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1. REPORT DATE (DD-MM-YYYY) 26-07-2018	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 13-May-2015 - 12-May-2018
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4. TITLE AND SUBTITLE Final Report: Reaction Network Reconstruction for Modeling of Dynamic Pathways	5a. CONTRACT NUMBER W911NF-15-1-0241
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 611102

6. AUTHORS	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Michigan - Ann Arbor 3003 South State Street Ann Arbor, MI 48109 -1274	8. PERFORMING ORGANIZATION REPORT NUMBER
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 66719-EG.4

12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Angela Violi
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	19b. TELEPHONE NUMBER 734-615-6448

RPPR Final Report

as of 16-Aug-2018

Agency Code:

Proposal Number: 66719EG

Agreement Number: W911NF-15-1-0241

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DUNS Number: 073133571

EIN: 386006309

Report Date: 12-Aug-2018

Date Received: 26-Jul-2018

Final Report for Period Beginning 13-May-2015 and Ending 12-May-2018

Title: Reaction Network Reconstruction for Modeling of Dynamic Pathways

Begin Performance Period: 13-May-2015

End Performance Period: 12-May-2018

Report Term: 0-Other

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees:

STEM Participants:

Major Goals: The goal of this work is to develop a descriptive model for the chemistry of alkanes in combustion conditions.

The new model will take into account experimental uncertainties. A recently developed computational method based on atomistic simulations is used to identify the most frequent reaction pathways for a given molecule, without any a priori knowledge - except for the chemical composition of the initial fuel. Given information on the chemical structure of the molecule, we aim at building a scalable random graphical model to represent chemical reaction mechanisms. With the aid of the established graphical model, we will employ spectral graph theory and machine learning techniques to infer the probability of reaction pathways, to estimate accurate model conditions in the presence of experimental uncertainties, and to identify the key characteristics of reaction networks, as well as common trends among different reaction networks that can be associated with molecular characteristics (e.g., branching, presence of rings).

Accomplishments: • Reaction network analysis.

- o Build physics-driven graphical models
- Derived graphical model physical reaction kinetic model
- Defined method to infer sparse graph topology and transition probability
- developed sparse-learning approach to analyze networks of reactions

Training Opportunities: Farshad Harirchi (postdoc)

Results Dissemination: 1. Khalil, O. A., Harirchi, F., Kim, D., Liu, S., Elvati, P., Violi, A., and Hero, A. O. "Model Reduction in Chemical Reaction Networks: A Data-Driven Sparse-Learning Approach" arXiv:1712.06281 [physics] (2017): Available at <http://arxiv.org/abs/1712.06281>

2. Wang, Q., Elvati, P., and Angela Violi. "Kinetic Model Reduction in Chemical Reaction Networks: A Data-Driven Sparse-Learning Approach" 37th International Symposium on Combustion (2018):

RPPR Final Report

as of 16-Aug-2018

Honors and Awards: 2017 Adel Sarofim Award, International Congress on Combustion By-Product and their Health Effects.

ASME George Westinghouse Silver Medal, 2015.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

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Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Co PD/PI

Participant: Alfred O Hero

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Farshad Harichi

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Reaction Network Reconstruction for Modeling of Dynamic Pathways

Final Report for W911NF-15-1-0241 (or W911NF-14-1-0359?)

Last revision: July 26, 2018

1 Mechanism reduction via reaction selection

In this section, we propose a data-driven sparse-learning approach towards identifying a reduced set of reactions, which approximately replicates the behavior of the detailed mechanism.

For each of N_r reactions, we introduce a binary selection variable $w_{i,t} \in \{0, 1\}$ to encode whether or not the i^{th} reaction is selected at time t . If reaction i is chosen for the reduced mechanism at time t , then $w_{i,t} = 1$; otherwise, $w_{i,t} = 0$. With the aid of the selection variables $\mathbf{w}_t = [w_{1,t}, w_{2,t}, \dots, w_{N_r,t}]^T$, we formally state the problem of mechanism reduction.

Given the measurements of species concentrations \mathbf{X}_t and reaction rates \mathbf{r}_t at all times, determine the smallest subset of reactions (in terms of \mathbf{w}) such that the estimation error induced by the reduced mechanism remains in a user-specified tolerance range (ϵ) at all time instances.

1.1 Sparse-Learning Mechanism Reduction (SLMR)

Let us first define the error induced by the reduced mechanism characterized by \mathbf{w}_t at time t on molar concentration of i^{th} species as follows:

$$\mathcal{E}_{i,t}(\mathbf{w}_t) = |\mathbf{X}_{t+1}(i) - \mathbf{X}_t(i) - \mathbf{M}_i(\mathbf{w}_t \odot \mathbf{r}_t)\Delta t|, \quad (1)$$

where \mathbf{M}_i denotes the i^{th} row of matrix \mathbf{M} and \odot denotes the element-wise product.

Error tolerance on individual concentrations We can enforce constraints on the error in the change of individual species concentrations for all time instances, *i.e.*,

$$\mathcal{E}_{i,t}(\mathbf{w}_t) \leq \epsilon \mathcal{N}_t(i), \quad \forall t, \quad \forall i \in \{1, \dots, N_s\}, \quad (2)$$

where \mathcal{N}_t is the normalization factor at time t , which is defined to be the summation of absolute changes of all concentrations at time t as described in Eq. (3), and ϵ is a tuning parameter that indicates the error tolerance that is acceptable in terms of the percentage of \mathcal{N}_t , *i.e.*, $\epsilon = 0.05$ indicates 5% error tolerance.

$$\mathcal{N}_t(i) = |\mathbf{M}_i| \mathbf{r}_t \Delta_t, \quad i \in \{1, \dots, N_s\}. \quad (3)$$

Constraint Eq. (4) is added to avoid the propagation of error through time. The size of time horizon can be chosen based on the speed of changes in concentrations. We indicate such time horizon with H . For the concentration change of each species i in time horizon $[t, t + H - 1]$, we have that

$$|\mathbf{X}_{t+H-1}(i) - \mathbf{X}_t(i) - \sum_{k=t}^{t+H-2} \mathbf{M}_i \mathbf{w}_k \odot \mathbf{r}_k \Delta_k| \leq \beta \epsilon \sum_{k=t}^{t+H-2} \mathcal{N}_k(i), \quad (4)$$

where β is a tuning parameter that indicates the tightness of the bound on propagated error, and $t = 0, H, 2H, \dots$

At each time instance t , we seek the minimum number of reactions that are required to be added to the previously selected reactions up to time t such that Eq. (2) and Eq. (4) are satisfied, *i.e.*,

$$\mathbf{w}_{t+1} \geq \mathbf{w}_t. \quad (5)$$

Now that the constraints that we consider for the optimization problem are described, we can formulate our data-driven sparse-learning mechanism reduction approach. For each time batch of size H , we solve the following mixed-integer linear programming problem:

$$\begin{aligned} \{\mathbf{w}_k^*\}_{k=t}^{t+H-1} = \underset{\{\mathbf{w}_k\}_{k=t}^{t+H-1}}{\text{minimize}} \quad & \sum_{k=t}^{t+H-1} \sum_{i=1}^{N_r} \mathbf{w}_{i,k} & (P_{SLMR}) \\ \text{subject to} \quad & \mathbf{w}_{i,k} \in \{0, 1\}, \quad i = 1, 2, \dots, N_r, \\ & \forall k \in \{t, t+1, \dots, t+H-1\} \\ & \text{Eqs. (2),(4),(5) hold.} \end{aligned}$$

where $\{\mathbf{w}_k\}_{k=t}^{t+H-1}$ are the optimization variables. Note that solving problem (P_{SLMR}) delivers the minimum number of reactions that are required to be added to the previously selected reactions, *i.e.*, incremental reaction inclusion Eq. (5) such that the error tolerance constraint on individual concentrations Eq. (2) and error propagation Eq. (4) are satisfied. The objective function minimizes the total number of selected reactions in the time horizon $[t, t + H - 1]$.

In order to have a global reduced mechanism that mimics the dynamical behavior of full mechanism, we need to use data from simulations over a sparse set of initial conditions that encompass the whole range of temperature T , equivalence ratio ϕ and pressure p . We refer to each initial condition as a point in the parameter space, namely $\theta = [T, \phi, p]$.

The next step is to find the reduced mechanism not just for the time horizon $[t, t + H - 1]$, but for the entire simulation time $[0, t_f]$, where t_f is the time that simulation ends. In order to do this, we solve problem (P_{SLMR}) for time intervals $[0, H - 1]$, $[H, 2H - 1]$, \dots , $[KH, t_f]$, where KH is the largest integer multiple of H that is smaller or equal to t_f , as described in Algorithm 1.

Global mechanism Assume that data is available for a sparse set of initial conditions that is denoted by Θ . In order to obtain a global reduced mechanism we calculate the set union of all

Algorithm 1 Calculating $\mathbf{w}(\theta)$

Input: $\{\mathbf{X}_t\}_{t=0}^{t_f}$, $\{\mathbf{r}_t\}_{t=0}^{t_f}$, $\{\Delta_t\}_{t=1}^{t_f}$, ϵ , β , $\theta = [\phi, T, p]$.Initialize: $t = 0$, $\mathbf{w}_{-1} = \mathbf{0}$.

1. While ($t \leq t_f$)
 - $W = \min\{H, t_f - t + 1\}$
 - set the time horizon to $[t, t + W - 1]$.
 - solve problem (P_{SLMR}) to obtain \mathbf{w}_{t+W-1}^*
 - $t + W \rightarrow t$.
 - $\mathbf{w}_{t-1} = \mathbf{w}_{t-1}^*$.
 - End while
 2. Return $\mathbf{w}_{t_f}^*$ as $\mathbf{w}(\theta)$.
-

selected reactions for all the conditions in Θ . In other words:

$$\mathbf{w}^* = \bigcup_{\theta \in \Theta} \mathcal{R}(\mathbf{w}(\theta)), \quad (6)$$

where $\mathcal{R}(\mathbf{w}(\theta))$ denotes the set of reactions corresponding to the output of Algorithm 1 for initial condition θ .

1.2 Computational Complexity

Problem (P_{SLMR}) is a standard mixed-integer linear programming (MILP) problem, and thus can be efficiently solved using state-of-the-art MILP solvers such as Gurobi [1] and CPLEX [2]. Even though these solvers can solve problems with large number of integer variables in a relatively fast manner by employing advanced branch and bounding algorithms, the worst-case complexity of MILP is exponential. In order to further reduce the complexity of our data-driven sparse-learning approach, we can utilize convex relaxation methods [3] by replacing the Boolean variable constraint with its convex compartment $0 \leq \mathbf{w}_{i,t} \leq 1$ for all i . The latter yields a linear programming problem, which can be solved efficiently in polynomial time, and therefore makes our approach promising for extremely large-scale chemical reaction networks at the cost of losing optimality guarantees.

2 Application

We applied the reduction algorithm presented in the previous section to the chemical mechanism of H_2 oxidation by Hong *et al.* [4]. We selected this mechanism for two reasons: first is a very small mechanism that is suitable for testing of different approaches and as such optimal to develop new methodologies; second, due to the small number of reactions and species, is very difficult to

reduce without affecting its accuracy. We want to stress, however, that the mechanism reduction of H_2 is intended to show the algorithm capabilities and not a real world application.

We first performed 48 simulations using the full mechanism in a H_2 /air 0-D homogeneous reactor for thermodynamic regimes that relevant to practical combustion devices by using Chemkin [5]. The species concentrations and reaction rates generated for initial conditions encompassing 5 – 20 atm, 800 – 1100 K, and equivalence ratios between 0.5 – 2 were used to generate the reduced mechanism. We first fix the time horizon for error propagation to be at $H = 10$. Then, by setting the tuning parameters β to 100 and ϵ , *i.e.*, the upper bound on the fitting error tolerance, to 0.02, 0.05, and 0.1 results in three reduced mechanisms with 47, 40 and 37 reactions (forward and reverse counted separately). Compared to the full mechanism, which includes 58 reactions excluding the reactions associated with Ar, that is a reduction of about 19%, 31%, and 36%, respectively.

Figure 1 shows, in the form of a directed bipartite graph, the comparison between the full mechanism and the 37-reactions reduced mechanism. In this representation, species are connected to the reactions in which they appear as reactants by red dashed lines, while reactions are connected to their products by blue dotted lines. Finally, gray lines show the reactions that were removed by the mechanism reduction.

To test the quality of the reduced mechanisms, we compared calculated ignition characteristics and the time evolutions of species concentrations in a range of conditions slightly wider than the one used to generate them (*i.e.*, 5 – 20 atm, 700 – 1300 K, equivalence ratio of 0.5 – 2) for the same homogeneous reactor. Figure 2 shows the ignition delay times, relative deviations in ignition delay time from the full mechanism, and maximum temperature increase at 10 atm, and equivalence ratios of 0.5 and 1. All three reduced mechanisms are in excellent agreement with the full mechanism, with, as expected, larger reduced mechanisms showing better agreements. The relative deviation in the ignition delay times are, however, even in the worst case scenario within 1% under all the tested conditions. Also the maximum temperature increase (bottom panels of Fig. 2) is well-maintained in the reduced mechanisms. This agreements are not limited to 10 atm and $\phi = 0.5$ and 1, as very similar observations can be made in all the condition tested (not shown).

Figure 3 shows the time evolutions of selected species for the simulations at 1000 K, 10 atm, equivalence ratios of 0.5 and 1. All reduced mechanisms generated very similar H_2O and H profiles throughout the whole ignition event compared to those from the full mechanism. However, OH profiles show that the correct concentrations after ignition is not completely matched by the 40- and 37-reactions mechanism. Considering the small size of the full mechanism this is not entirely unexpected and is exacerbated by the equilibrium reached in the concentrations after ignition. Overall, however, the above comparisons show that the reduced mechanisms generated by our new reduction approach are effective in reproducing key combustion properties such as ignition characteristics and heat release, as well as species profiles during pre-ignition and ignition.

3 Conclusions

In this work, we present a new method to reduce chemical reaction network by employing data-driven sparse learning approach to obtain a reduced mechanism that is valid for all process condi-

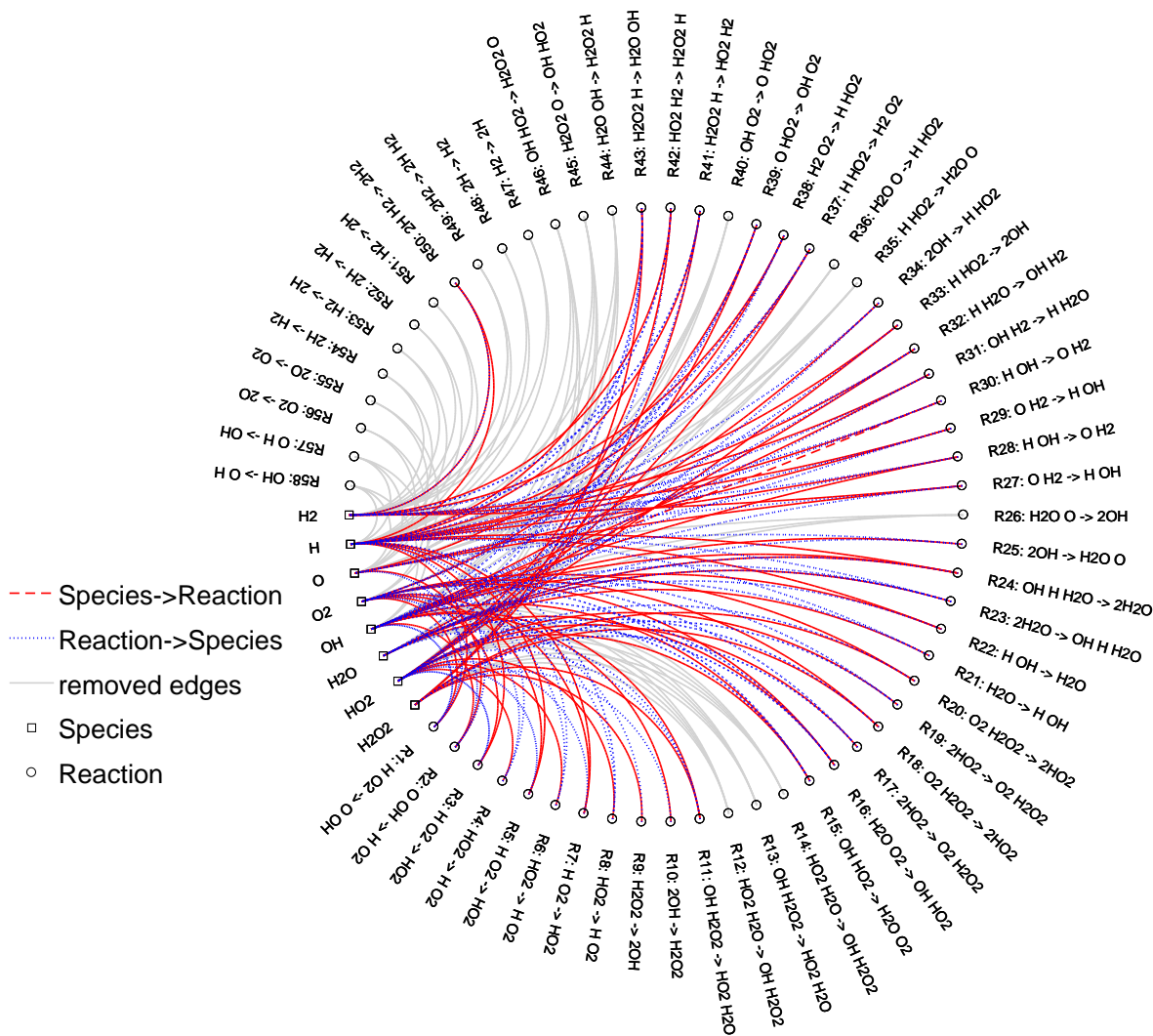


Figure 1: The directed bipartite graph for the reduced mechanism with 37 reactions ($\epsilon = 0.1$). Red dashed lines indicate the edges from species to reactions, blue dotted lines represent the edges from reactions to species, and light grey solid lines show the removed edges from the detailed mechanism.

tions (temperature, pressure and equivalence ration) and all ranges of species molar concentrations. In addition, our method incorporates a user-specified bound on the propagation of error cause by eliminating reactions. That is, the proposed approach ensures that the discrepancy between the original and the reduced mechanisms remains in the user-specified acceptable range in all time instances and in all time horizons of specified length. The reduction is performed without introducing any bias towards specific properties or species therefore providing a mechanism with optimal performance, which is independent of the chemical reaction network that is being considered. Finally, the approach has a low computational cost and scales gracefully with the size of the full mechanism, making it a viable option for the reduction of large mechanisms.

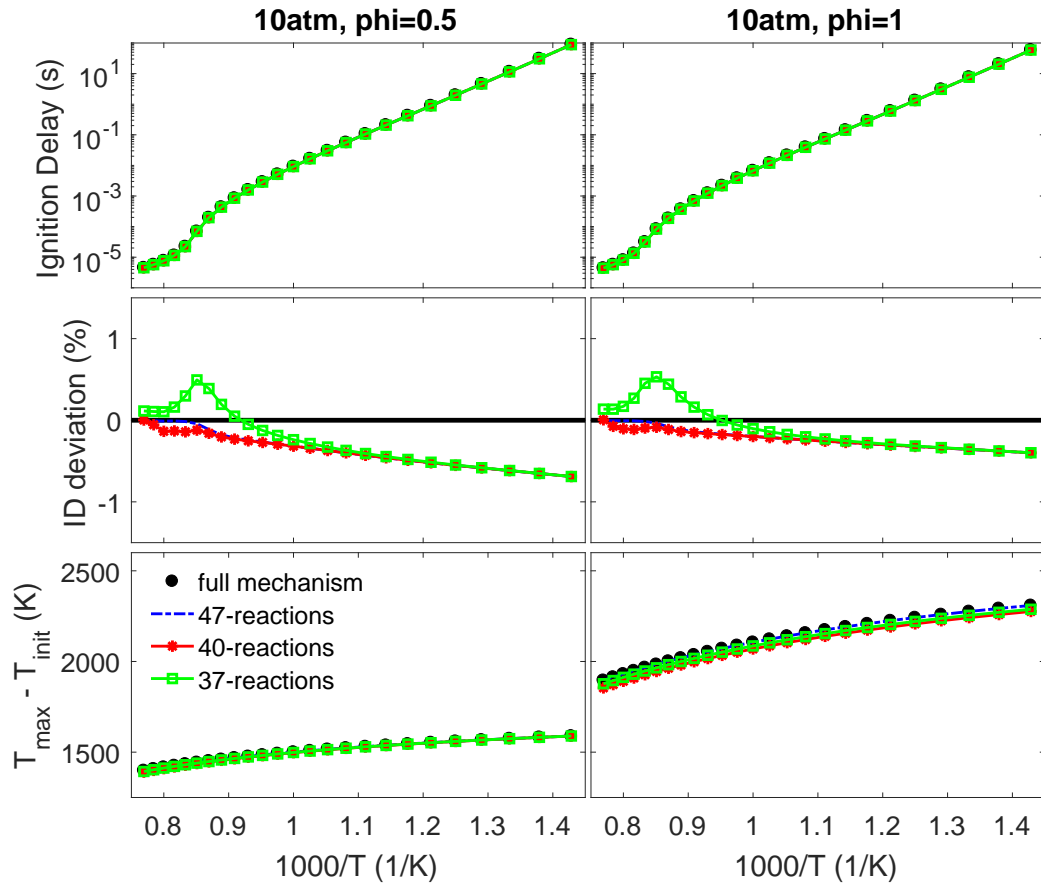


Figure 2: Computed ignition delay times (top), percent deviations in ignition delay from the full mechanism (middle), and maximum temperature increase (bottom) for 10 atm, equivalence ratios of 0.5 and 1 cases.

The performance of the method is evaluated on a H_2 mechanism, which due to its small initial size was expected to be difficult to reduce. Surprisingly, however, our method was able to reduced the number of reactions by more than one third without any notable discrepancy in ignition delay or heat release.

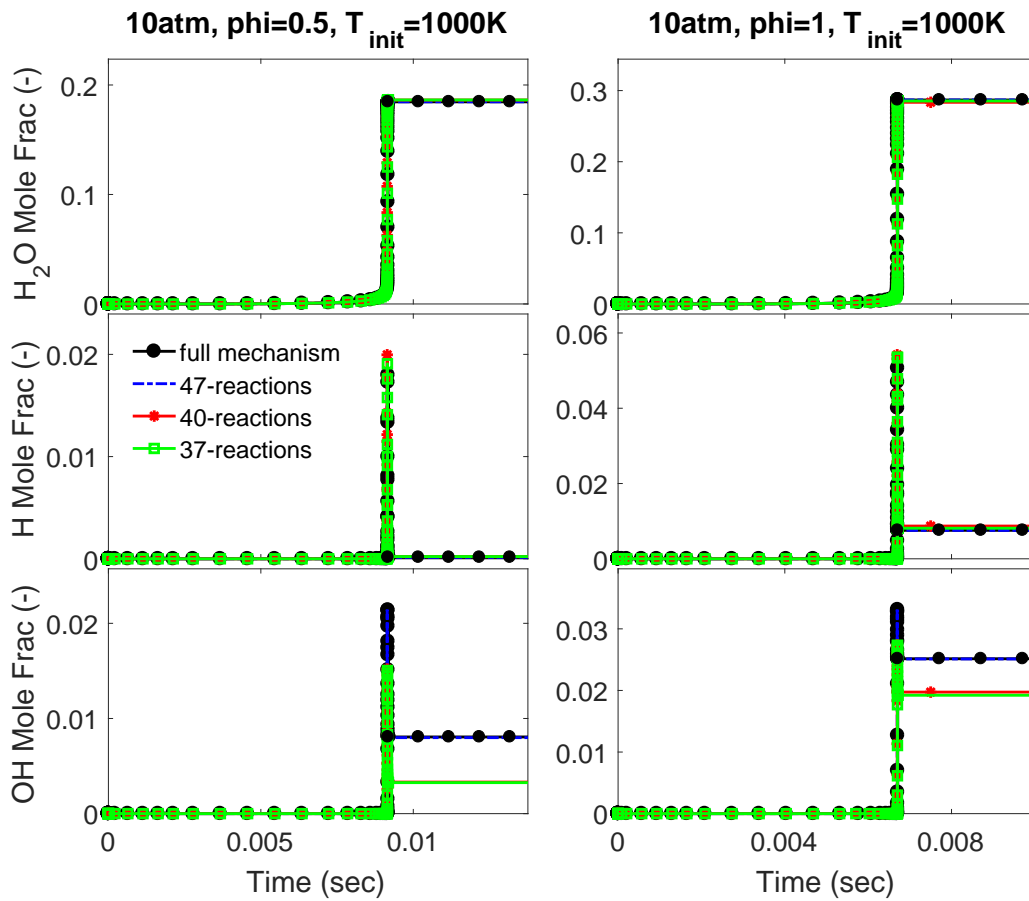


Figure 3: Time evolutions of H₂O, H, and OH in mole fractions from homogeneous reactor simulations with initial conditions of 1000 K, 10 atm, and equivalence ratios of 0.5 and 1.

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