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Article (Accepted Version)

Meng, Zhongwei, Liang, Kun and Fang, Jia (2019) Laminar burning velocities of iso-octane, toluene, 1-hexene, ethanol and their quaternary blends at elevated temperatures and pressures. *Fuel*, 237. pp. 630-636. ISSN 0016-2361

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Laminar Burning Velocities of Iso-octane, Toluene, 1-Hexene, Ethanol and Their Quaternary Blends at Elevated Temperatures and Pressures

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Abstract

Increasing environmental concerns caused interest in alternative fuels among which ethanol is regarded as possibly the best candidate to augment fossil fuels. Ethanol can easily be blended with hydrocarbons. Laminar burning velocity is a fundamental property of fuel for spark ignition engines. Adiabatic laminar burning velocities have been measured using the constant volume method along with the Schlieren optical system, for iso-octane, toluene, 1-hexene, ethanol and the quaternary blends with ethanol volume fractions of 0%, 20%, 50%, and 85% and equal fraction of other three components. Measurements were conducted for equivalence ratios from 0.7 to 1.4, temperatures of 298 K, 380 K and 450 K, and pressures of 1 bar, 2bar and 4 bar. Close agreements were found between the present results and literature data for pure components. Adding 20% ethanol doesn't increase the burning velocity of the blend by much, particularly for lean mixture. Higher volume fraction of ethanol (over 20%) leads to a higher laminar burning velocity of the blend and the burning velocity peaks at richer mixture. High temperature and high volume fraction of ethanol lead to earlier cellular flame of the quaternary blends.

Keywords: Laminar burning velocity, Iso-octane, Toluene, 1-Hexene, Ethanol, Quaternary Blends

Nomenclatures

A	area of flame surface
α	flame stretch rate
AFR	air-fuel ratio
DAQ	data acquisition
LHV	lower heating value
PRF	primary reference fuels
r	flame radius
RON	research octane number
S	flame speed
t	time
u	laminar burning velocity
ρ	density

1. Introduction

Ethanol is an attractive fuel for internal combustion engines to provide both security of supply and reduced net carbon oxide emissions. Ethanol can easily be blended with hydrocarbons and as a mixture of 85% of ethanol with gasoline (E85) is commercially available in Americas and Europe. Ethanol also has higher burning velocity, octane rating

and latent heat of vaporization compared to gasoline, which allow for the use of higher compression ratios, the possibility of more favourable spark timings, and thus increased engine efficiency [1]. Recently growing environmental concerns lead to increasing interest in sustainable fuels among which ethanol is regarded as promising candidate to augment or even replace traditional gasoline. With regard to gasoline fuel, it is currently not possible to represent the complex chemistry in a chemical kinetic model [2]. The term surrogate gasoline refers to a simple representation of a fully-blended fuel. The most common gasoline surrogates are iso-octane, binary blend of iso-octane and n-heptane, and the primary reference fuels (PRF's) for determining octane ratings for spark ignition engine fuels [3]. These surrogates from single to multi-components are intended for specific targets [4]. Toluene can be used as an octane booster in gasoline fuels. Pitz et al. [2] concluded that toluene should be included in surrogates because it is the most abundant aromatic in gasoline. Olefins are a family of hydrocarbons that are present in gasoline up to 20%. Olefins are hydrocarbon compounds with one or more carbon double bonds. Olefins can increase the reactivity of gasoline fuels in combustion processes. 1-hexene can be considered as representative of the unbranched olefins in gasoline [5].

One of the fundamental properties of the fuels for spark ignition engines is laminar burning velocity. The laminar flame speed is defined as the velocity at which the flame propagates into premixed unburned mixture ahead of the flame. The laminar burning velocity is a physicochemical property dependent on the temperature, pressure, and mixture composition (fuel type, equivalence ratio, and amount of diluents) [3]. The laminar burning velocity can be used to predict the turbulent burning velocity, to validate combustion kinetics model and to help with design of the combustion system. The laminar burning velocity can be measured by constant volume bomb [6-10], counter-flow flame [11 and 12], Bunsen burner [13], heat flux method [14 and 15], etc.

The laminar burning velocity for ethanol from measurements has been reported by [16-22]. Peak burning velocity can be found at slightly richer mixture for most of these studies. Several studies have been conducted to measure the laminar burning velocity of iso-octane including [3, 20, 22, 23, 24]. Laminar burning velocity for toluene has been measured at ambient pressure by [3, 22, 25, 26]. There is no laminar burning velocity data being reported so far for 1-hexene apart from Fan et al. [27] who measured the laminar flame speed of 1-hexene at elevated pressures with an initial temperature of 373 K by using a cylindrical combustion vessel. Several experimental studies have been conducted to determine the flame propagation characteristics of the gasoline surrogates and their blends with ethanol. Gülder [28] measured burning velocities of iso-octane-ethanol blends with up to 20% of ethanol by liquid volume over the range of equivalence ratios from 0.75 to 1.4, at initial temperatures from 350 to 600 K at ambient pressure. Broustail et al. [29] determined burning velocities of iso-octane-ethanol blends containing 25, 50 and 75 vol.% of ethanol over the range of equivalence ratios from 0.8 to 1.4, at initial temperature of 393 K at ambient pressure. Van Lipzig et al. [20] used a perforated plate burner for measurements of the adiabatic laminar burning velocities of n-heptane, iso-octane, ethanol and blends of their binary and tertiary mixtures. The adiabatic laminar burning velocities of a commercial gasoline and of a model fuel (n-heptane, isooctane, and toluene mixture) of close research octane number (RON) have been measured at 358 K by [22]. The influence of ethanol as an oxygenated additive has been investigated for these two fuels and has been found to be negligible for values up to 15% (vol). Sileghem et al. [3] measured the laminar burning velocities of iso-octane, n-heptane, toluene, a toluene reference fuel (mixture of iso-octane, n-heptane and toluene) and a commercial gasoline for an equivalence ratio from 0.7 to 1.3 and for a range of temperatures

between 298 K and 358 K at ambient pressure. However, there is still scarcity for laminar burning velocity at elevated pressure for binary, ternary and quaternary blends.

The objective of this work is to use the constant volume method and Schlieren image system to measure the laminar burning velocity of pure components including iso-octane, toluene, 1-hexene, ethanol and their quaternary blends with at elevated mixture temperatures and pressures. Ethanol with volume fraction of 0 (E0), 20% (E20), 50% (E50), 85% (E85) has been added to study the effect on the laminar burning velocity and the structure of the flame front.

2. Measurements

2.1 Constant Volume Bomb

A spherical stainless steel combustion vessel with 350 mm inner diameter (22.4 Litre) was constructed for the laminar burning velocity measurements. Fig. 1 shows the schematic diagram of the combustion bomb which has two orthogonal pairs of quartz windows with 100 mm in diameter. The bomb is capable of withstanding the pressures up to 7 bar. The vessel can accommodate both liquid and gaseous fuels. An electric heater (1 kW) located inside on the flange was used to heat the vessel and mixtures up to 600 K. The initial temperature of the fuel-air mixture was monitored during a mixture preparation by a thermocouple. Reactants were prepared in the combustion vessel using the partial pressure method, assuming an ideal gas. The amount of injected liquid fuel was calculated from the partial pressure and fuel density. The compressed intake air was controlled by a mass flow controller and heated before going into an injection block, which was also heated to ensure evaporation of the liquid fuel. A liquid fuel was injected with calibrated gas-tight micro-syringes using a needle valve. A Kistler 710A piezo-electric pressure transducer monitored the partial pressure of reactants during mixture preparation as well as initial pressure before ignition. Two piezo-resistive pressure transducers with different ranges were also used for measuring pressures during evacuation and mixture preparation. A lambda sensor was located in the exhaust system to monitor the air-fuel ratio (AFR) of the burned products. A data acquisition card USB 6251 from National Instruments was used to log the data. A LabVIEW programme was prepared to display the partial pressure and temperature during mixture preparation and record the pressure and temperature data after ignition. The sampling rate during combustion was 100 kHz. Spherical flame images were captured by adopting a Schlieren photography system. A high speed camera (Photron; FastCam Ultima APX 120K with 10-bit resolution) was used for image acquisition at 10k fps and 512*512 pixels.

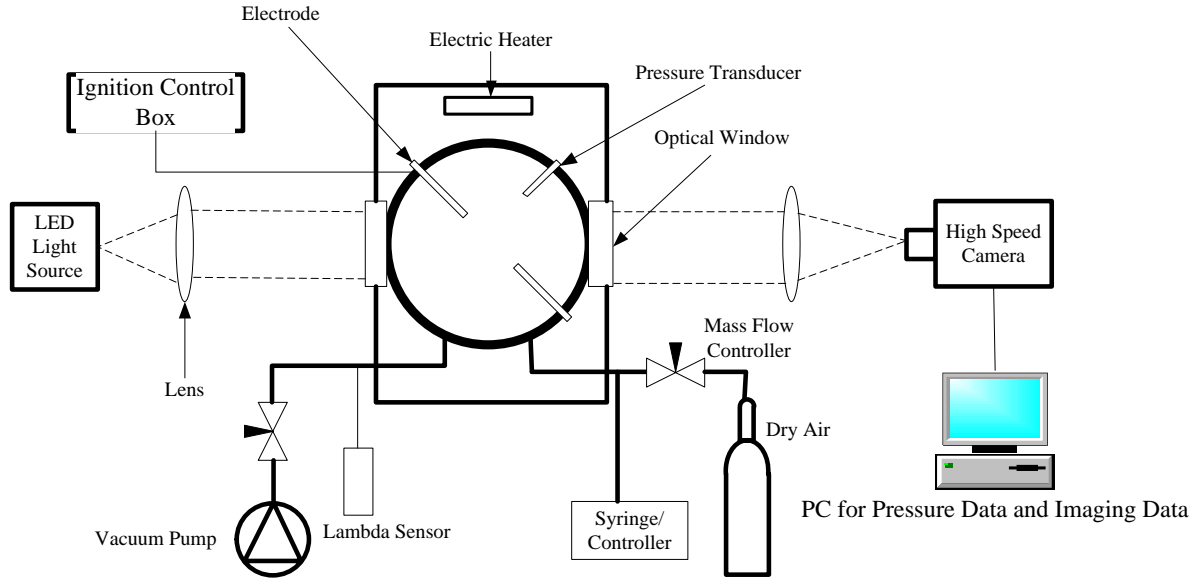


Fig. 1 Schematic of the experimental apparatus for laminar burning velocity measurements

Table 1 shows the test conditions for the four pure components and four quaternary blends. Initial pressures are 1 bar, 2 bar and 4 bar before ignition. Initial temperatures of the mixture are 300 K, 380 K and 450 K. Equivalence ratio ranges from 0.7 to 1.4.

Table 1 Test conditions of the pure components and quaternary blends

DAQ Sampling Rate (Hz)	100 K
Schlieren Imaging Speed (fps)	10 K
Fuel (pure components)	iso-octane, toluene, 1-hexene, ethanol
Fuel (quaternary blends)	E0, E20, E50, E85
Initial Pressure (bar)	1, 2, 4
Initial Temperature (K)	300, 380, 450
Equivalence Ratio	0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4

2.2 Data Analysis

The propagation speed of a spherical flame can be calculated by the flame radius versus time according to:

$$S_f = \frac{dr}{dt} \quad (1)$$

where r is the radius of the flame recorded.

The flame stretch rate can be calculated as

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

where A is the area of the flame surface.

The unstretched flame speed S_s can be found by linearly extrapolating zero stretch ($\alpha = 0$) due to linear correlation lines for the stretched flame speed against the flame stretch rate during the early stage of flame development

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

$$u_l = \rho_b S_s / \rho_u \quad (3)$$

where ρ_b and ρ_u are densities for burned gas and unburned gas respectively.

The images from Schlieren system were also used for detecting the onset of cellularity, after which the flame speed data was excluded.

2.3 Fuel Compositions

The properties of the four pure components for measurements are shown in Table 2. Toluene can boost the octane number of the fuel but the boiling temperature is highest. Ethanol has the highest latent heat of evaporation allowing for charge cooling effect but the lower heating value (calorific value) is the lowest. 1-hexene will increase the chemical reaction rate but reduce the RON.

Table 2 Properties of the pure components for measurements

	Formula	LHV (MJ/kg)	Density (kg/m ³)	RON	Boiling Point (K)	Latent Heat (kJ/kg)
Iso-octane	C ₈ H ₁₈	44.43	692	100	372	298
Toluene	C ₇ H ₈	40.59	867	120	384	330
1-Hexene	C ₆ H ₁₂	44.43	673	77	336	351
Ethanol	C ₂ H ₆ O	26.7	789	107	352	846

The quaternary blends consisting of the four pure components are listed in Table 3. The basic blend without ethanol consists of equal volume fraction of iso-octane, toluene, and 1-hexene. Mole fraction of the four blends as well as lower heating value (LHV), molecular weight, stoichiometric AFR and density are also shown in Table 3.

Table 3 Compositions and properties of the quaternary blends for measurements

	E0	E20	E50	E85
Volume fraction iso-octane	0.33	0.27	0.17	0.05
Volume fraction toluene	0.33	0.27	0.17	0.05
Volume fraction 1-hexene	0.33	0.27	0.17	0.05
Volume fraction ethanol	0	0.20	0.50	0.85
Mole fraction iso-octane	0.26	0.17	0.08	0.02
Mole fraction toluene	0.40	0.26	0.13	0.03
Mole fraction 1-hexene	0.34	0.22	0.10	0.03
Mole fraction ethanol	0	0.35	0.69	0.92
Formula	C _{6.9} H _{11.9} O ₀	C _{5.2} H _{9.8} O _{0.4}	C _{3.5} H _{7.9} O _{0.7}	C _{2.4} H _{6.4} O _{0.9}

Molecular Weight (g/mol)	95.1	77.8	61.4	49.7
LHV (MJ/kg)	43	40	35	29
Density (kg/m ³)	744	753	767	782
Stoichiometric AFR	14.3	13.2	11.5	9.7

3. Results for Pure Components

When possible the experimental laminar burning velocities from the present work are compared with the literature data. The results and comparisons for the four pure components are shown in Figs. 2–5.

Fig. 2 shows the burning velocity of iso-octane at 300 K and 1 bar in comparison with literature data [3, 20, 22, 24, 25]. Generally the results from present work are close to literature data. Van Lipzig et al. [20] over predicts the burning velocity using heat flux method. Kelly et al. [24] under predicts the burning velocity particularly for richer mixture using counterflow burner.

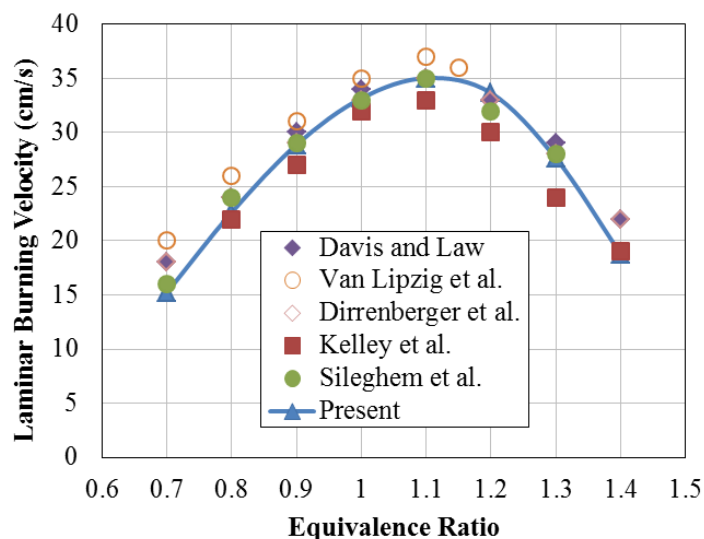


Fig. 2 Laminar burning velocities of iso-octane at 1 bar and 300 K

Fig. 3 shows the burning velocity results for toluene at 300 K and 1 bar. It can be seen that the burning velocity peaks at an equivalence ratio of 1.1. Generally the present results are in good agreement with the literature data, particularly Sileghem et al. [3] using heat flux burner and Davis et al. [25] using counterflow twin-flame technique. Hirasawa et al. [26] using similar approach to [25] presented much slower data than most of studies particularly for lean mixtures. The maximum percentage difference of peak burning velocity is only 8%.

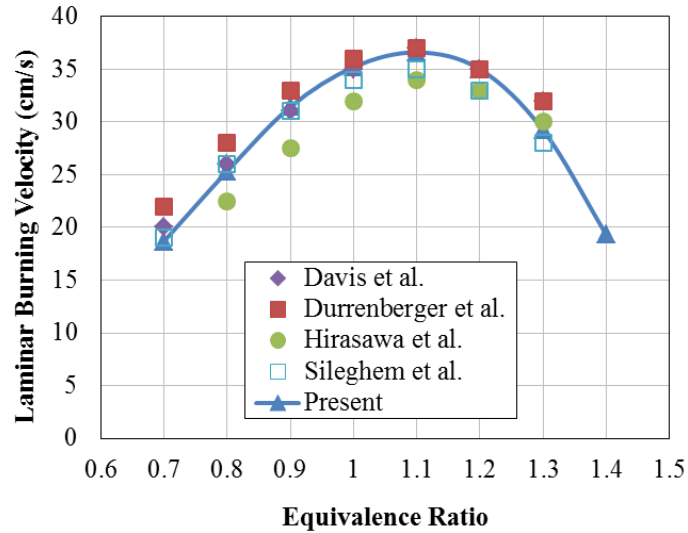


Fig. 3 Laminar burning velocities of toluene at 1 bar and 300 K

Fig. 4 shows the burning velocity results for 1-hexene at 1 bar, which has hardly been investigated before. The only available data from literature is Fan et al. [27] who adopted similar approach to measure the laminar flame speed of 1-hexene at 373 K at elevated pressures. The data at 373 K from present work for 1-hexene (300 K, 380 K and 450 K) has been interpolated for comparison with [27] considering the burning velocity as an exponential function of temperature. The average error percentage between the present work and [27] is 7%. The peak burning velocity of 1-hexene at 300 K and 1 bar is 46 cm/s.

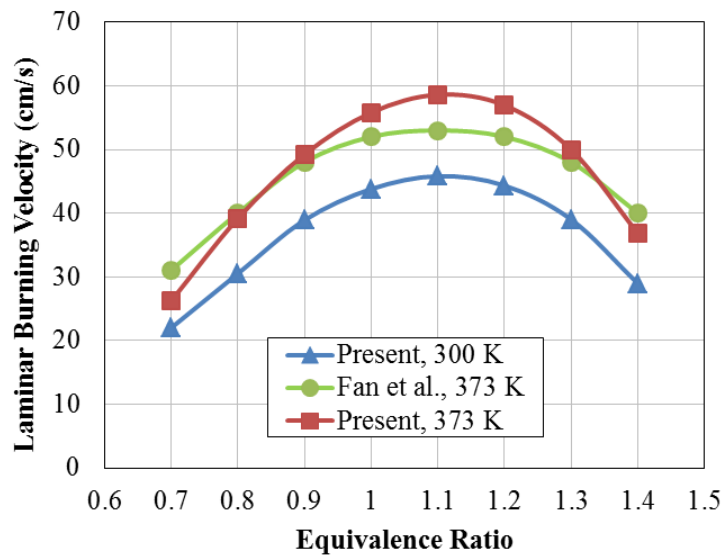


Fig. 4 Laminar burning velocities of 1-hexene at 1 bar

With regard to ethanol, which has been investigated by several studies [16, 17, 18, 19, 20, 21, 22], the burning velocity results are shown in Fig. 5 at 300 K and 1 bar. The present experimental results at 300 K are in very good agreement with literature data. A close agreement is observed with the measurements of Gulder [16], Liao et al. [18] and Bradley et al. [19] who also used constant volume bomb method and Schlieren imaging system. Gulder [16] over predicts the burning velocity due to no cellular flame being studied. The peak burning velocity from the present work is 45 cm/s.

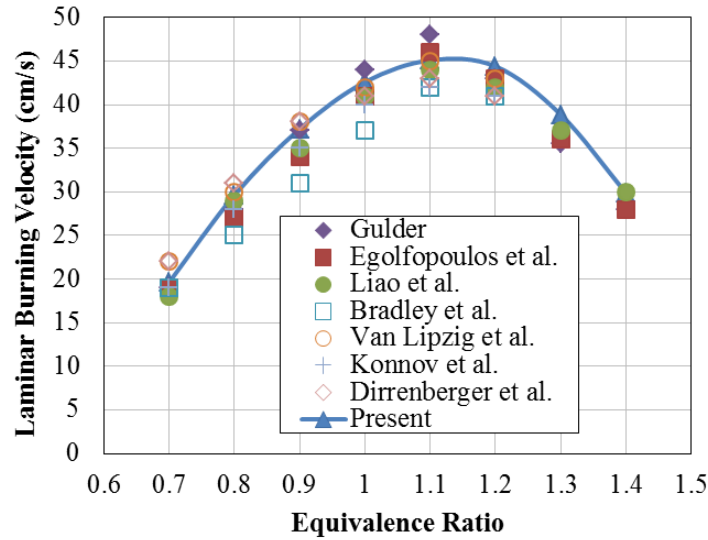
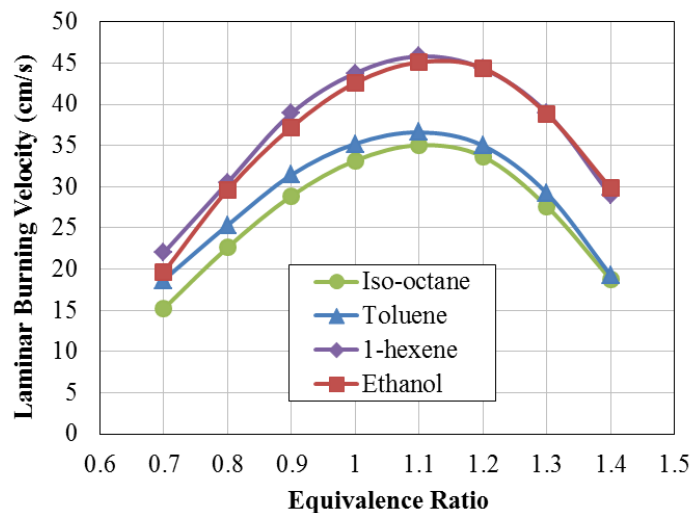
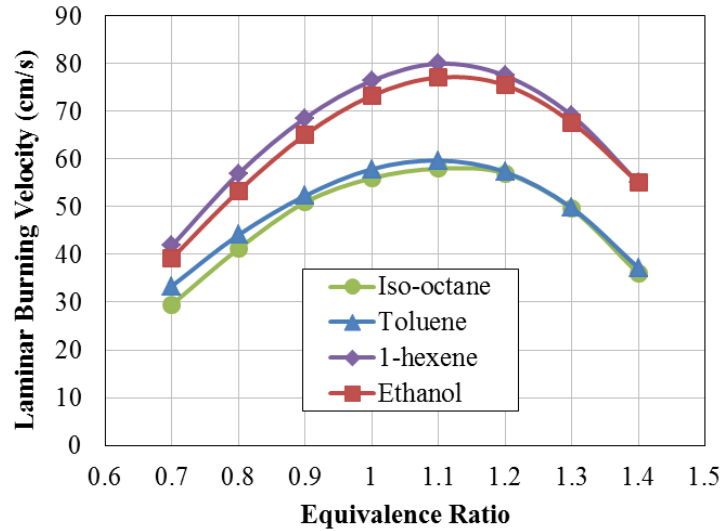


Fig. 5 Laminar burning velocities of ethanol at 1 bar and 300 K

Fig. 6 shows the burning velocity for the four pure components at 300 K and 1 bar (a) and 450 K and 2 bar (b). Amongst the four components, 1-hexene is the one with the highest velocities and ethanol has slightly lower values than 1-hexene at lean mixtures. At rich mixture, the difference between ethanol and 1-hexene is negligible. Very similar burning velocity values are found for toluene and iso-octane at 450 K and 2 bar, particularly for rich mixture. The peak burning velocities for toluene and iso-octane are 37 cm/s and 35 cm/s respectively. Burning velocities of toluene, 1-hexene and iso-octane all peak at an equivalence ratio of 1.1. The laminar burning velocity of ethanol reaches its peak value slightly richer mixture than other three pure components at an equivalence ratio of 1.15, due to a slight excess of fuel being required for all the oxygen to be combusted.



(a) 1 bar and 300 K



(b) 2 bar and 450 K

Fig. 6 Comparison between iso-octane, toluene, 1-hexene, and ethanol at 1 bar and 300 K (a) and 2 bar and 450 K (b)

4. Results for Quaternary Blends

Laminar burning velocities for the four quaternary blends are shown in Figs. 7-9 for different initial temperatures and pressures. It can be seen from three figures that the peak burning velocity occurs at richer mixture with increasing volume of ethanol for the quaternary blends. This is due to the fact that the burning velocity for ethanol peaks at richer mixture than other three pure components as shown in Fig. 6. Although ethanol has the largest values of the laminar burning velocities amongst the four pure components, the addition of up to 20% of ethanol has no effect on the laminar burning velocities, particularly at low initial pressures and temperatures as shown in Fig. 7. This is very close to conclusion by Dirrenberger et al. [22]. At 1 bar and 300 K, the burning velocity is almost the same for E0 and E20.

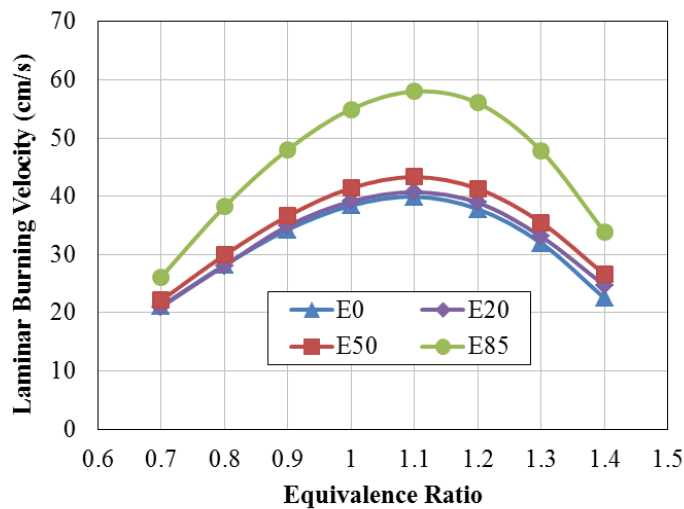


Fig. 7 Laminar burning velocities of the four quaternary blends at 1 bar and 300 K

It can be seen from Figs. 8 and 9 that at higher initial pressures and temperatures, with increase of ethanol volume fraction up to 50%, the increase in burning velocity is much smaller for lean mixture than for richer mixture. At 4 bar and 450 K, the peak burning velocities for E0, E20, E50 and E85 are 53 cm/s, 55 cm/s, 57 cm/s and 63 cm/s respectively.

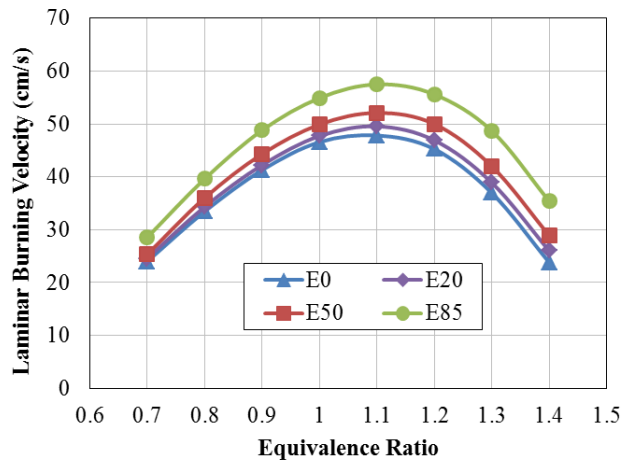


Fig. 8 Laminar burning velocities of the four quaternary blends at 2 bar and 380 K

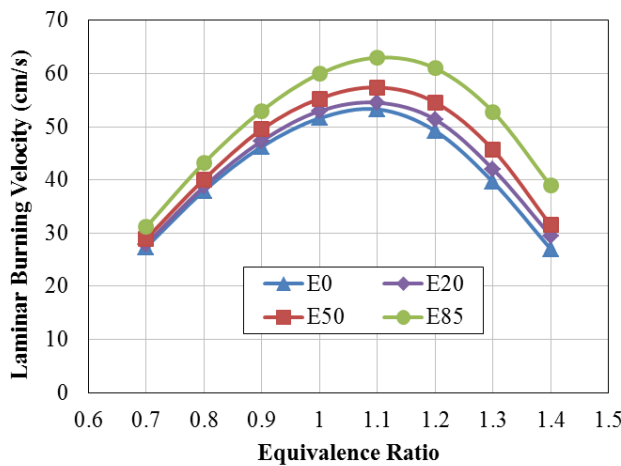


Fig. 9 Laminar burning velocities of the four quaternary blends at 4 bar and 450 K

The effect of pressure on the burning velocity of E85 at 450 K is plotted in Fig. 10. Higher pressure leads to lower laminar burning velocity. Higher pressure shifts the peak burning velocity towards stoichiometric mixture.

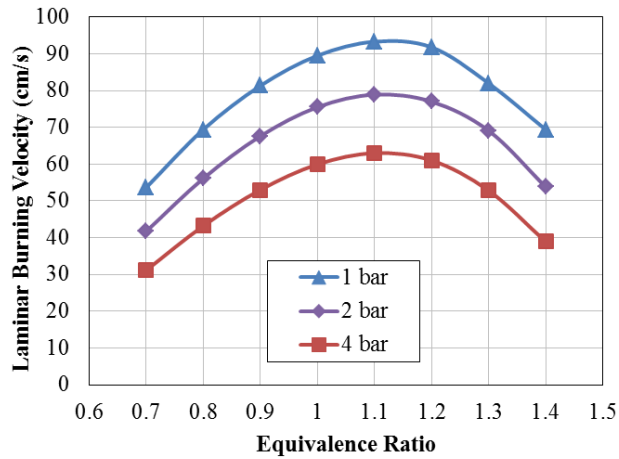


Fig. 10 Effect of pressure on the laminar burning velocity of E85 at 450 K

5. Cellular Flame

Cellular flame was detected during the experiments when the flame front became unstable causing a change of flame front structure from smooth to cellular. This is caused by local inhomogeneity in the mixture composition within the flame front. The burning rate after the onset of cellularity is no longer uniform resulting in the uneven surface. Fig. 11 shows the flame front images for stoichiometric E85 at 1 bar and 450 K at different times. There is a very smooth flame front at up to 15 ms. At 21 ms, the cellular structure occurs and at 30 ms, the flame front becomes purely cellular.

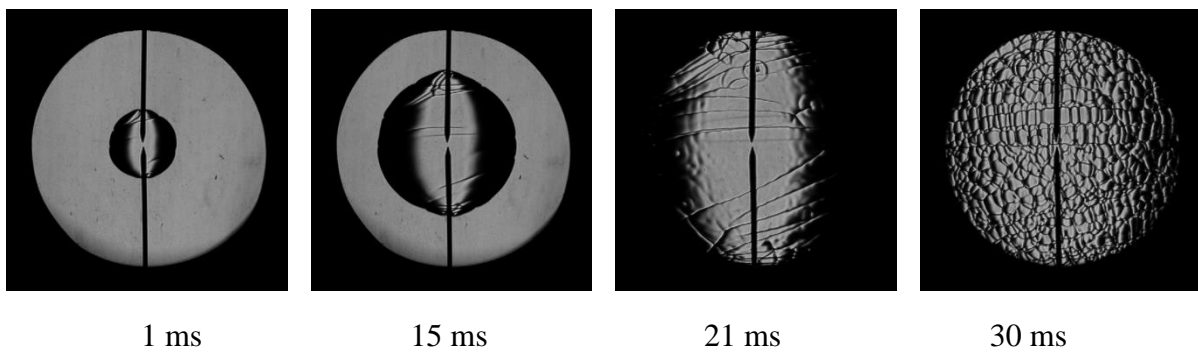


Fig. 11 Schlieren images of the flame front for stoichiometric E85 at 1 bar and 450 K

Fig. 12 shows the onset of cellularity for stoichiometric E0 and E85 against initial pressures. For both blends, higher initial pressures lead to early cellular flame. In general, cellularity occurs earlier as the initial pressure increases. It can also be seen that adding more ethanol leads to earlier cellular flame. As has been pointed out by Lawes et al. [30], rich mixtures could cause earlier cellular flame. Therefore it is necessary to determine an unstretched laminar burning velocity that is free from cellularity and the effect of ignition energy. Flame speed data after the onset of cellularity should be excluded when calculating the laminar burning velocity.

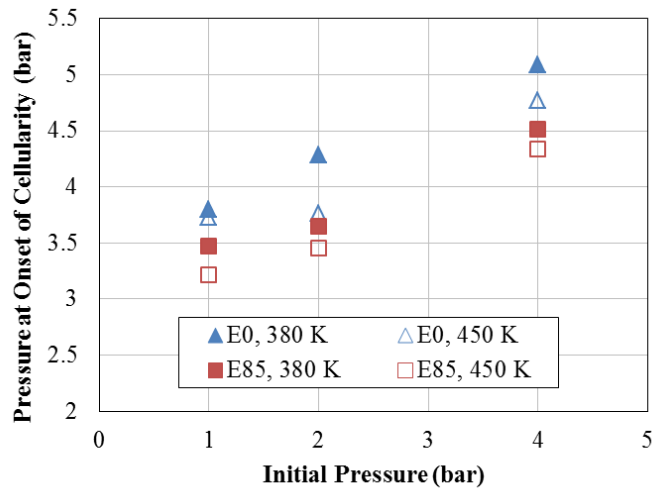


Fig. 12 Cellularity of stoichiometric E0 and E85 against initial pressure

6. Conclusions

The laminar burning velocities of four pure components toluene, iso-octane, 1-hexene and ethanol and their quaternary blends have been measured by using a constant volume combustion bomb and a Schlieren imaging system. Experiments over a wide range of initial temperatures, pressures and equivalence ratios have been conducted. Key findings are listed as below:

- (1) Close agreements were observed for toluene, iso-octane and ethanol for ambient conditions between the present work and literature data;
- (2) The burning velocity of 1-hexene was firstly presented for ambient condition. The only literature data is also close to present results at 373 K and 1 bar;
- (3) 1-hexene has similar values of burning velocity to ethanol at ambient conditions. Iso-octane and toluene have similar values as well. The burning velocity of ethanol peaks at slightly richer mixture than other three studied components;
- (4) Although ethanol itself has the highest burning velocity, the effect of adding ethanol of volume fraction up to 20% is negligible particularly for low pressures and temperatures;
- (5) For the quaternary blends, cellularity occurs earlier as the initial pressure increases. Adding more ethanol leads to earlier cellular flame.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China (51676167), the Science & Technology Department of Sichuan Province (2017TD0026, 2015TD0021), and the Sichuan Provincial Scientific Research Innovation Team Program (17TD0035).

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