-H01 is not without merit. However, it includes all the species found in the full mechanism, and its number of reactions is significantly larger than those of TMM-H01–TMM-H03.

Table 4. H₂-O₂ test case: eigenvalue and eigenelement values for $\lambda_{jmax} \geq 0.49$.^a

	Eigenvalues										
	2.30E+6	8.77E+2	2.49E+02	1.66E+02	9.22E+01	5.96E+01	3.86E+01	2.51E+01	2.30E+00	1.42E+00	7.62E-01
Rxn	Eigenvector Eigenelements										
1	-0.399	-0.704	0.386	0.202	-0.099	-0.090	0.199	-0.281	0.077	0.103	0.025
2	0.000	-0.004	0.055	0.018	-0.099	-0.001	-0.054	0.049	0.245	-0.153	-0.399
3	0.000	0.000	0.007	0.001	-0.012	0.002	-0.008	0.004	0.042	-0.009	-0.052
4	0.000	-0.009	0.097	0.039	-0.179	-0.016	-0.091	0.104	0.328	-0.300	-0.639
5	0.000	-0.035	0.278	0.142	-0.588	-0.170	-0.309	0.568	-0.255	0.023	0.199
6	0.000	-0.003	0.032	0.016	-0.060	-0.012	-0.032	0.048	0.059	-0.053	-0.148
7	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.001
8	0.001	-0.045	-0.247	0.404	0.273	-0.644	0.029	0.165	0.231	-0.319	0.240
9	0.058	-0.022	-0.037	-0.035	-0.031	0.040	-0.166	0.092	0.380	0.303	-0.025
10	0.022	0.046	0.582	-0.578	0.408	-0.360	-0.110	0.122	0.015	-0.041	0.008
11	0.908	-0.329	0.103	0.032	-0.103	-0.076	0.120	-0.141	0.022	0.035	0.016
12	0.095	-0.090	0.287	0.475	0.538	0.482	-0.245	0.298	-0.009	-0.001	0.002
13	-0.001	0.010	0.005	0.006	-0.010	-0.008	-0.030	-0.009	-0.021	-0.008	-0.009
14	0.047	0.596	0.479	0.415	-0.127	-0.131	0.077	-0.435	0.004	0.039	0.016
15	-0.001	0.011	0.005	0.007	-0.006	-0.003	-0.026	-0.008	0.020	0.018	-0.029
16	0.000	0.003	0.000	-0.025	-0.015	0.003	-0.002	-0.013	-0.065	-0.008	0.015
17	-0.018	0.091	-0.003	-0.020	-0.069	-0.021	-0.116	0.053	0.644	0.499	0.239
18	0.000	-0.134	-0.124	-0.013	0.004	-0.087	-0.846	-0.473	-0.081	-0.086	0.033
19	0.000	0.014	0.076	-0.123	-0.086	0.213	0.006	-0.048	0.012	-0.003	0.187
20	0.000	0.007	0.125	-0.152	-0.168	0.329	0.027	-0.064	0.362	-0.646	0.464

^a Bolded eigenelement values exceed the $u' = 0.2$ cutoff employed in Vajda et al.'s (1985) approach. PCA-H01 was constructed on this basis.

4.2.2 MMH-RFNA

In this case, $\mathcal{S}$ was constructed by selecting the $\mathcal{S}_k$ produced after every 4+ K change in temperature. This approach led to (1) 650 $\mathcal{S}_k$ (of the 1618 that were available) being included in $\mathcal{S}$ and (2) $\mathcal{S}$ having more than 2.7×10^7 elements. Based on equation 14, λ_{jmax} became 5.3 (compared to the largest single value of 3.9×10^8) and $jmax$ became 173. Coupled with $u' = 0.2$, this cutoff produced a 187 reaction-77 species mechanism (PCA-M01).

Figure 3 presents plots of the rate of heat release and temperature vs. time produced with PCA-M01 and compares them to the standards. The standard solution's three heat release features are reproduced reasonably well. For all corresponding features in the two solutions, the peak values and the times at which those values occur are within 3% of one another. (PCA-M01's solution fooled the automated screening method. Looking for the local maximum at $3.41 \mu\text{s}$ in a range that extended from only 3.39 to $3.45 \mu\text{s}$, it found a value much lower than the actual one at $3.51 \mu\text{s}$.) Also, the final temperatures for the two solutions are within 0.01 K of one another. Thus, similar to the reduced $\text{H}_2\text{-O}_2$ mechanism produced by this approach, PCA-M01 is not without merit. However, only 5 of 81 species were eliminated, and the number of reactions is more than 5 times larger than meritorious reduced mechanisms (such as TMM-M01) that were produced with the TMM.

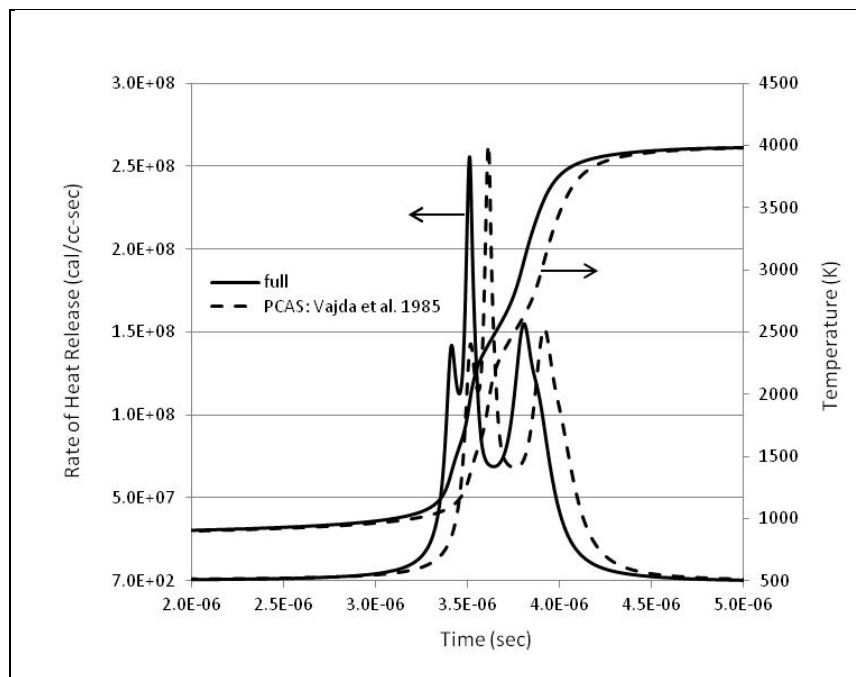


Figure 3. The MMH-RFNA homogeneous reactor test case: comparison of solutions generated by the full mechanism and the reduced mechanism produced by Vajda et al.'s (1985) PCAS approach.

4.3 Alternative Eigenvalue and Eigenelement Cutoffs

4.3.1 H₂-O₂

For this case, mechanisms with as few as 1 reaction and as many as 19 reactions were produced by adjusting λ_{jmax} and u' . Coupled with the restriction that $jmax$ not exceed the number of reactions targeted, 190 reaction sets were constructed. (This number included nonunique assemblages.) The smallest mechanism that produced a solution meeting the 10%–100 K agreement criteria (PCA-H02) had 12 reactions and 9 species. Thus, it was somewhat smaller than the mechanism produced by Vajda et al.'s (1985) approach. However, it still included all the species found in the full mechanism.

Despite the limited improvement found with respect to this approach's ability to produce mechanisms whose solutions for the test case met the 10%–100 K agreement criteria, other results suggested that further investigation of the approach was warranted. For example, a solution produced with a 10 reaction-9 species mechanism (PCA-H03) had a maximum rate of heat release parameter error of –11.9% and a final temperature within 0.03 K of the standard's. In another case, a solution produced with a 6 reaction-8 species mechanism (PCA-H04) had a maximum rate of heat release parameter error of –19.3% and a final temperature within 10 K of the standard's. Thus, the approach was applied to the MMH-RFNA test case.

4.3.2 MMH-RFNA

For this case, mechanisms with as few as 2 reactions and as many as 120 reactions were generated. (In all, 7140 mechanisms were produced, but the set included nonunique assemblages.) None of the mechanisms, however, produced a solution meeting the 10%–100 K agreement criteria. The failure of the approach for this case appears to be primarily attributable to the method's inability to identify as important the only reaction in the mechanism involving N₂O₄ (i.e., $N_2O_4 \leftrightarrow 2NO_2$). Without it, the N₂O₄ that is present as an initial reactant cannot react. In such cases, a significant fraction of the system's oxidizer existed essentially as an inert diluent over the entire course of the (simulated) process.

Figure 4a presents the full-mechanism-based model's predictions for the temperature and the concentrations of N₂O₄ and NO₂ during the first 5.1×10^{-10} s of the process. It shows that within 7.0×10^{-11} s, almost all the N₂O₄ is converted to NO₂. The first 4+ K temperature change also occurs at this same time, and it resulted in an S_k sample being taken. Since the next 4+ K temperature change did not occur for another 1×10^{-8} s, only one of the 650 S_k included in S corresponded to a time when a sensitivity coefficient for the reaction was large. Moreover, the reaction's importance to the formation of NO₂ was completely missed. (See figure 4b.) Thus, it is not surprising that the reaction's importance was not identified.

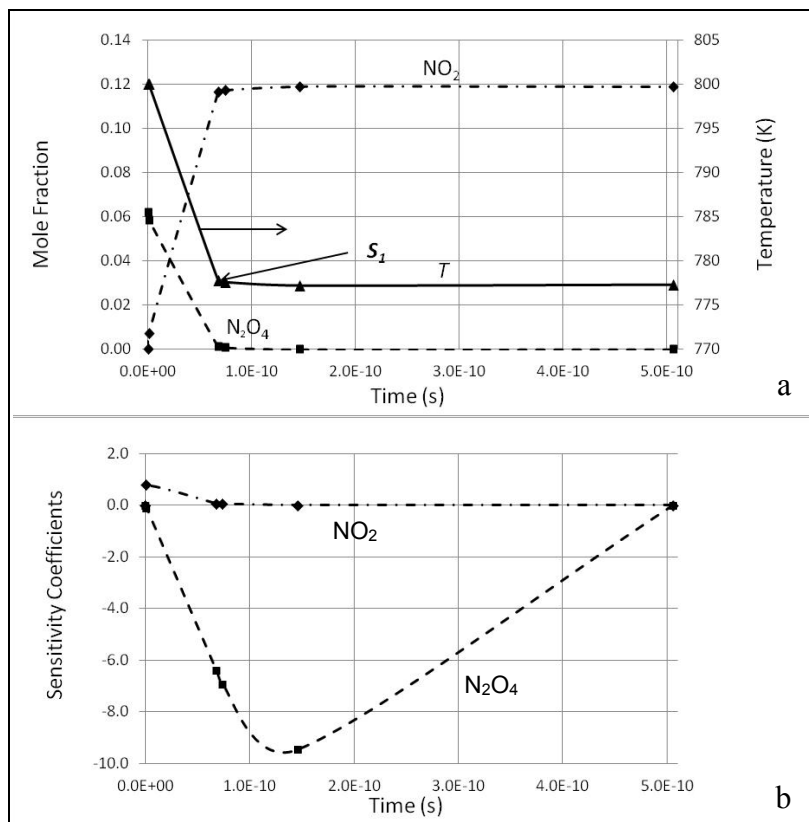


Figure 4. Plots of results relevant to identifying the importance of $\text{N}_2\text{O}_4 \leftrightarrow 2 \text{NO}_2$ in the MMH-RFNA mechanism.

While it might be argued that the introduction of the “obvious” inconsistency in the initial conditions should discount the results observed for this test, the reverse is true. Although the nature of the approach’s failure was easy to identify in this case, given the size and complexity of the systems ARL is interested in, it is clearly possible that similar but less obvious inconsistencies will be introduced. Thus, one would hope that the reduction method could not be so easily fooled. In an attempt to identify an approach that would be more foolproof, alternate S_k sampling strategies were investigated. They are discussed in sections that follow.

4.4 PCAS for Rate of Heat Release

4.4.1 $\text{H}_2\text{-O}_2$

A PCAS approach based on sensitivity coefficients for rate of heat release (and alternative eigenvalue and eigenelement cutoffs) proved to yield better results than Vajda et al.’s (1985) approach. It produced both PCA-H04 and TMM-H01. In addition, it produced a number of other mechanisms (PCA-H05–PCA-H08) with only eight species that, with the incremental addition of reactions, produced solutions in progressively better agreement with the standard (see table 2).

Beyond producing better results, this approach produces significantly smaller $\mathcal{S}$ matrices than those produced by Vajda et al.'s (1985) approach: $l*p$ vs. $l*(m+1)*p$. As such, it enables more extensive $\mathcal{S}_k$ sampling. This potential benefit was explored in the MMH-RFNA test case.

4.4.2 MMH-RFNA

The benefits of the PCAS approach based on sensitivity coefficients for rate of heat release observed in the H₂-O₂ test case were observed in the MMH-RFNA test case as well. The approach yielded a 55 reaction-43 species mechanism (PCA-M02) that produced a solution meeting the 10%–100 K agreement criteria. (See figure 5 and table 3.) While still not as small as mechanisms produced with the TMM, this result is clearly a significant improvement over the result obtained with Vajda et al.'s (1985) PCAS approach.

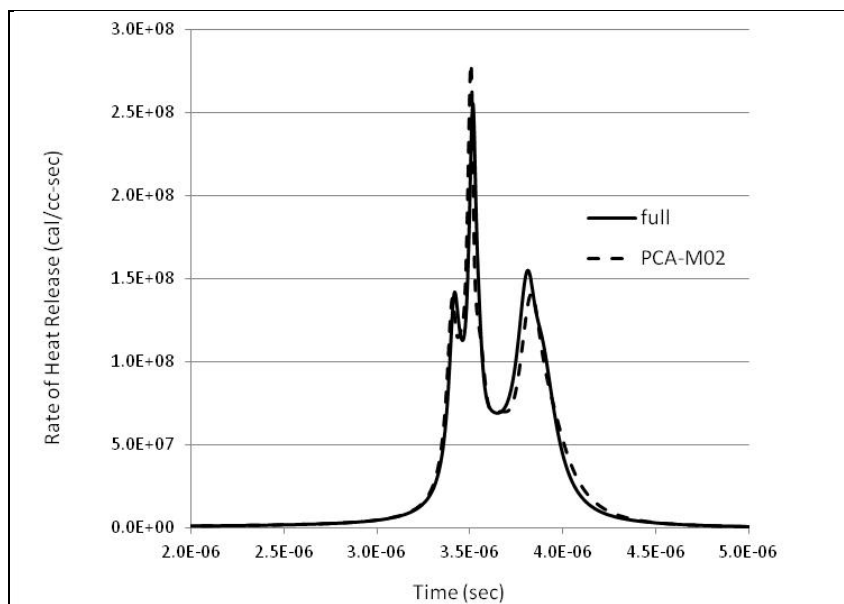


Figure 5. The MMH-RFNA homogeneous reactor test case: comparison of solutions generated by the full mechanism and a reduced mechanism produced by a PCAS approach based on sensitivity coefficients for rate of heat release.

To determine if even better results would be obtained if more $\mathcal{S}_k$'s were used in the construction of $\mathcal{S}$, advantage was taken of the fact that the number of elements in each $\mathcal{S}_k$ was simply $p = 513$. This allowed all (1618) available intermediate temporal solutions to be incorporated into $\mathcal{S}$. However, the results were worse; the smallest mechanism that was able produce a solution meeting the 10%–100 K agreement criteria had 87 reactions and 50 species (PCA-M02). There is the possibility that, as was the case with PCA-M01, some solutions associated with smaller mechanisms met the criteria but fooled the automated screening procedure. However, a review of the screening results indicated that the type of error seen in the case of PCA-M01 was unlikely to have occurred. Therefore, limited by time, the investigation of alternative $\mathcal{S}_k$ selection procedures was suspended.

4.5 Two-Step PCAS Approach

4.5.1 H₂-O₂

As discussed in the Computational Methods section, the two-step PCAS approach investigated in this study involved producing the kernel of a mechanism with a PCAS based on sensitivity coefficients for rate of heat release, then performing species-specific PCASs based on sensitivity coefficients for the concentrations of the species found in the kernel. To ensure that reactions important for species in the kernel would be identified, the $\mathcal{S}_k$ sampling procedure employed for the species-specific PCASs was designed so that sampling was conducted most frequently during times when changes in the concentration of the species under consideration were relatively large. Because of the complexity of programming a systematic approach for the investigation of this method's potential, a single reduced mechanism from the first step that produced a simulation that did not meet the 10%–100 K agreement criteria, but that came reasonably close, was chosen as a starting point for the second step. This choice reflected a belief that if the approach did not work for such a case, it would not work if the kernel produced a solution that agreed less with the standard.

For the H₂-O₂ test case, the 6 reaction-8 species mechanism PCA-H04 was chosen as the kernel. It was thought that the expansion of this mechanism on the basis of species-specific $q(\mathcal{A})$ s might produce the 8 reaction-8 species mechanism TMM-H01. However, that did not happen. There was no expansion of the mechanism if the expansion's basis was the modes/reactions with $u' \geq 0.2$ in the single most important eigenvector from each of the species-specific $q(\mathcal{A})$ s. When modes/reactions from the second most important eigenvector were made available for inclusion, reaction 5 was added on the basis of the $q(\mathcal{A})$ for O₂, and reaction 17 was added on the basis of the $q(\mathcal{A})$ for H₂O. Although having eight reactions and eight species, this mechanism (PCA-H09) was different than TMM-H01. It produced a solution with a maximum rate of release parameter error of 12.0% and had a final temperature that differed from the standard's by <0.03 K. As such, the simulation produced by this mechanism was closer to the standard than the one produced by PCA-H04. But unlike the solution produced by TMM-H01, it did not meet the 10%–100 K agreement criteria.

Further expansion of the kernel was also investigated. No reactions were designated for inclusion when modes of the third most important $q(\mathcal{A})$ eigenvectors were screened. When the modes for the fourth most important $q(\mathcal{A})$ eigenvectors were screened, two more reactions were added: reaction 4 (because of the $q(\mathcal{A})$ for H) and reaction 2 (because of the $q(\mathcal{A})$ for O₂). Combined with PCA-H09, the resulting mechanism became the same as TMM-H03, which, as noted, produces a solution meeting the 10%–100 K agreement criteria. Therefore, even though it did not produce TMM-H01, the two-step approach appeared to merit further investigation.

4.5.2 MMH-RFNA

The kernel chosen as the starting point for this case had 33 reactions and 36 species (PCA-M04). It produced the rate of heat release results shown in figure 6. The maximum rate of heat release parameter error (-63.8%) was associated with the magnitude of the heat release feature centered near $3.9 \mu\text{s}$. Despite this error, the final temperature of the solution produced with PCA-M04 was $<1 \text{ K}$ different from that of the standard's. The results produced by reduced mechanisms built from this kernel on the basis of species-specific $q(A)$ s were not, however, encouraging. No reactions were added until the third most important eigenvectors of the species-specific $q(A)$ s were screened. That led to the addition of 22 reactions and 6 species. However, the resulting 54 reaction-44 species mechanism (PCA-M05) produced results that agreed less with the standard than those produced by PCA-M04 (figure 6). Agreement did not improve until important modes for seven eigenvectors were added and the resulting mechanism included 83 reactions and 52 species. Even when important modes for the eigenvectors associated with the 9 largest eigenvalues were added, results produced by the resulting 91 reaction-54 species mechanism did not meet the 10%–100 K agreement criteria. Given these results, the investigation of the two-step approach was stopped.

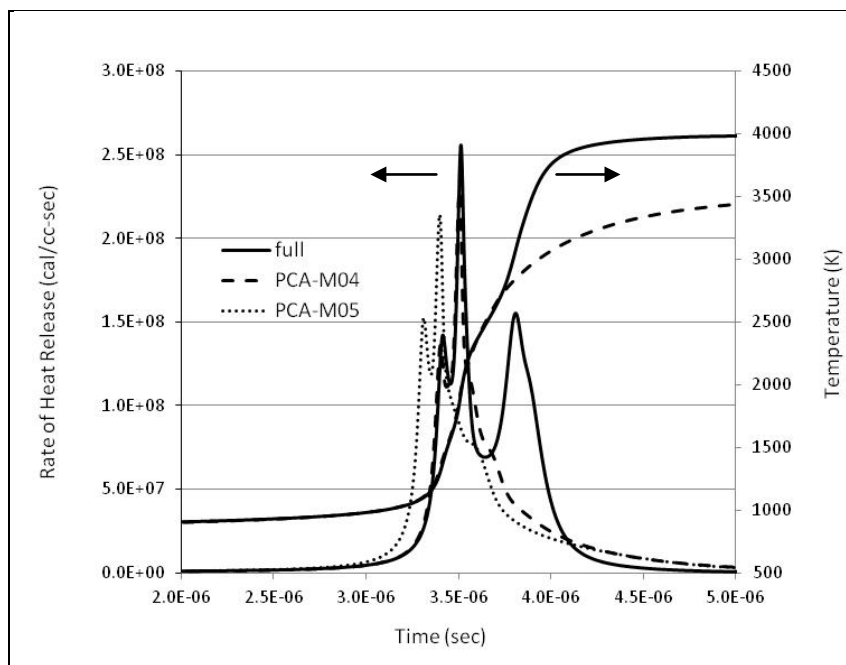


Figure 6. The MMH-RFNA homogeneous reactor test case: comparison of solutions generated by (1) the full mechanism, (2) a mechanism (PCA-M04) supplied to the second step of the two-step PCAS approach, and (3) a reduced mechanism (PCA-M05) derived by expanding PCA-M04 based on species-specific $q(A)$ s.

5. Summary

Various mechanism reduction approaches based on PCAS were developed and tested. For a test case involving a detailed MMH-RFNA mechanism with 81 species and 513 reactions, none of the implemented variations produced viable reduced mechanisms as small as those produced by the TMM. Although the sensitivity coefficients that are the foundation of the technique give an indication of the response of a process to a perturbation at a given time and set of conditions, they have no capacity for predicting whether that response will subsequently propagate or be damped out. That capacity is inherent in the perturbation approach underlying the TMM. As such, if mechanism size is the only concern, it will probably be preferable to use the TMM. However, employed as a means for understanding the role specific reactions play in sets produced by the TMM, a PCAS-based approach could prove useful. For example, any reaction that is included in a TMM-based mechanism but not a PCAS-based mechanism may represent a channel that can be modestly adjusted (say through a formulation change) such that a large change in the behavior of the propellant's ignition or combustion is achieved. In addition, because PCAS-based approaches have the potential to be less computationally demanding than the TMM, there may be applications for which it would be beneficial to employ a PCAS-based approach prior to employing the TMM.

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