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Skeletal Kinetic Mechanism of Methane Oxidation for High Pressures and Temperatures

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Abstract

A skeletal methane kinetic mechanism is developed for conditions which are the combustion of undiluted methane–oxygen mixtures at high pressures. The new skeletal mechanism is based on the detailed mechanism of alkanes oxidation by Zhukov (2009). The skeletal model has been created by cutting unimportant species and reactions from the detailed mechanism. The reduction technique is based on the reaction path and sensitivity analyses. They allow to determine the reactions and species that play important role in combustion in rocket combustion chambers. The skeletal mechanism consists of 23 species and 49 reactions. The final and intermediate versions of the skeletal mechanism are compared with the parent detailed mechanism, with other reduced kinetic models, and with experimental data on ignition of methane at high pressures. The comparison shows that the developed skeletal mechanism has a better performance than other kinetic mechanisms in terms of accuracy and required computational power.

1. Introduction

In the past decade, there has been increasing interest on fuel propellants for in-space and launcher rocket propulsion that reduce the operation cost of launching, and improve rocket operating efficiency and performance. Hydrogen provides the best performance in terms of specific impulse (I_{sp}) at a high cost of rocket engine while kerosene provides a cost optimized option for launch vehicle. Methane has intermediate properties between hydrogen and kerosene. In order to obtain good performance at moderate cost, methane has since stood out as a promising option for reusable boosters, main stage and upper stage rocket engines.

The use of methane instead of kerosene solves the problems of soot formation and coking in cooling channels. In addition, methane has cheaper cost in production and storage, and better cooling properties compatible with liquid oxygen due to similar thermodynamic properties [1]. Methane is also a green propellant with low pollution to the environment and is safe to handle and store. Rocket fuel tank size can be reduced due to the high density of methane as compared to hydrogen and a less complicated cooling system can be designed; thus, providing more payload mass in return [1]. Therefore, methane is an excellent choice for upper stage and main stage engine. With the increasing interest for Mars return missions, the motivation to use methane becomes prevalent. Studies have suggested that methane is abundant on Mars atmosphere and possibly under the surface crust [2]. This implies that methane could be synthesis on Mars into rocket fuel to be used for a return mission from Mars and in the future, facilities a manned mission to Mars. For the present work, the rocket operating condition of both upper stage and main stage rocket engines have been considered.

There are many simplified kinetic models for methane, for example the model by Westbrook and Dryer [3], the model by Jones and Lindstedt [4], and the model by Li and Williams [5]. However, all simplified (reduced) models are developed for a certain goal and for a certain range of parameters, and they are not valid outside this range of parameters. Petersen et al. [6] and Zhukov et al. [7] studied the ignition of methane–air mixtures at high pressures. They showed that the methane oxidation kinetics has its particularities at high pressures. In particular, the new reaction path appears at high pressures via the formation of CH_3O_2. Such important reaction as

$$H + O2 = OH + O \quad \textbf{(1)}$$

gives way to another reaction at high pressures:

$$H + O2 + M = HO2 + M\ . \quad \textbf{(2)}$$

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There is a natural trend in methane kinetics at the transition from low pressures to high pressures and from diluted mixtures to pure oxygen mixtures that is increasing the role of three-molecular reactions (i.e., recombination processes), the formation of peroxy species, and the transition to degenerate branching.
For high pressure conditions, it is known a reduced methane mechanism by Petersen and Hanson created called REDRAM [8]. The mechanism has been intended for the modelling of methane ignition at RAM accelerator conditions which means the pressures above 50 atm, the dilution below 70% (i.e., the fraction of inert component in the mixture), and the fuel-rich mixtures. Thereby, these conditions are the nearest to the conditions in rocket combustion chambers. The mechanism was derived from a detailed mechanism of the same research group [6]. The detailed mechanism called RAMEC was obtained from an earlier version of the GRI-Mechanism [9] by adding the reactions of peroxy species: CH_3O_2, CH_3O_2H, C_2H_5O, $C_2H_5O_2$, and $C_2H_5O_2H$. The addition of the kinetics of peroxy species improved significantly the agreement of RAMEC with experimental data at high pressures. The reduced (skeletal) mechanism was derived by Petersen and Hanson from RAMEC by systematic eliminating reactions and species that have no influence on the ignition delay time or on the final product temperature. (Such type of the reduced mechanisms is generally referred as skeletal.) The reduction technique was based on the sensitivity analysis.
Zhukov et al. developed a detailed kinetic mechanism of alkanes oxidation from methane to n-heptane at high pressures [10,11]. The mechanism was validated at pressures up to 500 atm. The methane sub-mechanism was based on RAMEC [6]. The mechanism of Zhukov et al. [10,11] have been selected as a basis for the new skeletal mechanism, because in contrast to RAMEC it contains the complete kinetics of propane and ethane derivatives whose role was not yet clear in the methane kinetics at rocket conditions which are the combustion of undiluted fuel–oxygen mixtures at high pressures.

2. Model reduction

2.1 General overview

Two types of chemical reactors have been used in the present work to simulate the combustion of methane: a constant pressure adiabatic batch reactor and a counterflow laminar burner. The constant pressure batch reactor has been used to simulate ignition behind shock waves, and the counterflow laminar burner has been used to simulate non-premixed flames. These two types of chemical reactors are supposed to be enough to simulate all chemical processes in rocket combustion chamber. The simulations have been performed with pure methane and oxygen as reagents at pressure of 60 bar. The calculations have been carried out using software package Cantera [12].
After narrowing the range of conditions to high pressures and pure methane–oxygen mixtures, the large detailed mechanism by Zhukov [10,11] becomes strongly overdetermined. This allows the reduction of the detailed mechanism to a skeletal one. The method used by Peterson and Hanson has a drawback. The sensitivity analysis shows only processes those are limiting. The alkane oxidation is characterized by degenerate chain branching at high pressures [10,11]. This means that the oxidation of methane occurs in the consequence of reactions where one reaction can be limiting while other reactions are equally important because the formation of final products is impossible without them. That is why the reaction path analysis has been carried out additionally to the sensitivity analysis. Alone the reaction path analysis is not sufficient because it is characteristic of chain processes that intermediate species formed in minor quantity may have a strong impact on the rate of chemical processes.
The reduction of the detailed mechanism [10] has been performed in three stages. On the first stage, the reaction path analysis has been done, since it requires less computational resources. Species, which are formed in a negligible quantity and do not participate in the formation of final products, were cut off from the mechanism after this stage. In the next stage, a sensitivity analysis has been carried out. It showed reactions that do not influence on flame temperature and ignition delay time, and therefore can be excluded from the mechanism. At the final stage, the reduction was performed by the “trial and error” method which is the most expensive from the point of view of spent time and efforts.
The hydrogen sub-mechanism has not been analysed for reduction because it was assumed already compact (or well-defined).

2.2 Reaction path analysis

The reaction path analysis consisted in determination of the amount of species containing a carbon atom formed from one mole of methane at certain conditions. The reaction path analysis shows the major pathways in the premixed stoichiometric methane–oxygen mixture for temperatures from 1000 K up to 3000 K at high pressures as follows:

$$CH_4 \rightarrow CH_3 \rightarrow CH_3O \rightarrow CH_2O \rightarrow HCO \rightarrow CO \rightarrow CO_2,$$

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$$CH_4 \rightarrow CH_3 \rightarrow C_2H_6 \rightarrow C_2H_5 \rightarrow C_2H_4 \rightarrow C_2H_3 .$$

The reaction path analysis shows the importance of C2 mechanism as the main alternative reaction pathway. The reactions with methanol (CH_3OH) and hydroxymethyl (CH_2OH) leading up to formaldehyde (CH_2O) are in low net flux and indicate a low production rate of these species during the combustion at the present conditions. CH_3O, CH_2O, and HCO are important intermediate species for methane combustion and included in the final skeletal mechanism. The analysis shows also the formation of C3 species, but their net flux amounts to about 1%. At higher temperatures (>3000 K), the reaction pathways shift after CH_3 from CH_3O and C_2H_6 to CH_2O and CH_2.
In case of non-premixed flames, the reaction pathways are determined by the position relative to flame front. On the flame part which is facing to the oxygen inflow, the H–O kinetics dominates. The C–O kinetics is represented only by the last stage of methane oxidation:

$$CO \rightarrow CO_2 .$$

On the fuel rich side, the formation of C2 species is the main reaction pathway:

$$CH_4 \rightarrow CH_3 \rightarrow C_2H_5 \rightarrow C_2H_4 \rightarrow C_2H_3 \rightarrow C_2H_2 .$$

The formation of a large amount of ethane and its derivatives is natural at this location due to high rate of CH_3 production at the lack of oxygen. However, the further formation of C3 and C4 species through the recombination of CH_3, C_2H_5 and other radicals of is not so pronounced. The amount of C3 species formed in the flame front is dozens of times less in comparison with the C2 species.

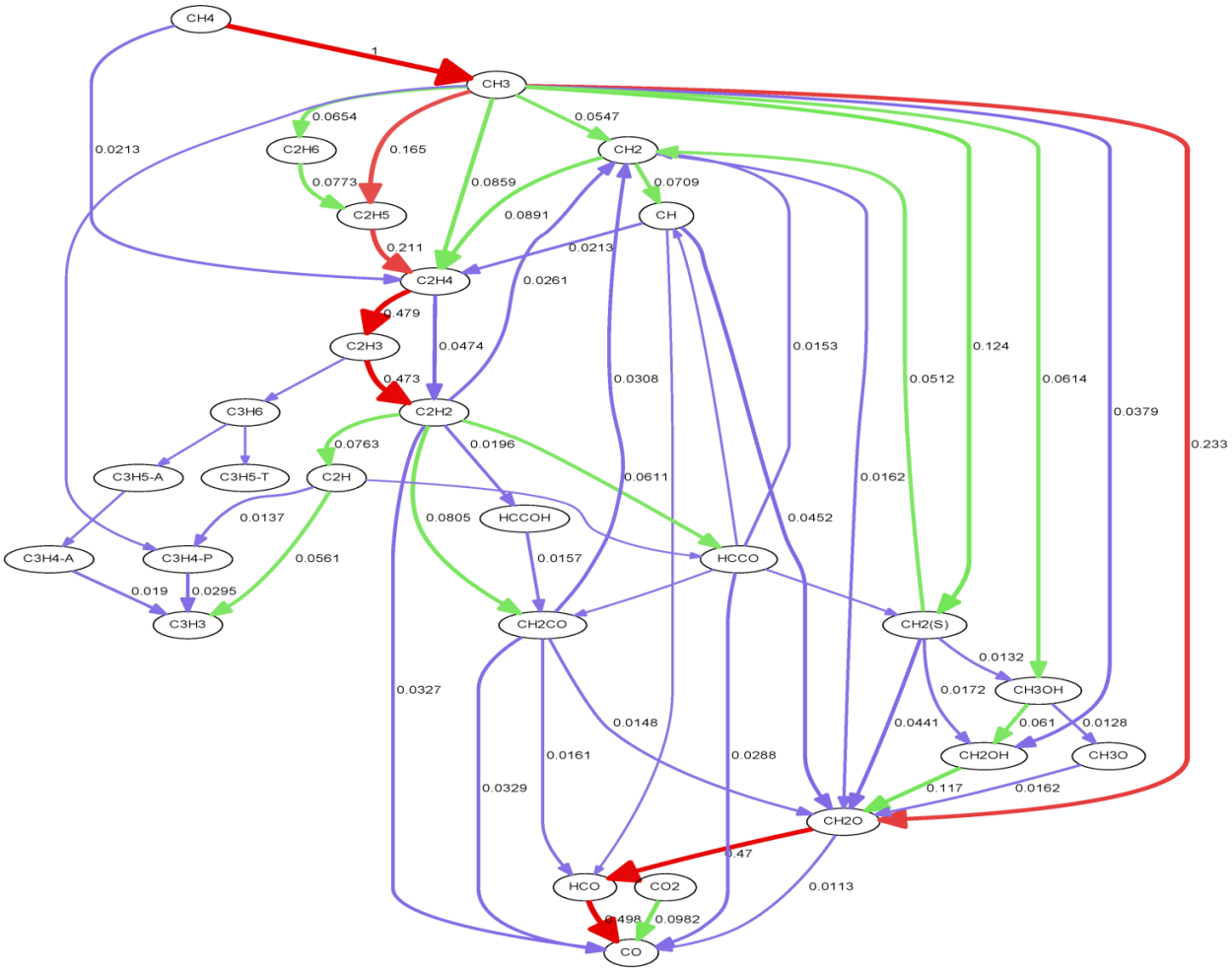

Figure 1: Reaction path diagram in the middle of non-premixed methane–oxygen flame at 60 bar.

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The most complex pattern of the reaction pathways is observed in the middle of the non-premixed flame, in the region where the local stoichiometry is close to unity, temperature and heat release reach the maximum. The corresponding reaction-path diagram is presented in Fig. 1. However, the diagram does not have any new reaction pathways with respect to the already mentioned results.
Summing up the results of the reaction path analysis, we can conclude that C3 and heavier species does not play a significant role in combustion of methane–oxygen mixtures at high pressures. Based on the results of the analysis of the reaction pathways, the reduction of the detailed mechanism by Zhukov [11] carried out. For the reduction, the truncated version of the detailed mechanism [10] was used, which contains species not larger than C4 and consists of 1260 reactions and 208 species. At first, all C3 and C4 species have been cut off. The initial hypothesis, that they might play a role in methane kinetics at the rocket combustion conditions, was not been confirmed. As we saw, the C4 species are formed in negligible amount in CH4/O2 flames, and the amount of the C3 species is too small. The hypothesis is not substantiated, because the transition to the rocket combustion conditions means not only high pressures but also high temperatures which reduce the role of the recombination processes. At the next step, the oxygenated C2 species were removed, which are also not involved in the major reaction pathways. The obtained skeletal mechanism has got the working name *ReduceRXN* and consists of 165 reactions and 26 species.

2.3 Sensitivity analysis

Sensitivity analysis has been carried to determine the rate limiting reaction steps of the kinetic mechanism *ReduceRXN*. For this purpose, sensitivity coefficients S_r of current temperature to reaction rates were calculated, which are defined as follows:

$$\boldsymbol{S_r = \frac{k_r}{T}\frac{\partial T}{\partial k_r}}, \tag{3}$$

where k_r is a reaction rate of reaction r. The sensitivity analysis demands significantly more computations than the reaction path analysis. Besides post-processing, the sensitivity analysis requires to perform simulations of ignition or flame twice for each reaction. Therefore, the sensitivity analysis has been done after the reaction path analysis and the intermediate reduction of the original mechanism. Figures 2 and 3 present the results of the sensitivity analysis for the stoichiometric methane-oxygen mixture in a constant pressure batch reactor and in a counterflow flame at a pressure of 60 bar. (The first 13 reactions with the highest S_r are only shown in the figures.) For ease of reference, the sensitivity coefficients were normalized to the largest sensitivity coefficient.
It was found that for methane combustion at elevated pressure, the reactivity of mixture is highly sensitive to reaction involving hydroperoxy radical and hydrogen peroxide, HO_2 and H_2O_2. This is due to the fact that HO_2 formation rate increases with pressure and becomes at high pressures higher than the rate of the formation of radicals OH and O. The sensitivity analysis also shows that the kinetics of premixed methane–oxygen mixture is sensitive to CH_3O_2 at high pressures.

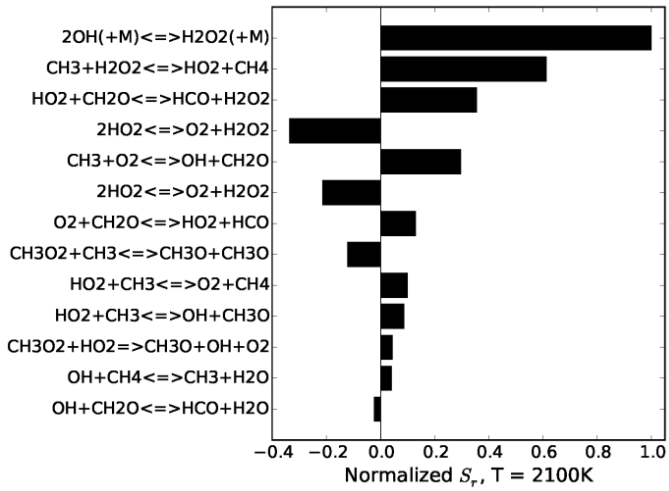

Figure 2: Sensitivity coefficients during the ignition of methane–oxygen mixture at 60 bar and 2100 K.

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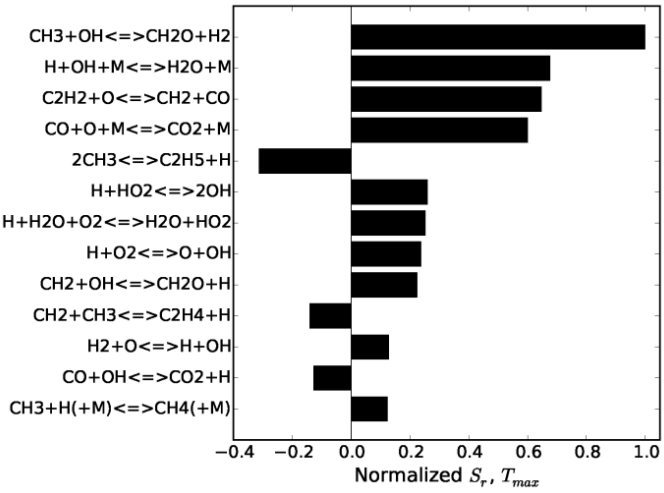

Figure 3: Sensitivity coefficients in the middle of non-premixed methane–oxygen flame at 60 bar.

The important reactions in the counterflow flame (see Fig. 3) are vastly different from the ignition of the premixed mixture in a batch reactor (see Fig. 2). The main distinctive feature of the kinetics of non-premixed methane–oxygen flames at high pressures is a relatively large contribution of C2 species. The sensitivity analysis of the counterflow flame has been performed not only in the middle of the flame but also on fuel and oxidizer sides of the flame. The sensitivity coefficients in a constant pressure batch reactor have been also calculated at different temperatures. However, these results do not add anything worthy of attention to the already obtained results.

Sensitivity analysis in a constant pressure batch reactor and in a counterflow flame has shown that up to 33 reactions along with 3 species contribute little effect on ignition delay times and on a temperature profile in counterflow flames. Following the results of the sensitivity analysis, the species C_2H_2, $CH_2(S)$ and CH were eliminated from the mechanism.

2.4 Cut and try method

After the two stages of the reduction, it was found that the difference in simulation results between the reduced and parent detailed mechanisms is invisible. This indicated that the reduced mechanism was still overdetermined, and there is potential for further reduction. The initial objective of the reduction was to obtain the skeletal mechanism that gives acceptable predictions of ignition delay times and predicts flame temperatures at rocket conditions within 2% margins relative to the original detailed mechanism. The overdetermination occurs as a result of very conservative criteria used for cutting off unnecessary reactions. Indeed, minor reaction pathways and sensitivity coefficients are not directly connected with ignition delay times and flame temperatures. Both species flows and sensitivity coefficients are not absolute values but normalised to the maximum value of species flow or to the maximum value of sensitivity coefficients. The used sensitivity coefficients connect temperatures with reaction rates but not with ignition delay times. The elimination of minor reaction pathways leads to the redistribution of flows on major reaction pathways. Therefore, the elimination of the species and reactions with flows and sensitivity coefficients of about 5% has not led to a visible difference between the detailed and reduced mechanisms.

For the further reduction the cut-and-try method was employed. This method is the most costly method from the point of view of time spent; thus, its application has sense only on the final stage when the kinetic mechanism is already compact. The used method is based on the results of the sensitivity analysis and is a continuation of the previously used reduction technique. In contrast to the previously used method, the reactions were not eliminated by one large group on this stage but individually. The comparison with the detailed mechanism and experimental data was performed not at the end of the work but after each try. Firstly, the reactions with low sensitivity coefficients were tried to be removed. This method has given the mechanism of 23 species and 49 reactions. This final version of the reduced mechanism has been labelled on graphs as *ReduceSens.*

With this method, the potential for the “simple” cutting of the detailed mechanism has been exhausted. Any further reduction of the methane mechanism requires other methods.

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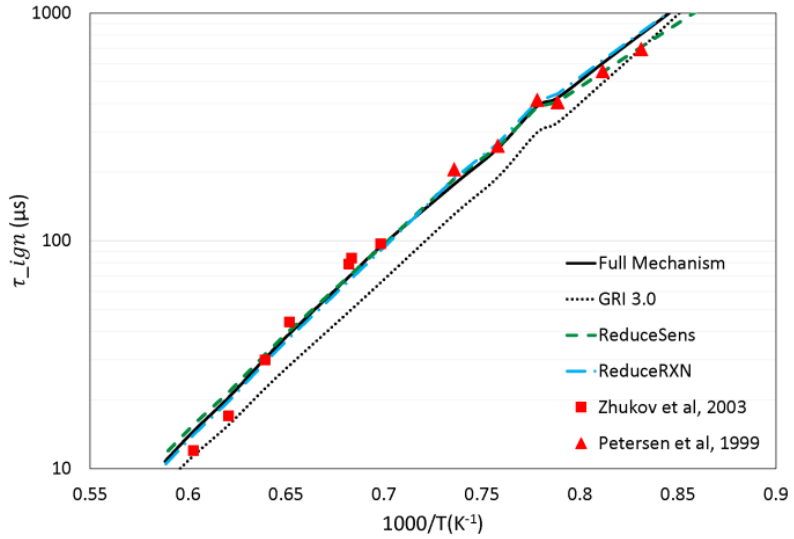

Figure 4: Calculated ignition delay times in comparison with experimental data, p=50 atm, lean methane–air mixture.

3. Verification and validation of skeletal mechanism

Two mechanisms, one from the reduction by reaction path analysis, *ReduceRXN*, and the final developed skeletal mechanism, *ReduceSens*, have been validated against two set of experimental data at 50 atm. The experimental data comes from shock tube experiment done by Petersen et al. [13] and by Zhukov et al. [7], and consisted of ignition delay times measured at highly elevated pressure of more than 40 bar. Petersen et al. [13] investigated the ignition delay times for CH_4/O_2/diluent at ϕ = 0.4, 3.0, 6.0 using either N_2, Ar or He as diluent gas. Zhukov et al. [7] investigated the ignition delay time for methane–air mixtures at ϕ = 0.5 and at pressures up to 450 atm. These two experiments were chosen for validation as they are closest to rocket engine conditions. Figure 4 shows that both *ReduceSens* and *ReduceRXN* are in good agreement with the full mechanisms and experimental data, with *ReduceSens* having a better fit to experimental data. Both *ReduceSens* and *ReduceRXN* are therefore within the desired error range of 5%.

As a comparison, the most widely used GRI-Mech 3.0 [14] is plotted. It was shown [6,7] that GRI-Mech 3.0 could not be used at high pressures (≥50 atm) due to the fact that it does not contain species such as CH_3O_2 that are important for low temperature and high pressure conditions. It is also worth mentioning that the pressures of about 60 bar exceed significantly the validity range of GRI-Mech 3.0 , 10 Torr to 10 atm [14]. Furthermore, it was found out that the lower diluent fraction is in mixture, the lower the accuracy of GRI-Meach 3.0 is [15]. Thus, GRI-Mech 3.0 should not be used for the rocket combustion conditions.

Due to the unavailability of experimental data for undiluted (pure methane-oxygen) mixtures, the new skeletal model cannot be validated at rocket engine relevant conditions. However, the skeletal and reduced models can be verified at these conditions against the parent detailed mechanism by Zhukov [10,11]. Figure 5 shows the comparison of the skeletal mechanisms with other methane mechanisms at the rocket engine relevant conditions: p=60 bar, and stoichiometric methane–oxygen mixture. The results from REDRAM kinetic mechanism [8] are also plotted to test the capability of the mechanism at the rocket combustion conditions. GRI-Mech 3.0 is also shown for comparison. Presently, there are no data available in literature from shock tube experiments at conditions similarly to the rocket combustion conditions, since all experiments have been done with either air as oxidizer or with an oxygen mixture diluted with inert gas such as nitrogen or argon. The result skeletal mechanism gives ignition delay times within 5% error from the parent detailed mechanism. From Fig. 5 it follows that the reduced mechanisms REDRAM, *ReduceSens*, and *ReduceRXN* have comparable accuracy in the prediction of ignition delay times as compared to the parent detailed mechanism.

The developed mechanism has been also verified with the temperature profile for counterflow flame. As a comparison, the results obtained using REDRAM [8] are plotted, see Fig. 6. The results obtained from Jones–Lindstedt mechanism [4] are also included to compare the performance between a skeletal mechanism of 49 reactions and a reduced mechanism of 4 reactions. The mechanism by Jones and Lindstedt was selected as it is widely used in many CFD simulations of methane combustion. Both REDRAM and Jones–Lindstedt mechanisms perform poorly in the case of non-premixed combustion at the rocket engine conditions. The peak temperature is underpredicted with error value up to 1500K. Jones–Lindstedt mechanism [4] does not contain OH, O, and H

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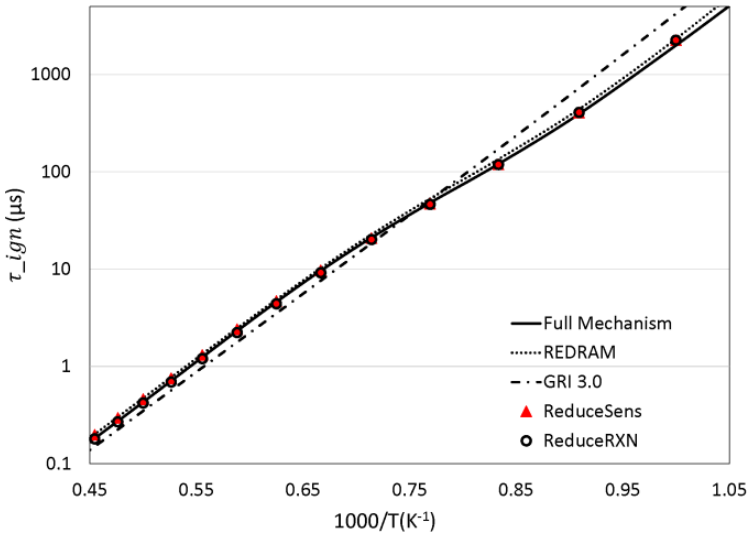

Figure 5: Comparison of different mechanisms at rocket engine relevant conditions: p=60 bar, stoichiometric methane–oxygen mixture.

radicals, and thus less heat release was accounted for in the formation and recombination of such radicals. The predicted peak temperature is thus much lower. For REDRAM, the skeletal mechanism was developed using ignition delay times as criteria, and the validation was carried out only for the ignition of premixed mixtures [8]. Hence, the resultant mechanism contains fewer reactions to account for fuel rich combustion, and the predicted peak temperature is lower by 500 K. This stresses the importance of correctly identifying the appropriate simulation conditions, which represent the desired application environment for reduced model, since this greatly influences which reactions to be eliminated and which to keep. From the Fig. 6, both *ReduceSens* and *ReduceRXN* are in a good agreement with the parent detailed mechanism. No comparison with experimental date has been done for the counterflow flame as there is no available experimental data at pressure above 10 atm. This suggested that more work needs to be done to obtain validation data for the developed kinetic mechanism. As a secondary verification, the comparison with species profiles of CH_4, O_2, CO_2, H_2O, CO and OH have been performed. The same observation can be made with the accuracy of Jones–Lindstedt and REDRAM mechanism for predicting these species' mole fractions. Both *ReduceSens* and *ReduceRXN* perform well in predicting the species profile within 5% error of the full mechanism with larger error seen in the prediction of CO and OH radicals, which is not critical for the simulations of rocket combustion chambers.

By reducing the size of the full mechanisms by around 25 times, the computation time has been reduced by a similar amount. The benefit of the reduction is more pronounced for the counterflow flame simulation where the computation time is reduced by two orders of magnitude. If the use of the mechanism will be extended to 2D and 3D simulations with hundreds of grid cells to solve, the advantage of having a smaller size mechanism will quickly become obvious.

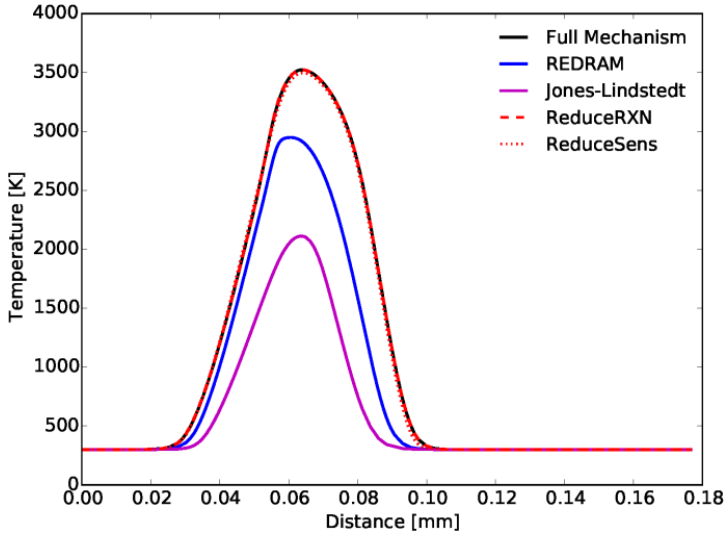

Figure 6: Simulated temperature profiles in counter flow methane–oxygen flame at 60 atm.

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4. Conclusions

The skeletal mechanism of 23 species and 49 reactions was developed from the detailed mechanism of Zhukov et al. [10] which consists of 1260 reactions and 207 species. Two of the species in the mechanism are neutral dilutants: N_2 and Ar.
The reduction of the detailed mechanism was done using reaction path analysis and sensitive analysis, which were carried out in a constant pressure batch reactor and in a counterflow flame at a pressure of 60 bar for pure methane-oxygen mixtures. The developed mechanism was shown to perform well in the predictions of ignition delay times and of temperature profile for counterflow flame at rocket operating conditions. The predicted values of temperature are within 5% error from the parent detailed mechanism and also within the error range of experimental data.
C3, C4 species are found to be insignificant in methane combustion under rocket operating conditions. The reaction path analysis in a constant pressure batch reactor and in a counterflow flame shows that species such as C, CH_3O_2H, CH_3OH, CH_2OH, HCO_2, HCO_3, and HCO_3H are formed in minor amounts and thus do not influence ignition delay times and temperature profile of counterflow flames at high pressures. C2 sub-mechanism consisting of C_2H_6 to C_2H_3 is considered important for fuel rich combustion of methane. However, the other C2 oxy species are found unimportant for rocket relevant conditions.

Acknowledgements

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References

[1] H. Burkhardt, A. Herbertz, J. Klevanski, and M. Sippel. 2004. Kerosene vs. Methane: A Propellant Tradeoff for Reusable Liquid Booster Stages, *J. Spacecraft Rockets.* 41(5):762–769
[2] Webster, C.R., Mahaffy, P.R., Atreya, C.K., et al. 2015. Mars methane detection and variability at Gale crater. *Science.* 347(6220):415–417.
[3] C.K. Westbrook, F.L. Dryer. 1981. Simplified Reaction Mechanisms for the Oxidation of Hydrocarbon Fuels in Flames, *Combust. Sci. Technol.* 27(1):31–43.
[4] Jones, W.P., and Lindstedt, R.P.. 1988. Global reaction schemes for hydrocarbon combustion. *Combust. Flame.* 73(3):233–249.
[5] Li S.C., Williams F.A.. 2002. Reaction Mechanisms for Methane Ignition, *J. Eng. Gas Turb. Power*. 124(3):471–480.
[6] Petersen, E.L., Davidson, D.F., Hanson, R.K. 1999. Kinetics modeling of shock-induced ignition in low dilution CH_4/O_2 mixtures at high pressures and intermediate temperatures. *Combust. Flame.* 117(1-2):272-290.
[7] Zhukov, V.P., Sechenov, V.A., Starikovskii, A.Yu. 2003. Spontaneous ignition of methane–air mixtures in a wide range of pressures. *Combust. Explo. Shock+*. 39(5):487-495
[8] Petersen, E.L., Hanson, R.K. 1999. Reduced kinetics mechanisms for ram accelerator combustion. *J. Propul. Power.* 15(4):591–600.
[9] M. Frenklach, H. Wang, C.L. Yu, M. Goldenberg, C.T. Bowman, R.K. Hanson, D.F. Davidson, E.J. Chang, G.P. Smith, D.M. Golden, W.C. Gardiner, V. Lissianski. GRI-Mech 1.2. http://www.me.berkeley.edu/gri_mech/
[10] Zhukov, V.P., Sechenov, V.A., Starikovskii, A.Yu. 2005. Autoignition of a lean propane-air mixture at high pressures. Kinet. Catal.+. 46(3):319-327.
[11] Zhukov, V.P. 2009. Kinetic model of alkane oxidation at high pressure from methane to n-heptane. Combust. Theor. Model. 13(3):427-442.
[12] Goodwin D.G., Moffat H.K., Speth R.L. 2015. Cantera: An Object-oriented Software Toolkit for Chemical Kinetics, Thermodynamics, and Transport Processes. http://www.cantera.org, Version 2.2.0.
[13] Petersen, E.L., Davidson, D.F., Hanson, R.K. 1999. Ignition delay times of ram accelerator CH_4/O_2/diluent mixtures. *J. Propul. Power*. 15(1):82–91.
[14] G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, S. Song, W.C. Gardiner Jr., V.V. Lissianski, Zh. Qin, GRI–Mech 3.0, http://www.me.berkeley.edu/gri-mech/version30/text30.html
[15] N. Donohoe, A. Heufer, W. K. Metcalfe, H. J. Curran, M. L. Davis, O. Mathieu, D. Plichta, A. Morones, E. L. Petersen, F. Güthe. 2014. Ignition delay times, laminar flame speeds, and mechanism validation for natural gas/hydrogen blends at elevated pressures, *Combust. Flame*, 161(6):1432-1443.