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Numerical Study of Water Effects on the Laminar Burning Velocity of Methanol

Kun Liang

Department of Engineering and Design, University of Sussex, Brighton BN1 9QT, UK

Tel: +44 1273 678573. Email address: kun.liang@sussex.ac.uk

Abstract

Using light alcohols in spark-ignition engines can improve energy security, engine performance and pollutant emissions. Methanol has gained popularity due to its ease in production compared to ethanol. Methanol could absorb water easily. In the present work, the adiabatic laminar burning velocity of methanol containing water is investigated both experimentally and numerically. Numerical simulations using CHEMKIN-PRO were undertaken to predict the burning velocities of six mixtures with different water volume fractions (up to 0.6) from the latest San Diego chemical-kinetic mechanism. The burning velocities of three mixtures with different water volume fractions (up to 0.4) were measured using a constant volume vessel and a Schlieren imaging system for a wide range of temperature (380-450 K), pressure (100-400 kPa) and equivalence ratio (0.7-1.4). Results showed a decrease in burning velocity with pressure and an increase with temperature. Water as a diluent led to reduction of the burning velocity. The chemical-kinetic mechanism over predicts the burning velocity.

Keywords: Methanol, Laminar burning velocity, Water, Constant volume, Chemical kinetic mechanism, Schlieren imaging

1. Introduction

Using light alcohols in spark-ignition engines can improve energy security, engine performance and pollutant emissions. Sustainable liquid alcohols, such as ethanol and methanol, are largely compatible with the existing fuelling and distribution infrastructure and are easily stored in a vehicle [1]. Methanol can be produced from a wide range of renewable sources such as gasification of wood, agricultural by-products and urban waste, in addition to fossil fuels based feedstock (coal and natural gas). For the purposes of energy sustainability and low carbon, methanol has been widely used in spark ignition engines in some countries like China and Iceland, as a single component and blend with gasoline [2]. Due to the high octane rating, high latent heat and low combustion temperatures, the power and efficiency is significantly higher for methanol (and ethanol) compared to gasoline. This is certainly true for highly pressure-charged engines, where aggressive downsizing is possible on these alcohols [3].

Methanol is very hygroscopic and even purified methanol by distillation will absorb water vapour directly from the atmosphere. Water in methanol will further improve the anti-knock rating. However, it dilutes the calorific value of methanol, and may cause phase separation of methanol-gasoline blends. The water is expected to reduce the burning velocity, the flame

38 stability and the flammability range, all of which would be adverse to the performance of the
39 engine.

40 The laminar burning velocity is a fundamental property of fuel for spark ignition engines,
41 which can also be used to validate the chemical-kinetic mechanism and estimate the turbulent
42 burning velocity. The laminar burning velocity depends on the initial pressure, mixture
43 temperature and equivalence ratio of the unburned mixture.

44 Many researchers have conducted experimental studies of pure methanol using different
45 methods: (1) constant volume vessel approach has been used by Saeed and Stone [4],
46 Metghalchi and Keck [5], Gulder [6], Liao et al. [7, 8], Zhang et al. [9, 10], and Beeckmann
47 et al. [11]. Note that [4, 7, 8, 9, 10 and 11] used optical access to the combustion vessel; (2)
48 counter flow flame configuration was used by Davies and Law [12] and Egolfopoulos et al.
49 [13]; (3) Bunsen burner was used by Gibbs and Calcote [14]; (4) heat flux burner was
50 adopted by Sileghem et al. [15] and Vancoillie et al. [16]; (5) meso-scale diverging channel
51 was recently used by Katoch et al. [17]. Constant volume vessel was also used by [18 and
52 19].

53 Numerical studies of laminar burning velocity has also been widely conducted but not for
54 methanol/water mixtures up to date. CHEMKIN based simulations can be used to predict
55 laminar burning velocity from different reaction mechanisms. The most widely used
56 mechanisms for development of alcohol chemistry are Li et al. [20] and San Diego
57 mechanism [21]. Li et al. [20] presented an updated C1 mechanism for methanol (CH₃OH)
58 combustion, which appeared to over predict the burning velocity as shown by Katoch et al.
59 [17]. The San Diego mechanism [21] is being frequently updated by latest published
60 experimental data. The correlations of burning velocity from experiments using constant
61 volume vessel for methanol/water mixtures have been reported by Liang and Stone [22].
62 Though Katoch et al. [17] states that the San Diego mechanism tends to over predict the
63 burning velocity for rich mixture of methanol and air, it is still unknown that how burning
64 velocity varies for methanol when water (H₂O) is added as a diluent. Therefore, the
65 capability of this mechanism in modelling methanol/water combustion still needs further
66 validation. This paper presents numerical work on laminar burning velocity using
67 CHEMKIN-PRO [23] in comparison with results from Schlieren imaging analysis that has
68 not been reported in [22].

69 **2. Computational Simulation**

70 The numerical simulations of laminar premixed flames were conducted using steady-state,
71 one-dimensional freely propagating laminar flame model in CHEMKIN-PRO. As the
72 adiabatic flame speed was determined from the heat flux method, no radiative heat loss was
73 considered in simulations. The hybrid time-integration/Newton-iteration technique with
74 adaptive meshes and mixture-averaged transport parameters is applied to solve the steady-
75 state mass, species and energy conservation equations of the flames.

76 A one-dimensional flow with uniform inlet conditions were assumed. The governing
77 conservation equations for the freely propagating flame are as follow:

78 For continuity:
$$\dot{M} = \rho u A \quad (1)$$

79 where \dot{M} is the mass flow rate, ρ is the mass density, u is the velocity of the fluid mixture and
80 A is the cross-sectional area of the stream tube encompassing the flame normalised by the
81 burner area.

82 For energy:
$$\dot{M} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left(\lambda A \frac{dT}{dx} \right) + \frac{A}{c_p} \sum_{k=1}^K \dot{\omega}_k h_k W_k \quad (2)$$

83 where x is the spatial coordinate, T is the temperature, c_p is the constant-pressure heat
84 capacity of the mixture, λ is the thermal conductivity of the mixture, $\dot{\omega}_k$ is the molar rate of
85 production by chemical reaction of the k th species per unit volume, h_k is the specific
86 enthalpy of the k th species, and W_k is the molecular weight of the k th species.

87 For species:
$$\dot{M} \frac{dY_k}{dx} + \frac{d}{dx} (\rho A Y_k V_k) - A \dot{\omega}_k W_k = 0 \quad (3)$$

88 where Y_k is the mass fraction of the k th species and V_k is the diffusion velocity of the k th
89 species.

90 For equation of state:
$$\rho = \frac{P \bar{W}}{RT} \quad (4)$$

91 where \bar{W} is the mean molecular weight of the mixture and R is the universal gas constant.

92 The computation domain was set from -2 cm to 10 cm to ensure the boundaries sufficiently
93 far from the flame itself so that there was negligible diffusion of heat and mass through the
94 boundary. The relative gradient and curvature parameters for the grid refinement are set to be
95 0.1 to ensure that the number of grids were over 150 for each condition. This number proved
96 sufficient in rendering the simulation as grid-independent. The fixed-flame coordinate system
97 is established by explicitly constraining the gas temperature to stay at the initial fixed value at
98 one grid point in the computational domain.

99 For the pre-mixed laminar flame speed model in CHEMKIN-PRO, chemistry set components
100 required include thermochemical data, gas-phase chemistry (chemical reactions and rate
101 parameters) and transport data. For the present work, the latest San Diego mechanism
102 published on 2016-12-14 [21] was employed, which has 57 species and 247 elementary
103 reactions. The chemistry set of the mechanism was created in ‘Pre-Processing’. A total
104 number of 504 computational simulations were conducted in CHEMKIN-PRO. Table 1 listed
105 the test conditions for methanol/water mixture. In ‘C1-Inlet’ of the model, equivalence ratio
106 and fractions of each species can be defined along with mass flow rate. The burning velocity
107 by using CHEMKIN-PRO is thus named as ‘CHEMKIN-PRO’ for comparison with
108 ‘Schlieren’ results. The equivalence ratio is the ratio of the fuel-to-air ratio to the
109 stoichiometric fuel-to-air ratio. Equivalence ratio over 1 means rich mixture.

110

111

Table 1 Simulation conditions of burning velocity for methanol/water mixtures

Water volume fraction	Initial pressure (kPa)	Initial temperature (K)	Equivalence ratio
0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6	100, 200, 400	300, 380, 450	0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4

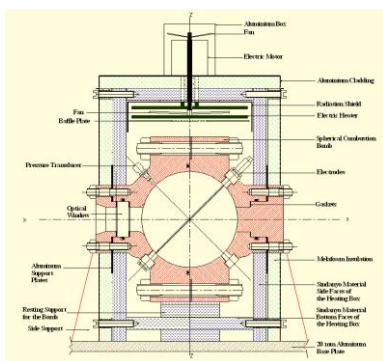
112

113 **3. Optical Measurement**

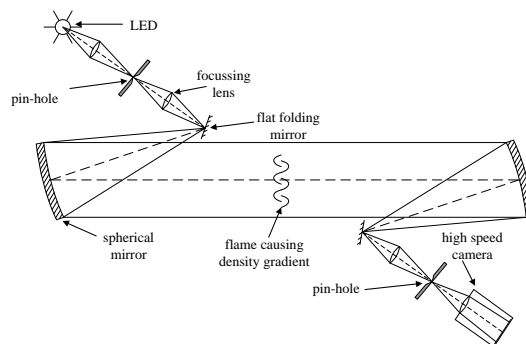
114 **3.1 Constant Volume Vessel and Schlieren Imaging System**

115 The constant volume vessel method is capable of exploiting the increase in pressure and the
 116 resulting increase in unburned gas temperature. Values of the burning velocity can be
 117 calculated for multiple temperatures and pressures from a single experiment as the pressure
 118 rise causes an isentropic temperature increase in the unburned gas. Therefore, the burning
 119 velocity can be determined from the pressure trace inside the combustion bomb (shown in Fig.
 120 1a) by assuming a smooth spherical flame front and an appropriate combustion mode. The
 121 details of the bomb have been reported by Liang and Stone [22].

122 A Schlieren imaging system was adopted for the purpose of imaging the flame front to
 123 determine flame speed in the initial stages of combustion and also for detection of cellularity
 124 in the later stages of combustion when the pressure rise is more significant. The Schlieren
 125 system for this work is a folded z-type arrangement shown in Fig. 1b. The system uses two
 126 oppositely tilted off-axis spherical mirrors to produce the collimated beam. Increasing
 127 pressure results in a change in density across the flame front and the flame front thickness,
 128 both of which affect the density gradient and hence the darkness of the detected Schlieren
 129 edge. The illumination source used is a 1 W green Prolight Power Star/O LED. The pressure
 130 vessel had a pair of windows with 40 mm diameter along the optical axis (see Fig. 1a) to
 131 allow the Schlieren imaging system. The Schlieren images were recorded using a Photron
 132 1024 PCI high speed camera with a 512*512 pixel resolution, allowing a frame rate of 3000
 133 frame per second (fps). The measured flame speed can be then used to determine the laminar
 134 burning velocity for validating the numerical simulation described in Section 2.



(a)



(b)

135

136

137 **Fig. 1** Schematic of the constant volume combustion bomb with optical window for Schlieren
 138 imaging system (a) [22] and arrangement of folded z-type Schlieren imaging system (b)

139 A total of 144 experiments were conducted over a wide range of initial temperatures (380 K
 140 and 450 K), pressures (100 kPa, 200 kPa and 400 kPa) and equivalence ratios (0.7 – 1.4) for 3
 141 methanol/water blends (W0, W20, and W40). W0 is pure methanol. W20 and W40 mean
 142 water volume fractions of 0.2 and 0.4, respectively.

143 The propagation speed of a spherical flame can be derived from the flame radius versus time
 144 as below:

$$145 \quad S_f = \frac{dr}{dt} \quad (5)$$

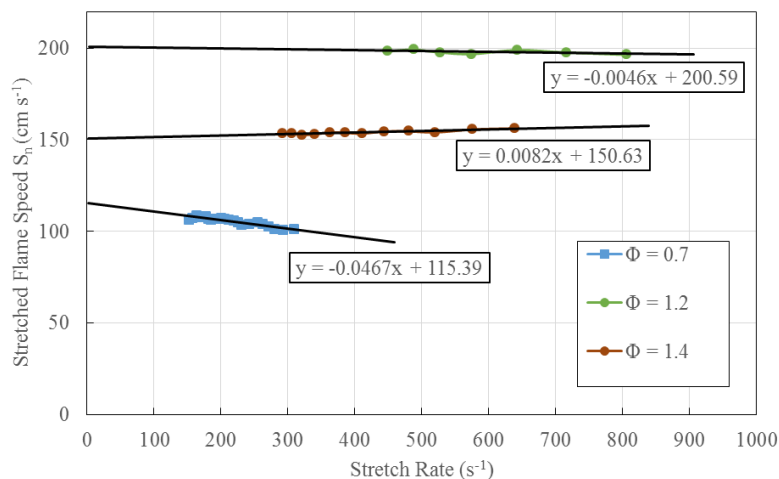
146 where r is the radius of the flame recorded by Schlieren imaging.

147 The flame stretch rate can be calculated as

$$148 \quad \alpha = \frac{1}{A} \frac{dA}{dt} = \frac{2dr}{r dt} \quad (6)$$

149 where A is the area of the flame surface.

150 Removing the stretched flame speed data affected by ignition energy and electrodes during
 151 the early stage of flame development gives a linear correlation line for the stretched flame
 152 speed and the flame stretch rate as shown in the Fig. 2. The unstretched flame speed S_s is
 153 found by extrapolating back to the case of zero stretch ($\alpha = 0$). It can be seen that the effect of
 154 the stretch rate on the burning velocity is not significant.



155

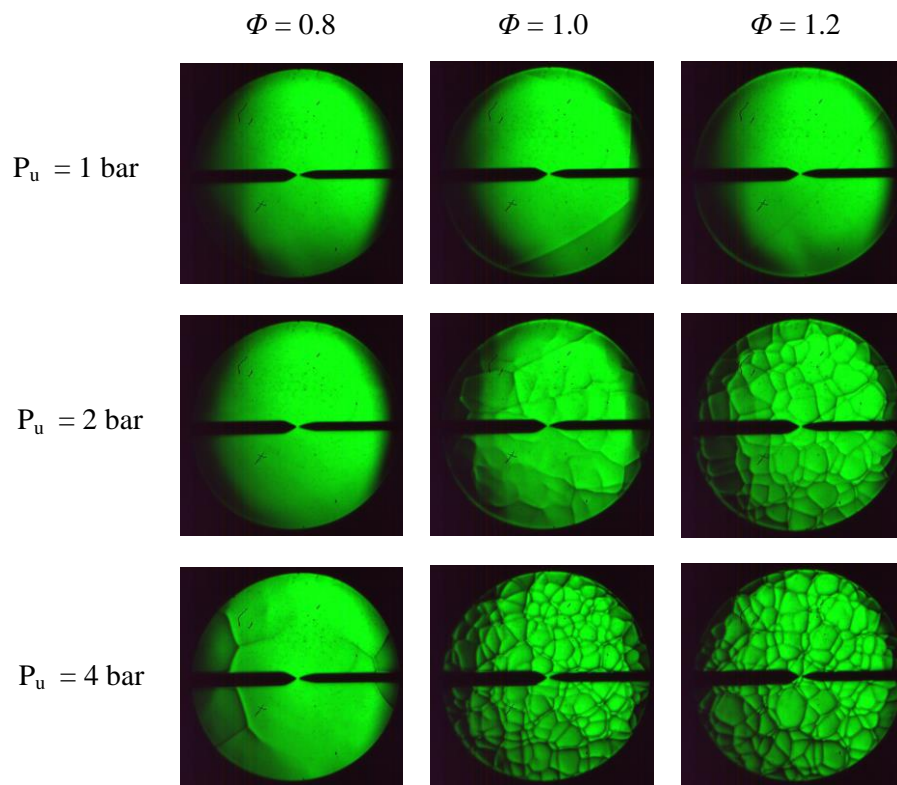
156 **Fig. 2** Extrapolations of unstretched flame speed (S_s) for W0 at $T_u = 380$ K and $P_u = 200$ kPa

157 The unstretched laminar burning velocity u_l can then be calculated according to

$$158 \quad u_l = \rho_b S_s / \rho_u \quad (7)$$

159 where ρ_b and ρ_u are densities for burned gas and unburned gas respectively. The laminar
 160 burning velocity calculated from Schlieren imaging data is named as ‘Schlieren’.

161 The Schlieren imaging data were also used for detecting the cellularity so that the data set for
 162 correlation can exclude the cellular data as has been described by Liang and Stone [22].
 163 Cellularity describes the phenomenon whereby a flame front develops an instability causing
 164 deviation from a smooth flame front to ‘cellular’ structure. These represent regions of
 165 intensified or weakened burning, caused by local inhomogeneity in the mixture composition
 166 within the flame front, meaning that the burning rate is no longer uniform over the flame
 167 front resulting in the uneven surface. Fig. 3 shows Schlieren images of the flame front of W0
 168 at 20 ms for different initial pressures (P_u) and equivalence ratios (Φ) when the initial
 169 temperature is 450 K. At the initial pressure of 100 kPa, a smooth flame front is observed at
 170 three equivalence ratios. When the initial pressure increases to 200 kPa, the cellular structure
 171 at the flame front begins to occur for stoichiometric and the rich mixtures. As the initial
 172 pressure increases to 400 kPa, a strong cellular flame front appears even for lean mixture. For
 173 a specific equivalence ratio, the cellular flame structure develops more easily with increased
 174 initial pressure.



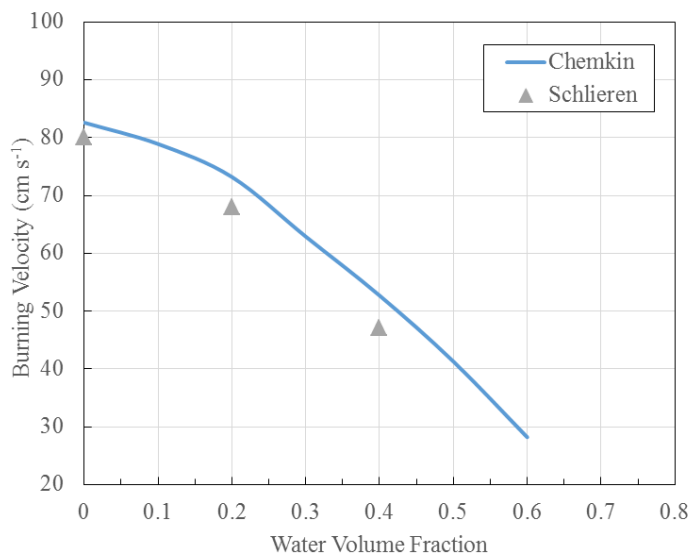
175
 176 **Fig. 3** Schlieren images of the flame front of W0 at 20 ms for different initial pressures (P_u)
 177 and equivalence ratios (Φ) at $T_u = 450$ K.

178 **4. Results and Discussions**

179 **4.1 Effect of Water**

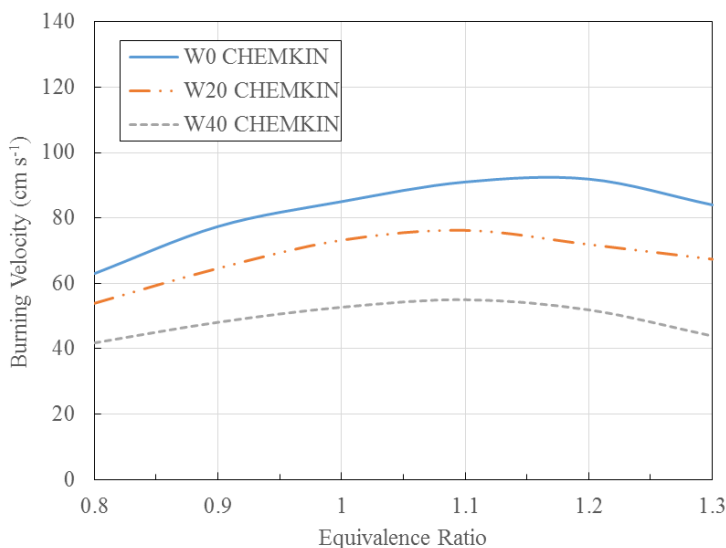
180 The laminar burning velocity of stoichiometric methanol and air mixture with different water
 181 fraction from 0 to 0.6 is shown in Fig. 4 using three methods described above for initial
 182 temperature of 450 K and initial pressure of 200 kPa. Water as a diluent clearly reduce the
 183 burning velocity of methanol linearly. Schlieren results show that the burning velocity

184 decreases from 80 cm s^{-1} to 46 cm s^{-1} when water fraction increase from 0 to 0.4. The
 185 CHEMKIN results using San Diego mechanism over predict the burning velocity by 5%.



186
 187 **Fig. 4** Laminar burning velocity variation of stoichiometric methanol/water and air mixtures
 188 against water fraction in volume using correlation, Schlieren and CHEMKIN methods at $T_u =$
 189 450 K and $P_u = 200 \text{ kPa}$

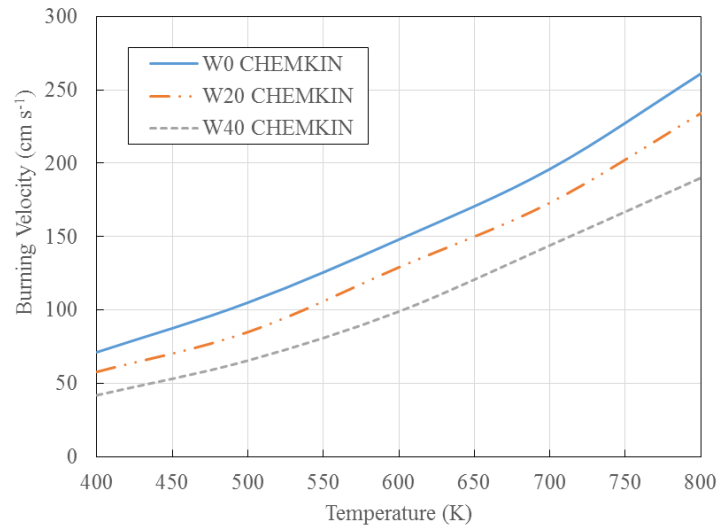
190 Fig. 5 shows CHEMKIN results for three methanol/water mixtures at different equivalence
 191 ratios. Increasing water fraction shifts the peak burning velocity towards stoichiometric
 192 probably due to the cooling effect of the increased water volume fraction lowering the
 193 adiabatic flame temperature leading to less dissociation and hence, a peak burning velocity
 194 occurring closer to stoichiometric.



195
 196 **Fig. 5** CHEMKIN results for the laminar burning velocity of methanol with different water
 197 fractions at $T_u = 450 \text{ K}$ and $P_u = 200 \text{ kPa}$

198 **4.2 Effect of Temperature**

199 Fig. 6 shows the CHEMKIN simulation for the laminar burning velocities at elevated
200 temperatures for stoichiometric methanol/water/air mixtures at $P_u = 200$ kPa. Increasing the
201 temperature of the mixture results in a faster burning velocity as expected. It can be seen that
202 temperature has hardly effect on the difference between methanol and hydrous methanol.
203 This may not be realistic because high temperature leads to increased dissociation, which
204 would affect the burning velocity.

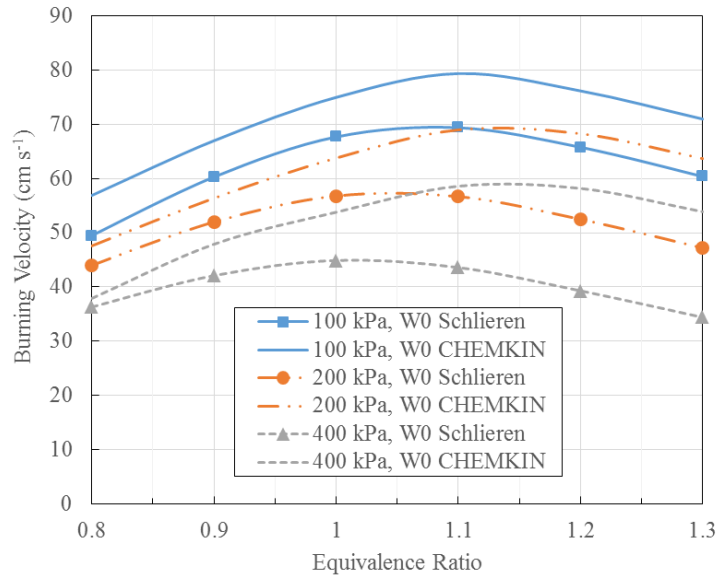


205

206 **Fig. 6** CHEMKIN results for the laminar burning velocity against temperature evaluated at
207 200 kPa for stoichiometric mixtures of methanol with different water fractions

208 4.3 Effect of Pressure

209 Fig. 7 shows the effect of pressure on the burning velocity of methanol with different water
210 fractions with initial temperature of 380 K. As expected, increasing the pressure results in a
211 lower laminar burning velocity. The peak burning velocity for W40 is lower than the
212 minimum for W0 as shown from both Schlieren and CHEMKIN simulation. This indicates
213 that adding 40% water (by volume) would make the methanol unsuitable for a spark ignition
214 engine. Schlieren imaging analysis results show that the peak burning velocity shifts towards
215 stoichiometric as pressure increases. This is because increased pressure would lead to less
216 dissociation. However, CHEMKIN simulation predicts an opposite trend. This further
217 indicates that the San Diego mechanism requires improvement.



218

219 **Fig. 7** Comparison between the Schlieren and CHEMKIN results for the laminar burning
 220 velocity of methanol with different water fractions at different pressures (P_u) and $T_u = 380$ K

221 5. Conclusions

222 The effect of water on the laminar burning velocity of methanol has been investigated by
 223 using a constant volume combustion bomb associated with a Schlieren imaging system and
 224 computational simulation using CHEMKIN-PRO based on the latest San Diego chemical
 225 kinetic mechanism. The data reported here has the expected trends:

- 226 (1) Increasing water fraction reduces the burning velocity of methanol. Methanol with
 227 water volume fraction of 0.4 (W40) appears to burn significantly more slowly.
 228 Correlation results in [22] show that adding more water will shift the equivalence
 229 ratio of the peak burning velocity away from stoichiometric due to more dissociation.
 230 However, CHEMKIN model using San Diego mechanism shows an opposite trend
 231 as shown in Fig. 5. San Diego mechanism over predict the burning velocity by 5% for
 232 stoichiometric mixture. This is within an acceptable range.
- 233 (2) Schlieren imaging data shows that the flame front of W0 becomes cellular very
 234 quickly after the ignition of a rich mixture. High initial pressure and rich mixture will
 235 lead to an early cellular flame for a constant initial temperature.
- 236 (3) Both Schlieren and CHEMKIN model show that higher pressures lead to a lower
 237 laminar burning velocity. Increasing the temperature increases the burning velocity.
 238 Schlieren result shows that the peak burning velocity appears to be close to
 239 equivalence ratio of 1.1 for pure methanol (W0), which agrees with most of the
 240 available results in the literature. However, CHEMKIN model shows a higher
 241 equivalence ratio at peak burning velocity.
- 242 (4) Though the San Diego mechanism can predict the burning velocity, it is strongly
 243 suggested that the mechanism should be updated, particularly for high temperature as
 244 well as the effect of pressure on the position of peak burning velocity.

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