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Temperature Dependence of the Laminar Burning Velocity of Methanol Flames

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ABSTRACT: To better understand and predict the combustion behavior of methanol in engines, sound knowledge of the effect of the pressure, unburned mixture temperature, and composition on the laminar burning velocity is required. Because many of the existing experimental data for this property are compromised by the effects of flame stretch and instabilities, this study was aimed at obtaining new, accurate data for the laminar burning velocity of methanol−air mixtures. Non-stretched flames were stabilized on a perforated plate burner at 1 atm. The heat flux method was used to determine burning velocities under conditions when the net heat loss from the flame to the burner is zero. Equivalence ratios and initial temperatures of the unburned mixture ranged from 0.7 to 1.5 and from 298 to 358 K, respectively. Uncertainties of the measurements were analyzed and assessed experimentally. The overall accuracy of the burning velocities was estimated to be better than ±1 cm/s. In lean conditions, the correspondence with recent literature data was very good, whereas for rich mixtures, the deviation was larger. The present study supports the higher burning velocities at rich conditions, as predicted by several chemical kinetic mechanisms. The effects of the unburned mixture temperature on the laminar burning velocity of methanol were analyzed using the correlation $u_L = u_{L0}(T_u/T_{u0})^{\alpha}$. Several published expressions for the variation of the power exponent α with the equivalence ratio were compared against the present experimental results and calculations using a detailed oxidation kinetic model. Whereas most existing expressions assume a linear decrease of α with an increasing equivalence ratio, the modeling results produce a minimum in α for slightly rich mixtures. Experimental determination of α was only possible for lean to stoichiometric mixtures and a single data point at $\phi = 1.5$. For these conditions, the measurement data agree with the modeling results.

■ INTRODUCTION

The use of light alcohols as spark-ignition engine fuels can help to increase energy security and offers the prospect of carbon-neutral transport. In comparison to other alternatives, such as hydrogen or battery-electric vehicles, liquid alcohols entail less issues regarding fueling and distribution infrastructure and are easily stored in a vehicle. In addition, the properties of these fuels enable considerable improvements in engine performance and efficiency, as several investigations on converted gasoline engines have demonstrated.[1]

In addition to bioethanol, methanol is interesting because it is versatile from a production point of view. Biofuels can only constitute part of our energy supply because of the limited area of arable land.[2,3] Methanol, on the other hand, can be produced from a wide variety of renewable (e.g., gasification of wood, agricultural byproduct, and municipal waste) and alternative fossil-fuel-based feedstocks (e.g., coal and natural gas). A sustainable closed-carbon cycle, where methanol is synthesized from renewable hydrogen and atmospheric CO_2 has been proposed.[4] For these reasons, there is renewed interest in methanol, particularly in China, which has chosen coal-based methanol as the strategic transportation fuel to ensure its energy independence.

A key parameter characterizing the combustion behavior of a combustible mixture is the laminar burning velocity (u_L). This physicochemical property is dependent upon the pressure, temperature, and mixture composition (fuel type, equivalence ratio, and amount of diluents). Whereas the laminar burning velocity at standard conditions provides invaluable information on the combustion properties and the underlying oxidation chemistry of the given fuel, most practical applications involve unburned mixture temperatures and pressures that are much higher. It is therefore important to quantify the effects of pressure and initial temperature on the adiabatic laminar burning velocity of renewable fuels. A convenient way to implement u_L data in turbulent combustion models is the use of a correlation that gives the laminar burning velocity in terms of pressure, unburned mixture temperature, and composition.

The most widely used correlation[5−7] is represented by eq 1

$$u_L = u_{L0}(T_u/T_{u0})^{\alpha}(p/p_0)^{\beta}(1 - Ff) \tag{1}$$

where T_u and p are the unburned mixture temperature and pressure, respectively. The subscript 0 refers to the values at reference conditions (usually 298 K and 1 bar). The amount of diluents is represented by f. The present work focuses on the temperature dependence of the laminar burning velocity of methanol flames. It has been shown that the power exponent α varies with the pressure and equivalence ratio.[8] However, these dependencies have often been neglected or averaged.

Table 1 summarizes published works on the methanol−air laminar burning velocity. The expressions for the power exponent α are also included. Early investigations by Wiser and Hill[9] and Gibbs and Calcote[10] employed measurement methods that have been shown to produce unreliable results.[8,11,12] Ryan and Lestz[13] were the first to report laminar

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Table 1. Experimental Data and Empirical Expressions for the Power Exponent α in Methanol−Air Flames at Fixed Pressure Close to 1 atm

T (K)	p (bar)	ϕ	technique	α	year	reference
298	0.85	0.7−1.4	horizontal tube		1955	9
298	1	0.8−1.4	Bunsen burner		1959	10
470−600	0.4−18	1	closed vessel, pressure-derived		1980	13
298−700	0.4−40	0.8−1.5	closed vessel, pressure-derived	$2.18-0.8(\phi-1)$	1982	5
298−800	1.0−8.0	0.7−1.4	closed vessel, flame ionization	1.75	1983	14
318−368	1	0.5−2	counterflow		1992	15
295−650	0.5−13.5	0.7−1.5	closed vessel, pressure-derived	$1.32-1.32(\phi-1)$	2004	12
385−480	1	0.7−1.4	closed vessel, Schlieren	$1.85-0.6(\phi-1)$	2006	7
373−473	1−7.5	0.7−1.8	closed vessel, Schlieren		2008	16
343	1	0.7−1.5	counterflow		2010	17
298−358	1	0.7−1.5	heat flux		2011	present work

burning velocities of methanol at elevated pressures and temperatures. The burning velocity was derived using the recorded pressure history during contained explosions inside a closed vessel in combination with a two-zone thermodynamic burning model. This model assumes negligible flame front thickness, which can lead to underprediction of the true burning velocities.[12] Metghalchi and Keck[5] used a similar method to measure burning velocities over a wide range of pressures (0.4−40 bar) and temperatures (298−700 K). These authors reported a linear decrease for the power exponent α in terms of ϕ (see Table 1).

Gülder performed an extensive study of the laminar burning velocity of iso-octane, methanol, ethanol, and their blends under engine-like conditions.[6,14] He measured the flame arrival time during contained explosions in a spherical vessel using flame ionization probes and derived the burning velocity from this. Gülder reported a constant value of 1.75 for the power exponent α of methanol− and ethanol−air flames, which was an average for equivalence ratios between 0.7 and 1.4.

None of the three above-mentioned closed vessel studies takes flame stretch and instabilities into consideration. Failing to perform stretch corrections for the spherical flames inside these closed vessels can lead to over- or underestimation of the true laminar burning velocity depending upon the sign of the Markstein number. Spherical flames are also sensitive to instabilities and can develop cellular structures. This is especially the case at elevated pressures, which can lead to overestimation of the true laminar burning velocities at these conditions. Because elevated pressures usually correspond to high temperatures during contained explosions, the power exponent α derived in these studies can be expected to be too high.

Egolfopoulos and co-workers were the first to take flame stretch effects into account for methanol−air flames. They used a counterflow twin-flame burner to measure the burning velocity of various hydrocarbons, including methanol and ethanol, at temperatures between 318 and 453 K for a wide range of equivalence ratios (0.5−2).[15,18] Because the typical strain rate in their flames was quite small (about 100 s^{-1}), they used a linear extrapolation to zero stretch. This linear extrapolation has recently been reported to lead to overestimations of the burning velocity by 5−10%.[17,19] Egolfopoulos et al.[15,18] extrapolated values down to room temperature from their experimental range of 318−368 K. This linear extrapolation to 298 K might result in an underestimation of the true burning velocity at that temperature.

More recently, Saeed and Stone[12] employed a multiple-zone thermodynamic burning model to find the relationship between the mass fraction burned and the recorded pressure rise during contained explosions. They performed no stretch correction but analyzed the data only after the flame radii were above 50 mm, claiming that the effect of stretch on the burning velocity is smaller than 1% at these conditions. They studied the burning velocity for pressures up to 13.5 bar but observed cellular flame structures at pressures beyond 6 bar and, consequently, removed these cellular flame points from their data set. As a result, the validation of their proposed u_L correlation is quite limited at elevated pressures and temperatures. This might explain why the reported power coefficient is considerably lower than in other works.

Liao et al.[7] and Zhang et al.[16] investigated the flame propagation properties of methanol and ethanol, using a closed vessel, in which the flame growth was captured by a high-speed camera and a Schlieren optical system. To correct for stretch, they use a linear relationship between flame speeds and flame stretch, following a method proposed by Markstein.

Veloo et al.[17] recently repeated the measurements by Egolfopoulos et al.[15,18] on methanol− and ethanol−air flames under a restricted set of conditions. They used the counterflow twin-flame burner in combination with a particle image velocimetry method. The unstretched laminar burning velocity was derived using a nonlinear extrapolation approach based on direct numerical simulations of the experiments. This led to an improved accuracy of the measured burning velocity compared to the linear extrapolation employed by Egolfopoulos et al.[15,18]

The different methodologies to deal with flame stretch and instability effects have led to significant scattering of the obtained results at similar conditions (see for example Figure 5).[8,12] Computationally, these effects can be avoided by assuming one-dimensional, planar adiabatic flames. Over the years, a number of detailed and reduced methanol oxidation reaction mechanisms have been developed and validated using experimental data on methanol oxidation in jet-stirred and flow reactors, ignition delays, flame structure, and laminar burning velocity.[15,20−28] The characteristics and accuracy of these mechanisms have been discussed elsewhere.[8,28] The derivation of the power exponent α based on calculation results using these mechanisms has not yet been not attempted for methanol. Therefore, the goal of the present work was 2-fold: first, to provide accurate experimental laminar burning velocity data at atmospheric pressure for methanol−air flames obtained using the heat flux method and, second, to analyze the temperature dependence of the laminar burning velocity of methanol−air flames, both experimentally and numerically.

EXPERIMENTAL DETAILS

The heat flux method for the stabilization of adiabatic premixed laminar flames on a flat flame burner has been proposed by de Goey et al.[29] and further developed by van Maaren and de Goey.[30] This method was extensively used for measuring laminar burning velocities of gaseous fuels[30,31] and has recently been applied for liquid ethanol.[19] A detailed description of the method and associated experimental uncertainties for gaseous fuels are given elsewhere.[32,33] Important features of the method common for gaseous and liquid fuels are, therefore, only shortly outlined in the following. The present experimental rig is similar to that used by Konnov et al.[19] and has been constructed and certified in previous work.[34]

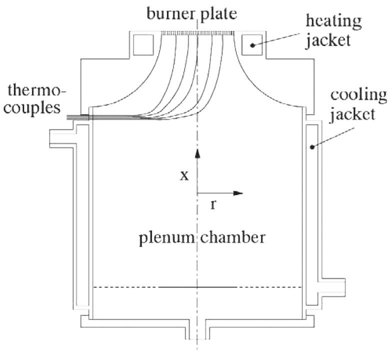

Figure 1. Perforated plate burner.

The experimental setup for the adiabatic flame stabilization using the heat flux method is shown in Figure 3. A 2 mm thick burner plate perforated with small holes (0.5 mm in diameter) is attached to the burner outlet (see Figure 1). The burner head has a heating jacket supplied with thermostatic water to keep the temperature of the burner plate constant. During the experiments, this temperature (T_1) was fixed at 368 K. The plenum chamber has a separate temperature control system supplied with water at a temperature (T_0), which enables a temperature range of the fresh gas mixture from 298 to 358 K. The heating jacket keeps the burner plate edges at a certain temperature higher than the initial gas temperature, thus warming the (unburned) the flow of gases. Conductive heat transfer of the flame to the burner plate cools the gas flow on its turn. When the flow rate of the gas mixture is changed, an appropriate value of the gas velocity can be found to nullify the net heat flux. In this case, the radial temperature distribution in the burner plate is uniform and equal to the temperature of the heating jacket.[34] A theoretical analysis of the heat flux method has been given by Bosschaart and de Goey,[33] where it was shown that the temperature profile of the burner plate can be approximated by a parabolic function

$$T_p(r) = T_c - \frac{q}{4\lambda_p h} r^2 = T_c + Cr^2 \tag{2}$$

where $T_p(r)$ is the mean temperature of the perforated plate (averaged over the burner thickness) at radial position r. T_c is the thickness-averaged temperature of the perforated plate at the center of the plate ($r = 0$). h is the thickness of the perforated plate ($h = 2$ mm). λ_p is the heat conductivity of the plate, and q is the net heat flux (the difference between the heat flux from the flame to the plate and the heat flux from the plate to the unburned mixture).

A series of thermocouples attached to the burner plate as shown in Figure 1 allow for measuring the temperature distribution at different radial positions. A polynomial fit is performed to find the heat flux constant C in eq 2. Figure 2 shows an example of the results for methanol–air flames at atmospheric pressure and an unburned mixture temperature (T_0) of 308 K. As seen from this figure, close to $C = 0$, the heat flux constant C can be well-approximated by a linear fit. This was the case for all flames considered in this study. The interpolated flow velocity at which the net heat flux was zero is shown to be the adiabatic flame burning velocity of the unburned gas mixture at temperature T_0.[29,30]

A mixing panel shown in Figure 3 was used to provide controlled flow of the vaporized fuel and air of the required equivalence ratio. The key part of this mixing panel is the CORI-FLOW liquid mass-flow controller (MFC) connected to the controlled evaporator mixer (CEM), both from Bronkhorst B.V. The liquid fuel flow from the fuel reservoir, pressurized by nitrogen, is metered by the CORI-FLOW MFC and fed to the CEM. Part of the air flow controlled by the gas MFC-1 is used as a carrier gas to facilitate vaporization at temperatures up to 423 K. Another part of the air flow controlled by the gas MFC-2 and mixed downstream is varied to provide the required mixture composition.

ERROR ASSESSMENT

Two major sources of experimental uncertainties for gaseous fuels pertinent to the heat flux method were identified as (1) irregular thermocouple placement in the burner plate and (2) inaccuracy in the mass-flow control.

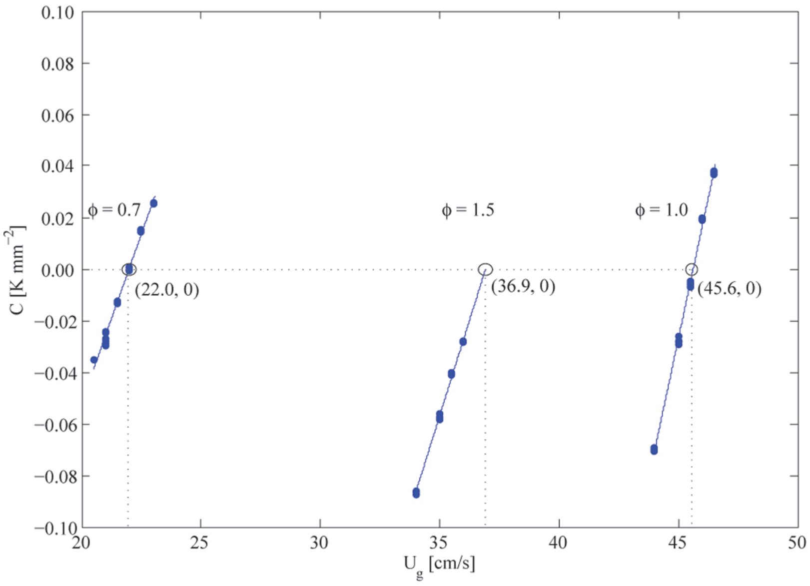

Figure 2. Heat flux constant [$C = -q/(4\lambda_p h)$] as a function of the unburned gas velocity U_g (T_0 = 308 K, and p = 1).

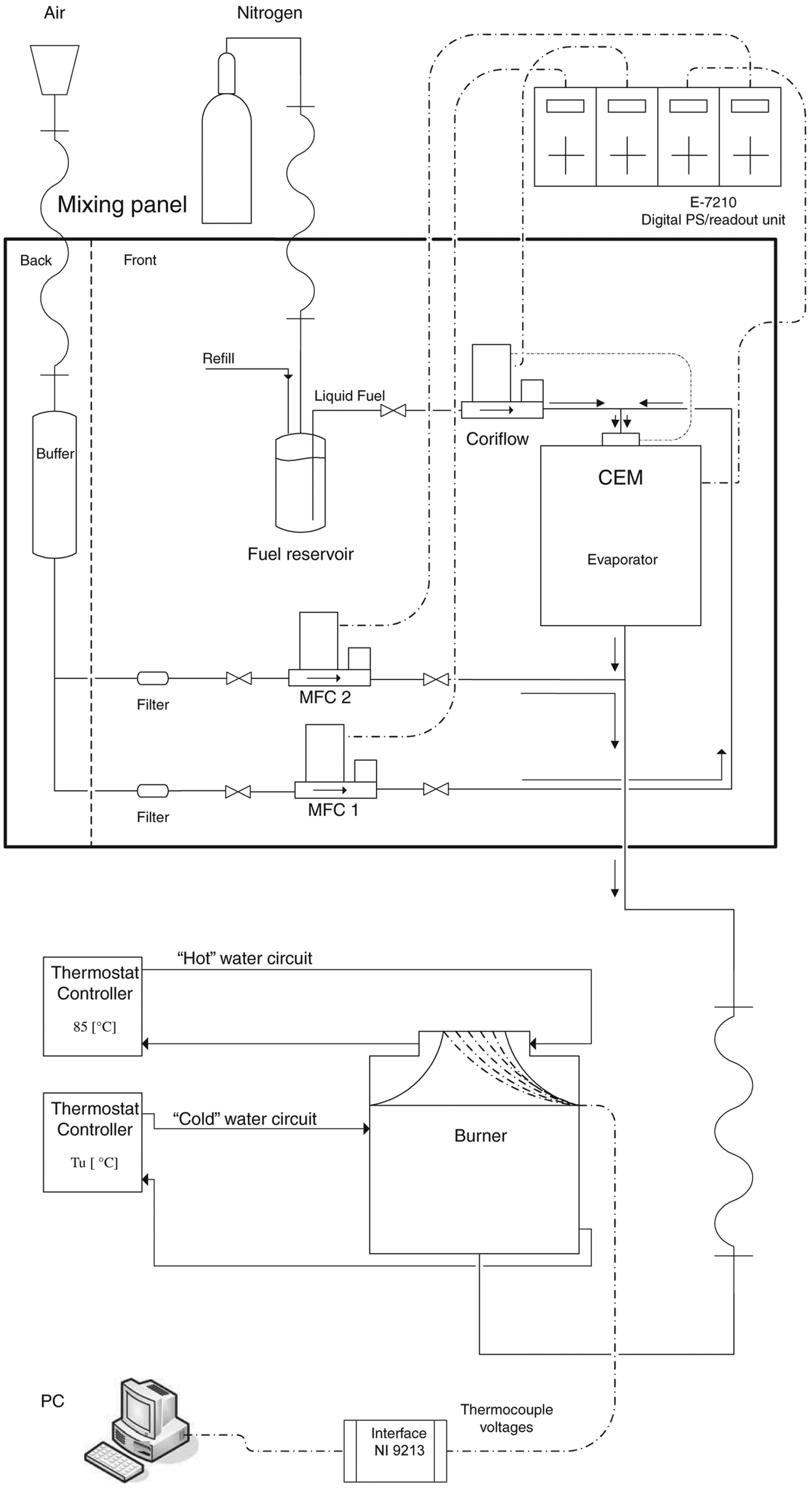

Figure 3. Schematic of the experimental heat flux setup for liquid fuels.

Detailed analyses of these uncertainties were performed earlier[32,33] and repeated for the present installation and showed that the overall accuracy of the burning velocity measurements is better than ±0.8 cm/s (double standard deviation with a 95% confidence level). The relative inaccuracy of the equivalence ratio was found to be below 1.5%.

Additional possible sources of experimental uncertainties associated with liquid fuels are the following: (1) variable flow ratio of the air between MFC-1 and MFC-2, (2) influence of the CEM operating temperature, (3) fuel purity, (4) dissolution of nitrogen in the liquid fuel, and (5) hygroscopic nature of the liquid fuel.

These five sources were assessed experimentally as described in ref 19, and relevant procedures were repeated for the present installation.[34] It was shown that the ratio of the flows via MFC-1 (carrier gas for the CEM) and MFC-2 (balance) does not affect the measured burning velocity within the expected accuracy of the measurements. No influence of the CEM operating temperature was observed when it was set well above boiling temperatures of methanol (423 K in the present work).

The purity of the methanol, delivered in sealed bottles, was better than 99.9% with less than 0.1% water. The purity could potentially deteriorate because of hygroscopy when refilling the fuel reservoir and dissolution of nitrogen, which pressurizes it. The refilling was short in time, and the amount of water that could be dissolved in the methanol during it was estimated to be less than 0.01%. The methanol was then kept in the reservoir sealed from the ambient air by pressurization using nitrogen (see Figure 3).

Certification of the present new installation took an extended period of time. Some series of experiments, for instance, for ethanol−air at 298 K, have been repeated many times.[34] The scattering of the laminar burning velocities at the same conditions never exceeded 1.8 cm/s. The maximum scattering was observed in the very lean and very rich mixtures, where set points of the MFCs approached the recommended low limit of 10% from the total scale. The overall accuracy of the measurements presented in this work can thus be conservatively evaluated as ±1 cm/s.

■ MODELING DETAILS

For the modeling of adiabatic premixed flames, the one-dimensional chemical kinetics code CHEM1D was used.[35] This code was developed at Eindhoven University of Technology and employs the EGLIB complex transport model,[36] including multi-component transport and thermal diffusion. In each case, the solution was calculated using the exponential differencing technique in a grid consisting of 200 points, with most of the detail centered at the inner flame layer. Radiation was neglected, and solver convergence was confirmed by ensuring that all residuals were below 10^{-10} and the laminar burning velocity had reached a stable value. A grid independence test was performed to eliminate the large tructation errors from inadequate grid resolution. It was found that the laminar burning velocity differed by less than 1% between 200 and 400 grid points.

Methanol−air flames were modeled using the detailed $CO/CH_2O/CH_3OH$ oxidation mechanism by Li et al.[27] This mechanism consists of 89 reactions among 22 species and is based on an earlier comprehensive mechanism by Held and Dryer[24] updated with the latest work on H_2/O_2 kinetics and recent thermochemical and kinetic information for the CO/O_2, CH_2O/O_2, and CH_3O/O_2 submechanisms. It is regarded as one of the most comprehensive and widely applicable methanol oxidation mechanisms available.[8,28] In the present work, the modeling was used to compare experimentally observed trends for the laminar burning velocity to those predicted by the calculations. No attempts were made to modify the mechanism to improve its performance and agreement with experiments.

■ RESULTS AND DISCUSSION

Laminar burning velocities of methanol−air flames measured using the heat flux method at different initial temperatures are summarized in Table 2. Note that the measurements are limited to equivalence ratios below 1.1 and equal to 1.5. Between ϕ = 1.1 and 1.5, the required fuel mass flow to attain the laminar burning velocity exceeded the upper limit of the fuel mass flow controller. The results at ϕ = 1.5 were obtained by linear extrapolation to $C = 0$ instead of interpolation (see Figure 2). The resulting additional uncertainty on u_l is estimated from the standard deviation of the slope of the linear fit. The linear extrapolation is expected to yield reasonable results because the maximum attainable flow velocity at ϕ = 1.5 is close to the laminar burning velocity. For ϕ = 1.1−1.4, this is not the case. In a wider range of variation of the flow rate, the dependence of C from it is not linear anymore; therefore, linear extrapolation is not accurate. Also, equivalence ratios below 0.7 and above 1.5 were not investigated, because these resulted in unstable or nonflat flames. All measurements have been repeated separated by a 2 month interval, and differences were below the assessed experimental uncertainty of 1 cm/s.

Table 2. Laminar Burning Velocities of Methanol−Air Flames at Different Initial Temperatures (cm/s)

ϕ	298 K	308 K	318 K	328 K	338 K	343 K	348 K	358 K
0.7	20.5	22.0	22.8	25.3	25.5	26.0	27.5	29.4
0.8	29.2	31.0	32.2	34.4	36.5	36.4	37.4	40.7
0.9	37.1	39.3	40.7	43.4	46.5	45.8	46.9	50.5
1.0	43.2	45.6	47.4	50.2	53.3	53.4	54.0	57.8
1.1	46.3	50.1						
1.5	34.6	36.9	38.9	41.2	42.9	44.3	44.5	45.8

Results at 298 K and Varying Equivalence Ratios. The experimental values obtained at 298 K are compared to relevant literature data in Figure 4. The differences between the results from Metghalchi and Keck[5] and ours are within experimental uncertainty for lean to stoichiometric flames. At rich conditions, they are lower. Saeed and Stone[21] attribute the low values of Metghalchi and Keck to the negligence of flame thickness in their burning model. Further underestimation of the burning velocity might be caused by flame stretch, which was not taken into account.

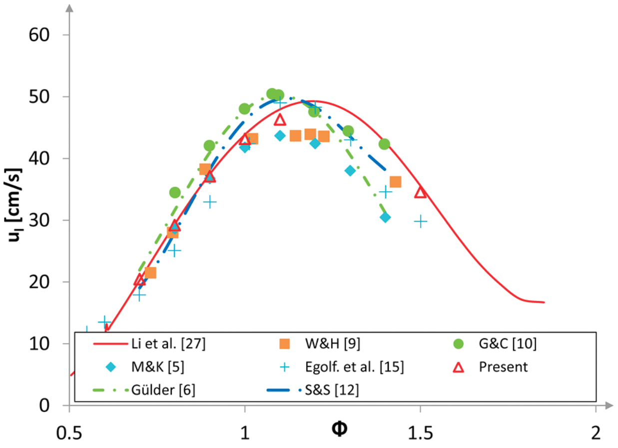

Figure 4. Laminar burning velocities of methanol−air flames at atmospheric pressure and initial temperature of 298 K.

Also included in Figure 4 are the laminar burning velocity correlations derived from different experimental investigations (dotted lines) and the modeling results using the methanol oxidation mechanism by Li et al.[27] (full line). The correlation by Gülder[6] generates quite low u_L values for equivalence ratios above 1.1. According to Saeed and Stone,[12] this is due to the use of an exponential form to fit the data for u_L in terms of ϕ, leading to a too steep decrease in the burning velocity for rich mixtures. The correlation by Saeed and Stone[12] agrees with the present data for $\phi \leq 0.9$. Closer to stoichiometry, the differences are somewhat larger.

The modeling results using the methanol oxidation mechanism by Li et al.[27] are in agreement with the present experimental results for $\phi \leq 1$, within the evaluated experimental uncertainty of ±1 cm/s. For rich mixtures, they are slightly higher. It is interesting to note that the mechanism by Li et al. places the maximum burning velocity at $\phi = 1.2$, whereas most experimental studies have it at $\phi = 1.1$. For reasons mentioned above, the present data set did not include measurements at $\phi = 1.2$.

None of the above experimental studies presents a clear uncertainty analysis of their results. Gülder[6] estimated the accuracy of his closed vessel measurements to be better than 2 cm/s. However, in a detailed analysis, Liao et al.[7] evaluated the uncertainty of the burning velocity measured in their constant volume bomb to be ±8%.

Results at 343 K and Varying Equivalence Ratios. A comparison of the present data at 343 K to results from the literature is shown in Figure 5. Relevant data have been obtained at 340 K by Egolfopoulos et al.[15] and are also included in the figure. These can be compared against the results by Veloo et al.,[17] which were measured at 343 K using the same counterflow twin-flame technique but with a nonlinear extrapolation approach to zero stretch. This results in laminar burning velocity values that are 5−10% lower for $\phi \leq 1.2$. Thanks to the meticulous effort to account for stretch and instability effects, the data set by Veloo et al.[17] can be regarded as one of the most reliable. The present results agree rather well with this data set for lean to stoichiometric mixtures. For the data point at $\phi = 1.5$, the values by Veloo et al. are significantly lower. The same can be seen when comparing the u_L data for ethanol−air mixtures obtained by Konnov et al.[19] using the heat flux method to the data by Veloo et al.[17] for ethanol−air: very good correspondence for lean mixtures and larger differences for increasingly rich mixtures, with the values by Konnov et al. being higher.[8]

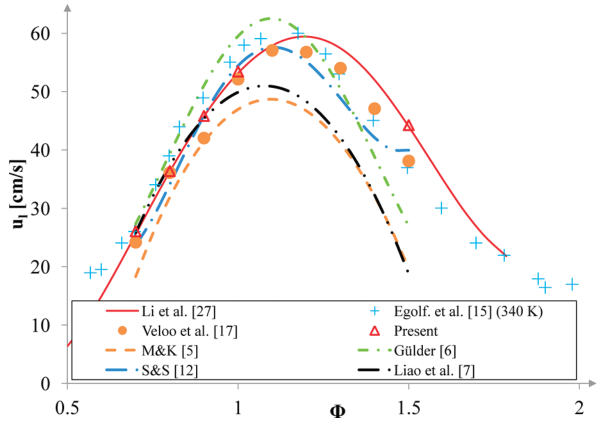

Figure 5. Laminar burning velocities of methanol−air flames at atmospheric pressure and initial temperature of 343 K (unless otherwise stated in the legend).

Liao et al.[7] fitted their results to a correlation, which is included in Figure 5. It can be seen that, for lean to stoichiometric mixtures, their results agree well with the data set by Veloo et al., whereas for rich mixtures, the differences are beyond the reported experimental uncertainties of 8%. The same differences between the counterflow twin-flame technique by Veloo et al. and the closed vessel method by Liao et al. can be seen when comparing their work on ethanol−air flames.[17,37] Because the bomb by Liao et al. is relatively small (<1.6 L), the systematic difference could be due to restrainement of the flame propagation, resulting from pressure build-up inside the vessel. This effect can be expected to be more important for rich flames because of the higher density ratio ρ_u/ρ_b.

The results from the correlations by Gülder[6] and Saeed and Stone[12] compared to the present data set are the same as discussed for Figure 4. The correlation by Metghalchi and Keck[5] underpredicts the burning velocity over the entire range of equivalence ratios. Because their correlation was fitted to measurements in an experimental range of 350−700 K and their power exponent α is too high compared to other values (as will be shown in Figure 7), an underestimation of u_L at this low temperature can be expected. Again, the calculations using the scheme by Li et al.[27] are in good agreement with the present results.

In summary, for lean to stoichiometric mixtures, the present data agree well with previously reported values in the literature. Whereas the spread on the reported burning velocities is limited at these conditions (≃10%), the differences are much larger at rich conditions. The present study supports the higher burning velocities at rich conditions, as measured by Veloo et al. and predicted by several reaction mechanisms. The modeling results using the Li et al.[27] mechanism correspond well to the present experimental data for the entire range of equivalence ratios.

Results at Varying Unburned Mixture Temperatures. Measured laminar burning velocities of methanol−air flames at atmospheric pressure and different initial temperatures are shown in Figure 6 using log−log scales. Apart from the experimental data represented by symbols, lines are included to show the best fits to eq 1 using the least-squares method. The slopes represent the power exponent α.

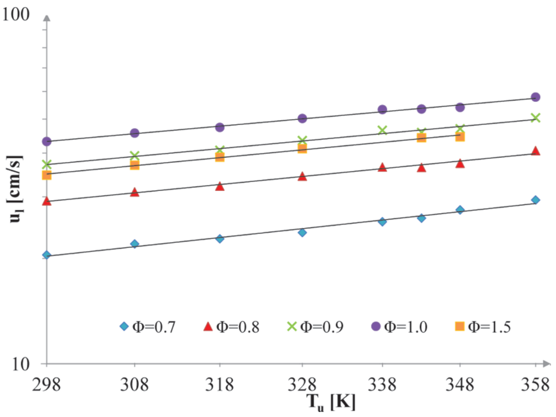

Figure 6. Log−log plot of selected laminar burning velocities of methanol−air flames at atmospheric pressure and different initial temperatures. Symbols, experiments; lines, best fits to eq 1 using the least-squares method.

In Figure 7, the derived α values are compared to the proposed empirical expressions for the power exponents as a function of the equivalence ratio (see Table 1). Error bars on the current values represent the uncertainty on the power exponent α stemming from the error on the individual u_L measurements at different temperatures. Because of the narrow range of temperatures (298−358 K), they are rather high.

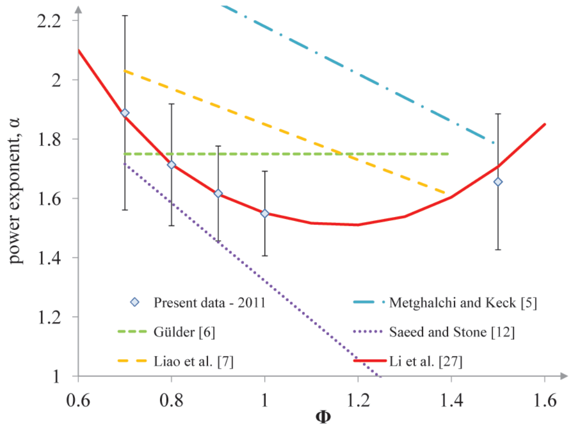

Figure 7. Power exponent α, in eq 1 for methanol−air flames. The full red line represents α values derived from modeling using the mechanism by Li et al.[27]

The laminar burning velocities calculated using the mechanism by Li et al.[27] were also processed to derive the power exponents α. At each equivalence ratio, the least-squares procedure was used for Figure 7 temperature points in the range of 298−358 K. No deviations from the power law dependence (eq 1) was found in the modeling.

The present experimental data for α agree well with the values resulting from modeling, especially in lean and stoichiometric conditions. Whereas most correlations predict a linear decrease of α as a function of ϕ, the mechanism by Li et al.[27] produces a minimum in the power exponent α for slightly rich mixtures. A similar minimum in the power exponent was reported for slightly rich ethanol−air flames and close to stoichiometric methane−air flames.[19,31] The present data for α at ϕ = 1.5 agrees with the modeling results. However, it is unclear from the experimental results if the power exponent α for methanol−air flames will keep increasing after the minimum or if the trend will level off with an increasing equivalence ratio (as reported for ethanol−air flames[19]) or even exhibit a local maximum (as reported for methane−air flames[31]). Further measurements of the laminar burning velocity of rich methanol−air flames are desirable.

In comparison to the present measurements, the correlation by Metghalchi and Keck[5] predicts α values that are too high, especially for lean to stoichiometric mixtures. This is probably due to the inclusion of cellular flames in their data set, which leads to overestimations of the true burning velocity at elevated temperatures. The correlation by Gülder[6] does not include the effect of the equivalence ratio on the power exponent. For lean to stoichiometric mixtures, the correlation by Liao et al.[7] is slightly higher and that by Saeed and Stone[12] is slightly lower than the present measurements. For rich mixtures, further measurements of the temperature variation of u_L are needed to confirm the local minimum, as predicted by the calculations.

Note that the experimental α values are only valid in the investigated temperature range (T_u = 298−358 K). However, now that the mechanism by Li et al.[27] has been shown to correctly predict the temperature effect, it can be used with confidence to cover engine-relevant conditions.

■ CONCLUSION

The heat flux method was used to obtain new, accurate measurements of the laminar burning velocity of methanol−air flames at unburned mixture temperatures of 298−353 K and atmospheric pressure. Uncertainties in the measurements were analyzed and assessed experimentally. The overall accuracy of the burning velocities was estimated to be better than ±1 cm/s in fast propagating flames. An attempted range of equivalence ratios was from 0.7 to 1.5; however, because of fuel mass flow controller limitations, some rich mixtures were not accessible for measurements. Further extension of the temperature range and assessment of moderately rich mixtures will require redesign of the present installation, which is the objective of the authors. In lean conditions, the present experimental results are in good agreement with the recent literature data obtained using various measurement methods. The correspondence with older data is worse because of the absence of stretch corrections in these investigations. At rich conditions, the spread between recent data sets is larger. The present study supports the higher burning velocities at these conditions, as measured by Veloo et al.[17] and predicted by several chemical kinetic mechanisms. The calculation results from the Li et al. mechanism[27] correspond well to the present experimental data for the entire range of equivalence ratios.

The effects of the unburned mixture temperature on the laminar burning velocity of methanol were analyzed using the correlation $u_L = u_{L0}(T_u/T_{u0})^{\alpha}$. Several published expressions for the variation of the power exponent α with equivalence ratio were compared against the present experimental results and calculations using the detailed kinetic model by Li et al. Whereas most existing expressions predict a linear decrease of α with an increasing equivalence ratio, the calculation results produce a minimum in α for slightly rich mixtures. The experimental α values for lean to stoichiometric mixtures and at ϕ = 1.5 agree with the modeling results. However, further measurements of rich methanol−air flames remain desirable to confirm the accuracy of the model in these conditions.

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Notes

The authors declare no competing financial interest.

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