Exercise 10: Reduction of a kinetic mechanism using pyMARS

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1. Introduction & Problem

In combustion modeling, detailed kinetic mechanisms are essential for understanding fundamental combustion characteristics, but their computational complexity often limits their practical application in large-scale simulations. Detailed mechanisms can contain hundreds of species and thousands of reactions that accurately predicts behavior in combustion. However, as all of these reactions and species are not relevant for the overall behavior, effective reduction methods can be used to reduce the mechanisms while still retaining accurate modeling data. Thus, drastically lowering the computational cost of these models.

In this report, we employ pyMARS (Python-based Mechanism Automatic Reduction Software) to reduce the GRI-Mech3.0 kinetic mechanism for methane-air combustion. We will use Directed Relation Graph with error propagation (DRGEP) with initial sensitivity analysis (DRGEPSA). The reduction will be performed under specified conditions of 1 atm pressure, reactor temperature ranging from 700-2000 K and equivalence ratio of 1.1: The reduced model will be compared with the unchanged GRI-Mech3.0 and the generated RMG mechanism from exercise 9. The cases for comparision are

- Ignition Delay Time for 1 bar, temperature ranging from 700-2000 K and equivalence ratio of 1.1:
- Laminar Flame Speed for 1 bar, temperature of unburnt gas mixture at 298 K and equivalence ratio between 0.5 to 1.5:

2. Theory and Method

2.1 Mechanism Reduction Fundamentals

Mechanism reduction techniques are categorized by their approach to identifying and eliminating less important species and reactions. The primary methods include sensitivity analysis, detailed reduction, computational singular perturbation (CSP), and directed relation graph (DRG) approaches. Each method balances performance against computational cost, with more sophisticated techniques generally providing better reduction quality at higher computational expense. Figure 1 shows an overview of the performance against computational cost for different reduction techniques.

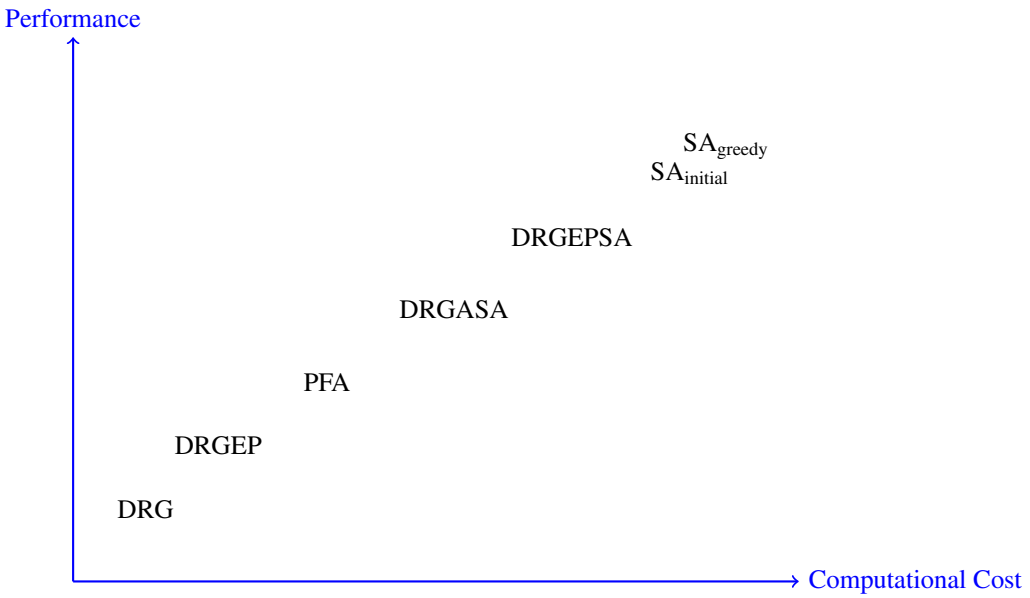

Figure 1: Performance vs computational cost comparison of different mechanism reduction methods

The reduction techniques can remove important and wanted reactions as well as make the mechanism unreliable with a to high error rate. Retained species, threshold and error limit values needs to be specified accordring to know theory in order to ensure the accuracy of the reduced model.

2.2 Directed Relation Graph (DRG)

The DRG method identifies and eliminates species of negligible importance by calculating interaction coefficients between target species and candidate species for removal. For a target species A, the method calculates the interaction coefficient (r_{AB}) representing the production rate dependency of A on species B, see equation (1)

$$r_{AB} \equiv \frac{\sum_{k=1,K} |\nu_{A,k}\omega_k\delta(B)_k|}{\sum_{k=1,K} |\nu_{A,k}\omega_k|} \tag{1}$$

where $\delta(B)_k = \begin{cases} 1, & \text{if the } k^{th} \text{ elementary reaction involves species B} \\ 0, & \text{otherwise} \end{cases}$

The parameters $\nu_{A,k}$ represents the stoichiometric coefficient of species A in the k^{th} elementary reaction, ω_k is the overall rate of reaction for K, and K is the total number of reactions. If $r_{AB} < \varepsilon$ (cutoff threshold), species B is removed from the mechanism, provided this removal does not eliminate reactions essential for important pathways. Meaning that an unimportant reaction will not be removed in case it's necessary to produce antoher species which has an important reaction. For example in figure 2, if reaction A⇒B is unimportant, but B⇒C is. Then A⇒B will remain as it solely produce species B which is necessarily for the important reaction of B⇒C.

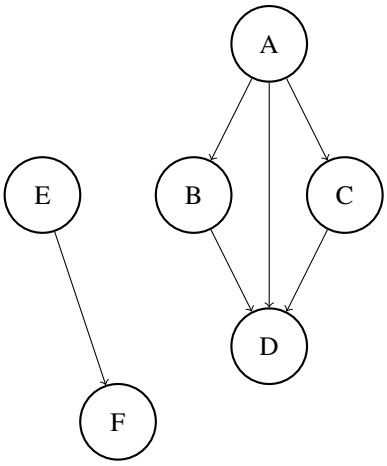

Figure 2: Reaction pathways, connections between different species in Directed Relation Graph theory

2.3 Directed Relation Graph with Error Propagation (DRGEP)

DRGEP represents an improved version of DRG that better accounts for indirect species dependencies through graph pathways. In figure 2, we see that A is directly affects B,C and D, but also effects D indirectly through A⇒B⇒D and A⇒C⇒D

DRGEP uses the overall interaction coefficients (R_{AB}) to decide which species to keep. (R_{AB}) is calculated with the maximum product for all paths between the chosen two species, see equation (2)

$$R_{AB} = \max_{\text{all paths } p}(r_{AB,p}) \tag{2}$$

Where the updated formula for interaction coefficients (r_{AB}) is calculated thorugh equation (3)

$$r_{AB} = \frac{\sum_{k=1,K} |\nu_{A,k}\omega_k \delta(B)_k|}{max(P_A, C_A)} \tag{3}$$

$P_A = \sum_{k=1,K} max(0, \nu_{A,k}\omega_k)$ represents production and $C_A = \sum_{k=1,K} max(0, -\nu_{A,k}\omega_k)$ represents consumption. $r_{AB,p} = \prod_{j=1}^{n-1} r_{s_j s_{j+1}}$ is used to calculates the paths for n species between A and B.

So for figure 2, R_{AB} would be calculated according to equation (4)

$$R_{AB} = \max_{\text{all paths } p}(r_{ad,p}) = \max(r_{AD,1}, r_{AD,2}, r_{AD,3}) = \max(r_{AB}r_{BD}, r_{AD}, r_{AC}r_{CD}) \tag{4}$$

2.4 Sensitivity Analysis Integration

Due to the high computational cost of sensitivity analysis, it is typically applied in combination with DRG or DRGEP methods. The combined approaches (DRGASA and DRGEPSA) first remove a significant fraction of species using graph-based methods, then apply sensitivity analysis to the smaller mechanism.

Two sensitivity analysis algorithms are implemented in pyMARS:

Initial Algorithm: Error induced by limbo species removal is evaluated once at the beginning, with species considered for removal in ascending order of induced error.

Greedy Algorithm: The induced error of remaining limbo species is re-evaluated after each removal, selecting the species with the lowest induced error at each step.

2.5 pyMARS Implementation

pyMARS requires input files in cti format specifying the detailed mechanism, target species, retained species, reduction method, error limits, and reactor conditions. The software implements various reduction methods with different performance-cost trade-offs, from simple DRG to computationally expensive sensitivity analysis approaches.

Key input parameters include:

- Detailed mechanism (RMG-generated mechanism or GRI-Mech3.0)
- Target species (fuel, oxidizer)
- Retained species (species that must remain in reduced mechanism, such as CO_2 and intermediate species)
- Reduction method specification (DRG, DRGEP, with or without sensitivity analysis)
- Error tolerance limits for the reduced model (Maximum acceptable deviation between detailed and reduced mechanism predictions.)
- Threshold values for species interaction coefficients (ε-value, removed from model if R_{AB} or r_{AB} is lower)
- Reactor conditions (temperature, pressure, equivalence ratio ranges)

pyMARS evaluates mechanism accuracy based on ignition delay time rather than laminar flame speed. The software systematically removes species while monitoring error accumulation to ensure the reduced mechanism remains within specified accuracy bounds.

3. Results

For the results, two reduced `.cti` files were generated from pyMars reduction of GRI-Mech3.0, R-17 and R-24. The two reduced mechanism were compared to the already establishes GRI-Mech3.0, our previously generated RMG-mechanism from exercise 9 and experimental data. Amount of species and reactions generated is presented in table 1 for all four mechanisms.

Table 1: Amount of Core species and reactions present in the different mechanisms

Mechanism	**Species**	**Reactions**
GRI-Mech 3.0	53	325
RMG 99% conv (700-2000K)	48	839
GRI reduced 17 (R-17)	17	58
GRI reduced 24 (R-24)	24	102

Freely propagating laminar flame speed was calculated at 298 K, 1 bar and equivalence ratio ranging from 0.5-1.5 for all four mechanism. The experimental data conditions used for comparison where taken during the following conditions, 1 atm, equivalence ratio between 0.65 to 1.25 at unburnt gas temperture of 298 K, see figure 3.

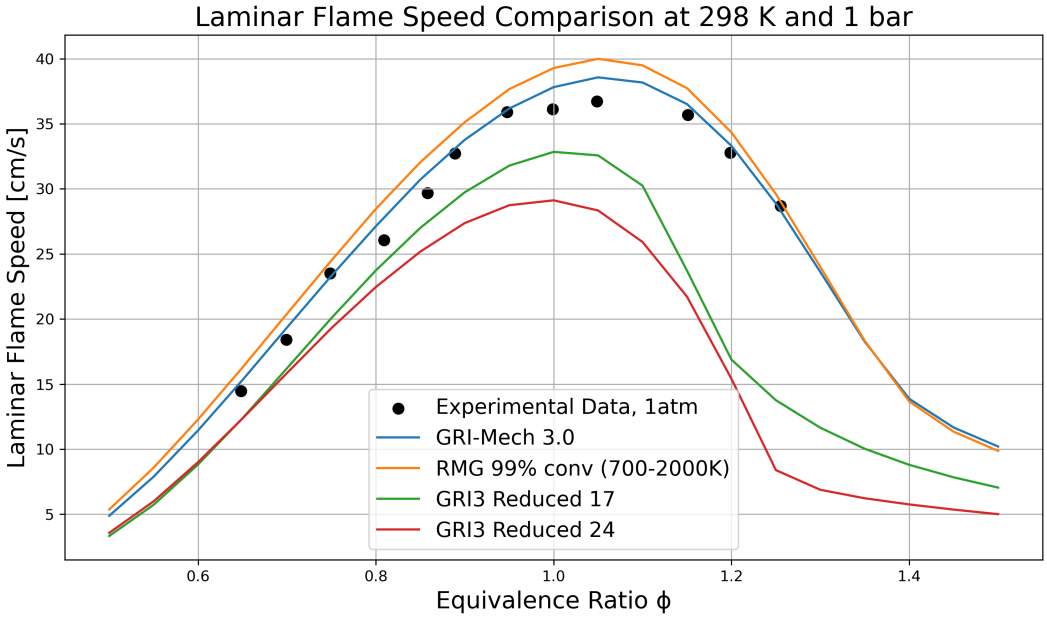

Figure 3: Comparison of Laminar Flame Speed Delay Time between GRI-Mech3.0, RMG-mechanism, R-17 and R-24. Lines represent Canteras calculations and dots represent the experimental data.

Ignition delay time was calculated at equvilance ratio 1.1; 1 bar and tempertures ranges from 700-2000 K. The experimental data conditions used for comparison where taken during the following conditions, 1 atm, interval between 1500-1950 K and equivalence ratio of 1.0; see figure 4.

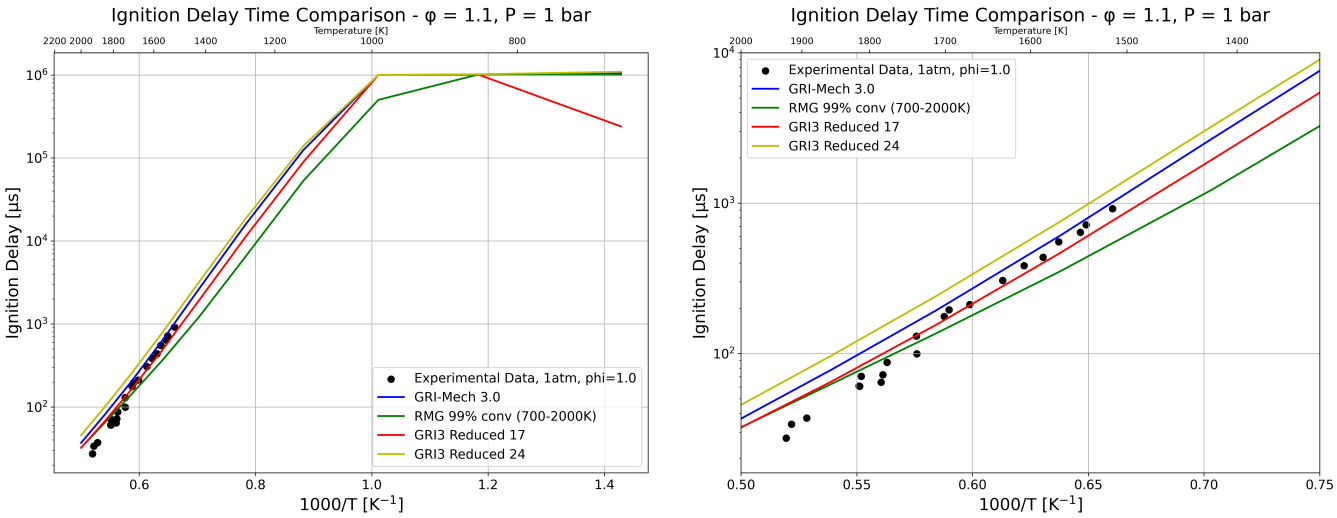

Figure 4: Comparison of Laminar Flame Speed Delay Time between GRI-Mech3.0, RMG-mechanism, R-17 and R-24. Lines represent Canteras calculations and dots represent the experimental data. Left is the full figure while right plot is zoomed in where the experimental data is present.

A laminar flame speed sensitivity analysis was performed to compare R-17 and R-24 and GRI-Mech3.0, presented in figure 5 was performed for pressure at 1 bar, unburnt gas temperature 298 K and equivalence ratio 1.1. The generated laminar flame speed was 38.21 cm/s for GRI-Mech3.0, 30.30 cm/s for R-17, 25.92 cm/s for R-24 and 39.80 cm/s for RMG 99% conversion.

R-17 generated 14 and R-24 generated 21 sensitive reactions respectively. These reactions are compared to the top 15 sensitivity reactions in the GRI-Mech3.0 mechanism that fulfilled the conditions of of sensitivity values within -0.03 to 0.03, presented in table 2. In table **??** the sensitivity reactions between R-17 and R-24 are compared.

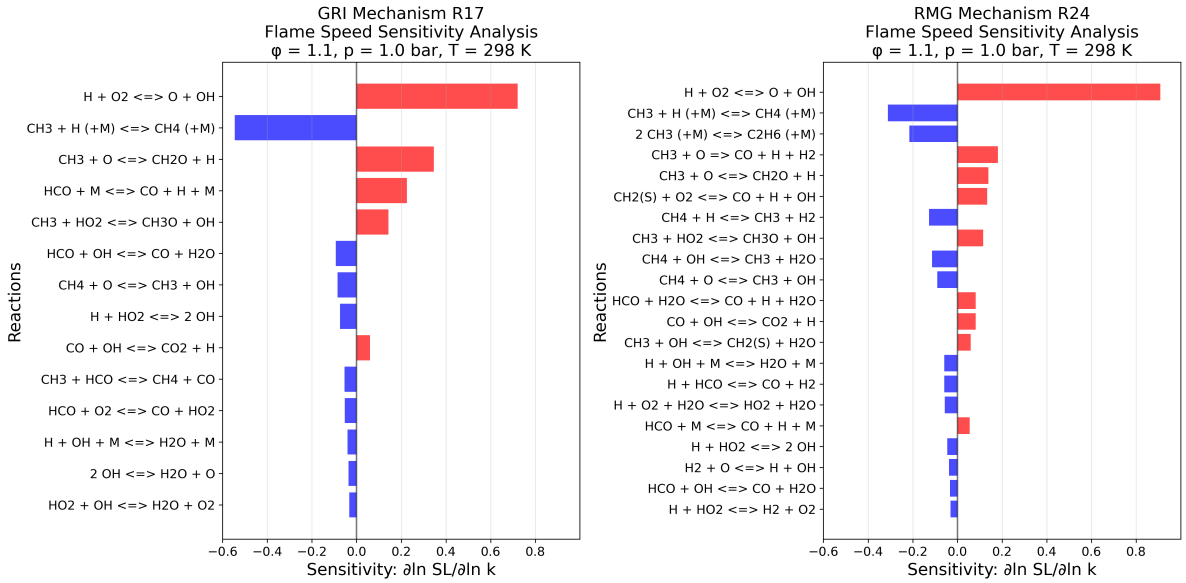

Figure 5: Laminar Flame Speed sensitivity analysis performed for methane-air combustion. Comparison between GRI-Mech3.0 (left) and RMG generated mechanism for 99% conversion (right)

Table 2: Sensitivity Analysis Comparison for Methane-Air Combustion between GRI-Mech3.0, RMG with 99% conversion, R-17 and R-24

Reaction	**GRI-Mech 3.0**	**RMG 99%**	**GRI-R17**	**GRI-R24**
$H + O_2 \Leftrightarrow O + OH$	+0.5586	+0.5715	+0.7210	+0.9085
$CH_3 + H\ (+M) \Leftrightarrow CH_4\ (+M)$	-0.1836	-0.1983	-0.5459	-0.3112
$CO + OH \Leftrightarrow CO_2 + H$	+0.0715	+0.0786	+0.0596	+0.0814
$CH_3 + HO_2 \Leftrightarrow CH_3O + OH$	+0.0711	+0.0533	+0.1424	+0.1151
$CH_3 + OH \Leftrightarrow CH_2(S) + H_2O$	+0.0672	+0.0669	–	+0.0594
$H + O_2 + H_2O \Leftrightarrow HO_2 + H_2O$	-0.0451	-0.0633	–	-0.0569
$HCO + H_2O \Leftrightarrow CO + H + H_2O$	+0.0594	+0.0488	–	+0.0816
$CH_3 + O \Rightarrow CO + H + H_2$	+0.0532	+0.0598	–	+0.1817
$CH_4 + H \Leftrightarrow CH_3 + H_2$	-0.0404	-0.0470	–	-0.1268
$2\ CH_3\ (+M) \Leftrightarrow C_2H_6\ (+M)$	-0.0404	-0.0416	–	-0.2150
$H + OH + M \Leftrightarrow H_2O + M$	-0.0366	-0.0418	-0.0405	-0.0593
$CH_4 + OH \Leftrightarrow CH_3 + H_2O$	-0.0405	-0.0383	–	-0.1136
$HCO + M \Leftrightarrow CO + H + M$	+0.0439	+0.0364	+0.2254	+0.0546
$H + HCO \Leftrightarrow CO + H_2$	-0.0461	-0.0357	–	-0.0584
$H + HO_2 \Leftrightarrow H_2 + O_2$	-0.0355	–	–	-0.0311

Table 3: Sensitivity Analysis Comparison for Methane-Air Combustion between reduced mechanism R-17 and R-24

Reaction	**GRI-R17**	**GRI-R24**
$H + O_2 \Leftrightarrow O + OH$	+0.7210	+0.9085
$CH_3 + H\ (+M) \Leftrightarrow CH_4\ (+M)$	-0.5459	-0.3112
$CH_3 + O \Leftrightarrow CH_2O + H$	+0.3460	+0.1385
$HCO + M \Leftrightarrow CO + H + M$	+0.2254	+0.0546
$2\ CH_3\ (+M) \Leftrightarrow C_2H_6\ (+M)$	–	-0.2150
$CH_3 + O \Rightarrow CO + H + H_2$	–	+0.1817
$CH_3 + HO_2 \Leftrightarrow CH_3O + OH$	+0.1424	+0.1151
$CH_2(S) + O_2 \Leftrightarrow CO + H + OH$	–	+0.1337
$CH_4 + H \Leftrightarrow CH_3 + H_2$	–	-0.1268
$CH_4 + OH \Leftrightarrow CH_3 + H_2O$	–	-0.1136
$HCO + OH \Leftrightarrow CO + H_2O$	-0.0936	-0.0329
$CH_4 + O \Leftrightarrow CH_3 + OH$	-0.0849	-0.0898
$HCO + H_2O \Leftrightarrow CO + H + H_2O$	–	+0.0816
$CO + OH \Leftrightarrow CO_2 + H$	+0.0596	+0.0814
$CH_3 + OH \Leftrightarrow CH_2(S) + H_2O$	–	+0.0594
$H + OH + M \Leftrightarrow H_2O + M$	-0.0405	-0.0593
$H + HCO \Leftrightarrow CO + H_2$	–	-0.0584
$H + O_2 + H_2O \Leftrightarrow HO_2 + H_2O$	–	-0.0569
$CH_3 + HCO \Leftrightarrow CH_4 + CO$	-0.0543	–
$HCO + O_2 \Leftrightarrow CO + HO_2$	-0.0527	–
$H + HO_2 \Leftrightarrow 2\ OH$	-0.0747	-0.0454
$H_2 + O \Leftrightarrow H + OH$	–	-0.0376
$2\ OH \Leftrightarrow H_2O + O$	-0.0359	–
$HO_2 + OH \Leftrightarrow H_2O + O_2$	-0.0329	–
$H + HO_2 \Leftrightarrow H_2 + O_2$	–	-0.0311

4. Discussion and Conclusion

In figure 3, we clearly see that the reduced mechanism follows the same trend but lower LFS-value than the original GRI-Mech3.0 mechanism until $\varphi = 1.1$ where the laminar flame speed value starts to drop. This trend does not follow the experimental data, so the reduced mechanism has lost severe accuracy.

In contrast to the IDT-calculations, seen in figure 4. Where the reduced mechanism follows the same trend as GRI-Mech3.0 with the variation that R-17 undershoots and R-24 overshoots in comparision to GRI-Mech3.0.

The over- and undershoot of IDT calculations is most likley due to what type of reactions where left in the reduced mechanism. As seen in table 2 and table 3 that R-24 includes more chain termination reactions such as 2 CH_3 (+M) $\Leftrightarrow$ C_2H_6 (+M). This increase in chain termination and lack of branching and propagation in comparison would explain why R-24 overshoots the IDT and R-17, which lacks these terminations reactions, would undershoot and have a lower IDT value than the base mechanism.

The reason why IDT still provides accurate values and LFS loses a great deal of accuracy even though they contain the same sensitivity reactions according to table 2, is most likely because the least important reactions that were removed in the reduction still serve a purpose and have an impact on the LFS value.

This happens because pyMars is currently designed to calculate its error rate according to IDT. pyMars uses `Autoignition parameters` to sample its thermochemical data and bases which species and reactions should remain. As a result, pyMars considers IDT and not LFS for the reducing, which will result in IDT still being fairly accurate while LFS can have severe accuracy damages which pyMars simply ignores. There is currently implements ongoing to update pyMars to include LFS in it's error calculations. These implements are currently not available and thus we get this error.

This is the cost of using reduction tools such as pyMars. The computational cost is dropped and the mechanism becomes more available for practical applications. However, it loses its accuracy, and in some cases like this, completely makes the mechanism unusable in some areas. This can be minimized with theory and improved reduction tools, but the problem will always remain there. There will always be a trade off between accuracy and practicality.