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NUMERICAL EVALUATION OF THE LAMINAR FLAME SPEED OF ETHANOL WITH LOW WATER CONCENTRATIONS

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Abstract. Bioethanol is an important biofuel that has contributed to reducing of the pollutant emissions and dependence on fossil fuels. One important fact of ethanol production is the great amount of water present after the fermentation process, demanding a high amount of energy to separate trough distillation up to azeotropic concentration and another amount of energy for higher purity. This work aims to present a better understanding of the combustion properties of ethanol in the presence of water close to the azeotropic region. The property evaluated was the laminar flame speed using three combustion mechanisms most reported in the literature. First, a mesh analysis and the parameters defined for the simulation are presented. Then, the laminar flame speed was simulated for various water/ethanol mixtures (0%, 4%, 7.5% and 24% water by mass), equivalence ratio between 0.7 and 1.3 and unburned temperature of 358K, 450K and 600K. A small influence was observed of the water concentration on the flame speed for the poor mixtures. However, for rich mixtures this effect was more significant.

Keywords: *ethanol water fraction, laminar flame speed, reaction mechanism, adiabatic flame temperature.*

1. INTRODUCTION

There are many discussions regarding global warming and if it is a consequence of greenhouse gas emissions or a simple cyclical phase of the planet. However, some facts are indisputable, the first is that each portion of oil, shale or coal extracted from the depth of crust, brings to the surface a portion of carbon atoms that for millennia did not participate in the natural cycle, and the second is that these reserves will certainly end one day.

Thus, the biofuels represent a good option to reduce the dependence of fossil fuels. Currently, the most common biofuels are bioethanol and biodiesel, which can be produced and distributed on a large scale. However, understanding the process of combustion of these biofuels in a combustion system is important to improve the equipment efficiency and reduce pollutant emissions (Saxena and Williams, 2007; Konnov, Meuwissen and De Goey, 2011).

The main combustion parameter that must be evaluated to design a combustion system is the laminar flame speed. Several numerical and experimental analyzes have been reported for the laminar flame speed of anhydrous ethanol premixed with air, for various ranges of equivalence ratio, pressure and temperature of the reactants (Gülder, 1982; Liao *et al.*, 2007; Leplat *et al.*, 2011; Sileghem *et al.*, 2014).

However, the most common routes for ethanol production result in high water concentration, in general the ethanol obtained from fermentation has a volumetric concentration around 12% (Hinton *et al.*, 2018). Thus, to obtain pure ethanol, a large energy consumption is necessary, increasing the production cost. Producing ethanol with 92% of purity instead of 96 % means a 154% specific energy saving on the distillation process, comparing the respective distillation energy-to-lower heating value ratios (Kun-Balog et al., 2017). In this context, knowing the influence of the presence of water premixed with ethanol (hydrous ethanol) and air on the laminar flame speed becomes important to obtain a balance between production cost and combustion efficiency. This influence has been studied by some researchers and Tab. 1 gives a brief summary of the reported results.

Table 1. Summary of the existing data of the laminar burning velocity of ethanol/water/air mixtures for different equivalence ratios, temperatures, and pressures of the reactants.

Reference	Method*	Ø	T_0 (K)	P_0 (bar)	% H_2O by vol.
Lama et al. (2020)	CV	0.7-1.4	380, 450	1, 2, 4, 5	0, 5, 10, 20, 30
Van Treek et al. (2019)	HF	0.7-1.4	358	1	0, 9, 17, 23, 29
Hinton et al. (2018)	CV	0.7-1.4	380, 450	0.5, 1, 2, 4	0, 20, 40
Haas-Wittmüß and Hermanns (2015)	HF	0.7-1.4	318, 358, 383	1	0, 10, 20
Liang et al. (2014)	CV	0.7-1.6	383	1	0, 10, 20, 30

**CV – Constant volume method, HF – Heat-flux method and CF – Counter flow burner method.*

It can be seen that most of the experiments were carried out for water concentrations above 10 %, preheating temperatures below 450 K and a pressure at 1 bar. Only the works presented by (Garzón Lama, Sotton and Martins, 2020)and Hinton et al. (2018) evaluated the effect of pressure on the laminar flame speed of hydrous ethanol. However, the effect of water in mixtures with ethanol and air on the laminar flame speed, with concentrations close to the azeotropic mixture (4.3 % by mass of water) and high temperatures is even less studied.

Thus, in the present work it is proposed to numerically evaluate the behavior of the laminar flame speed for commercial mixtures of hydrous ethanol fuel (EHC). Mixtures of water/ethanol containing 0 %, 4 %, 7.5 % and 24 % water by mass were evaluated, respectively. In Brazil, EHC is available in the common version with 7.5% water (6 % by vol.) and in the premium version with 4 % by mass (3 % by vol.). The results obtained with anhydrous ethanol and water concentration of 24% by mass, have been compared to the experimental data from literature.

Although actual vehicles run most of the time on stoichiometric mixture to keep the catalytic converter in its optimum window, some newer engines under development shows great efficiency improvement using lean burn, stratified mixtures, homogeneous charge compression ignition or other kind of combustion strategies (SAHARIN, 2013; Lee *et al.*, 2017; Ran *et al.*, 2019), thus this work will cover a equivalence ratio range of interest.

2. METHODOLOGY

Laminar flame speed of premixed ethanol/water/air mixtures are evaluated using ANSYS CHEMKIN-PRO 2019 R3, to solve the steady state 1-D premix model using component averaged transport properties. The mechanisms used were LLNL (Mehl *et al.*, 2010), San Diego (Chemical-Kinetic Mechanisms, 2016) and Konnov (Capriolo, Alekseev and Konnov, 2018), as listed in Tab. 2.

Table 2. Mechanism specifications used in the present work.

Mechanism	Species	Reactions
San Diego	57	268
Konnov	119	1419
LLNL	323	1486

The LLNL mechanism was developed for higher hydrocarbons and is well accepted for gasoline and its substitutes studies (Javed *et al.*, 2016). The San Diego and Konnov mechanisms were developed for lower hydrocarbons and are widely used for ethanol analysis. In the present work, it was checked the influence of the adaptive mesh parameters GRAD and CURV, using the data listed in Tab.3.

Table 3. Adaptive grid parameters used for numerical analysis of laminar flame speed.

Set of parameters	Gradient	Curvature	Grid limit
A	0.01	0.01	2000
B	0.02	0.02	2000
C	0.02	0.10	1000
D	0.10	0.50	250

Simulations were conducted over a range of initial temperatures (358 K, 450 K and 600 K) and equivalence ratios (0.7–1.3). For the investigation of water content, the purest commercial ethanol available was selected, with a minimum mass purity of 99.8%, the two automotive classes with a minimum purity of 96% and 92.5%, and a fourth class of 76 % to evaluate the extrapolation trend. The pressure was kept constant at 1 bar for all mixtures. Table 4 shows the fuel composition of the water/ethanol blends used in the present work.

Table 4. Water/ethanol blends evaluated in the present work.

Mixtures	**Ethanol (% v/v)**	**Water (% v/v)**	**Ethanol (% m/m)**	**Water (% m/m)**	**$T_{ad}^{(1)}$ (K)**	***LHV* (kJ/kg)**
M0	99.8	0.2	99.8	0.2	2295	30371
M3	96.8	3.2	96.0	4.0	2280	29156
M6	94.0	6.0	92.5	7.5	2266	28093
M20	80.0	20.0	76.0	24.0	2185	23082

(1) Calculated considering complete combustion with standard dry air, for Ø=1.0, P_0= 1 atm and T_0= 358 K.

The addition of 20% water by volume results in a reduction of the adiabatic flame temperature by around 4.8%, while *LHV* has a reduction of 24%.

3. RESULTS AND DISCUSSIONS

Initially, the simulation parameters applied in the Chemkin-Pro software were evaluated, to reduce the error in the calculation of the laminar flame speed. Then, mixtures M1 and M4 were simulated (see Table 4) and the values were compared with the experimental data reported in the literature. In this way, it was possible to evaluate the reaction mechanism more adequately for these mixtures.

3.1. Analysis of CURV and GRAD parameters

The GRAD and CURV parameters were changed as showed in Tab. 3. Figure 1 shows the effect of GRAD and CURV settings on the laminar flame speed (S_L) and adiabatic flame temperature (T_{ad}) as a function of the equivalence ratio (Ø).

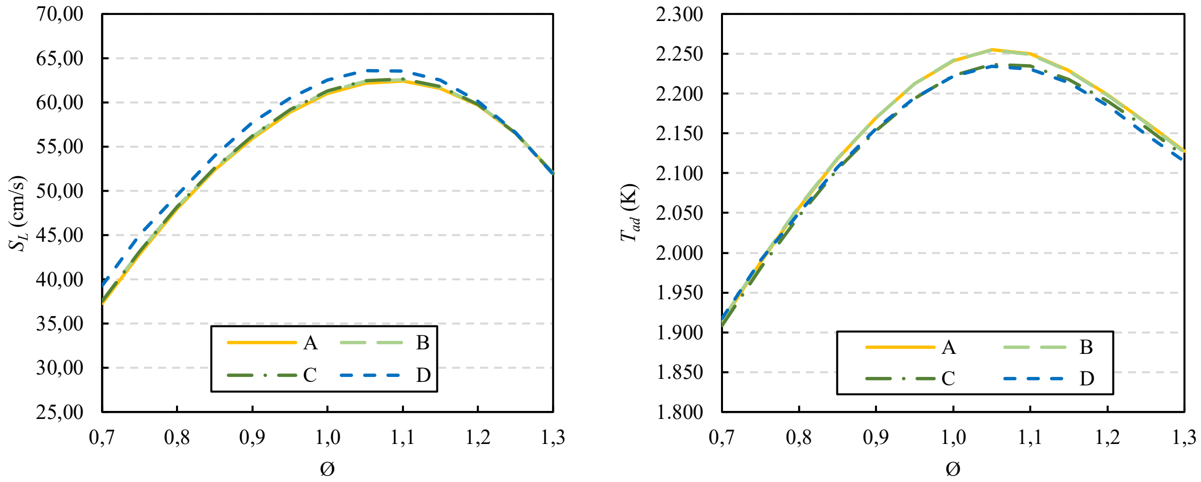


Figure 1. Effect of adaptive grid parameters on (a) laminar burning velocity and (b) flame temperature.

Figure 1(a) shows the laminar flame speed for the equivalence ratio between 0.7 and 1.3, where can be noted that the coarse grid provided a laminar flame speed of 2 cm/s higher for equivalence ratio up to 1.0. For rich mixtures, was observed a slight increment of the laminar flame speed, around of 1 cm/s, and some convergence for the equivalence ratio from 1.2 to 1.3. The three other meshes give similar results over all points.

Figure 1 (b) shows the effect of the GRAD and CURV parameters on the flame adiabatic temperature as a function of the equivalence ratio. It is possible to notice a point of displacement from the two coarser meshes (C and D) to the finer ones (A and B). In addition, the effect of the adaptive parameters is more significant for the equivalence ratio between 0.9 and 1.15.

Thus, sets A and B show similar satisfactory results, but set A takes about 3 to 5 times the computational time spent on B, depending on the equivalence ratio. Table 5 shows the average grid size for each test condition. Parameter B presented results similar to A, but with minimal computational effort, so it was selected for this work.

Table 5. Average grid size obtained with the parameters listed in Tab. 3.

Set of parameters	Average grid Points
A	1737
B	877
C	708
D	141

3.2. Effect of the reaction mechanism on the laminar flame speed

The most suitable reaction mechanism for the present work was evaluated by comparing the numerical results with the experimental values obtained from van Treek et al. (2018) and Haas and Hermanns (2015), for mixtures containing 0% and 20% water by volume. Figure 2 shows the laminar flame speed (S_L) as a function of the equivalence ratio (Ø), for the mixtures M0 and M20 listed in Tab.4 and the mechanisms listed in Tab.2.

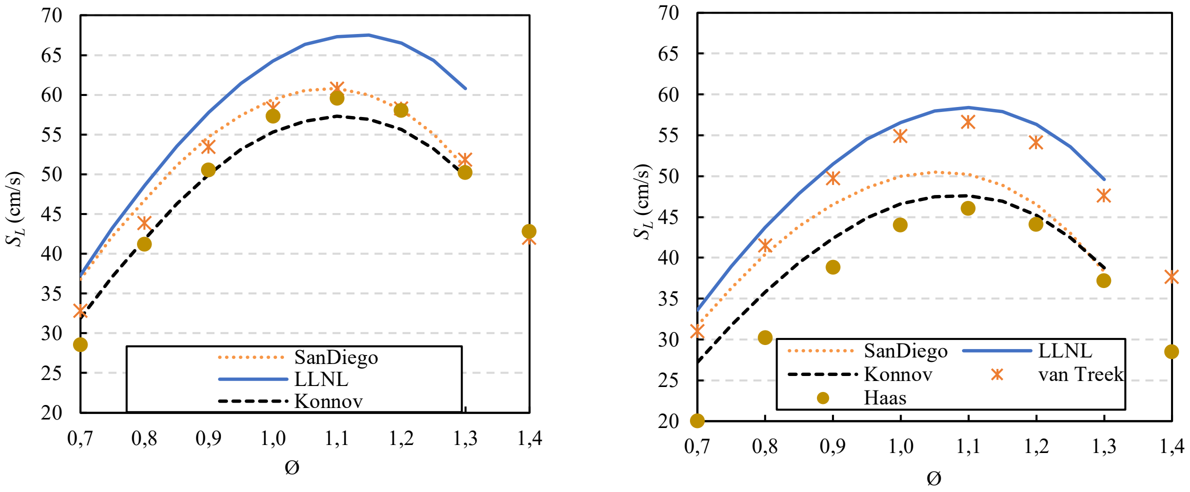


Figure 2. Effect of mechanism on the laminar burning velocity for fuel mixtures with 0% (a) and 20% (b) water by volume, initial temperature of 358 K and pressure 1 bar. Symbols are experimental and lines are numerical results.

Simulation results for pure ethanol are in agreement with simulations and experimental results reported in previous articles (Bradley *et al.*, 2014; Katoch, Millán-Merino and Kumar, 2018; Konnov *et al.*, 2018). It can be seen that the experimental S_L values for 0% of water showed by van Treek et al. (2019) and Haas and Hermanns (2015) were very close, while for the mixture with 20% water the differences are more significant.

For a mixture of fuel with 0% water, it is possible to observe that the San Diego mechanism is more adequate compared to van Treek et al. (2019), while Konnov mechanism is better when compared to Haas and Hermanns (2015). For fuel mixture with 20% water by volume, the experimental results show a variation up to 19% for Ø = 1.1.

The percentage differences of the experimental S_L in relation to the numerical results for 0% water are shown in Tab. 6.

Table 6. Percentage deviation of the S_L calculated with reaction mechanism in relation to the experimental results presented by Hass and Hermanns (2015) and van Treek et al. (2019), for 0% water.

Ø	***Compared to Haas and Hermanns (2015)***			***Compared to van Treek et al. (2019)***		
	San Diego	**LLNL**	**Konnov**	**San Diego**	**LLNL**	**Konnov**
0.7	29.1	30.9	11.9	12.2	13.7	-2.7
0.8	13.6	18.0	1.7	6.8	11.0	-4.3
0.9	8.3	14.5	-1.0	2.4	8.2	-6.4
1.0	3.7	12.0	-3.5	2.1	10.3	-5.0
1.1	2.2	13.1	-3.7	0.2	10.9	-5.6
1.2	0.2	14.7	-4.1	-0.2	14.3	-4.5
1.3	1.4	21.1	-0.8	-1.7	17.4	-3.9

As the water concentration range of interest in this work is closer to the results for 0% water, the mechanism selected for analysis was San Diego. In addition, this mechanism presented the best result for the stoichiometric mixture.

3.3. Effect of the water concentration on the laminar flame speed

Simulations of the laminar flame speed to evaluate the effect of water concentration were conducted using the reaction mechanism of San Diego, for atmospheric pressure and initial temperatures of 358 K, 450 K and 600 K. Figure 3 shows the effect of water concentration on the laminar flame speed as a function of the equivalence ratio (Ø), for the three initial temperature and pressure at 1 atm.

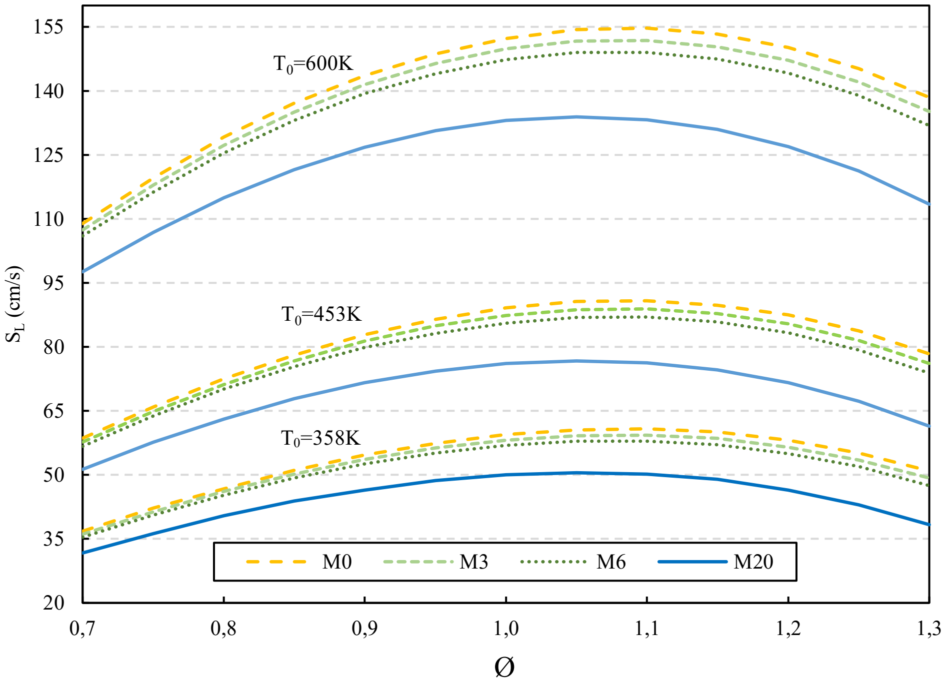


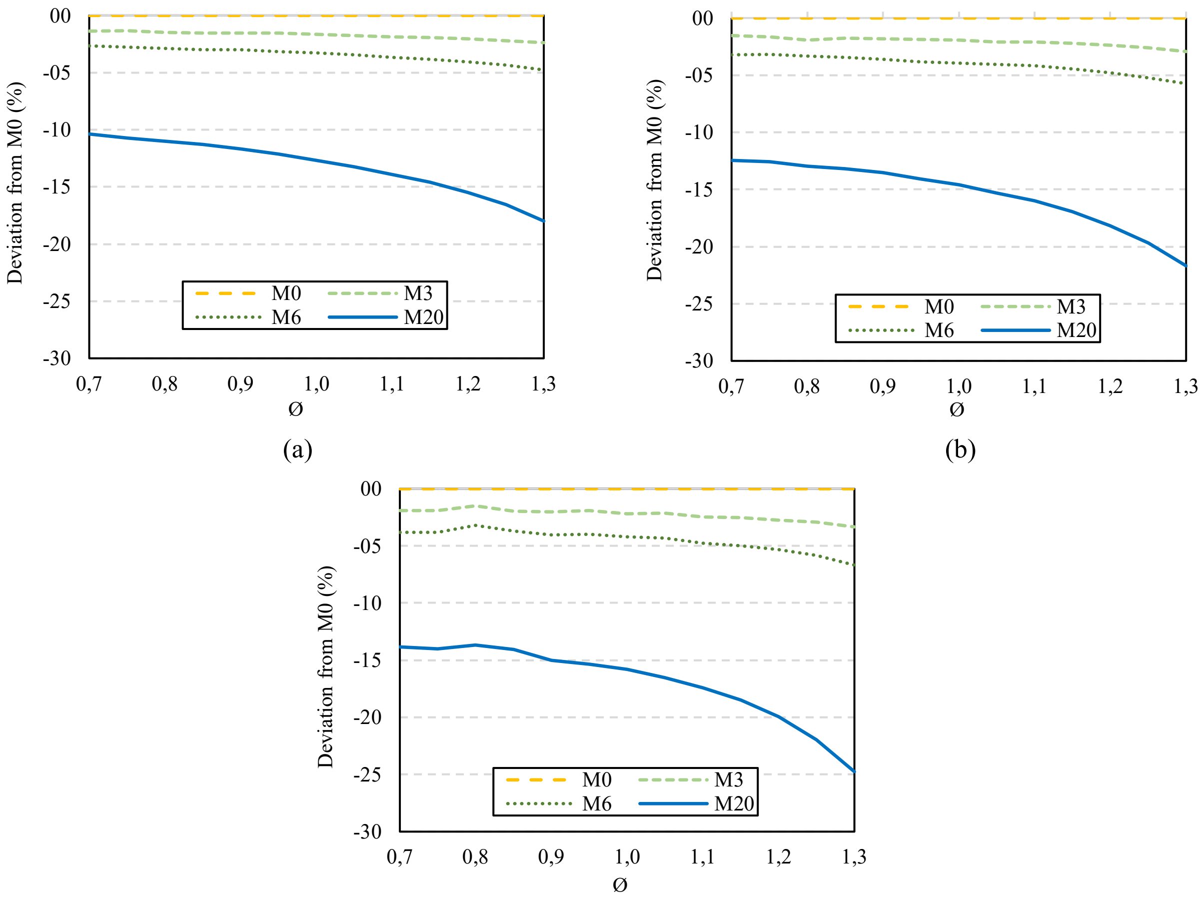
Figure 3. Effect of water addition on the laminar flame speed calculated with San Diego mechanism, for atmospheric pressure and initial temperature of 358 K, 453K and 600K.

In Fig. 3 it can be seen that the flame speed decreases with increasing water concentration, for all initial temperatures. This effect is more significant for Ø > 1.0. In addition, it can be observed that the increase of the reactant's temperature has a greater influence on the flame speed than the addition of water. Also, the adiabatic flame temperature decreases 5 % between the fuel with 0 and 20% water, however the *LHV* reduced 23% (see Tab. 4), evidencing the influence of the heat release of the fuel mixture on the laminar flame speed.

Liang et al. (2014) evaluated the effect of water content on the ethanol laminar flame speed for temperature of 383 K, atmospheric pressure, and concentrations of 0%, 10%, 20% and 30% water by volume. The physical effect of water was separated from its chemical effect by designing a type of fictitious water in the simulation, with the same thermodynamic and transport properties as real water. Results show that laminar flame speed decrease with increasing the water content, due to physical and chemical effects of water that suppress laminar burning velocities. Also, was observed that the physical effect is dominate.

Figure 4 shows the percentage deviation of S_L in relation to pure ethanol (M0), for fuel mixtures with 3%, 6% and 20% water by volume.

Although the absolute values of S_L are higher for elevate temperatures, the effect of adding water on the laminar flame speed is relatively less for temperature of 600 K than to 358 K. For equivalence ratio of 1.0 and using the fuel mixture with 0% water as reference, the S_L of the M20 decreases 16% at 358K, 15% at 453K and 13% at 600K.



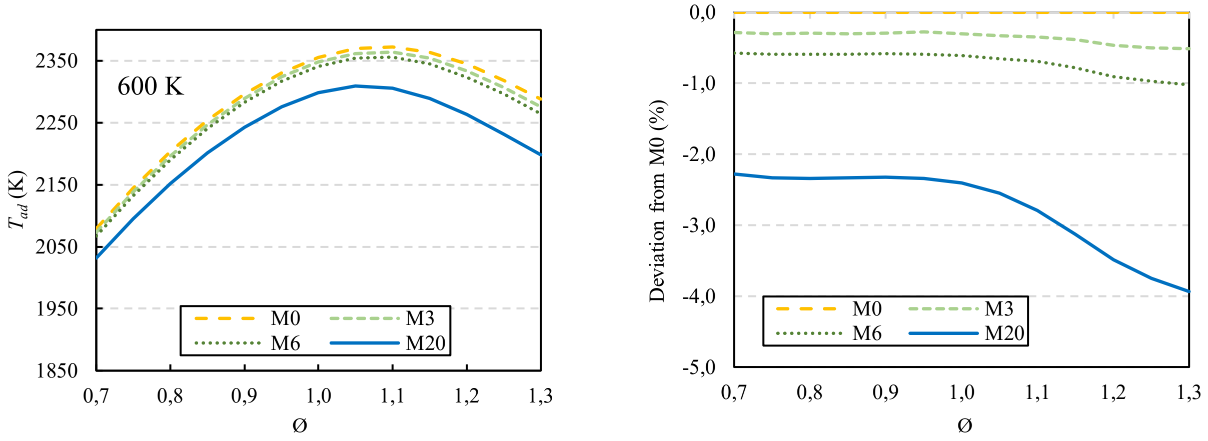
(a)

(b)

(c)

Figure 4. Percentual deviation of the S_L in relative to pure ethanol (M0), for fuel mixtures with 3%, 6% and 20% water by volume, calculated with San Diego mechanism, for atmospheric pressure and initial temperature of (a) 600 K, (b) 453 K and (c) 358 K.

Figure 5 shows the simulation results of the adiabatic flame temperature as a function of equivalence ratio calculated using San Diego mechanism, for all fuel mixture evaluated. It can be noted that the increase in unburned temperature has a small effect on T_{ad}.



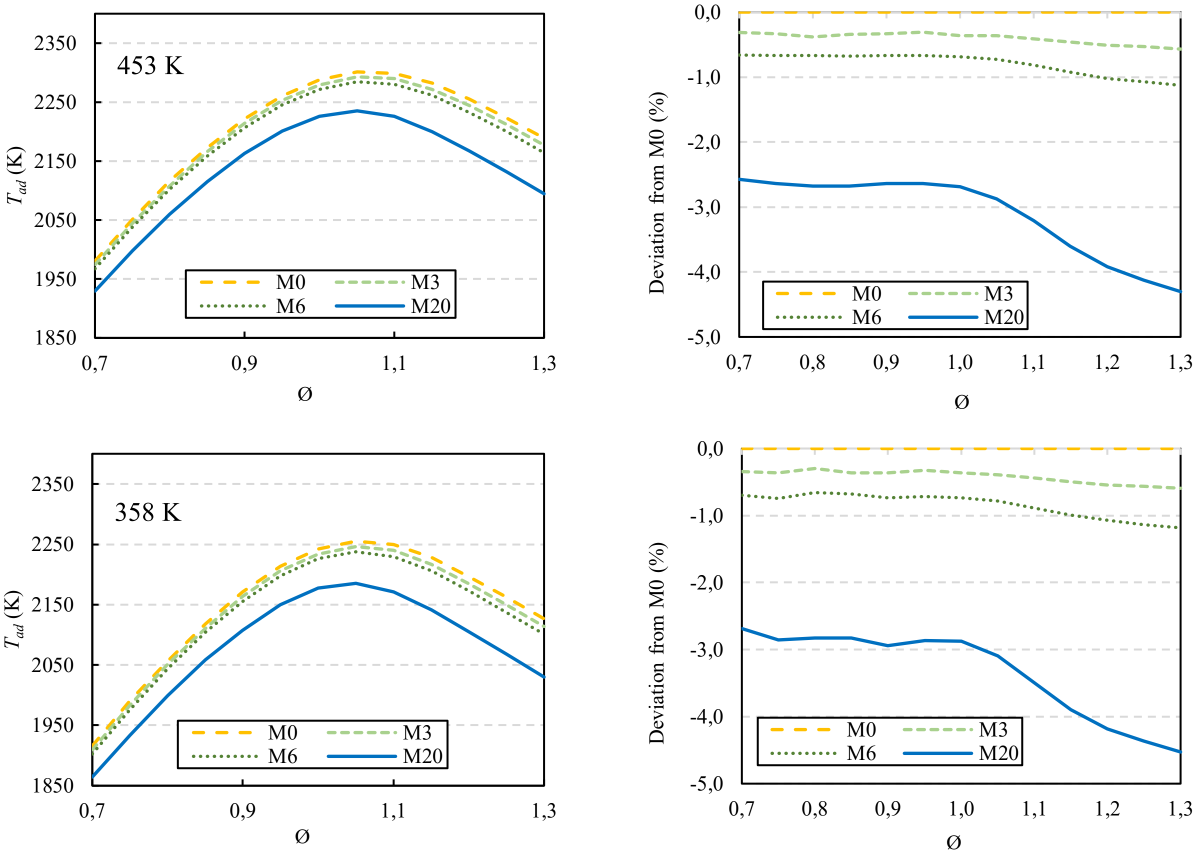


Figure 5. Effect of water addition on the adiabatic flame temperature calculated using San Diego Mechanism, for atmospheric pressure and T_0 of 358 K, 453 K and 600 K. Percentual deviation of T_{ad} is presented using M0 as reference.

It was found that adiabatic flame temperature decreases with water addition, but in different ratio depending on the equivalence ratio. For leaner mixtures up to stoichiometric there is almost constant offset proportional to water content and very little dependency on unburned temperature. For richer mixtures water effect became higher and varied almost linearly with equivalence ratio. Also, the slope of this increment seems to be independent of the reactant's temperature.

4. CONCLUSIONS

Simulations of ethanol combustion were performed and a mesh study is presented. The numerical values for pure ethanol are consistent with experimental results presented in the literature. The evaluated mechanisms were San Diego, Konnov and LLNL. The first and second are widely used for ethanol studies and the third was developed for higher hydrocarbons, mainly gasoline substitutes. The absolute values of flame speed calculated with LLNL tend to be higher than the experiments with pure ethanol, but they present good agreement with the experimental results presented by van Treek et al. (2019) using 20% water by volume. However, in the present work the water concentration of interest is lower than 6% by volume, so the mechanism used to evaluate the effect of the water concentration was San Diego.

For the fuel mixture with 3% and 6% water by volume, the laminar flame speed reduced 2 and 4% in comparison with pure ethanol, respectively, for initial temperature of 358 K and equivalence ratio of 1.0. The water addition has a greater influence on the laminar flame speed for equivalence ratios above stoichiometry. This effect was observed for all initial temperatures evaluated. The reduction of the laminar flame speed with water addition is a result of both physical and chemical effects, but probably the physical effect is dominate. A sensitivity analysis of the reaction coefficients should be conducted to better understand the chemical effect of the water addition on the laminar flame speed for the fuel mixtures evaluated.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Bradley, D. *et al.* (2014) 'Laminar mass burning and entrainment velocities and flame instabilities of i-octane, ethanol and hydrous ethanol/air aerosols', *Combustion and Flame*. The Combustion Institute., 161(6), pp. 1620–1632. doi: 10.1016/j.combustflame.2013.12.011.

Capriolo, G., Alekseev, V. A. and Konnov, A. A. (2018) 'An experimental and kinetic study of propanal oxidation', *Combustion and Flame*. Elsevier Inc., 197, pp. 11–21. doi: 10.1016/j.combustflame.2018.07.004.

Chemical-Kinetic Mechanisms for Combustion Applications (2016), San Diego Mechanism web page, Mechanical and Aerospace Engineering (Combustion Research), University of California at San Diego (http://combustion.ucsd.edu)

Garzón Lama, L., Sotton, J. and Martins, C. A. (2020) 'Experimental burning velocities of ethanol-water-air at elevated pressure and temperature', *Fuel*. Elsevier, 265(December 2019), p. 116933. doi: 10.1016/j.fuel.2019.116933.

Gülder, Ö. L. (1982) 'Laminar burning velocities of methanol, ethanol and isooctane-air mixtures', *Symposium (International) on Combustion*, 19(1), pp. 275–281. doi: 10.1016/S0082-0784(82)80198-7.

Haas, R. and Hermanns, E. (2015) 'Measurements of the Laminar Burning Velocity of Ethanol-Water-Air Mixtures', *OWI Oel-Waerme-Institut GmbH*, p. 6.

Hinton, N. *et al.* (2018) 'Aqueous ethanol laminar burning velocity measurements using constant volume bomb methods', *Fuel*. Elsevier, 214(July 2017), pp. 127–134. doi: 10.1016/j.fuel.2017.10.113.

Javed, T. *et al.* (2016) 'Ignition studies of n-heptane/iso-octane/toluene blends', *Combustion and Flame*, 171. doi: 10.1016/j.combustflame.2016.06.008.

Katoch, A., Millán-Merino, A. and Kumar, S. (2018) 'Measurement of laminar burning velocity of ethanol-air mixtures at elevated temperatures', *Fuel*. Elsevier, 231(May), pp. 37–44. doi: 10.1016/j.fuel.2018.05.083.

Konnov, A. A. *et al.* (2018) 'A comprehensive review of measurements and data analysis of laminar burning velocities for various fuel+air mixtures', *Progress in Energy and Combustion Science*. Elsevier Ltd, 68, pp. 197–267. doi: 10.1016/j.pecs.2018.05.003.

Konnov, A. A., Meuwissen, R. J. and De Goey, L. P. H. (2011) 'The temperature dependence of the laminar burning velocity of ethanol flames', *Proceedings of the Combustion Institute*. Elsevier Inc., 33(1), pp. 1011–1019. doi: 10.1016/j.proci.2010.06.143.

Kun-Balog, A., Sztankó, K. and Józsa, V. (2017) 'Pollutant emission of gaseous and liquid aqueous bioethanol combustion in swirl burners', Energy Conversion and Management. Elsevier Ltd, 149, pp. 896–903.

Lee, C. *et al.* (2017) 'Autoignition characteristics of oxygenated gasolines', *Combustion and Flame*. Elsevier Inc., 186, pp. 114–128. doi: 10.1016/j.combustflame.2017.07.034.

Leplat, N. *et al.* (2011) 'Numerical and experimental study of ethanol combustion and oxidation in laminar premixed flames and in jet-stirred reactor', *Combustion and Flame*. The Combustion Institute., 158(4), pp. 705–725. doi: 10.1016/j.combustflame.2010.12.008.

Liao, S. Y. *et al.* (2007) 'Determination of the laminar burning velocities for mixtures of ethanol and air at elevated temperatures', *Applied Thermal Engineering*, 27(2–3), pp. 374–380. doi: 10.1016/j.applthermaleng.2006.07.026.

Mehl, M. *et al.* (2010) 'Detailed Kinetic Modeling of Low-Temperature Heat Release for PRF Fuels in an HCCI Engine', *SAE Technical Paper Series*, 1. doi: 10.4271/2009-01-1806.

Ran, Z. *et al.* (2019) 'Experimental study of lean spark ignition combustion using gasoline , ethanol , natural gas , and syngas', *Fuel*. Elsevier, 235(May 2018), pp. 530–537. doi: 10.1016/j.fuel.2018.08.054.

SAHARIN, S. B. (2013) 'Vaporization and autoignition characteristics of ethanol and 1-propanol droplets: influence of water', p. 204. Available at: https://tel.archives-ouvertes.fr/tel-00909646.

Saxena, P. and Williams, F. A. (2007) 'Numerical and experimental studies of ethanol flames', *Proceedings of the Combustion Institute*, 31 I(1), pp. 1149–1156. doi: 10.1016/j.proci.2006.08.097.

Sileghem, L. *et al.* (2014) 'Laminar burning velocities of primary reference fuels and simple alcohols', *Fuel*. Elsevier Ltd, 115, pp. 32–40. doi: 10.1016/j.fuel.2013.07.004.

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