

A Reduced Mechanism for Ethanol Oxidation

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Abstract

To account for the increasing share of alternative fuels, reliable chemical kinetic mechanisms are needed. For ethanol, as one of the most important alternative fuels, Marinov [1] proposed a high-temperature mechanism consisting of 57 chemical species and 383 elementary reactions. In the present work, this mechanism is systematically reduced, finally leading to 38 species and 228 reactions. For validation, numerical results using the reduced mechanism are compared to experimental ignition delay times and laminar burning velocities, as well as results obtained with the original mechanism.

Introduction

Numerical simulation of combustion processes, for example in internal combustion engines, has become an important tool in research and development. Therefore, chemical mechanisms are required as a basis for combustion models used in CFD. With respect to times needed for computations, these mechanisms have to be as small as possible. Nevertheless, the chemical mechanisms must capture the main phenomena of the combustion process.

Based on the ethanol mechanism by Marinov [1], a reduced mechanism is presented. The new mechanism is validated against the detailed mechanism by Marinov and experimental data from literature. Therefore, ignition delay times from shock tubes [2, 3] and laminar burning velocities from a constant-volume bomb [4, 5] at various conditions are considered. An overview of the conditions investigated can be found in Table 1 (ignition delay times) and Table 2 (laminar burning velocities).

T [K]	p [bar]	ϕ [–]	X_{Ar} [%]
1110-1540	3.3	0.5	91.25
1110-1540	3.5	1.0	95
1110-1540	3.4	2.0	93.25
1250-1670	1+2	0.5	90
1250-1670	1+2	1.0	90
1250-1670	1+2	2.0	90

Table 1: Ignition delay times investigated

T [K]	p [bar]	ϕ [–]
300	1.0	0.5-1.5
300	2.0	0.5-1.5
453	1.0	0.5-1.8
400	10.0	0.5-1.8
600	40.0	0.5-1.8
800	80.0	0.5-1.8

Table 2: Laminar burning velocities investigated

Mechanism Reduction

The reduction process is based on a straightforward approach, whereas the sensitivity of each chemical kinetic species to a user-given quantity is evaluated. The mechanism presented in this work has been derived on the basis of a sensitivity analysis of the ignition delay time and the adiabatic temperature at two different conditions. If a certain threshold is not exceeded, the chemical species is removed from the mechanism, thus reducing the number of species and reactions. During the reduction process, the laminar burning velocity was not considered because it mainly depends on the adiabatic temperature.

The computations for the reduction process were performed using an in-house code combined with the homogeneous reactor model from the Cantera package [6, 7]. Finally, the following species were removed from the detailed mechanism:

- $HCOH$
- $HCOOH$
- CH_3OH
- C_2O
- $CHOCHO$
- $HOC_2H_4O_2$
- CH_2CHCO
- CH_2CHCHO, CH_3CHCO
- CH_2CHCH_2O
- $a - C_3H_4, p - C_3H_4$
- $a - C_3H_5, p - C_3H_5, s - C_3H_5$
- C_3H_6
- $i - C_3H_7, n - C_3H_7$
- C_3H_8

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Unsurprisingly, most of the species that have been removed are from the C_3 -chain. Only two C_3 -species are found to be of importance to the oxidation of ethanol. These species are C_3H_2 and H_2CCCH . Furthermore, $HCOH$ was found to be negligible, whereas the isomer CH_2O remains in the reduced mechanism. $HCOOH$ and C_2O , which are (with regard to the detailed mechanism) in each case mostly formed by a single H -atom abstraction reaction, have also been found to be unimportant. Finally, CH_3OH (methanol) as the next smaller alcohol to ethanol and $HOC_2H_4O_2$ are found to be insignificant for the oxidation of ethanol.

The reduced mechanism, along with the original thermodynamic and transport data by Marinov, is available online [8]. As part of a future work, further reduction of the mechanism could be obtained by introducing steady state assumptions for some of the remaining species.

Results and Discussion

In the following section the reduced mechanism is validated against experimental ignition delay times and laminar burning velocities, as well as results obtained using the original mechanism by Marinov.

The experimental ignition delay times are taken from Dunphy and Simmie [2] (Figs. 1, 2, and 3) as well as Natarajan and Bhakaran [3] (Figs. 4, 5, and 6). They measured ignition delay times using different ethanol/oxygen/argon mixtures. The equivalence ratios investigated were 0.5, 1.0, and 2.0. The temperature ranges from 1100-1670 K and pressure from 1-3.5 bar. As in the case of the reduction process, the numerical ignition delay times have been computed using the isochoric homogeneous reactor model from the Cantera package.

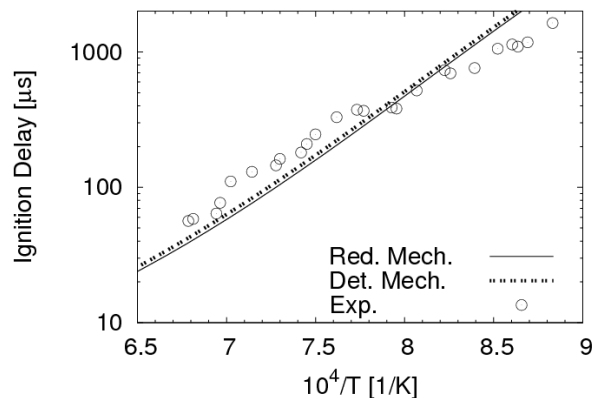


Figure 1: Ignition delay times at $p=3.3$ bar. Experimental data are from Dunphy and Simmie [2]. Mixture composition (molar): 1.25 % C_2H_5OH , 7.5 % O_2 , 91.25 % Ar . $\phi=0.5$.

Figure 1 contains the results for an equivalence

ratio $\phi = 0.5$ at a pressure of 3.3 bar. The reduced mechanism gives almost identical ignition delay times compared to the original mechanism. Both mechanisms slightly overpredict the experimental results for temperatures below 1200 K and underpredict the experiments for temperatures above 1300 K.

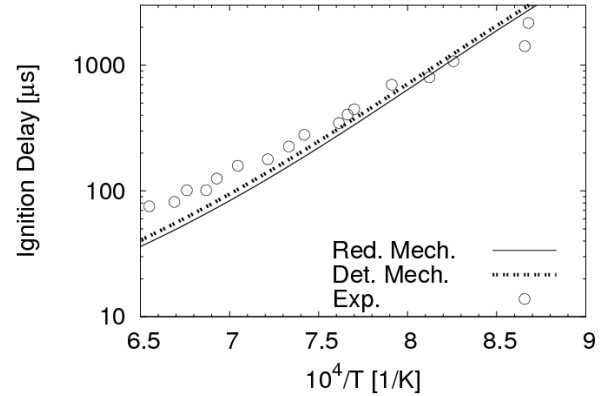


Figure 2: Ignition delay times at $p=3.5$ bar. Experimental data are from Dunphy and Simmie [2]. Mixture composition (molar): 1.25 % C_2H_5OH , 3.75 % O_2 , 95.0 % Ar . $\phi=1.0$.

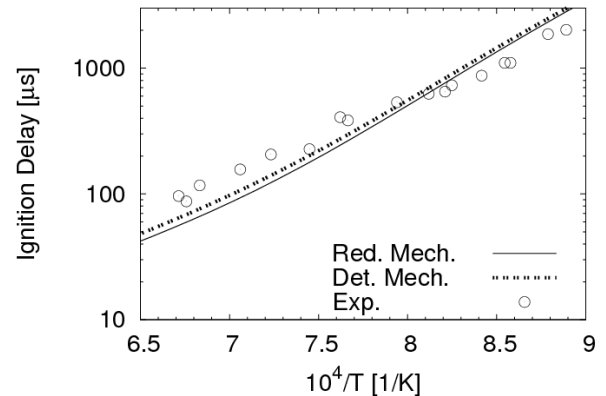


Figure 3: Ignition delay times at $p=3.4$ bar. Experimental data are from Dunphy and Simmie [2]. Mixture composition (molar): 2.5 % C_2H_5OH , 3.75 % O_2 , 93.25 % Ar . $\phi=2.0$.

Figure 2 shows the results at stoichiometric conditions and 3.5 bar. Again, both mechanisms give almost identical ignition delay times. Here, good agreement is found for relatively low and intermediate temperature, whereas at very high temperatures both mechanisms underpredict the experiments.

Under rich conditions ($\phi = 2$, Fig. 3), similar results as in the case of $\phi = 0.5$ are obtained (i.e., slight overprediction in case of low and underprediction in case of high temperatures).

The following results are based on the experi-

ments by Natarajan and Bhaskaran [3], who kept the molar fraction of argon constant (90 %) and varied the ratio of fuel and oxygen to achieve three different equivalence ratios. They investigated two different pressures (1 and 2 bar) at all three mixture conditions.

Figure 4 shows the results for $\phi = 0.5$. At both pressures, the mechanisms match very well the experiments with slightly higher ignition delay times above 1600 K and below 1300 K.

The ignition delay times at stoichiometric conditions can be found in Fig. 5. The mechanisms show very good agreement at all temperatures and pressures investigated.

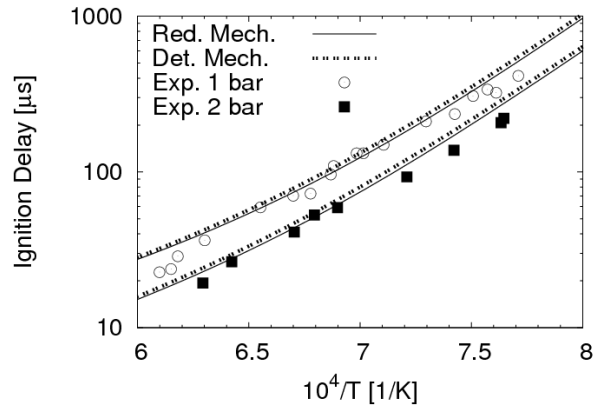


Figure 4: Ignition delay times at $p=1$ and 2 bar. Experimental data are from Natarajan and Bhaskaran [3]. Mixture composition (molar): 1.43 % C_2H_5OH , 8.57 % O_2 , 90.0 % Ar . $\phi=0.5$.

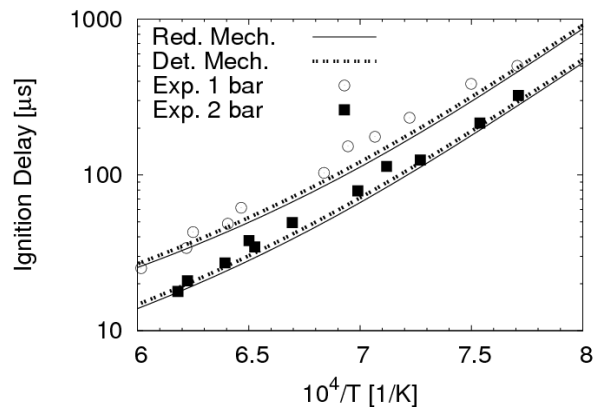


Figure 5: Ignition delay times at $p=1$ and 2 bar. Experimental data are from Natarajan and Bhaskaran [3]. Mixture composition (molar): 2.5 % C_2H_5OH , 7.5 % O_2 , 90.0 % Ar . $\phi=1.0$.

Finally, rich mixtures ($\phi = 2$) have been investigated and the results are given in Fig. 6. Again, very

good agreement could be obtained with both mechanisms. At very high temperatures (above 1600 K), the numerical results give slightly higher ignition delay times.

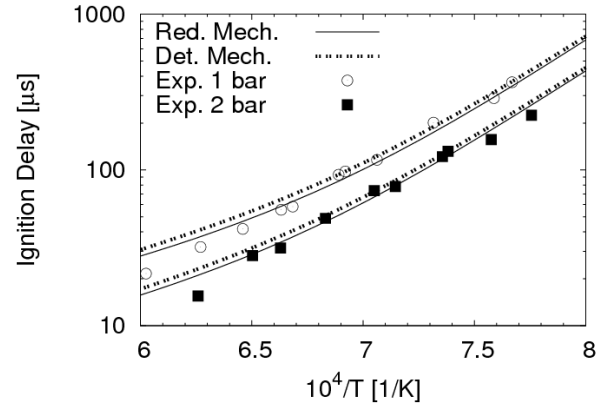


Figure 6: Ignition delay times at $p=1$ and 2 bar. Experimental data are from Natarajan and Bhaskaran [3]. Mixture composition (molar): 4.0 % C_2H_5OH , 6.0 % O_2 , 90.0 % Ar . $\phi=2.0$.

Generally, in all cases investigated, the numerical ignition delay times match the experimental results very well. Furthermore, the difference between the detailed mechanism and the reduced mechanism is insignificant, whereas the reduced mechanism gives slightly lower ignition delay times than the detailed mechanism. Both mechanisms are able to reliably predict ignition delay times.

The following Figs. 7, 8, and 9 show the comparison of numerical and experimental laminar burning velocities over equivalence ratio at different temperatures and pressures. The computations of all laminar burning velocities presented were carried out using the model for a freely propagating flame contained in the Cantera software package.

The experimental values presented in Fig. 7 are taken from Gülder [4] and Egolfopoulos [5]. Gülder investigated laminar burning velocities at 300 K and 1 bar and values from Egolfopoulos are at 298 K and 1 atm. The numerical results are at 300 K and 1 bar. As in the case of the ignition delay times, the reduced and the detailed mechanism give almost identical results, whereas in case of the laminar burning velocity the reduced mechanism gives slightly higher values. In comparison to the experiments one can see that for $\phi = 0.7 - 0.9$, the numerically obtained burning velocities overpredict the experiments while the maximum is underpredicted. For all other equivalence ratios numerical and experimental values agree very well.

Gülder also investigated laminar burning velocities at higher pressure (2 bar) and 300 K. The re-

sults can be found in Fig. 8 along with the numerical values. Similar to the results in Fig. 7, both mechanisms give higher values compared to the experiments in case of lean mixtures, but lower values close to stoichiometric conditions. Overall good agreement is obtained and the location of the maximum laminar burning velocity is well predicted.

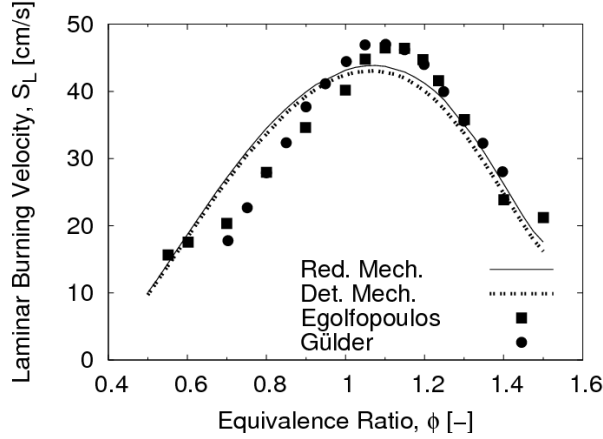


Figure 7: Laminar burning velocities at $p=1$ bar and $T=300$ K. Experimental data are from Gülder [4] and Egolfopoulos et al. ($T=298$ K, $p=1$ atm) [5].

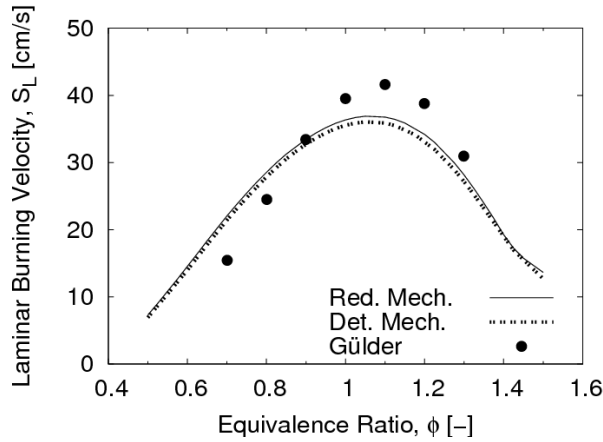


Figure 8: Laminar burning velocities at $p=2$ bar and $T=300$ K. Experimental data are from Gülder [4].

Additionally, laminar burning velocities at a temperature of 453 K and ambient pressure are compared. Experimental values are taken from Egolfopoulos [5]. The numerical results are lower for equivalence ratios $\phi = 1.2 - 1.6$, but match the experiments very well for all other equivalence ratios. The location of the maximum laminar burning velocity is slightly shifted towards lower equivalence ratios.

Finally, laminar burning velocities at higher pressures and temperatures are investigated numerically to validate the reduced mechanism at engine-relevant conditions. As mentioned above in Table 2 three

different conditions are presented. The results can be found in Fig. 10. The reduced mechanism gives slightly higher values for lean mixtures and lower values around $\phi = 1.1 - 1.3$. The difference between the mechanisms becomes larger at higher temperatures and pressures but is always below 10 %. Altogether, the laminar burning velocities obtained with the reduced mechanism match very well the values computed using the detailed mechanism.

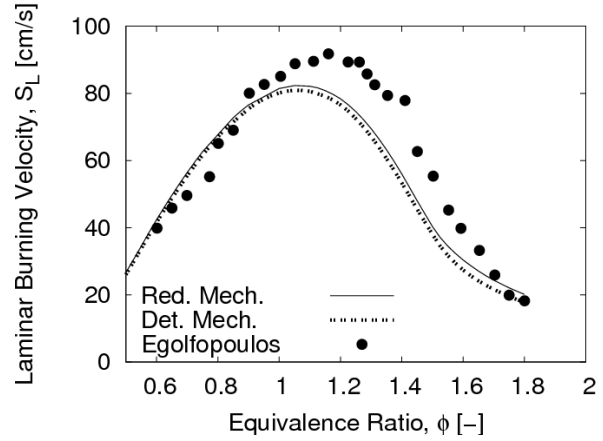


Figure 9: Laminar burning velocities at $p=1$ atm and $T=453$ K. Experimental data are from Egolfopoulos et al. [5].

It may be additionally mentioned here that the results of the ignition delay time and laminar burning velocity calculations have also been used to compare the profiles of important chemical species predicted by the original and the reduced mechanism. As a result, no significant difference could be found at all conditions investigated.

Furthermore, in case of the laminar burning velocities an overall speedup of the computations of about 60 % could be obtained with the reduced mechanism.

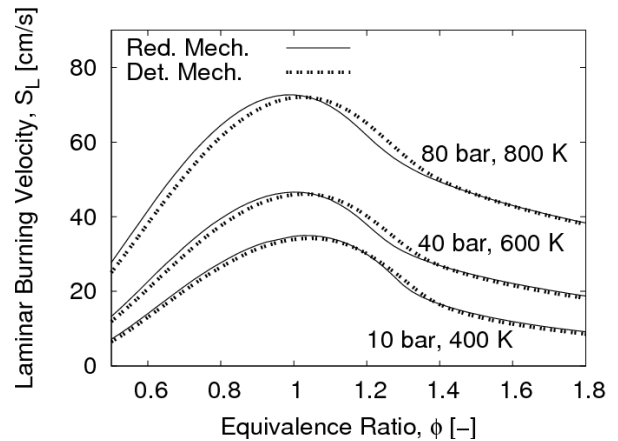


Figure 10: Laminar burning velocities at engine-relevant conditions.

Conclusions

The detailed high-temperature ethanol mechanism by Marinov [1], incorporating 57 chemical species and 383 reactions, was reduced to 38 species and 228 reactions. To validate the reduced mechanism, ignition delay times and laminar burning velocities were calculated and compared to numerical results using the detailed mechanism and experimental data from literature.

In case of ignition delay times, equivalence ratios of 0.5, 1.0, and 2.0 at pressures of 1, 2 and 3.3-3.5 bar were investigated.

Numerically obtained laminar burning velocities at 300 K and 1 and 2 bar and at 453 K and 1 atm were compared to experimental values. Additionally, to validate the reduced mechanism at engine-relevant conditions, laminar burning velocities at 10 bar and 400 K, 40 bar and 600 K, as well as 80 bar and 800 K were considered.

It was shown that the results obtained with the reduced mechanism are almost identical to the results using the detailed mechanism, and both match the experimental values very well within the accuracy of the measurements.

The reduced mechanism gives the opportunity to calculate reliable ignition delay times and laminar burning velocities. Furthermore, the mechanism is small enough to be applied to combustion models used in CFD calculations.

Acknowledgments

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