Exercise 9: Development of a mechanism for a methane-air mixture using Reaction Mechanism Generator (RMG)

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23th of July 2025

1. Introduction & Problem

In combustion modeling, reaction mechanisms are crucial tools for accurately simulating and calculating important characteristics such as laminar flame speed and ignition delay time. In some cases, existing reaction mechanisms can be used, which is the case for methane (CH_4) combustion where GRI-Mech3.0 can be employed. However, in several cases, there is a need to generate custom mechanisms, either because no current reaction mechanism exists or the existing ones do not suit the specific requirements of one's simulation. In these cases, constructing reaction mechanisms by hand is time-consuming, and therefore there is a need for tools such as RMG (Reaction Mechanism Generator) to generate reaction mechanisms efficiently and according to one's specific needs.

In this report, we will use RMG to generate a detailed kinetic mechanism for methane-air combustion and compare the results with GRI-Mech3.0. The conditons for RMG reactor was specified as, pressure of 1 bar, temperature between 700 K to 1400 K and 700 K to 2000 K, equvilance ratio between 0.5 to 1.5 by using initial fractions for ranges of [0.0499, 0.1361] for CH_4 and [0.1815, 0.1996] for O_2. N_2 was set to 0.71645 and later `BalanceSpecies` was used to ensure the sum of mole fractions is one. The temperature was The cases we will compare are the following:

- Determine freely propagating laminar flame speed of the RMG-generated mechanism for unburnt mixture temperature 298 K, initial pressure 1 bar and equivalence ratio ranging from 0.5-1.5
- Calculate the ignition delay time for temperatures ranging from 700-1400 K (700-2000K for experimental data comparision) at equivalence ratio 1.1 and pressure 1 bar
- Generate a reaction flux diagram at pressure 1 bar, temperature 1200 K and equivalence ratio 1.1
- Perform flame speed sensitivity analysis for the created mechanism at initial pressure 1 bar, unburnt gas temperature 298 K and equivalence ratio 1.1

The theory behind these calculations and the implementation in Cantera was covered in previous exercises 6, 7, and 8.

2. Theory and Method

2.1 Mechanism Development

The development of chemical kinetic mechanisms is a systematic process that involves multiple stages of refinement and validation. As shown in Figure 1, the process begins with user input defining the desired model conditions, which are then fed into RMG to generate a detailed kinetic model. This initial model undergoes validation against experimental or quantum calculation data to assess its accuracy.

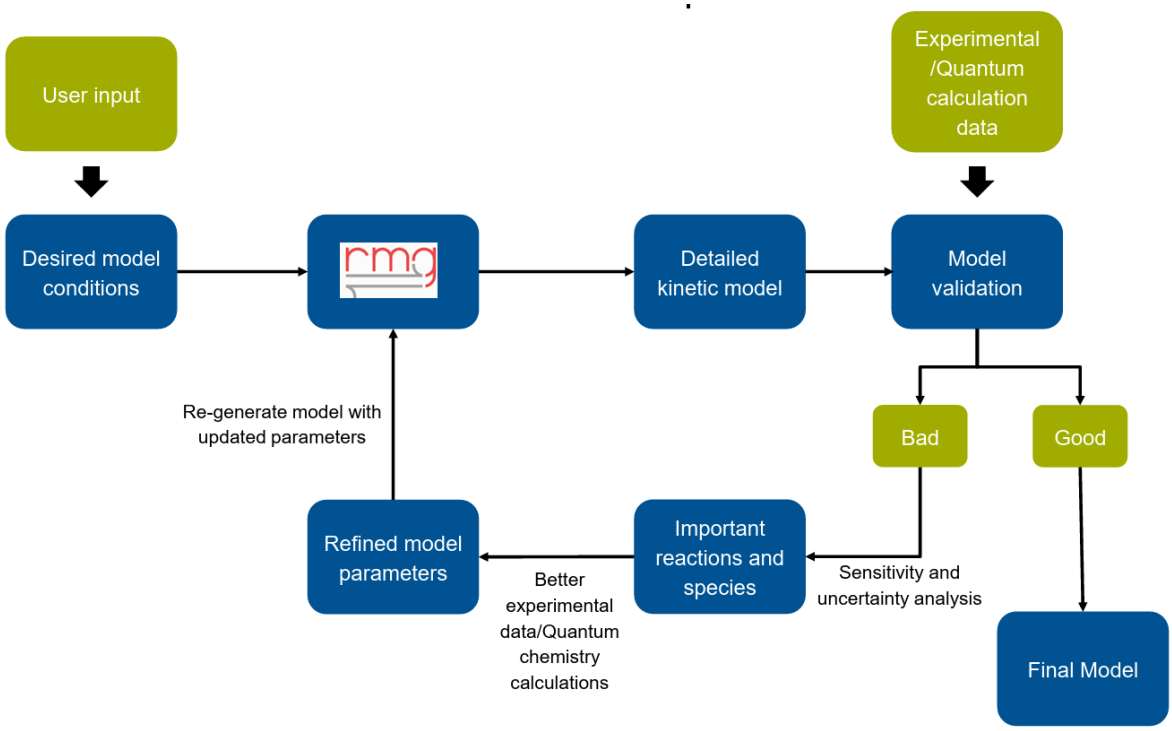


Figure 1: Flow chart illustration of mechanism development.

The validation process determines whether the model is satisfactory or requires further refinement. If the model performs poorly, sensitivity and uncertainty analysis are conducted to identify the most important reactions and species that significantly influence the combustion characteristics. Based on this analysis, better experimental data or quantum chemistry calculations are obtained to refine the model parameters. The updated parameters are then used to regenerate the model. This process is repeated until a satisfactory result is achieved and the model is ready to be used.

2.2 Model generation and expansion in RMG

RMG is an automatic chemical reaction mechanism generator that constructs kinetic models composed of elementary chemical reaction steps using a general understanding of how molecules react. The software employs a systematic approach to mechanism generation through a core-edge methodology.

Initially, reactants are placed at the model core, representing the main mechanism that forms the foundation of the model. All possible reactions are then generated for the species present in the model core. As the generation process continues, new species and reactions are evaluated for inclusion in the core based on conditions defined in the input file, see figure 2

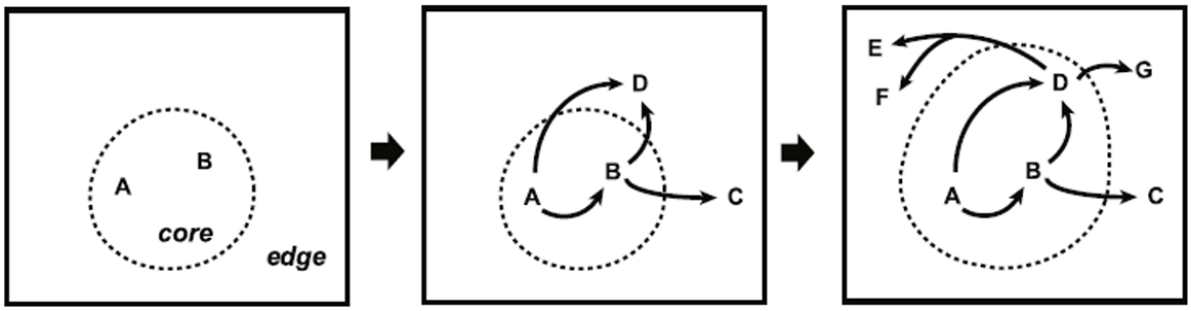


Figure 2: RMG core-edge model generation.

The decision to move species from the edge to the core is based on flux analysis. RMG adds species to the core when the species edge flux $R_i = \frac{dC_i}{dt}$ exceeds εR_{char}, where C_i is the concentration of species i, ε is the tolerance for moving to core, and $R_{char} = \sqrt{\sum_j R_j^2}$ represents the characteristic flux of the system for species j belonging to the core.

Species and reactions that do not meet the specified criteria remain in the model edge, which represents all species and reactions that RMG has produced but are not considered sufficiently important for the current simulation conditions. The core plus edge represents the complete set of species and reactions generated by RMG, while the core alone constitutes the final mechanism used for simulations.

2.3 RMG Input

The RMG input system is structured around several databases and parameters that control mechanism generation. The software follows a hierarchical order of preference for obtaining kinetic and thermodynamic data: seed mechanisms take highest priority, followed by reaction libraries, kinetic depositories, and finally rate rules. One also needs to add the species information, reactor system, tolerances and dependencies,

The input database consists of several different libraries and reference rules. `Kinetics Families` define reaction classes such as hydrogen abstraction and unimolecular fuel decomposition. `Thermo Libraries` provide species thermodynamics data or employ group additivity methods when unavailable. `Reaction Libraries` contain experimentally validated kinetic parameters. `Seed Mechanisms` include pre-existing reactions that are automatically incorporated. These are also the base for the model generation as they are added first and highest in the hierachical order. `Kinetics Depositories` store reactions organized by type for rate estimation and `Kinetics Estimator` specifies methodologies for unknown reaction rates, with the use of models such as rate rules.

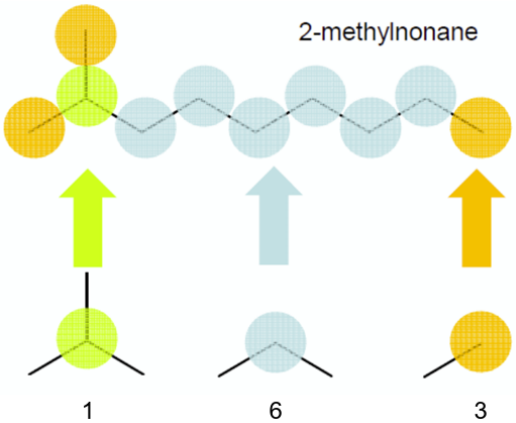


Figure 3: Illustration of Group Additivity theory for larger molecules.

The group additivity method estimates thermodynamic properties by decomposing molecules into functional groups, calculating properties as the sum of group contributions, illustrated in Figure 3. Rate rules use a tree structure to determine unknown kinetic parameters, descending to find the most specific applicable rule or falling back to more general estimates when needed. The drawback with rate rules and why it's often avoided is that rate rules don't take into consideration molecules that have the same molecular formula but with different structures, see figure 4

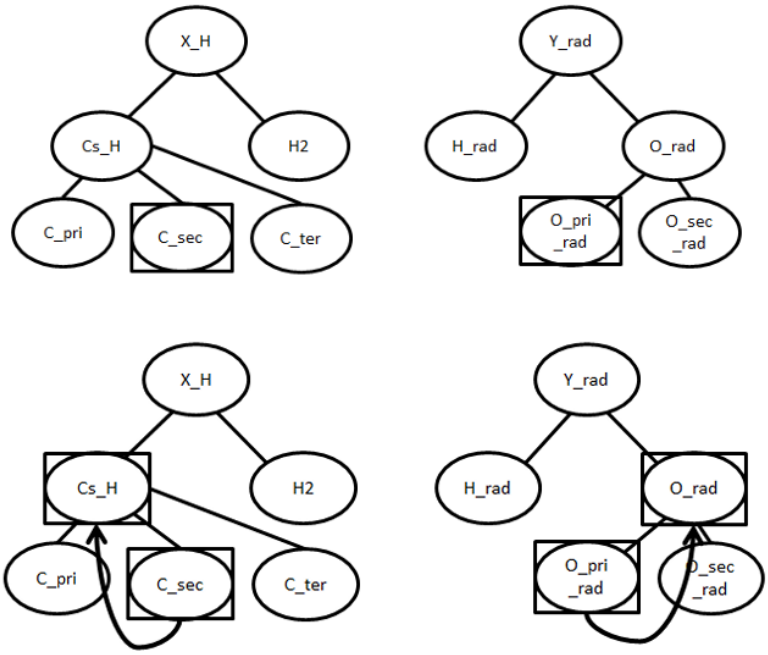


Figure 4: Rate Rules Tree structure for estimating kinetics.
Illustrates the backtracking in rate rules calculating and missing out of key information such as radical placement

Reactant species are defined using SMILES, adjacency lists, or InChI notation, with reactive flags controlling whether species participate in reactions. For example if both O_2 and N_2 are present but O_2 is True and N_2 is False, then we have reactions in air where nitrogen is not participating in the reactions.

The reactor system uses `simpleReactor` for gas-phase isothermal and isobaric conditions. With parameters for temperature/pressure ranges, simulation cycles, and mole fractions. Mole fractions can be added in ranges to calculate over varying equivalence ratios. For this to work one molecule need to be added as single value, otherwise the reactor becomes redundant. For balancing the system. `BalanceSpecies` can be used to ensure the mole fractions adds up to 1. Termination criteria specifes when the generation should stop, can be based either on species conversion (often the fuel is specified) or time limits.

Tolerances control mechanism accuracy: simulator tolerances (`atol`, `rtol`) ensure numerical stability, while model tolerances (`toleranceMoveToCore`, `toleranceInterruptSimulation`, `maximumEdgeSpecies`) determine when species move from edge to core and when simulations are interrupted for model expansion.

Pressure dependence accounts for molecular energy effects at low pressures and high temperatures, with rate coefficients $k(T, P)$ obtained from $k(E)$ using Modified Strong Collision or Reservoir State methods.

Species constraints limit mechanism scope through parameters like `maximumCarbonAtoms`, which limits chemistry up to certain amount of specified atom and `allowed` which allows specified species from lists to bypass previous mentioned constraints.

Output control options include HTML generation for species visualization, statistical plots, CSV simulation profiles,

verbose Chemkin commentary and edge species files. RMG operates exclusively with SI units across all calculations and outputs.

2.4 Model format and duplicate reactions

The final RMG-generated mechanism is typically output in Chemkin format (.cti files), which can be converted to YAML format using Cantera's built-in conversion function. The command `python -m cantera.cti2yaml "<filename>.cti"` performs this conversion. Using the newest version of RMG, this feature is built in, and therefore you immediately generate `chem.yaml` and `chem_annotated.yaml` files.

However, this update does not handle a common problem with duplicate reactions which still needs to be solved to use the mechanism. These duplicates typically arises when the same reaction is represented in multiple ways ($(+M)$ or with specific molecules) or when different rate rules generate similar reactions with slightly different rate parameters. The standard approach to resolve this issue is to retain the more generalized reaction while commenting out or removing the duplicate entries.

3. Results

For the results, three mechanism where generated, one for where the mechanism generation was to be stopped when the fuel (CH_4) reached 95% conversion and the other two when the conversion reached 99%. The difference between the 99% conversion mechanism are that one is generated between 700-1400K and the other one is generated for temperature ranges between 700-2000K. The generated mechanism were compared to the already establishes GRI-Mech3.0 and experimental data. Generation of 95% conversion took around 26 minutes and 99% conversion took around one and a half hour to generate. The re-run of 99% mechanism took 30 minutes with the additional temperature ranges. Amount of species and reactions generated is presented in table 1 for all three mechanisms.

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

Mechanism	**Species**	**Reactions**
GRI-Mech 3.0	53	325
RMG 95% conv (700-1400K)	46	779
RMG 99% conv (700-1400K)	45	790
RMG 99% conv (700-2000K)	48	839

Freely propagating laminar flame speed was calculated at 298 K, 1 bar and equivalence ratio ranging from 0.5-1.5 for all three machismen. The experimental data conditions used for comparison where taken during the following conditions, 1 atm, equvilance ratio between 0.65 to 1.25 at unburnt gas temperture of 298 K, see figure 5.

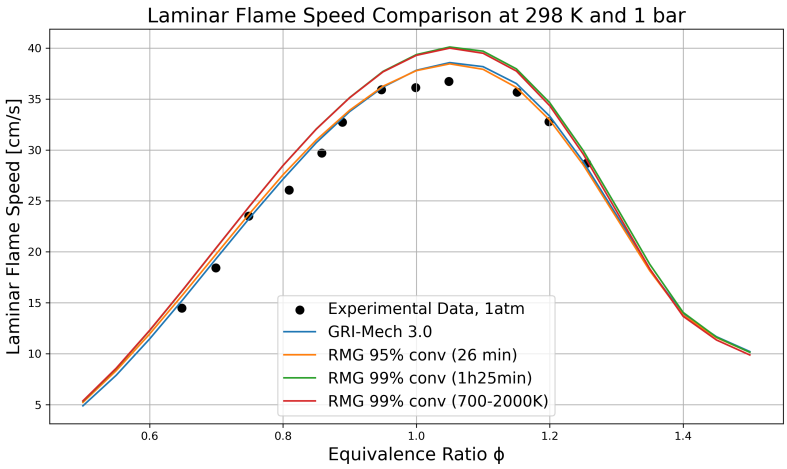


Figure 5: Comparison of Laminar Flame Speed Delay Time between GRI-Mech3.0, 95% conversion, 99% conversion and 99% conversion for 700-2000K. Lines represent Canteras calculations and dots represent the experimental data.

Ignition delay time was calculated at equvilance ratio 1.1; 1 bar and tempertures ranges from 700-2000 K for RMG and between 700-2000 K for GRI-Mech3.0. 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 6.

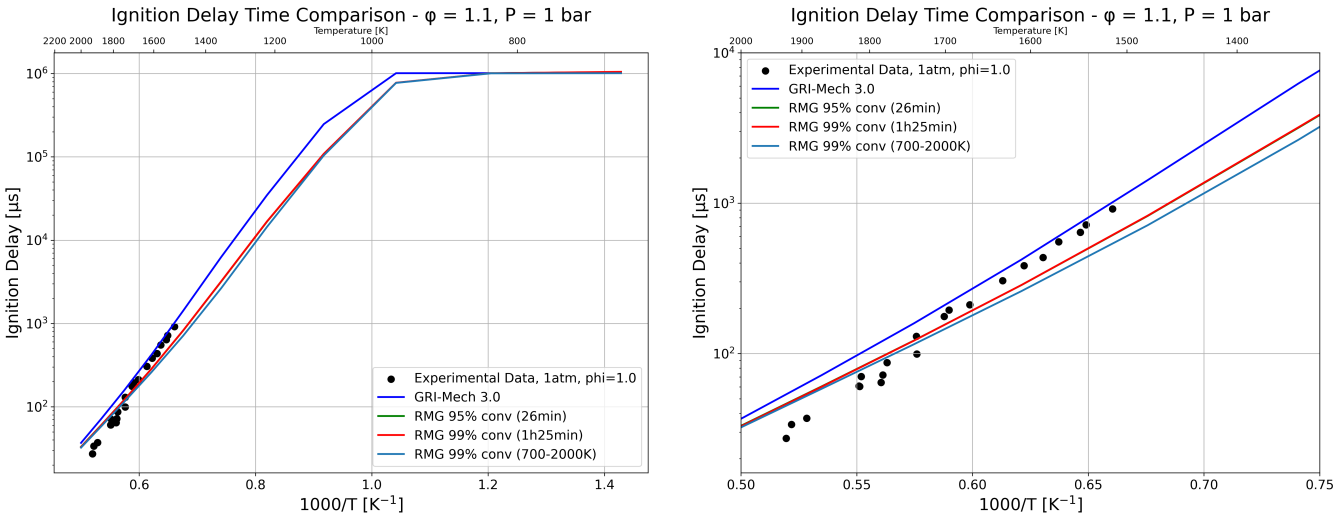


Figure 6: Comparison of Ignition Delay Time between GRI-Mech3.0, 95% conversion, 99% conversion and 99% conversion for 700-2000K. Lines represent Canteras calculations and dots represent the experimental data. Left is the full figure while right plot is zoomed in where the experimental data is present.

For the laminar flame speed sensitivity analysis, figure 7 compares the GRI-Mech3.0 and 99% conversion sensitivity conditions 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 and 39.61 cm/s for GRI-Mech3.0 and 99% conversion (700-2000K) respectively.

GRI-Mech3.0 generated 15 sensitive reactions and RMG generated 14 reactions that fulfilled the conditions of sensitivity values within -0.03 to 0.03, presented in table 2. Of these reactions, only one reaction, $H + HO_2 \Leftrightarrow H_2 + O_2$, was unique to GRI-Mech3.0, RMG hade no unique reactions that fulfilled the conditions.

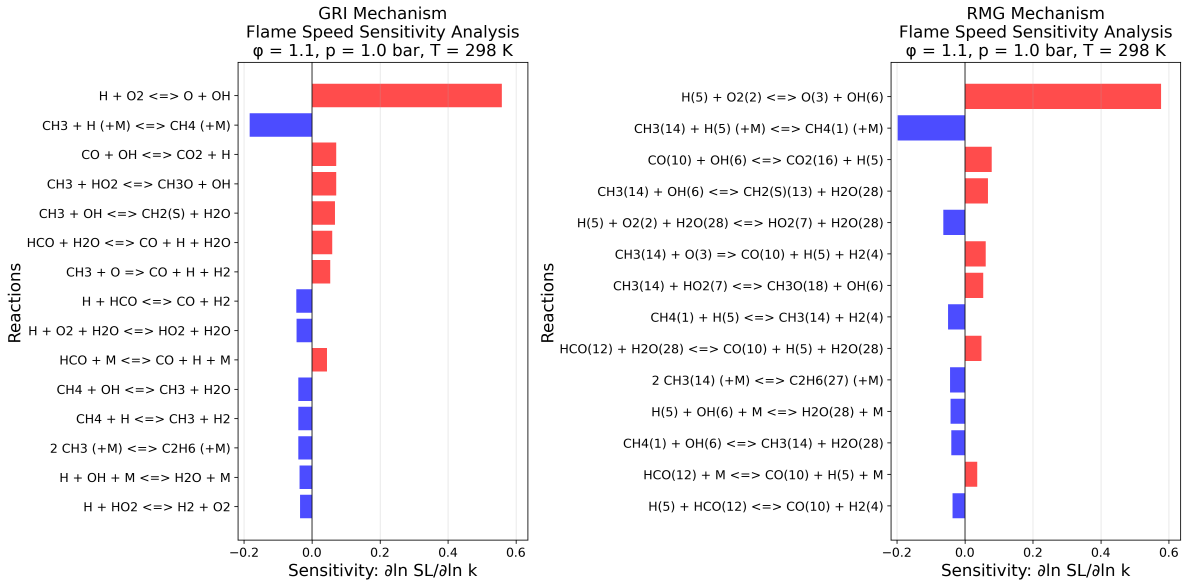
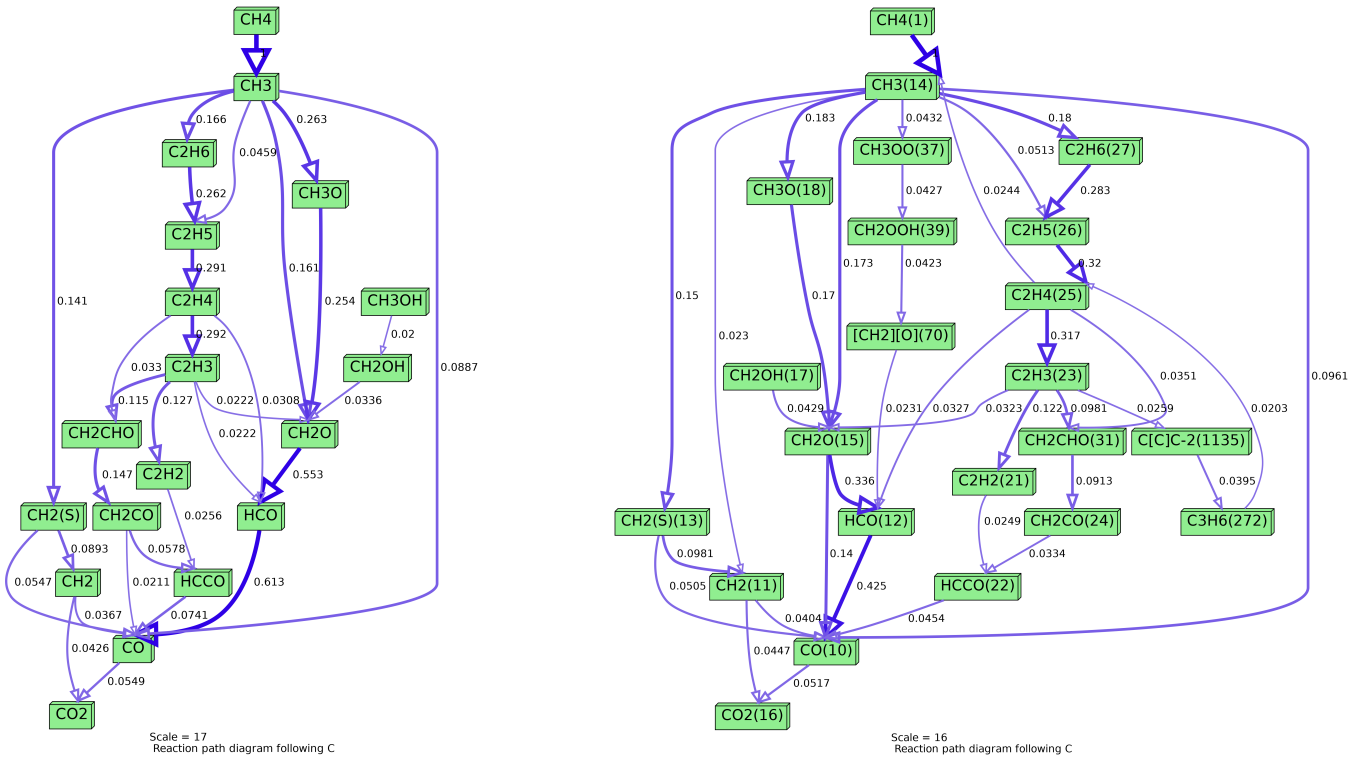


Figure 7: Laminar Flame Speed sensitivity analysis performed for methane-air combustion. Comparison between GRI-Mech3.0 (left) and RMG generated mechanism for 99% conversion (right)

Table 2: Sensitivity Analysis Comparison for Methane-Air Combustion between GRI-Mech3.0 and RMG with 99% conversion (700-2000K)

Reaction	**GRI-Mech 3.0**	**RMG 99%**
$H + O_2 \Leftrightarrow O + OH$	+0.5586	+0.5767
$CH_3 + H\ (+M) \Leftrightarrow CH_4\ (+M)$	-0.1836	-0.1980
$CO + OH \Leftrightarrow CO_2 + H$	+0.0715	+0.0786
$CH_3 + HO_2 \Leftrightarrow CH_3O + OH$	+0.0711	+0.0542
$CH_3 + OH \Leftrightarrow CH_2(S) + H_2O$	+0.0672	+0.0678
$H + O_2 + H_2O \Leftrightarrow HO_2 + H_2O$	-0.0451	-0.0637
$HCO + H_2O \Leftrightarrow CO + H + H_2O$	+0.0594	+0.0491
$CH_3 + O \Rightarrow CO + H + H_2$	+0.0532	+0.0610
$CH_4 + H \Leftrightarrow CH_3 + H_2$	-0.0404	-0.0492
$2\ CH_3\ (+M) \Leftrightarrow C_2H_6\ (+M)$	-0.0404	-0.0434
$H + OH + M \Leftrightarrow H_2O + M$	-0.0366	-0.0421
$CH_4 + OH \Leftrightarrow CH_3 + H_2O$	-0.0405	-0.0400
$HCO + M \Leftrightarrow CO + H + M$	+0.0439	+0.0366
$H + HCO \Leftrightarrow CO + H_2$	-0.0461	-0.0361
$H + HO_2 \Leftrightarrow H_2 + O_2$	-0.0355	–

For the Flux path diagram, figure 8 shows the reaction path from our fuel of methane and following the element of carbon. A threshold of 0.02 was chosen to restrict the size of the diagram and still keep the important reactions.



(a) GRI-Mech 3.0

(b) RMG 99% conversion (700-2000K)

Figure 8: Path flux diagrams following Carbon in methane-air combustion at pressure of 1 bar, temperature range 1200-1800 K, and equivalence ratio 1.1: Green boxes show the current followed chemical structure and numbers next to arrows show the net flux of the reaction path. All values are normalized against the largest flux.

4. Discussion and Conclusion

Despite the RMG-95% conversion mechanism showing better overall agreement with GRI-Mech3.0 in laminar flame speed calculations, the RMG-99% conversion mechanism was selected for sensitivity analysis and reaction path flux diagrams. This decision was based on the principle that a more complete mechanism (99% conversion) would provide a more comprehensive representation of chemical kinetics for reaction pathways, minimizing the chances of missing minor but important reactions that might provide insight into rate-controlling steps during sensitivity analysis. Maximizing combustion through a more complete combustion is also the preferred answer in industrial and academic applications. The updated temperature range mechanism for the conversion of 99% was used to ensure that the mechanism was designed to calculate the ranges of our experimental data in the intervals.

4.1 Laminar Flame Speed

The laminar flame speed comparison in figure 5, shows that GRI-Mech3.0 and RMG-95% generate similar values, with greater differences observed at higher and lower equivalence ratios, which also matches the experimental data well. RMG-99% shows a similar structure to the other mechanisms but overshoots the flame speed values. The difference between RMG-95% and RMG-99% (1400K) is one species and 11 reactions with RMG-99% (2000K) adding additional 50 reactions. As both RMG-99% shows almost identical LFS-values and overshoot, there is reasonable conclusion that the 11 additional reactions between 95% and 99% for the lower temperature mechanism is the likely reason for this overshoot. Investigating whether these reactions originate from one of the libraries or were generated by group additivity or rate rules could result in

improved kinetic values and a more accurate model, especially since rate rules might ignore important molecular structures.

4.2 Ignition Delay Time

The ignition delay time in figure 6 shows a clear difference between GRI-Mech3.0 and the RMG-generated mechanisms, with all RMG conversions showing shorter ignition delay times (IDT) for the same temperature. A likely reason for RMG's faster response can be seen table 1, where RMG is missing the termination reaction H + $HO_2 \rightleftarrows H_2 + O_2$, which lowers the IDT value as radical termination reactions decrease the amount of radicals present in the system.
It can also be observed that all mechanisms reach a plateau at IDT = 1s. This is a numerical limitation in the code where the estimated ignition time acts as a hard limit for the generated IDT. The estimated IDT value would need to be increased to 1000 s to avoid this plateau. Results at low temperatures are not reliable as GRI-Mech3.0 was designed for temperatures above 1000 K. RMG, which uses GRI-Mech3.0 as a base in thermoLibraries, reactionLibraries, and as a seed mechanism, inherits these limitations and must rely on group additivity and rate rules at such low temperatures. For improved low-temperature performance, specialized mechanisms or kinetic data designed for these conditions would be required.

4.3 Sensitivity Analysis

The sensitivity analysis comparison between GRI-Mech3.0 and RMG-99% (2000K) shows great similarity in identifying rate controlling reactions. Both mechanisms identify the same critical reactions, with H + $O_2 \rightleftarrows$ O + OH showing the highest positive sensitivity coefficient (0.5586 for GRI and 0.5767 for RMG-99%), confirming this reaction's role as the primary chain-branching step.

The CH_3 + H (+M) $\rightleftarrows$ CH_4 (+M) reaction shows the strongest negative sensitivity in both mechanisms (-0.1836 for GRI and -0.1980 for RMG-99%), indicating its role in chain termination.

While the top three most sensitive reactions remain the same in both mechanisms, some changes in importance order can be noticed among the other sensitive reactions, though they still present similar sensitivity values to GRI.

As mentioned above, the biggest difference is the absence of the H + $HO_2 \rightleftarrows H_2 + O_2$ reaction from the RMG-99% mechanism's sensitivity list.

4.4 Reaction Path Analysis

The overall reaction path flux is similar for both GRI-Mech3.0 and RMG-99% (2000K), with RMG-99% containing more reaction pathways as a result of having more than twice the number of reactions compared to GRI-Mech3.0. Both mechanisms contain similar reaction paths from the fuel (CH_4) to the end products of CO_2 and important species such as C2H2 (acetylene) to confirm the reliability.

The variation in scale and normalized fluxes can also be contribiuted to the additional reaction pathways. One clear example of the differences is the additional reaction branch containing CH_3OO(37), CH_2OOH(39), and [CH_2]O(70), which is not present in GRI-Mech3.0.

4.5 Conclusions

The differences between GRI-Mech3.0 and RMG's mechanisms can be attributed to the increased number of reactions present in RMG compared to GRI-Mech3.0. Since GRI-Mech3.0 serves as the seed and first library in many of RMG's databases, the fundamental reactions originate from GRI-Mech3.0, while newly generated reactions (over 300) likely obtain their kinetics from group additivity and rate rules, which might provide incorrect values as observed in the laminar flame

speed results. This explains why the path flux and sensitivity analyses are similar for both RMG and GRI-Mech3.0, as the fundamental chemistry is comparable.

For better model accuracy, RMG would need to examine both the reactions added between RMG-95% and RMG-99% to understand how they affected the laminar flame speed predictions. The mechanism would also require investigating the reactions that the sensitivity analysis identified, especially H + $HO_2 \rightleftarrows H_2 + O_2$, to determine if these kinetic values are accurate or need adjustment according to the literature. These corrections are post-fixes and would work to ensure our model fits our experimental data, but might lack aspects for scientific uses as the model could potentially leave out important kinetics for understanding the reactions. Thus, another approach of looking into the chemistry of the whole reaction and updating the input file in accordance with important chemical reaction pathways and radicals which might been left out previously to ensure that RMG generation an accurate model. This would allow us to generate mechanisms for other reactor conditions and avoid the post-work of checking kinetic values and thus reduce the amount of work needed to be done manually.