Benchmarking of Alcohol
Chemical Kinetic Mechanism
for
Laminar Flame Speed Calculations [+]

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Abstract

Methanol and ethanol have been investigated as very high octane fuels for knock control/avoidance in spark ignition engines. Direct injection of the alcohol results in substantial cooling of the cylinder charge, decreasing the chemical kinetic rates that result in autoignition. However, decreasing the temperature of the cylinder charge also affects the initial flame propagation. The purpose of this paper is to benchmark the Marinov mechanism developed for ethanol oxidation when used for methanol, and to compare it with the Li mechanism developed for methanol. Flame speeds from the chemical kinetics model are compared with published experimental results for both methanol and ethanol.

I. Introduction

Methanol is a very attractive fuel for operation in spark ignited engines [Nichols, Reed, George, O'Blenes, West, Brusstar]. Although toxic, it is being used today in most automotive applications as a fluid for windshield washer, which instead of being burned is actually sprayed onto the roadway.

One of the main attractiveness of methanol is that it has high octane. It is used in drag racing, where peak power is desired for relatively short periods of time. [O'Blenes] It has also been proposed as a fuel for conventional passenger vehicles, and substantial fleet of vehicles existed in the US up to the mid-90's, accumulating about half-a-decade of data on performance, degradation and consumer acceptance [West]. In addition, there is substantial interest in this fuel in the developing countries, in particular, China, where a fuel specification for methanol fuels is expected in the first half of 2008. [Wu, Volvo]

Direct injection of the alcohol (either methanol or ethanol) has a substantial effect in cooling the air-fuel charge, decreasing the propensity of a fuel to autoignite (knock) and thus allowing for increased pressure in the manifold or increased compression ratio, or both. [Bromberg] In a previous paper, the effective octane of methanol and ethanol were calculated, simulating a Cooperative Fuels Research (CFR) engine with different alcohol mixes. [Bromberg1] It was determined that both ethanol and methanol had effective octane numbers higher than 150.

It is possible that when used as a large fraction of the fuel, the flame propagation is not an issue in warm engines if there is substantial fuel reformation in the region around the spark plug [Turner1], which is warmer than the other surfaces in the cylinder walls or piston. It is desired to prevent the local reformation of the fuel, as it could result in pre-ignition. The cooling effect may be sufficiently large to impact the flame propagation speed, decreasing it to the point where misfire could occur. In order to be able to compute the effect, it is necessary to evaluate the adequacy of established chemical kinetic mechanism for these alcohols, in order to determine whether new mechanisms need to be developed. In this paper, a published mechanism for the oxidation of ethanol is evaluated for determining the flame speed of methanol, and the results are compared with experimental data on methanol combustion.

II. The fuel properties

Table 1 shows the properties of gasoline, ethanol and methanol. [SAEJ1297, Hara, Liao] It also shows the flame speed of octane, n-heptane, ethanol and methanol. The flame speed of stoichiometric air mixtures with ethanol and methanol at 1 bar, 300K are comparable to that of n-heptane, which is in small amounts present in Primary-Reference-Fuel (PPRF) gasoline. The flame speed of iso-octane, which is in high concentration in PRF gasoline, is substantially smaller than the flame speed of either alcohol or n-heptane.

It should be stressed that the Primary Reference Fuels (PRF) have been used as the standard to determine the propensity of the fuels to autoignite, not to determine the flame

speed. Thus, the properties presented in Table 1 for iso-octane and n-heptane are only indicative on the situation with gasoline. In other words, it is not clear that conventional 87 octane gasoline would have the same flame speed properties of a PRF with the same octane rating. Low temperature chemistry is associated with knock propensity, while flame speed is more related to high temperature kinetics.

Table 1. Properties of the alcohol fuels and gasoline

Fuel type		Gasoline	iso-octane	n-heptane	Ethanol E100	Methanol M100
Chemical formula			C_8H_{18}	C_7H_{16}	C_2H_5OH	CH_3OH
RON			100	0	129	133
MON			100	0	102	105
(R+M)/2					115	119
Specific gravity	kg/l	0.75			0.794	0.796
Net heat of Combustion (LHV)	MJ/l	32			21	16
Net heat of Combustion (LHV)	MJ/kg	43			27	20
Latent heat of vaporization	BTU/gal	800			2600	3300
Latent heat of vaporization	MJ/kg	0.30			0.91	1.16
Vaporization energy/heat of combustion		0.007			0.034	0.058
Stoic air/fuel ratio		14.6			9	6.4
Equiv. Latent heat of vaporization	MJ/kg air	0.02			0.10	0.18
ΔT air	K	-28			-138	-246
Laminar flame speed (1 bar, 300K)	cm/s		33	39	41	50

A simplified cooling effect has been estimated in Table 1. ΔT in Table 1 refers to the change in temperature of a stoichiometric mixture when the alcohol evaporates, assuming constant air properties. It is an indication of the evaporating cooling property of the fuel, as opposed to a precise number, which depends on initial temperature, evaporation rate, time of injection, compression heating during evaporation, and others complications in the real system. In a stoichiometric mixture, ethanol has a cooling of about 4 times that of gasoline, while methanol has the effect of about 9 times larger than gasoline. These numbers are large, and projection of the effect of these large numbers on turbocharging and increased compression ratio have been presented elsewhere [Bromberg]. It is this thermal effect that may affect the start of combustion, resulting in misfire. In addition, it is desired to be able to determine the effect of water dilution of the alcohol mixture when calculating the effect on laminar flame speeds.

The temperature and pressure conditions for the flame speed shown in Table 1 are different from those around spark timing in the engine, which are closer to 10 bar and about 640 K in normal operation of spark ignition engines operating at maximum brake torque timing (MBT). Once benchmarked, the code can then be used to determine the laminar flame speed at conditions more relevant to spark ignition engines.

III. Mechanism

Two mechanisms have been used in the calculations. The first one is the mechanism by Marinov [Marinov]. This is a detailed chemical kinetic mechanism that has been validated for ethanol by comparisons to experimentally measured laminar flame speeds and shock tube ignition delay times. The results of the model were also compared to species concentrations measured in a stirred reactor and a flow reactor. This mechanism has been included in the Curran mechanism [Curran] used previously by our group to determine the knock conditions of ethanol addition and the octane of methanol and octane blends [Bromberg, Bromberg1]. Since methanol is on the path of ethanol oxidation, there are reactions for methanol, although the mechanism has not been validated for methanol.

The second mechanism, which we found recently, has been developed by the Princeton's Fuel and Combustion Research Laboratory [Li]. This mechanism has been validated for methanol (and other C1 compounds) using data from laminar premixed flame speed, shock tube ignition delay and flow reactor measurements.

The adiabatic flame speed is a characteristic property of a gas mixture at a given temperature and pressure.
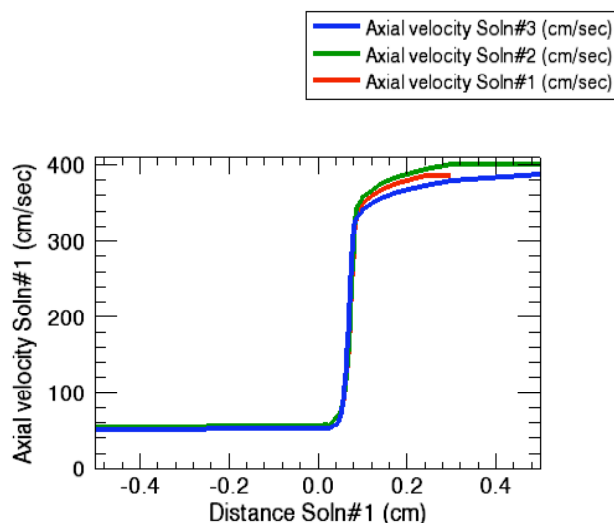

Figure 1. Axial velocity from the three iterations of the calculations of flame speed of methanol (stoichiometric air/methanol, 1 bar, 300 K, Marinov mechanism)

The premixed laminar flame speed calculations were performed using the CHEMKIN 4.1 package [CHEMKIN] from Reaction Design for freely propagating flames. The Pre-Mixed Flame Speed calculator uses a fixed flame coordinate system. The length of the calculating zone has been chosen large enough so that the calculations are not affected by the boundaries. Three iterations are used to increase convergence and minimize running

time. The first one uses only 6 points, allowing the code to adapt the grid points as needed, starting with loose grid resolution criteria. In most cases three additional iterations (continuations) are used to adjust the relative curvature and the gradient controls. The first one has adaptive grid control based on solution curvature of 0.7 and on solution gradient of 0.5, while the second iteration has controls of curvature of 0.5 and of gradient of 0.2. The third iteration has a curvature and of gradient of 0.05 and 0.02 for the Li mechanism, but was limited to 0.1 and 0.04 respectively for the Marinov mechanism because of convergence issues. In general, the second iteration requires less than 100 points, while the third iteration requires between 200 and 500 points.

The flame velocity decreased by about 10% as a consequence of the increased number of point in the third iteration. Increasing the number of points further changed the results by only a couple of percentage points.

Typical results from the three iterations are shown in Figure 1. The figure shows the velocity of the gas across the calculation zone. The final computational grid is 12 cm wide.

These computations assume that the flame front be one-dimensional with no heat loss to the surroundings. Thermal diffusion was not included in the adiabatic freely propagating flame calculations. Mixture averaged transport was used, as multicomponent transport changed the results by about 1% but increased substantially the computation times. Also, the Correction Velocity Formalism was used. The AURORA program [CHEMKIN] has been used to determine the approximate composition in the combustion process (at some point), a required input to the laminar flame propagation code.
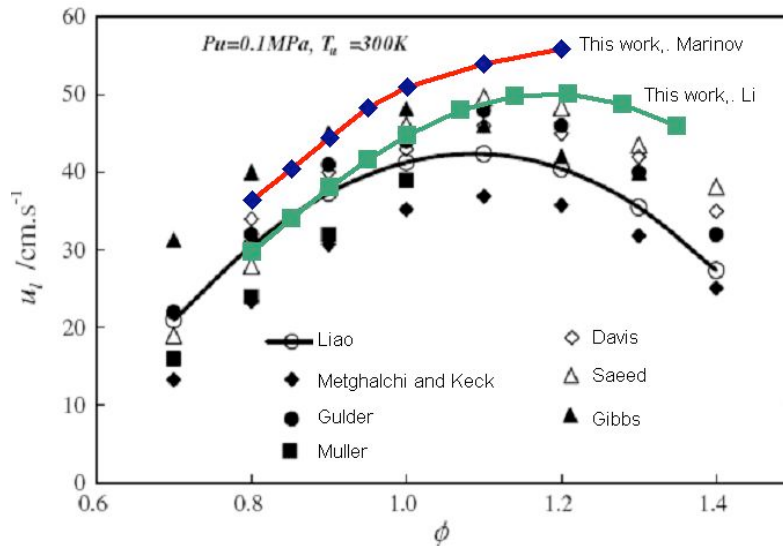

Figure 2. Calculated methanol flame speed as a function of equivalence ratio (1 bar, 300 K), as well as several experimental results (adapted from Liao).

IV. Methanol flame speed

The flame speeds of methanol has been measured by several groups, following the lead paper of Metghalchi and Keck [Metghalchi]. We have used and adapted the recent work by Liao [Liao] and Li [Li], which compares previous experimental result, superimposing our results on curves presented in these works.

Figure 2 shows the results of the flame speed as a function of the equivalence ratio, for an initial temperature of the air/fuel of 300 K. Both the results using the Marinov and the Li mechanisms are compared with published experimental data. In addition to the results by Liao and those of Metghalchi and Keck, the results from Davis [Davis], Saeed [Saeed], Gibbs [Gibbs], Muller [Muller] and Gulder [Guler] are also presented.

The code had convergence problems with the Marinov mechanism for $\phi < 0.8$ and $\phi > 1.2$ at 1 bar and 300 K, and with the third continuation. In Figure 2, only results for the second continuation for the Marinov mechanism are shown. The Li mechanism resulted in much faster convergence, and there were no regions of convergence difficulty through the parameter space used in this paper, including the third continuation. There is relatively good agreement for equivalence ratios lower than stoichiometry. However, as will be also shown later, the flame speed for equivalence ratios above stoichiometric conditions are overestimated.
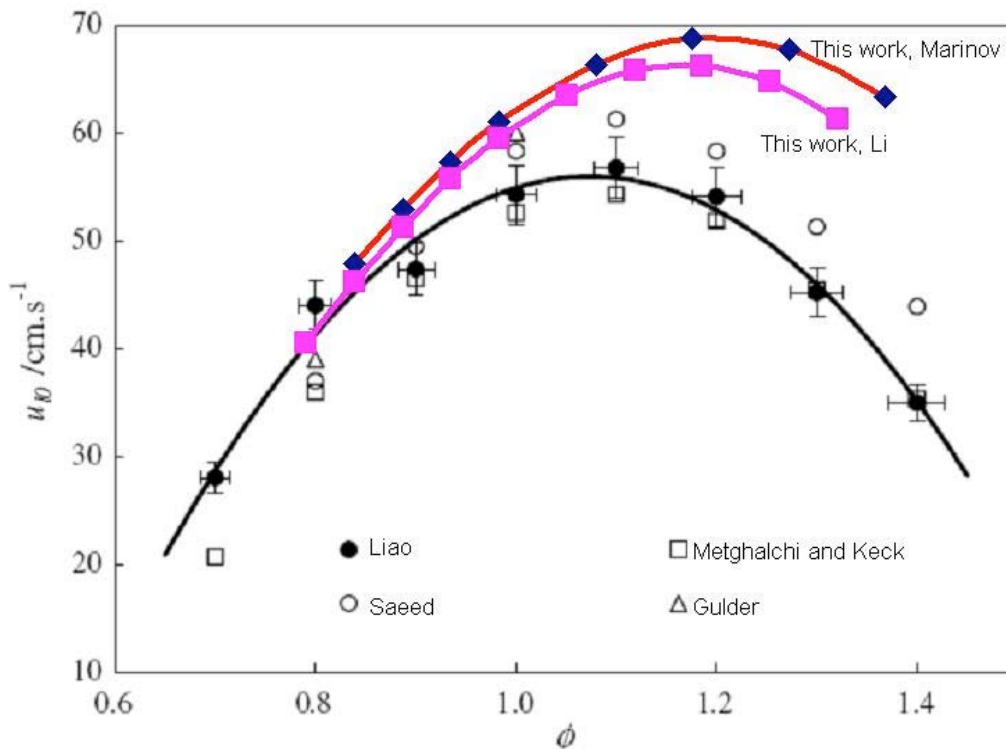

Figure 3. Same as Figure 2 but at 358 K, 1 bar (adapted from Liao).

Figure 3 shows similar results from Figure 2 but at higher temperatures, in this case 358 K. For the Marinov mechanism, in cases of higher temperature it was easier to achieve convergence of the flame speed calculation over a larger range of equivalence ratios, but still the solution curvature and gradients were limited to higher values, as indicated above. As partly indicated in Figure 2, the peak flame speed is substantially higher (10-20%) for $\phi > 1.1$, and the peak of the flame speed is also shifted to about $\phi \sim 1.2$, vs $\phi \sim$ 1.1 for the experimental results. Although Li is slightly closer to the experimental data at fuel rich operation, both models overestimate the flame speed
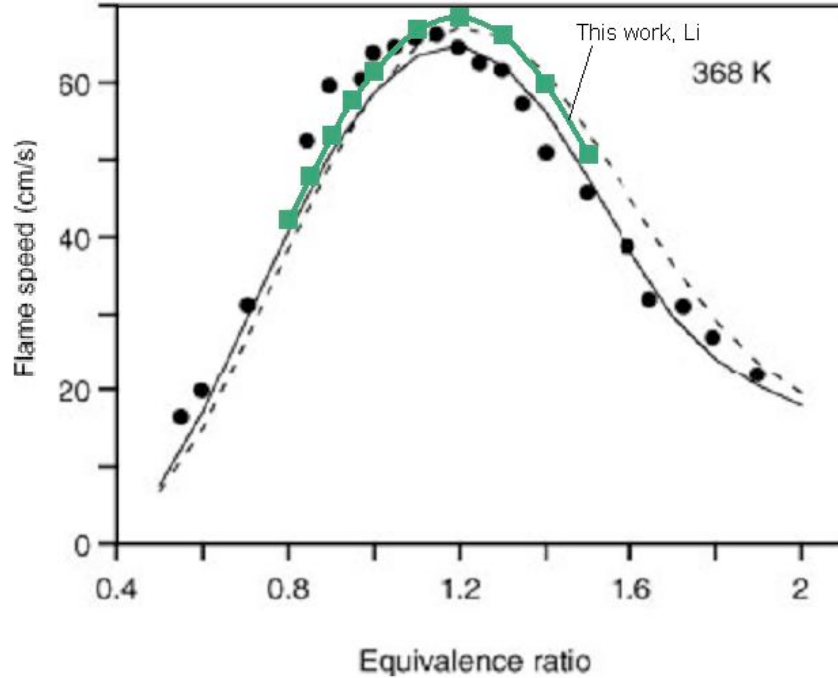

Figure 4. Similar results than Figure 4, but showing the experimental results from Egolfopoulos [Egolfopoulos]; adapted from Li [Li].

There is a substantial spread on the methanol flame speed measurements. Figure 4, adapted from Li [Li], shows a much better agreement between the measurements and the results of the Li mechanism, at 368 K, in contrast to the substantial discrepancy of the measurements and the calculations shown in Figure 3 (for both mechanisms). There is no much difference from multicomponent transport and mixture average transport (about 1%). The results of the third continuation (with about 400 points) are shown in Figure 4.

Figure 5 shows the same as Figures 2 - 4, but for still higher temperatures, in this case, 400 K. The difference between the calculated and experimentally determined laminar flame speeds show the same trends as those in Figures 2 - 4. The convergence problems of the Marinov mechanism limited, as indicated above, the resolution of the solutions. There is, however, very good agreement between the two mechanisms.
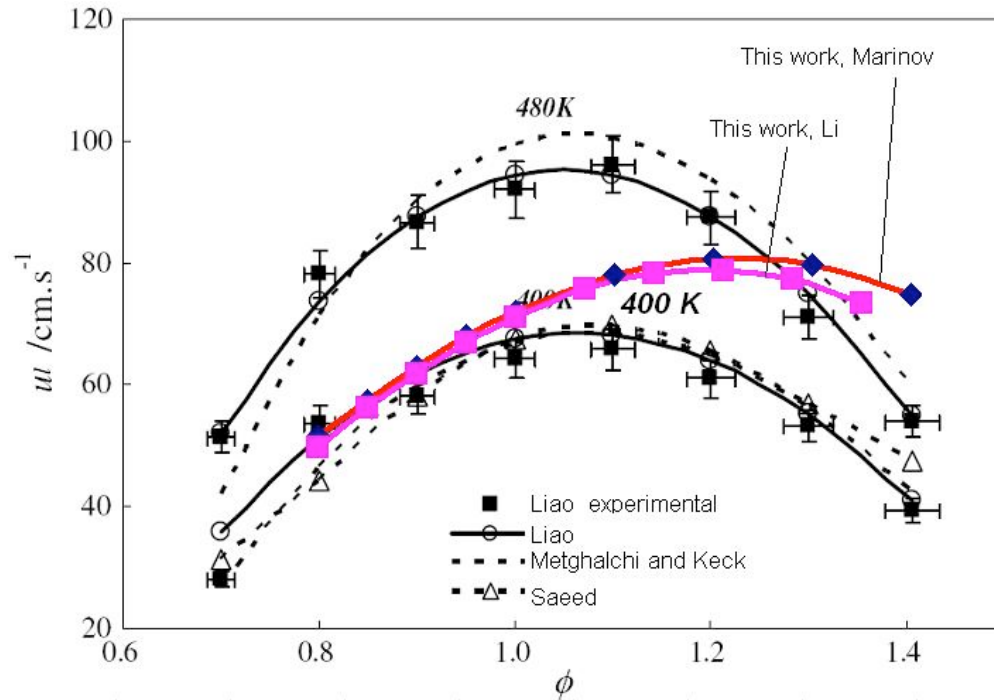
Figure 5. Laminar Flame speed of Methanol/air mixtures, 1 bar, 400 K (adapted from Liao) for both the Marinov and the Li mechanisms.
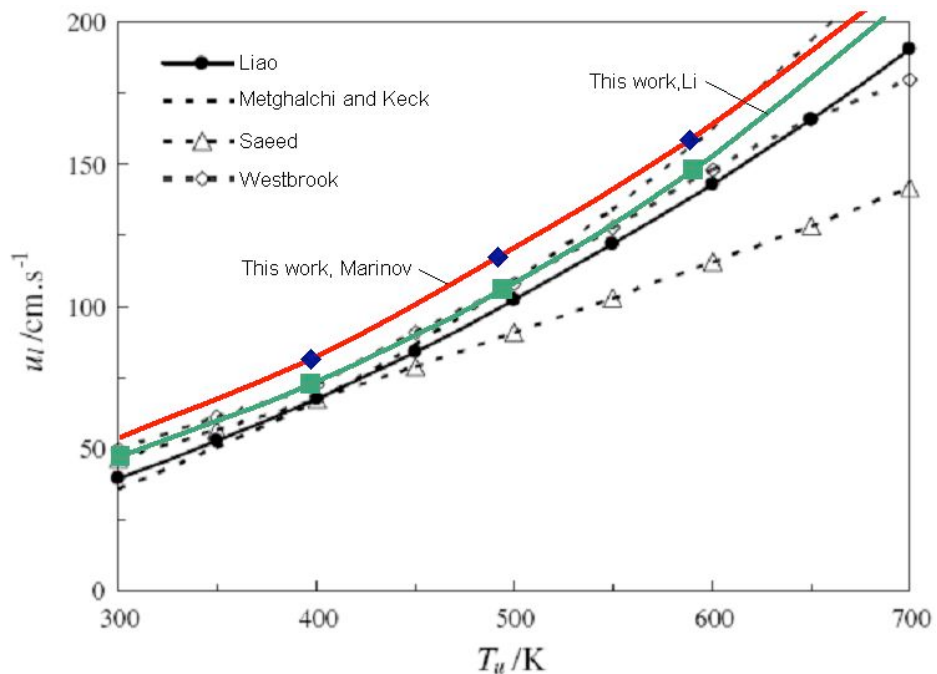

Figure 6. Calculated and experimentally determined laminar flame speeds using the Marinov mechanism as a function of temperature, 1 bar (adapted from Liao).

Figure 6 shows the laminar flame speeds at stoichiometric conditions for both mechanisms, as a function of temperature. Because of the convergence problem at the low temperature, the same low resolution was used for all the points presented in Figure 6 for the Marinov mechanism. The Li mechanism fits the data better than the Marinov one, although even the Marinov mechanism seems to reproduce the main trends in the experimental data.
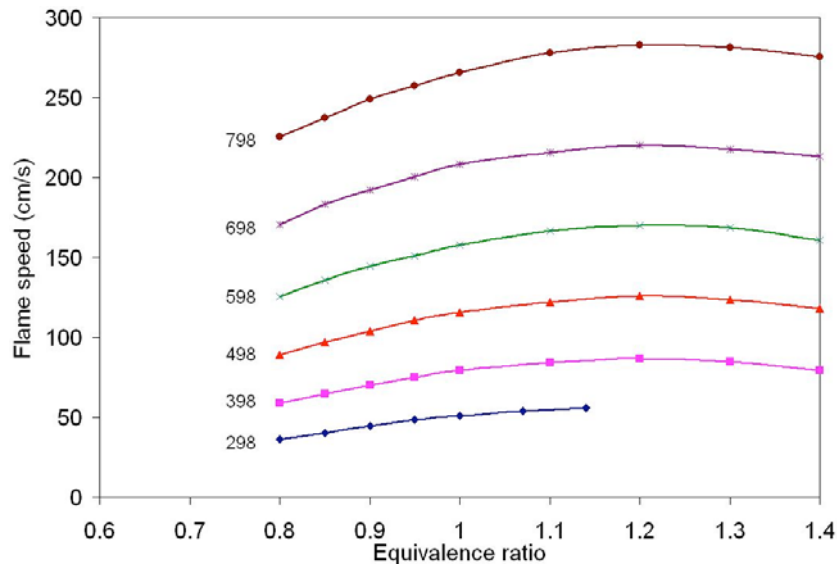

Figure 6. Laminar flame speed calculations of methanol/air mixtures vs equivalence ratio and for different initial temperatures.

Finally, Figure 6 extends the flame speeds as a function of temperature and stoichiometric, at 1 bar. The model will be used to determine the laminar flame speed at pressures and temperatures that are relevant to spark ignition conditions.

V. Ethanol flame speed comparison.

We used the same formalism above to examine the flame speed of ethanol, and compare it with those results shown by Marinov [Marinov].

Figure 7 shows the laminar flame speed of ethanol for 300 K, 1 bar conditions, and compares those with the calculations by Marinov and the experimental results by Egolfopoulos {Egolfopoulos1] and Gulder [Gulder], adapted from Marinov. There is better agreement in this case of fuel rich operation than in those for methanol, shown in the previous section.
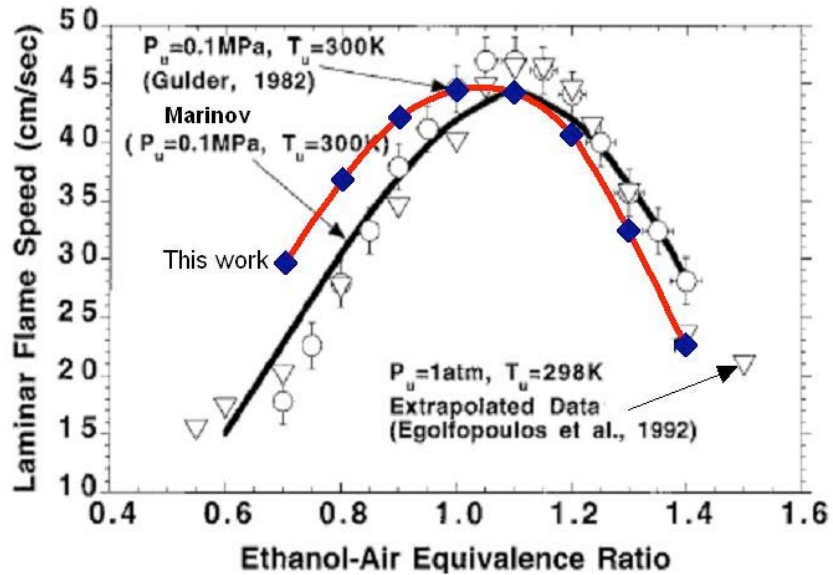
Figure 7. Laminar flame speed calculations and comparison with previous work (adapted from Marinov [Marinov])

VI. Conclusions

The Marinov and the Li mechanisms have been benchmarked for use with methanol flame speed calculations. The models are accurate for stoichiometric methanol/air mixture and lean stoichiometric methanol/air mixtures, but the model overestimates the flame speed by 10-20% for methanol rich mixtures. The Li mechanism has no convergence difficulties, and runs much faster than the Marinov mechanism.

The model can be used to determine effect of methanol addition to gasoline, even when operating overall stoichiometrically, as the methanol/air mixture in those circumstances would be lean.

Acknowledgements

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