N. Slavinskaya, M. Abbasi, Mehdi, J.H. Starcke, O. Haidn, Methane Skeletal Mechanism for Space Propulsion Applications. In: Proceedings. 52nd AIAA/SAE/ASEE Joint Propulsion Conference, AIAA 2016-4781, 25.-27.07.2016, Salt Lake City, USA.

The AIAA version of the paper is accessible at
http://dx.doi.org/10.2514/6.2016-4781

Methane Skeletal Mechanism for Space Propulsion Applications

N.A. Slavinskaya[1], M. Abbasi[2], J.-H. Starcke[3],
German Aerospace Center (DLR), Institute of Combustion Technology, 70569, Stuttgart, Germany

O.J. Haidn[4]
Lehrstuhl für Flugantriebe, Technische Universität, München, Germany

A skeletal chemical kinetic model for CH_4/air combustion with 100 reactions and 24 chemical species was developed from the detailed mechanism, with 42 species and 298 reactions. The mechanism reduction was performed with the multi target reduction strategy realized in the in-house developed DLR RedMaster code. RedMaster is able to analyze the different chemical processes (ignition delay time and laminar flame speed) in the given time and height points.
The obtained reduced model describes satisfactory experimental data for ignition delay and flame speed under conditions: p_5 = 1-50 bar, T_5= 940K - 210K, ϕ = 0.5–2; p = 1-60 bar, T_0= 300K, ϕ = 0.6–1.4.

Some problems related to reaction mechanism reduction are analyzed.

I. Introduction

Within the last ten recent years, the propellant combination LOX/CH_4 has received considerable attraction worldwide as a propellant combination for space propulsion applications [1-5]. The advantages are numerous: a specific impulse better than that of oxygen/kerosene, reduced cost and complexity in in handling compared to hydrogen and reduced requirements for turbomachinery. In Germany, this propellant combination is investigated both experimentally and numerically within the collaborative research center TRR40 on 'Technological foundations for the design of thermally and mechanically highly loaded components of future space transportation systems' [6-8]. Within this project, specific effort is put on developing design tools for thrust chambers which requires validated numerical tools for the prediction of combustion and heat transfer in such devices. In an effort to compare different numerical approaches, a special workshop will be organized later this year at the Technical University of Munich where teams from all over the world which apply RANS, URANS, LES and hybrid models will try to reproduce combustion efficiency and heat transfer of a test case provided by one of the TRR 40 projects [9]. Generally, different groups not only use different approaches to handle fluid mechanics as mentioned above, their way to treat combustion differs substantially, too. In order to allow for a more detailed comparison of the applied numerical tools, a reduced chemical kinetic scheme has been developed and will be provided to the workshop participants. The extremely large CPU times for CFD calculations with detailed chemical mechanisms necessitate that the applied kinetic models must be as simple as possible. However, any accurate modelling of diffusion flames and in general combustion processes in liquid propellant rocket engines are of this type requires that the chemical model must be able to sufficiently describe these combustion processes for a wide range of parameters: propellant mixture ratios, temperatures and pressures. Obviously, such a reduced mechanism can be generated only on the base of sensitivity analyses performed for the large number of simulations related to the different chemical processes (ignition delays, flame speeds, concentration profiles in chemical reactors) under different operating conditions. The reduction of chemical species or reactions held on such integrated information allows keeping most facilities of the input detailed model. The presented work reports the results of the methane (CH_4)/oxygen (O_2) reaction mechanism reduction performed with the DLR RedMaster code [10]. The methane skeletal mechanism applicable for the CFD

[1]Senior research fellow, Chemical Kinetics Department, Nadja.Slavinskaya@dlr.de, AIAA Senior Member.
[2] PhD Student, Chemical Kinetics Department, Mehdi.Abbasi@dlr.de.
[3] Senior research fellow, Chemical Kinetics Department, JanHendrik.Starcke@dlr.de.
[4] Prof. of Technical University Munich, haidn@lfa.mw.tum.de , AIAA Senior Member

simulations of rocket combustion chamber under pressure 20 bar was developed through simulations and reactions/species local sensitivity analysis performed for 65 experimental targets for ignition delay times and 15 targets for laminar flame speed. These experimental measurements cover the next operating conditions: p_5 = 1-50 bar, T_5= 940K - 2100K, $\phi = 0.5–2$ (for ignition delay time); p = 1-60 bar, T_0= 300K, $\phi = 0.6–1.4$ (for laminar flame speed).

II. Reaction Model

The input detailed mechanism is a sub-model of C_1-C_2 reaction mechanism [11], which was uploaded and improved [12, 13] related the some pressure depending and multichannel reactions. The input CH_4 model has 42 species (including Ar, He and N_2) and 298 reactions.

The uncertainty factors, lower, $f_l(T) = k_0(T)/k_{lower}(T)$, and upper, $f_u(T) = k_{upper}(T)/k_0(T)$, boundaries ($k_0$ is the nominal rate coefficient, k_{lower} and k_{upper} are lower and upper bounds), for rate coefficients were assumed equal to the proposed ones in the sources or evaluated from statistical treatment of the different data. Uncertainties of the rate coefficients were used to study their influence on the thresholds in sensitivity analysis to select unimportant reactions.

III. Experimental Targets

A. Ignition delay times

Quantification of uncertainties in the shock tube is ultimately needed prior to undertaking any tuning of the kinetic parameters to match ignition targets. If some active phenomena in the shock tube experiments cannot be described by assuming homogeneous conditions (constant V, U system) behind the reflected shock, they areclassified as “non-idealities” in the shock tube experiments. Both, facility-dependent effects and energy-release phenomena can increase the non-idealities and influence the instrument readings, thus adding to the uncertainty of experimental data. To evaluate the uncertainty bounds of the measured observations included in the dataset, the empirical algorithm is proposed [12]. For that, the most strong non-ideality phenomena were determined across the investigations. The facility-related and fuel-related factors, which affect these phenomena, have been identified and possible errors, caused by these factors have been evaluated. It was found that experimental data obtained by using large diameter shock tubes (~ 10cm), dilute fuel/oxidizer mixtures in monoatomic gases, and short test times (less than about 500 μs) have the lowest uncertainty level. A correspondence with the diameter of the shock-tube and weak ignition is found: the larger diameter leading to an ignition delay close to that of a homogeneous reactor.

It was assumed, that in the best case (strong ignition, diluted mixture, t_{meas} = 50ms – 500ms, shock tube diameter > 10 cm) the uncertainty can be assumed ~15%. Deviations from these conditions are evaluated by adding a 5% uncertainty for each criterion not satisfied to the ideal case. For measured ignition delay time longer as 1000 μs 5% uncertainty is added per every 1000 μs. Radical impurities were evaluated as extra 5% uncertainty, Table 1.

Table 1. Evaluation of uncertainty intervals for the selected shock tube experimental data. The beginning uncertainty is 20 %.

Driven section				Temperature interval, K		Pressure, atm		Dilution		t meas, μs	
Length, m		Internal diameter, cm									
>8		>10		T<1000	+5%	P>15	+5%	yes		0-50	+5%
<8	+5%	<10	+5%	T>1600	+5%	P>30	+10%	none (air)	+5%	100-500	+0%
						every 15	+5%			500-1000	+5%
										1000-1500	+10%
										every 500	+5%

In Table 2 the selected shock tube experiments [13-25] are collected. Uncertainty intervals evaluated with the proposed empirical rule will be show on the graphics with model validations.

Table 2. Ignition delay time measurements used for model validation and reduction.

P, atm	Composition	φ	T_5, K	Ref.
1; 11-31	$CH_4/O_2/Ar$	0.5; 1.0; 2.0	1337-2246	[13]
10-44	$CH_4/O_2/N_2$	0.3; 0.5; 1.0	970-1533	[14]
40; 25-50	$CH_4/O_2/Ar/N_2$	1.0	908-1041	[17]
14.1-41.9	$CH_4/O_2/N_2$	0.7; 1.0; 1.3	1004-1348	[18]
0.85-1.7	$CH_4/O_2/Ar$	0.5; 1.0; 2.0	1685-2175	[19]
1.2- 1.7	$CH_4/O_2/Ar$	0.5; 1.0; 2.0	1739-2158	[20]
5; 10; 20	$CH_4/O_2/Ar$	0.5	1284-2034	[21]
2.5-175	$CH_4/O_2/Ar$	0.5	1209-1722	[22]
4-17	$CH_4/O_2/Ar$	0.5; 1.0; 2.0	1521-1983	[23]
0.5-24	$CH_4/O_2/N_2$	0.5	1243-2001	[24]
0.9	$CH_4/O_2/Ar$	0.98-1	1687-2242	[25]

B. Laminar flame speed

Methane flame velocities at 0.1-0.6 MPa have been investigated by using almost all known techniques [26-38]. The flame velocity data at high pressures are relatively sparse. Experimentalists consider the current uncertainties of laminar flame speed measurements to be in a range of about 5–10%, but also indicating its increase with pressure (>0.5 MPa) and fuel-air ratio (φ>2). Figure 1 collects the literature experimental data for laminar flame velocity. From data analysis following from Figure 1, the uncertainty of available data can be assumed to be 25% for φ< 0,8, 15% for 0.8 < φ< 1.2, and 30% for φ>1.2. The uncertainties for experimental data measured at higher pressure have been evaluated by adding 5%.

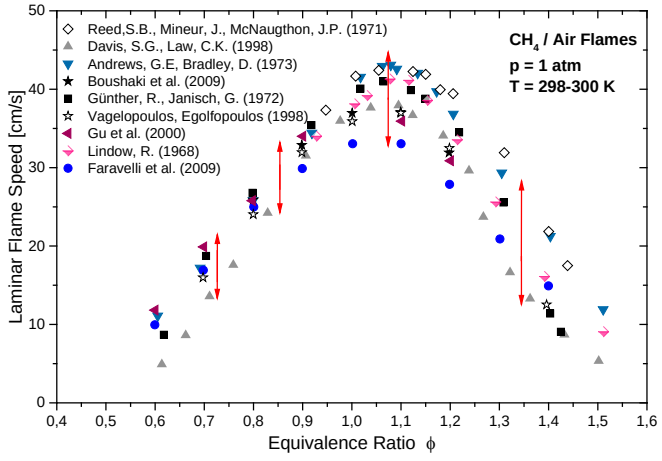


Figure 1. Comparison of literature [26-34] experimental data for atmospheric CH_4/air laminar flame speed with evaluated uncertainty bars.

The laminar flame speed data included in the dataset are presented in Table 3.

Table 3. Laminar flame speed measurements selected for for model validation and reduction.

P, atm	Composition	φ	*T*, K	Ref.
1	CH_4/air	0.6-1.5	298	[26]
1	CH_4/air	0.6-1.4	298	[27]
1	CH_4/air	0.6-1.5	298	[28]
1	CH_4/air	0.95-1.45	298	[29]
1	CH_4/air	0.9-1.5	298	[30]
1	CH_4/air	0.8-1.2	300	[31]
1	CH_4/air	0.6-1.4	300	[32]
1	CH_4/air	0.7-1.4	300	[33]
1;5	CH_4/air	0.6-1.4	300	[34]
0.5-4	CH_4/air	0.6-1.35	298	[35]
2	CH_4/air	0.55-1.4	298	[36]
2-20 10-60	CH_4/air CH_4/O_2/He	0.6-1.4 0.8-1.4	298	[37]
5; 10	CH_4/air	0.6-1.4	298	[38]

IV. Reduction strategy

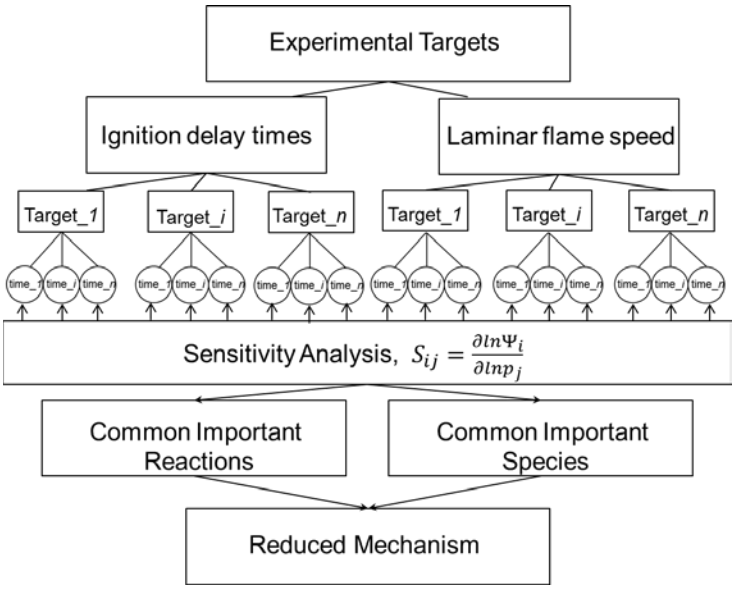


Figure 2. Principal scheme of the RedMaster code for the multi target reaction mechanism reduction.

The multi target reduction strategy was realized in the in-house developed RedMaster code [10]. The global sensitivity analysis implemented in the RedMaster allows determination and elimination of unimportant species and reactions code has been applied to reduce the basic mechanism to the skeletal one. RedMaster manages calculations of chemical processes with the CHEMKIN code [39], calculations of the sensitivity of the species production rate to the rate constants and calculations of the sensitivity of the species production rate to the species concentrations. These sensitivities are calculated with procedures adopted from KINALC code [40]. RedMaster treats the integrated information from the sensitivity coefficients calculated in the ignition delay times and laminar flame simulations at different time and height points, Fig.2. On this basis the reduced mechanism is produced through iterative procedure. After each iteration step the reduced model validation is performed through simulations of selected experimental data. Uncertainty boundaries of experimental data were evaluated how it was described below.

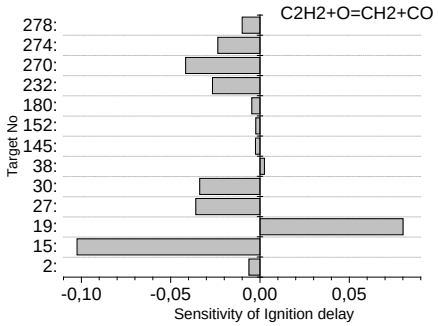


Figure 3. Normalized time integrated sensitivity coefficient of the ignition delay time targets relatively the rate coefficient of reaction C_2H_2+O=CH_2+CO.

As the mechanism reduction is in general a strongly problem oriented procedure, the special attention should be paid to the targets selected for the analysis and validation. They cover as optimal as possible the full range of operating conditions available in the literature to avoid the loss of model predictive facilities. It can be highlighted with Fig. 3, which demonstrates the normalized time integrated sensitivity coefficient of the ignition delay time targets relatively the rate coefficient of reaction C_2H_2+O=CH_2+CO. How it can be seen, the different targets have the different sensitivities to the studies reaction. As the reactions with the maximum sensitivities have a maximal chance to be kept in reduced mechanism, the analysis performed without targets No19 and No15 can lead to reaction elimination and consequently to increase in the reduced model facilities. The dependence of the important reaction pool on the time points of process is evident.

It must be mentioned the second problem here. The normalized sensitivity coefficient S_{ij} contains quantitative information about a ration between the relative changes in the model output δ_i^{out} to the relative change in the model parameter δ_j^{par}, $S_{ij} = \delta_i^{out} / \delta_j^{par}$. The changes in model parameters must lie in the intervals of the rate coefficient uncertainties f_l and f_u.

For the reduction loop 66 ignition delay time and 15 laminar flame speed targets have been selected.

A. Reduction of the reaction number

The contribution of reaction steps to the production rate is based on the sensitivity of production rates to changes in reaction rate coefficients. The effect of changing the reaction rate coefficient k_i on the rate of production of species *i*, R_i, in a mechanism with *N* species is calculated as the sum of squares of the *overall normalized sensitivity coefficient*

$$A_i = \sum_i^N \left(\frac{\partial \ln R_j}{\partial \ln k_i} \right)^2$$

R_j - the rate of production of species *j*, k_i – rate coefficient of reaction *i*. The reaction *i* is considered important if its coefficients A_j, calculated as the sum for all species, e.g. *N*, are larger than a pre-defined threshold value Δ.

B. Reduction of the species number

A species is considered redundant if its concentration change has no significant effect on the production rate of necessary species. The influence of a change of the concentration of species *j* on the rate of production of a *p*-membered group of important species *i*, are calculated as the sum of squares of the *overall normalized sensitivity coefficient*

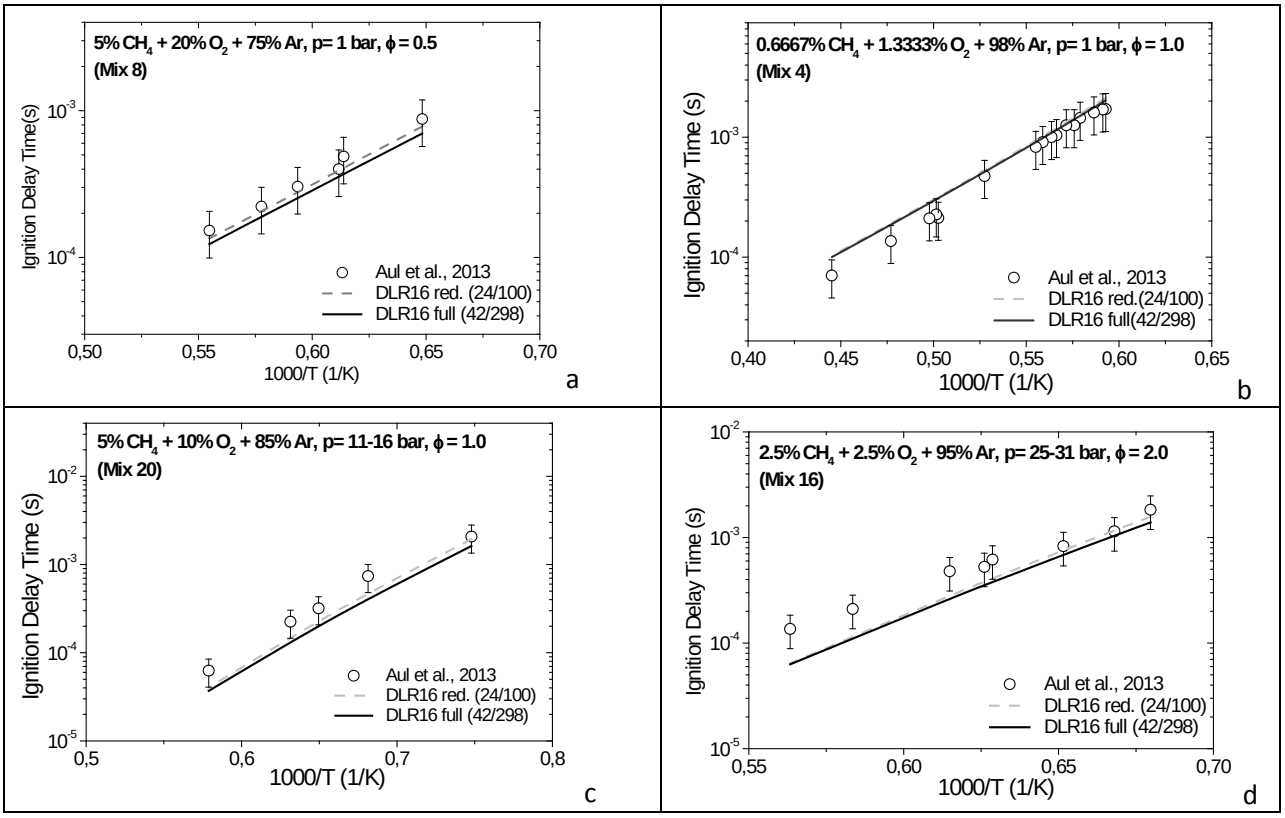
$$B_j = \sum_i^p \left(\frac{\partial \ln R_i}{\partial \ln c_j} \right)^2$$

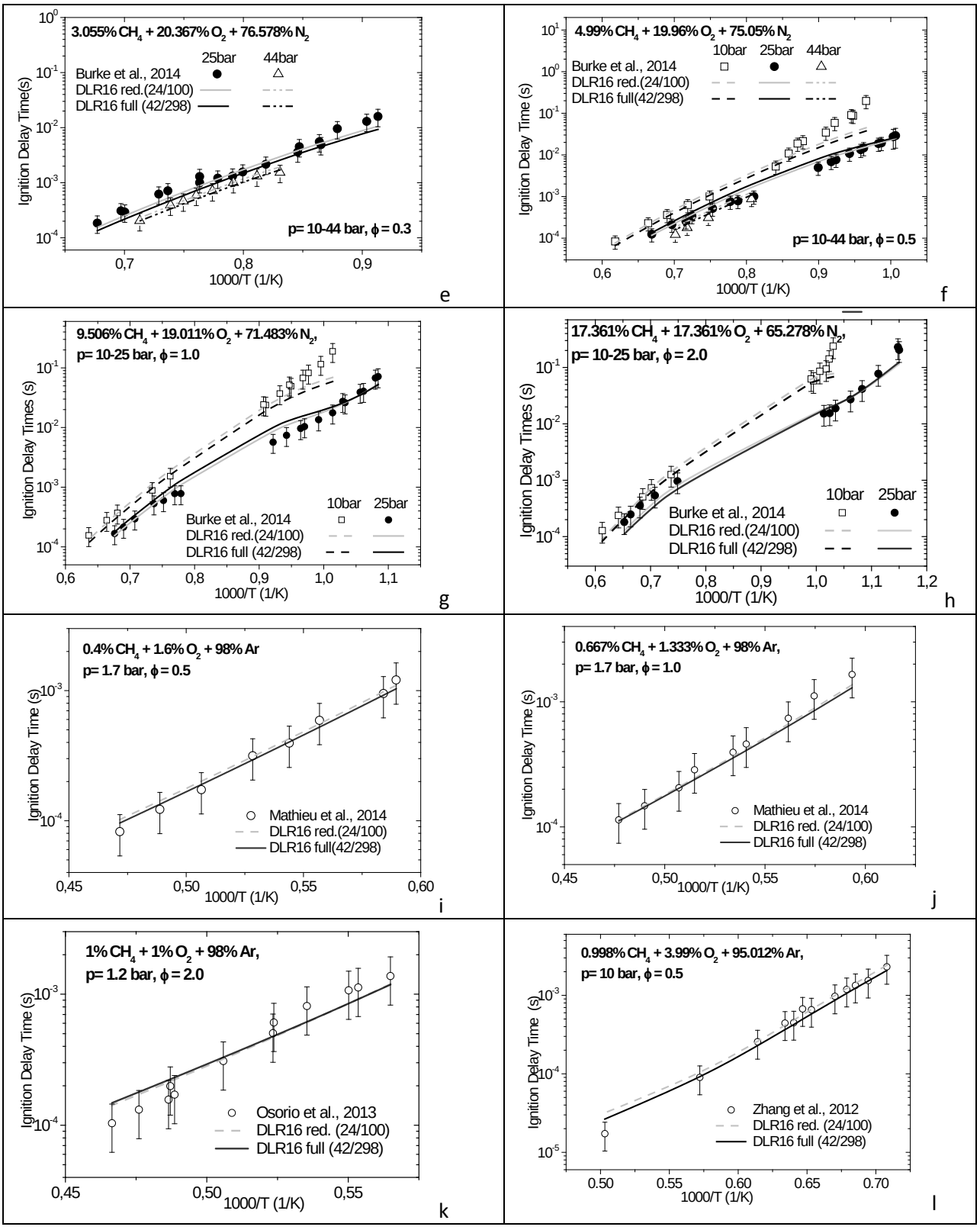
B_j yields the integrated effect of a change of the concentration of species c_j on the rate of production of species *i*, R_i, from a group of *p* important species, *i* = 1, 2, …., *p*. Number of *p* is changed during iterative procedure. The number of "primary" necessary species is given by the investigator. After each step *n* of B_j calculation only one species with the greatest value B_j is added to the group of necessary and important species (p_n+1). After last iteration, those species which were added to the first main group at the last iterations can be considered as redundant species. In the present reduction process 11 species were nominated as "primary" necessary species: H_2, CH_4, OH, O, CO, O_2, HO_2, H, CO_2, HCO, H_2O_2.

A reduction cycle has to be repeated several times until no more species and reactions are found to be unimportant and the simulations with the resulting reduced mechanism reveal that the results achieved fulfil the pre-defined agreement requirement with experimental data.

V. Results

The input reaction mechanism with 42 species and 298 reactions was reduced to one with 24 species and 100 reactions on the base of 65 different ignition delays simulations and 15 calculations of flame speed. This mechanism has the capability to reproduce with good agreement both the experimental data selected for model reduction and experimental data which were not included in reduction loup, Table 2-3, Figures 4-5.
Each additional step for further model reduction with the applied procedure would reduce sufficiently the model predictive capability. Further reduction is possible only with chemical lumping methods and algorithms of the global model production. On the Figs. 4 - 5 the results of calculations of ignition delay times and laminar flame speed with detailed and reduced mechanism are shown. Simulations are in good agreement with experimental data in both cases. The proposed skeletal mechanism for the methane combustion under rocket engine conditions can be successfully used in CFD modeling. It is free for use on the https://teamsites-extranet.dlr.de/vt/DLR-Mechanism/SitePages/Home.aspx




3.055% CH4 + 20.367% O2 + 76.578% N2
25bar 44bar
Burke et al., 2014
DLR16 red.(24/100)
DLR16 full (42/298)
p= 10-44 bar, ϕ = 0.3
Ignition Delay Time(s)
1000/T (1/K)
e
4.99% CH4 + 19.96% O2 + 75.05% N2
10bar 25bar 44bar
Burke et al., 2014
DLR16 red.(24/100)
DLR16 full(42/298)
p= 10-44 bar, ϕ = 0.5
Ignition Delay Time (s)
1000/T (1/K)
f
9.506% CH4 + 19.011% O2 + 71.483% N2,
p= 10-25 bar, ϕ = 1.0
10bar 25bar
Burke et al., 2014
DLR16 red.(24/100)
DLR16 full (42/298)
Ignition Delay Times (s)
1000/T (1/K)
g
17.361% CH4 + 17.361% O2 + 65.278% N2,
p= 10-25 bar, ϕ = 2.0
10bar 25bar
Burke et al., 2014
DLR16 red.(24/100)
DLR16 full (42/298)
Ignition Delay Times (s)
1000/T (1/K)
h
0.4% CH4 + 1.6% O2 + 98% Ar
p= 1.7 bar, ϕ = 0.5
Mathieu et al., 2014
DLR16 red.(24/100)
DLR16 full(42/298)
Ignition Delay Time (s)
1000/T (1/K)
i
0.667% CH4 + 1.333% O2 + 98% Ar,
p= 1.7 bar, ϕ = 1.0
Mathieu et al., 2014
DLR16 red. (24/100)
DLR16 full (42/298)
Ignition Delay Time (s)
1000/T (1/K)
j
1% CH4 + 1% O2 + 98% Ar,
p= 1.2 bar, ϕ = 2.0
Osorio et al., 2013
DLR16 red. (24/100)
DLR16 full (42/298)
Ignition Delay Time (s)
1000/T (1/K)
k
0.998% CH4 + 3.99% O2 + 95.012% Ar,
p= 10 bar, ϕ = 0.5
Zhang et al., 2012
DLR16 red. (24/100)
DLR16 full (42/298)
Ignition Delay Time (s)
1000/T (1/K)
l

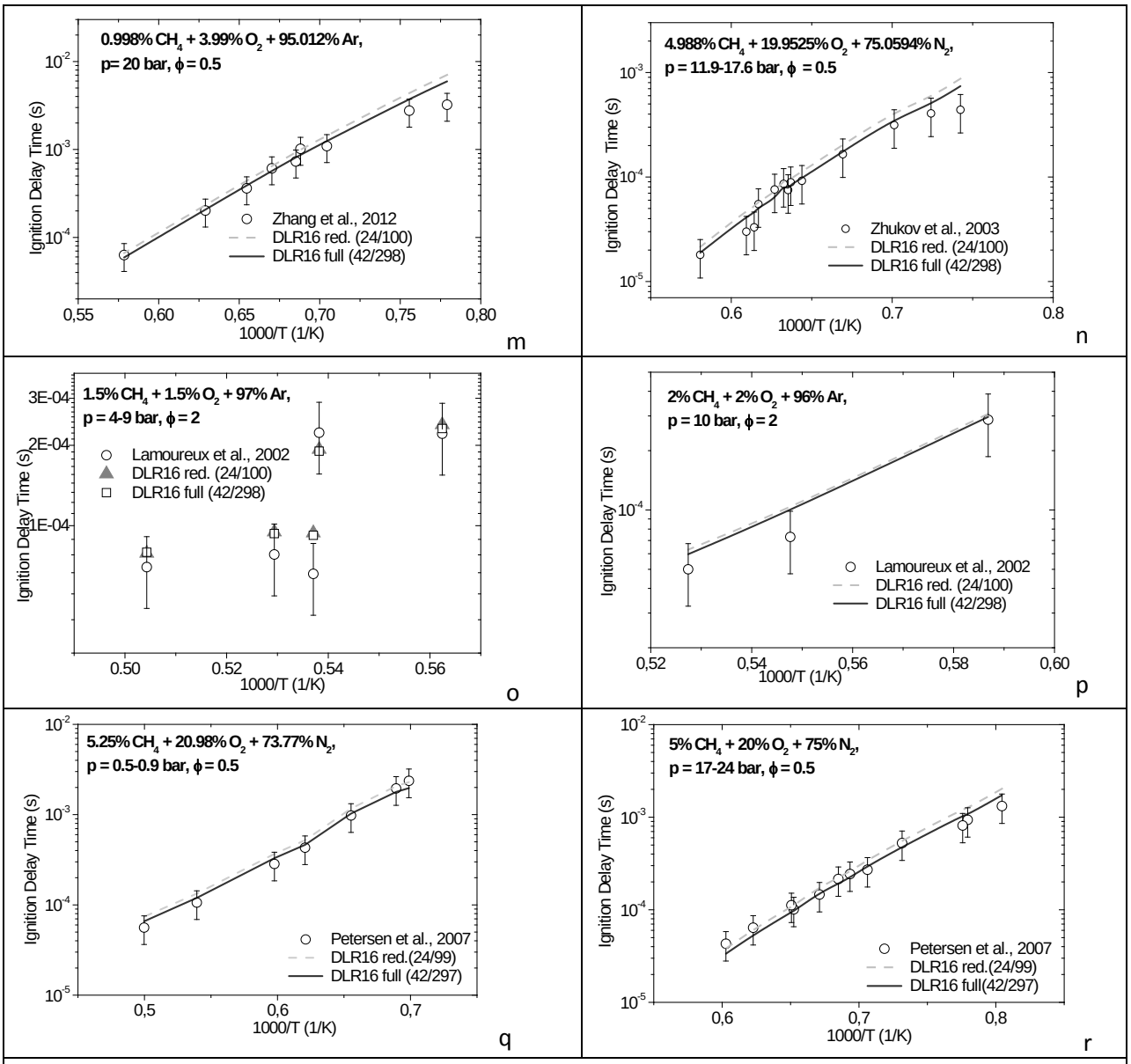
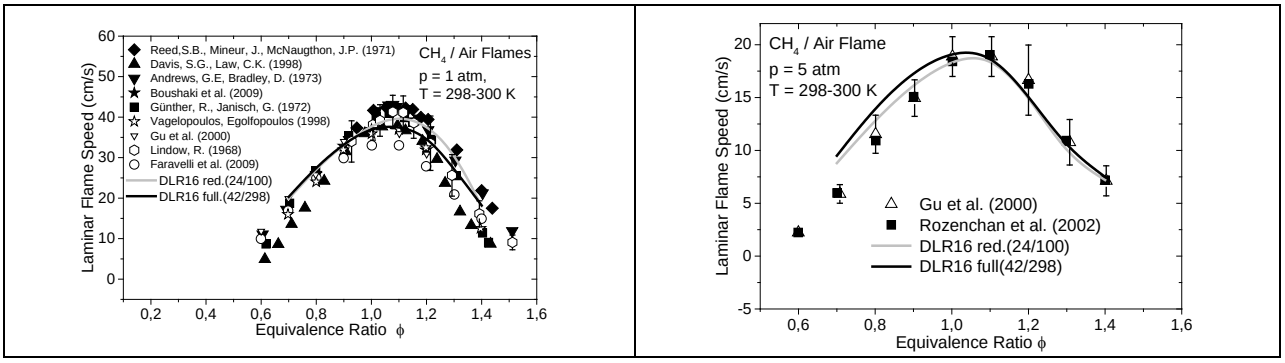


Figure 4. Modeling the ignition delay time [13,14,19-24] with full and reduced mechanism.



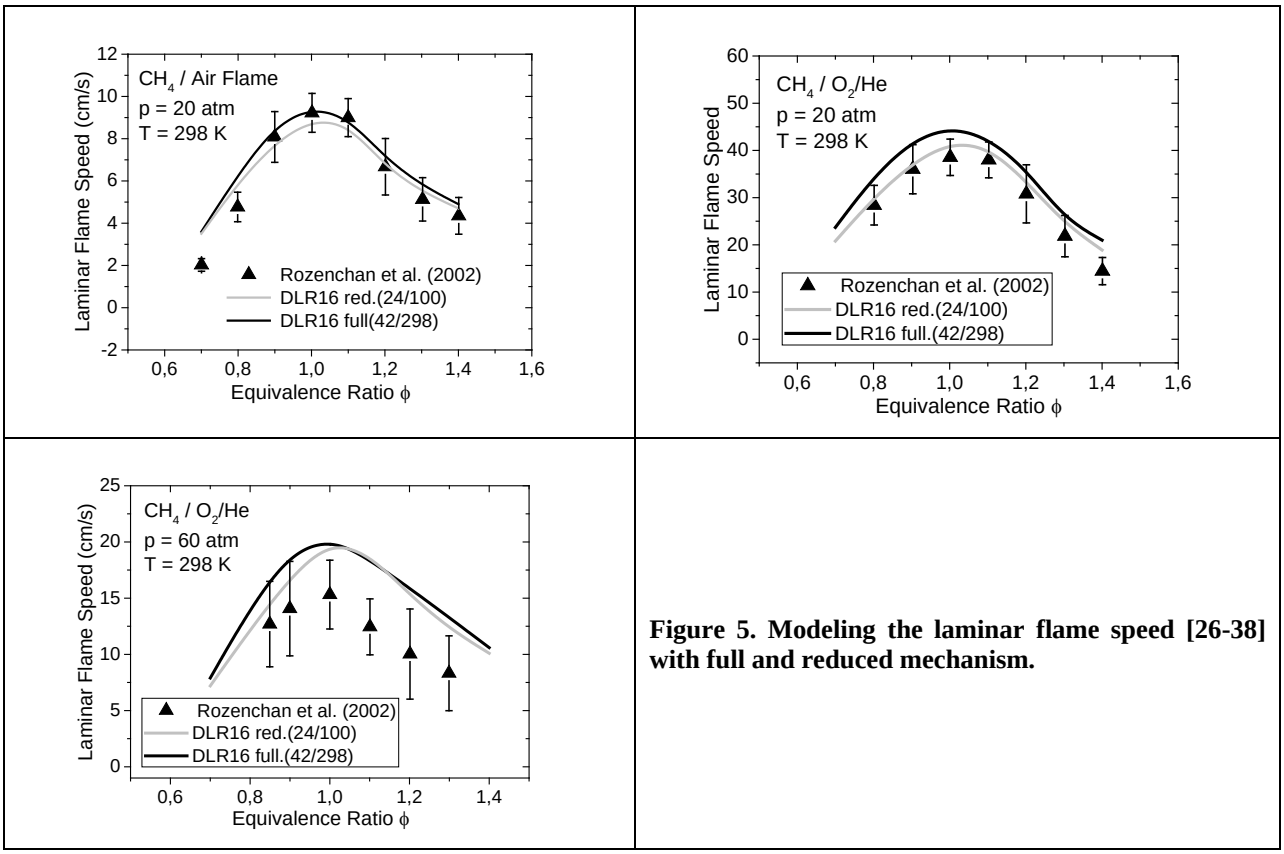


Figure 5. Modeling the laminar flame speed [26-38] with full and reduced mechanism.

VI. Conclusions

A skeletal chemical kinetic model for CH_4/air combustion with 100 reactions and 24 chemical species was developed from detailed mechanism, with 42 species and 298 reactions. The mechanism reduction was performed with the multi target reduction strategy realized in the in-house developed DLR RedMaster code. RedMaster is able to analyze the different chemical processes (ignition delay time and laminar flame speed) in the given time and height points.

The obtained reduced model describes satisfactory experimental data for ignition delay and flame speed under conditions: p_5 = 1-50 bar, T_5= 940K - 210K, $\phi = 0.5–2$; p = 1-60 bar, T_0= 300K, $\phi = 0.6–1.4$.

Further reduction is possible only with chemical lumping methods and algorithms for a global model production. The proposed skeletal mechanism for the methane combustion under rocket engine conditions can be successfully used in CFD modeling. It is free for use on the https://teamsites-extranet.dlr.de/vt/DLR-Mechanism/SitePages/Home.aspx

VII. Acknowledgment

Part of the work has been funded by the German Research Foundation (Deutsche Forschungsgemeinschaft-DFG) Collaborative Research Center TRR 40 – "Technological foundations for the design of thermally and mechanically highly loaded components of future space transportation systems".

References

[1]Stone, R., Tiliakos, N., Balepin, V., Tsai, C.-Y., Engers, R., "ALTITUDE Testing of LOX-Methane Rocket Engine at ATK-GASL," *26th AIAA Aerodynamic Measurement Technology and Ground Testing Conference*, Seattle, Washington, 2008, pp. 2008-3701.

[2]Arione, L"Development Status of the LM10-MIRA Engine for the LYRA Launch Vehicle," *Proceedings of the "Space 2010" Conference*, San Sebastian, 2010.

[3]Kawashima, H., Okita, K., Aoki, K., Azuma, N., Kumakawa, A., Onodera, T., Yoshida, S., Negishi, H., Manako, H., Koganezawa, T., Combustion and Regenerative Cooling Characteristics of LOX/Methane Engine, Transactions of the Japan Society For Aeronautical and Space Sciences, Space Technoogy Japan, Vol. 7 (2009), ists 26 (ISTS Special Issue: Selected papers from the 26th International Symposium on Space Technology and Science), pp Ta_7 – Ta_11.

[4]Preclik,D., Hagemann, G., Knab, O., Mäding, C., Haesler, D., "Lox/Hydrocarbons Preparatory Thrust Chamber Technology Activities in Germany," *AIAA-2005-4555, 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, July 10th to 13th, 2005, Tucson, Arizona, USA.

[5]Burkardt, H., Sippel, M., Herbertz, A., Klevanski, J., "Kerosene vs Methane: A Propellant Tradeoff for reusable Liquid Booster," *Journal of Spacecraft and Rockets*, Vol. 41, No. 5, September-October 2004.

[6]Adams, N., Haidn, O., Schröder, W., Radespiel, R., Sattelmayer, T., Weigand, B., "Collaborative Research Center TRR 40 - Technological foundations for the design of thermally and mechanically highly loaded components of future space transportation systems," accepted for publication at EUCASS 2015, Krakov, Poland, 2015.

[7]Keller, R., Gerlinger, P., "Numerical simulations of a gaseous methane rocket combustion chamber," accepted for publication at EUCASS 2015, Krakov, Poland, 2015.

[8]Celano, M. P., Silvestri, S., Schlieben, G., Kirchberger, C., Haidn, O. J., Knab. O., "Injector Characterization for a GOX-GCH4 Single Element Combustion Chamber," Space Propulsion 2014, Cologne, 2015.

[9]Haidn, O. J., Knab. O., Celano, M. P., Silvestri, S., Kirchberger, C., Schlieben, G., "Test Case 1: Single Element Combustion Chamber – GCH/GOX," TR40 Website, URL: http://www.sfbtr40.de/index.php/de [cited 20 June 2016].

[10]Slavinskaya, N. A., Lenfers, C., "Skeletal Mechanism Production for n-Decane," *2nd Int. Workshop on Model Reduction in Reacting Flow*, 2007,September 3-5, University of Rome "La Sapienza", Rome, Italy.

[11]Slavinskaya, N. A., Riedel, U., Dworkin, S. B., Zhang, Q., Thomson, M. J., "Detailed Numerical Modelling of PAH Formation and Growth in Non-Premixed Ethylene and Ethane Flames," *Combustion and Flame*, Vol. 159, 2012, pp. 979-995.

[12]Slavinskaya, N. A., J.H.Starcke , M.Abbasi , A.Mirzayeva , U.Riedel, M. Frenklach , A. Packard , W. Li , J. Oreluk , A. Hedge, "Consistent Chemical Mechanism from Collaborative Data Processing" submitted in Energy&Fuel issue honoring Prof. Brian Haynes.

[13]Aul, C. J., Metcalfe, W. K., Burke, S. M., Curran, H. J., Petersen, E. L., "Ignition and kinetic modeling of methane and ethane fuel blends with oxygen: A design of experiments approach," *Combustion and Flame*, Vol. 160, No. 7, 2013, pp. 1153–1167.

[14]Burke, U., Somers, K.P., O'Toole, P., Zinner, C. M., Marquet, N., Bourque, G., Petersen, E. L., Metcalfe, W. K., Serinyel, Z., Curran, H. J., "An ignition delay and kinetic modeling study of methane, dimethyl ether, and their mixtures at high pressures," *Combustion and Flame*, Vol. 162, No.2, 2015, pp. 315–330.

[15]Brett, L., Macnamara, J., Musch, P., Simmie, J. M.,"Simulation of methane autoignition in a rapid compression machine with creviced pistons," *Combustion and Flame*, Vol. 124, No.1-2, 2001, pp. 326–329.

[16]de Vries, J., Petersen, E. L.,"Autoignition of methane-based fuel blends under gas turbine conditions," *Proceedings of the Combustion Institute*, Vol. 31, No. 2, 2007, pp. 3163–3171.

[17]Gersen, S., Mokhov, A.V., Darmeveil, J. H., Levinsky, H. B., Glarborg, P., "Ignition-promoting effect of NO2 on methane, ethane and methane/ethane mixtures in a rapid compression machine," *Proceedings of the Combustion Institute*, Vol. 33, No. 1, 2011, pp.433–440.

[18]Huang, J., Hill, P. G., Bushe, W. K., Munshi, S. R., "Shock-tube study of methane ignition under engine-relevant conditions: experiments and modeling," *Combustion and Flame*, Vol.136, 2004, pp.25–42.

[19]Mathieu, O., Goulier, J., Gourmel, F., Mannan, M. S., Chaumeix, N., Petersen, E. L., "Experimental study of the effect of CF3I addition on the ignition delay time and laminar flame speed of methane, ethylene, and propane," *Proceedings of the Combustion Institute*, Vol.35, No. 3, 2015, pp. 2731–2739.

[20]Osorio, C. H., Vissotski, A. J., Petersen, E. L., Mannan, M. S., "Effect of CF3Br on C1–C3 ignition and laminar flame speed: Numerical and experimental evaluation ," *Combustion and Flame*, Vol. 160, 2013, pp. 1044–1059.

[21]Zhang, Y., Huang, Z., Wei, L., Zhang, J., Law, C.K., "Experimental and modeling study on ignition delays of lean mixtures of methane, hydrogen, oxygen, and argon at elevated pressures ," *Combustion and Flame*, Vol. 159, 2012, pp. 918–931.

[22]Zhukov, V. P., Sechenov, V. A., Starikovskii, A. Yu., "Spontaneous Ignition of Methane–Air Mixtures in a Wide Range of Pressures ," *Combustion, Explosion, and Shock Waves*, Vol. 39, No. 5, pp. 487-495, 2003.

[23]Lamoureux, N., Paillard, C. E., Vaslier, V., "Low hydrocarbon mixtures ignition delay times investigation behind reflected shock waves ," *Shock Waves*, Vol.11, 2002, pp. 309–322.

[24]Petersen, E. L., Hall, J. M., Smith, S. D., de Vries, J., Amadio, A. R., Crofton, M. W., "Ignition of Lean Methane-Based Fuel Blends at Gas Turbine Pressures," J. *Eng. Gas Turbines Power*, Vol. 129, 2007, No. 4, pp.937-944.

[25]Petersen, E. L., Kalitan, D.M., "Reflected Shock Ignition of SiH4/H2/O2/Ar andSiH4/CH4/O2/Ar Mixtures," *Journal of Propulsion and Power*, Vol. 20, No. 4, pp. 665-674, 2004.

[26]Davis, S.G., Law, C.K.; "Determination of and Fuel Structure Effect on Laminar Flame Speeds of C1 to C8 Hydrocarbons," *Combustion Science and Technology*, Vol. 140, 1998, pp. 427-449.

[27]Günther, R., Janisch, G.,"Measurements of burning velocity in a flat flame front," *Combustion and Flame*, Vol. 19, 1972, pp. 49-53.

[28]Andrews, G. E., Bradley, D.,"The Burning velocity of methane-air mixtures," *Combustion and Flame*, Vol. 19, 1973, pp. 275-288.

[29]Reed, S. B., Mineur, J., McNaugthon, J. P.,"The effect on the burning velocity of methane vitiation of combustion air," *J. Inst. Fuel*, Vol. 44, 1971, pp. 149.

[30]Lindow, R., " Eine verbesserte Brennermethode zur Bestimmung der laminaren Flammenge-schwindigkeiten von Brenngas/luftgemischen,"Brennstoff Wärme Kraft, Vol. 20, 1968, pp. 8-14.

[31]Boushaki, T., Ferret, B., Selle, L., Dhue, Y., Poinsot, T.," Experimental and numerical study of the accuracy of flame-speed measurements in Bunsen burner," 6th *Mediterranean Combustion Symposium*, MCS 6 (2009).

[32]Faravelli, T., Ranzi, E., Candusso, C., Frassoldati, A., Cuoci, A., Tolazzi, D.,"Simplified kinetic schemes for oxy-fuel combustion," *1st International Conference on Sustainable Fossil Fuels for Future Energy (S4FE)*, 2009.

[33]Vagelopoulos, C.M., Egolfopoulos, F., "Direct experimental determination of laminar flame speeds," *27th Symp. (Int.) on Combustion*, *The Combustion Institute*, Pittburgh, pp. 513-519 (1998).

[34]Gu, X. J., Haq, M. Z., Lawes, M., Woolley, R.," Laminar burning velocity and markstein lengths of methane-air mixtures," *Combustion and Flame*, Vol. 121, 2000, pp. 41-58.

[35]Hassan, M. I., Aung, K. T., Faeth, G. M., "Measured and Predicted Properties of Laminar Premixed Methane/Air Flames at Various Pressures," *Combustion and Flame*, Vol. 115, 1998, pp. 539-550.

[36]Egolfopoulos, F. N., Law, C. K.,"An experimental and computational study of the burning rates of ultra-lean to moderately-rich H2/O2/N2 laminar flames with pressure variations," *Proc. Combust. Inst*. Vol. 23, 1990, pp. 333-340.

[37]Rozenchan, G., Zhu, D. L. Law, C. K., Tse, S. D., "Outward Propagation, Burning Velocities and Chemical Effect of Methane Flames up to 60 atm," *Proc. Combust. Inst.* Vol. 29, 2002, pp. 1461-1470.

[38]Lowry, W., de Vries, J., Krejci, M., Petersen, E., Serinyel, Z., Metcalfe, W., Bourque, G.; "Laminar Flame Speed Measurements and Modeling of Pure Alkanes and Alkane Blends at Elevated Pressures," *Journal of Engineering for Gas Turbines and Power*, in press. (2011).

[39]Kee, R. J., Rupley, F. M., Miller, J. A., CHEMKIN, A FORTRAN chemical kinetics package for the analysis of gas phase chemical kinetics, Ver. 2.0, Sandia Laboratories Report, SAND89-8009B, 1993.

[40]KINALC version 1.71; see http://www.chem.leeds.ac.uk/Combustion/Combustion.html or (Turanyi et al.) http://garfield.chem.elte.hu/Combustion/Combustion.html [cited 20 June 2016].