Research Article

The Role of Hydrogen Bonding on Laminar Burning Velocity of Hydrous and Anhydrous Ethanol Fuel with Small Addition of n-Heptane

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The molecular structure of mixed hydrous and anhydrous ethanol with up to 10% v n-heptane had been studied. The burning velocity was examined in a cylindrical explosion combustion chamber. The result showed that the burning velocity of hydrous ethanol is higher than anhydrous ethanol and n-heptane at stoichiometric, rich, and very rich mixtures. The burning velocity of hydrous ethanol with n-heptane drops drastically compared to the burning velocity of anhydrous ethanol with n-heptane. It is caused by two reasons. Firstly, there was a composition change of azeotropic hydrous ethanol molecules within the mixture of fuel. Secondly, at the same volume the number of ethanol molecules in hydrous ethanol was less than in anhydrous ethanol at the same composition of the n-heptane in the mixture. At the mixture of anhydrous ethanol with n-heptane, the burning velocity decreases proportionally to the addition of the n-heptane composition. The burning velocity is between the velocities of anhydrous ethanol and n-heptane. It shows that the burning velocity of anhydrous ethanol mixed with n-heptane is only influenced by the mixture composition.

1. Introduction

Combustion is the best way to obtain large amounts of energy in a short time. Burning velocity is the most important parameter in the fuel combustion process, of either external or internal combustion engines. The burning velocity is influenced by several factors like fuel, air fuel ratio, and onset combustion pressure and temperature.

Hydrous ethanol (4.0–4.9% v of water) is intensively developed as fuel due to its characteristics like being renewable, having low NO_x emission, increasing engine working pressures, and reducing production cost [1–4]. In Brazil, Flex-Fuel vehicles that can be operated with 100% hydrous ethanol have been in the market since 2003. In the vehicles, ethanol can be used separately as fuel or combined with gasoline as the octane enhancer and oxygenate.

The n-heptane is one of the fuel main references [5]. The mixture of n-heptane and isooctane is considered as the major component of gasoline. This combination at any number of octane has also been researched for many times.

Unfortunately, either n-heptane or isooctane is fossil fuel in which it is nonrenewable energy.

Nowadays, since the issues on the fossil fuel stock and environment are oftentimes discussed, this increases the interest in using the alternative-renewable fuel that is also good for environment. Hydrous and anhydrous ethanol are renewable fuel with the higher octane number compared to isooctane. Until today, hydrous ethanol is considered as candidate to be set as additive or even substitution for the fossil fuel. It is because hydrous ethanol can be easily combined with hydrocarbon and produced by simple process.

The burning velocity of the mixture of n-heptane and ethanol had been observed by [6, 7]. Their results showed that the burning velocity of ethanol is higher than n-heptane at either the lean, stoichiometric, or rich mixtures. The burning velocity of n-heptane and ethanol is among those two [6]. The results of [7] showed that the addition of alcohol does not cause the decomposition of hydrocarbon. The addition of alcohol on n-heptane gave a little effect to the fuel's chemical interaction.
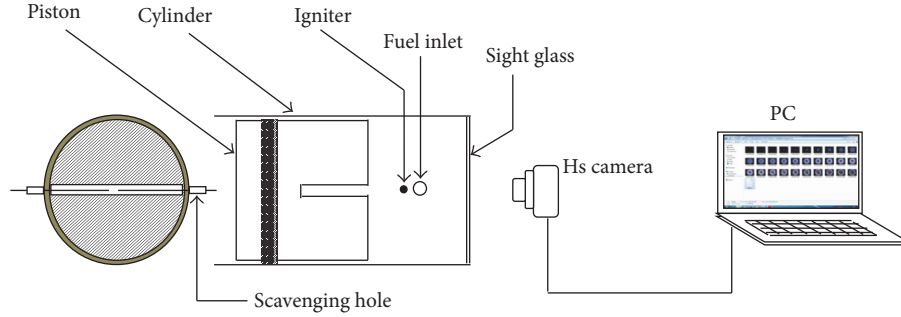
FIGURE 1: Experimental setup.

The examination of the mixture of ethanol and n-heptane used directly as fuel for engine has been executed by [8–11]. The study of [8] denoted that alcohol has a better prospect within engines since it possesses higher latent heat of evaporation and larger number of oxygen molecules. The result of [9] showed that when the system uses ethanol/n-heptane fuel, the ignition delay increases very high but the temperature and pressure in the cylinder decrease drastically in a higher ratio. But, based on some existing studies, there is no fundamental data covering the premixed combustion behavior of hydrous and anhydrous ethanol with n-heptane, especially the ones related to laminar burning velocity.

Therefore, the objective of this study is to acquire new data about laminar burning velocity of the mixtures of anhydrous ethanol (99.7% v) and hydrous ethanol (95.5% v) with n-heptane in varied composition at lean (ϕ = 0.9), stoichiometric (ϕ = 1), rich (ϕ = 1.1), and very rich mixture (ϕ = 1.2). It is motivated by the characteristics of hydrous ethanol fuel which is better than anhydrous ethanol at the sto-ichiometric and rich mixture [12]. The mixture of ethanol/n-heptane can combine the renewable fuel with fossil fuel.

2. Experiment Design, Procedure, and Data Analysis

The premixed combustion of hydrous and anhydrous ethanol mixed with n-heptane was observed in a cylindrical explosion combustion chamber as shown in Figure 1. Its diameter is 135 mm and the length is 270 mm. This model had also been used in [13–16]. The frontal end of the chamber was closed with transparent glass wall for capturing the fireball growth with a high speed camera. The other end was a piston which could move freely during the development of fireball. The left side wall of the cylinder was fitted with positive (+) terminal of an igniter and fuel inlet for insertion of fuel mixture, while the right side was negative (−) igniter and scavenging manifold.

Anhydrous ethanol with purity of 99.7% v was used as fuel and hydrous ethanol of 95.5% v was made in the analytical chemical laboratory. The test was conducted at atmospheric pressure and room temperature at 303 K.

Liquid hydrous ethanol fuels and air are introduced into the mixing chamber at the desired equivalence ratio. After that, the latent heat for evaporation of the fuels was supplied by blowing air to the surface of mixing chamber at room temperature so it turns into the gas state. The mixture was put into the combustion chamber to test its burning velocity. Flame radius was visualized from the frontal end of the combustion chamber. Before igniting, the camera was firstly turned on and set up at a speed of 420 fps.

3. Data Processing

Broustail et al. [13], Beeckmann et al. [14], Zhang et al. [15], and Johnston and Farrell [16] studied the characteristic of laminar burning velocity from a variety of fuels in spherical combustion bomb and developed a theory of developing flame ball. According to this theory, the stretched laminar flame propagation speed (S_n) can be calculated from the growth rate of flame radius as

$$S_n = \frac{dr}{dt} \tag{1}$$

in which r is the radius of spherical flame front and t is the time when the radius is measured. The stretched rate (α) of spherical flame is obtained at any captured image on the flame surface [12], as follows:

$$\alpha = \frac{d(\ln A)}{dt} = \frac{dA/A}{dt} = \frac{dA}{A \cdot dt} \tag{2}$$

in which A is the surface area of the flame. In the case of spherical propagating flame, the flame stretched rate can be calculated as

$$\alpha = \frac{dA}{A \cdot dt} = \left(\frac{2}{r}\right)\left(\frac{dr}{dt}\right) = \left(\frac{2}{r}\right)S_n. \tag{3}$$

A linear relationship between the unstretched flame speed (S_s) and stretched flame speed has been reported in [15–17] as

$$S_s - S_n = L_b \cdot \alpha. \tag{4}$$

Based on (4), it can be seen that S_s is the same with S_n when $\alpha = 0$.

Laminar burning velocity (S_L) is derived from S_s as

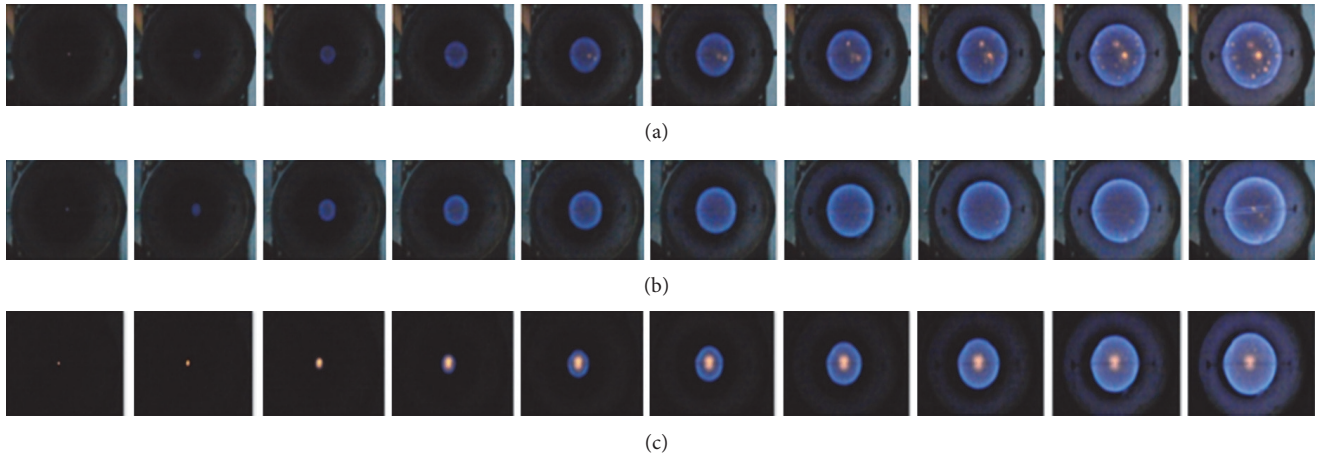$$S_L = \frac{\rho_b}{\rho_u} S_s. \tag{5}$$

(a)

(b)

(c)

FIGURE 2: Typical growing image of flame radius with time interval of 2.381 ms (ϕ = 1.1, T = 305 K, and P = 1 atm) for (a) hydrous ethanol (95.5% v); (b) anhydrous ethanol (99.7% v); (c) n-heptane.

ρ_b and ρ_u are, respectively, the density of combustion gases and the density of the reactants. ρ_b is calculated at adiabatic flame temperature.

4. Results and Discussion

Laminar burning velocity of hydrous and anhydrous ethanol and their respective mixture with n-heptane had been measured from flame images at any equivalence ratio (ϕ), fuel heating value, and adiabatic flame temperature in which all of them were affected by the addition of n-heptane and water content of the fuel.

Low Heating Value (LHV) of hydrous ethanol was determined based on the water content in the ethanol. LHV of hydrous ethanol was obtained by multiplying the mass percentage of hydrous ethanol with LHV of anhydrous ethanol in which its value is 26.8 MJ/kg. The LHV of n-heptane is 44.50 MJ/kg [8, 9]. Meanwhile, LHV of the mixture of hydrous and anhydrous ethanol with n-heptane was obtained by averaging both LHV values of those fuels. The adiabatic flame temperature was calculated using the formula in [18].

4.1. The Pure Fuel Laminar Burning Velocity. When the mixture of fuel and air had been filled into the combustion chamber, the sparker (igniter) was ignited in the middle of combustion chamber, and the fire then spread towards reactant in the direction of combustion chamber's radius. Figure 2 shows the development of the fireball of hydrous ethanol, anhydrous ethanol, and n-heptane with the increase of diameter at each 2.381 ms.

The flame front was determined by using color differences which occur between the color of fire (bright blue) and reactants color (dark blue) as shown in Figure 3 which shows the photo of flame ethanol 95.5% v, at ϕ = 1 after 23.81 ms from the ignition. Good quality pictures could be taken in this experiment due to a good blocking of the outside light from the environment to the apparatus. The light from the environment was blocked so that the border between the
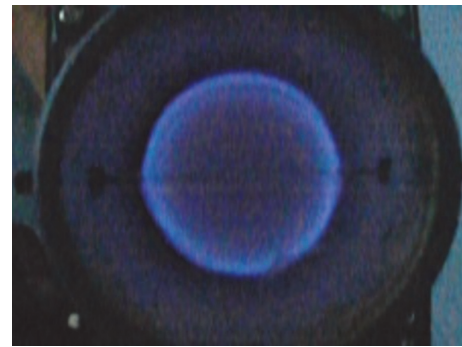

FIGURE 3: Photo of flame ethanol 95.5% v; at ϕ = 1 after 23.81 ms.

surface of fire and the reactants is very thin, less than 1% of the flame radius. This means that there is almost no significant measurement error on flame radius (r).

From Figure 2, the stretched flame speed (S_n) could be determined by using formula (1). Unstretched flame speed (S_s) was obtained by extrapolating the value of S_n at α = 0. Figure 4 shows S_s for hydrous ethanol, anhydrous ethanol, and n-heptane at stoichiometric, rich, and very rich mixture. It is seen that S_s at the very rich mixture is higher than at the rich and stoichiometric mixture.

By using (5), each fuel's laminar burning velocity (S_L) can be determined. Figure 5 shows S_L of each fuel. S_L of hydrous ethanol is higher than anhydrous ethanol and n-heptane at the stoichiometric and rich mixture. Though the calorific value of hydrous ethanol is lower than anhydrous ethanol and n-heptane, and since the molecular structure of hydrous ethanol is shorter, with a centered oxygenate, the burning velocity increases.

4.2. The Effect of n-Heptane Blending to Hydrous and Anhydrous Ethanol on Laminar Burning Velocity. Figure 6 shows the value of S_s for hydrous and anhydrous ethanol fuel mixed with n-heptane. The legend 95.5 + 2 means ethanol 95.5% v
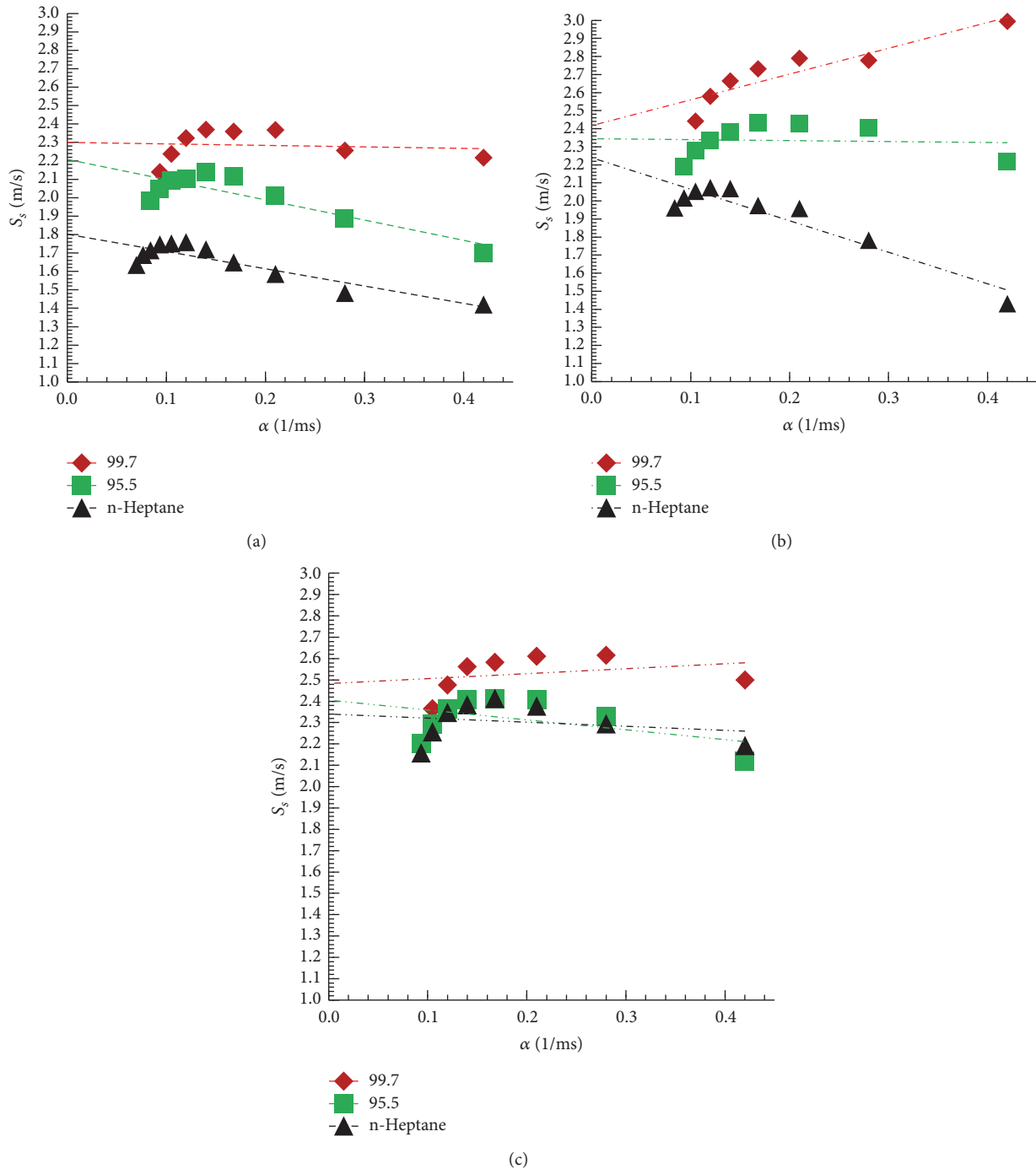
(a)

(b)

(c)

FIGURE 4: Flame stretch rate for the hydrous ethanol, anhydrous ethanol, and n-heptane. (a) Stoichiometric mixture; (b) rich mixture; (c) very rich mixture.

was added with 2% v of n-heptane. The 99.7 + 2 means ethanol 99.7% v was added with 2% v of n-heptane. In Figure 6(a), it is shown that there is a very significant change of flame speed after the hydrous ethanol was added with 2% v of n-heptane. The increasing percentage of n-heptane, furthermore, up to 10% v reduced the speed proportionally to the increase of n-heptane.

In Figure 6(b), it is shown that there is a decreasing value of S_s after the anhydrous ethanol was mixed with n-heptane.

S_s decreases proportionally to the addition of n-heptane. S_s of mixed fuel is between S_s of pure anhydrous ethanol and S_s of n-heptane.

When compared with the data of Bradley et al. [19] for anhydrous ethanol containing very small liquid phase with liquid droplet of diameter 31 μm, the trend of the data agrees very well (see Figure 7). Differences in flame speed between this study and that of [19] can be caused by several factors such as measurements, temperature, and research apparatus
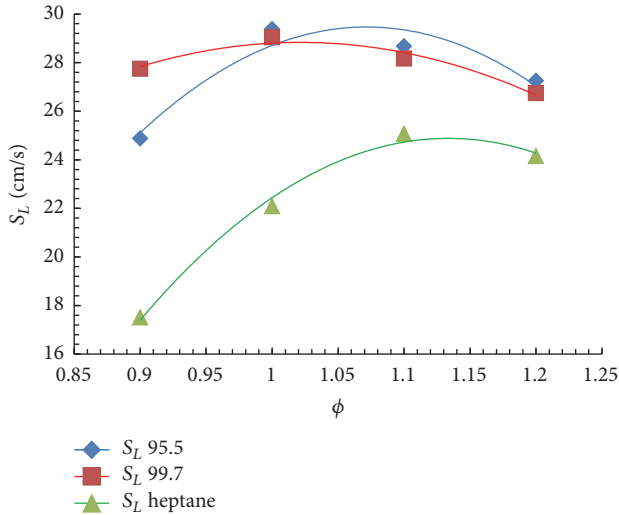
FIGURE 5: Laminar burning velocity of hydrous ethanol, anhydrous ethanol, and n-heptane fuels.

factors. For measurements, the error in this study is very small, less than 1%. For the temperature, all studies were conducted at room temperature which has low possibility of providing a difference in the results. Then, the difference is considered to come from the research apparatus factor. There was little friction between the piston and the cylinder in the combustion chamber of current research that led to a slight increase in pressure that decreases the speed of combustion, compared with research conducted by Bradley without piston.

There are limitations to doing experiment at equivalent ratio (ϕ) below 0.9 and above 1.2. At $\phi < 0.9$, because the fuel contains a small amount of water, the calorific value of the fuel is very low and the water in the fuel absorbs energy so that reactants become difficult to be ignited. At $\phi > 1.2$ the fuel is too saturated so it is difficult to evaporate it in the mixing chamber because the reactants quickly turn into droplets that cause the mixture to become nonhomogeneous.

The burning velocity, S_L, of hydrous and anhydrous ethanol mixed with n-heptane on each equivalence ratio can be seen in Figure 8. In Figure 8(a), it is shown that S_L for hydrous ethanol drastically drops after being added with 2% v of n-heptane. The further addition of n-heptane up to 10% v reduces the laminar burning velocity, proportionally to the increasing of n-heptane volume.

S_L of anhydrous ethanol mixed with n-heptane decreases from S_L of ethanol. The burning velocity of the mixed fuel is between S_L of anhydrous ethanol and n-heptane. The burning velocity decreases proportionally to the increasing volume of n-heptane can be seen in Figure 8(b).

5. Discussion

The burning velocity of a fuel is highly influenced by heat value, length of the chain, and molecular structure of the fuel. A shorter carbon chain in the fuel will increase the burning velocity [20]. In the previous study, Suarta et al.
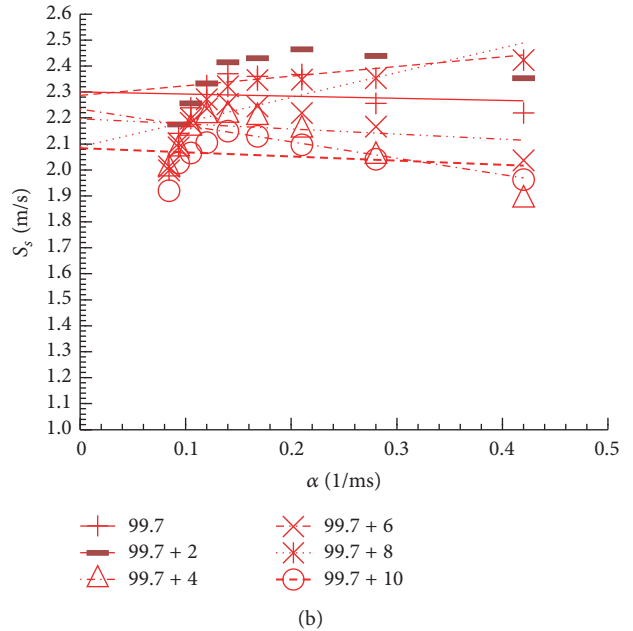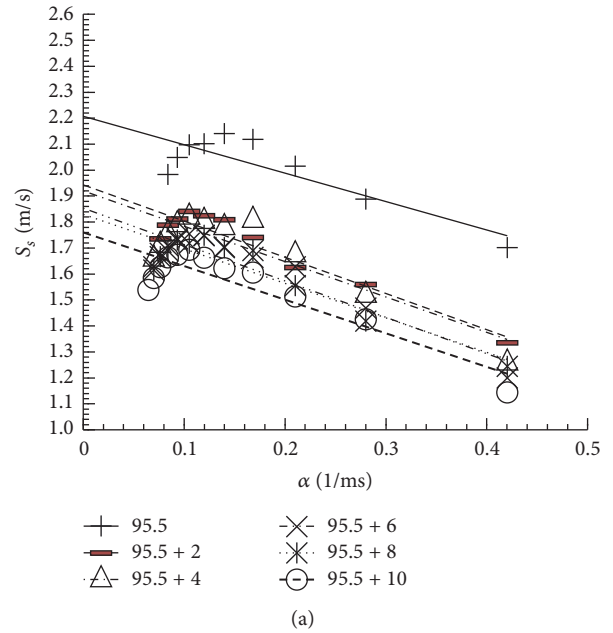

(a)

(b)

FIGURE 6: The flame speed for the stretch at $\phi = 1$. (a) Hydrous ethanol is added with n-heptane. (b) Anhydrous ethanol is added with n-heptane.

[12] showed that the composition of azeotropic hydrous ethanol occurs at a 95.1% v composition with the molecular structure as in Figure 9(a). The maximum burning velocity of hydrous ethanol occurs at a 95.5% v composition with the molecular structure as in Figure 9(b). The molecular structure of anhydrous ethanol is in Figure 9(c) and the molecular structure of n-heptane is in Figure 9(d).

The laminar burning velocity of hydrous ethanol decreased drastically with the addition of n-heptane. It was caused by the composition change of azeotropic group within the fuel. The presence of n-heptane molecule within the
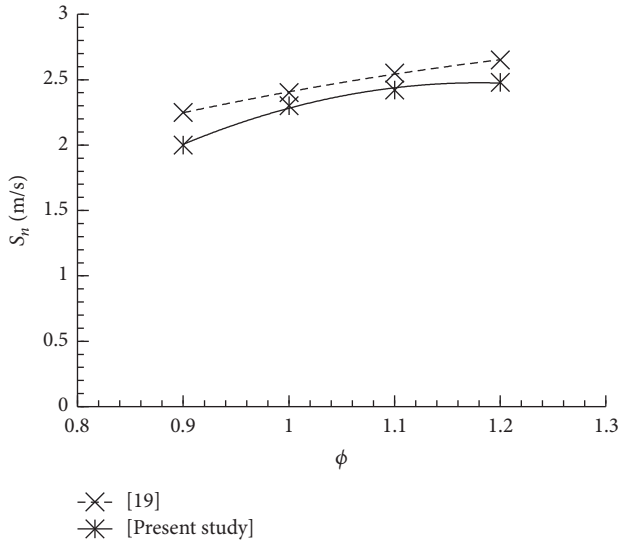
FIGURE 7: Comparison of the value of S_s for anhydrous ethanol between [19] and present study.

95.5% v of hydrous ethanol fuel elevates the calorific value but there would be a molecule that disrupts its azeotropic characteristic.

From the molecular structure point of view, when hydrous ethanol 95.5% v is added with 8% v of n-heptane, then, in the mixed fuel, there will be two molecules of ethanol 95.5% v and one n-heptane molecule. This composition can be said as 4 azeotropic molecules (95.1% v) with two free ethanol molecules and one n-heptane molecule. This composition is depicted in Figure 10.

The presence of n-heptane would disrupt the azeotropic characteristic. The burning velocity of hydrous ethanol with h-heptane decreased drastically from the velocity of hydrous ethanol.

The burning velocity of anhydrous ethanol decreased with the addition of n-heptane. The burning velocity decreased proportionally to the addition of % v of n-heptane as shown in Figure 8(b). The burning velocity is between the burning velocity of anhydrous ethanol and n-heptane. It is caused by the chain of anhydrous ethanol that has hydrogen bond which becomes a long chain having structure almost similar to the chain of n-heptane. Thus, the burning velocity is only influenced by the burning velocity of each fuel. From molecular structure shown in Figure 11, it is seen that when anhydrous ethanol is added with 8% v of n-heptane then, in 29 molecules of ethanol, there is only one n-heptane molecule. It is also declared in [7] that the addition of alcohol does not influence the decomposition of hydrocarbon fuel.

The addition of n-heptane on hydrous ethanol of 95.5% v caused a very sharp decrease of velocity, compared to the addition on anhydrous ethanol. It is because of the different number of ethanol molecules. In hydrous ethanol, the number of ethanol molecules is less than the number of anhydrous ethanol molecules in the same mixture ratio with n-heptane. It can be seen from molecular structures in Figure 10 that, with 8% v of n-heptane, at hydrous ethanol of 95.5% v, there
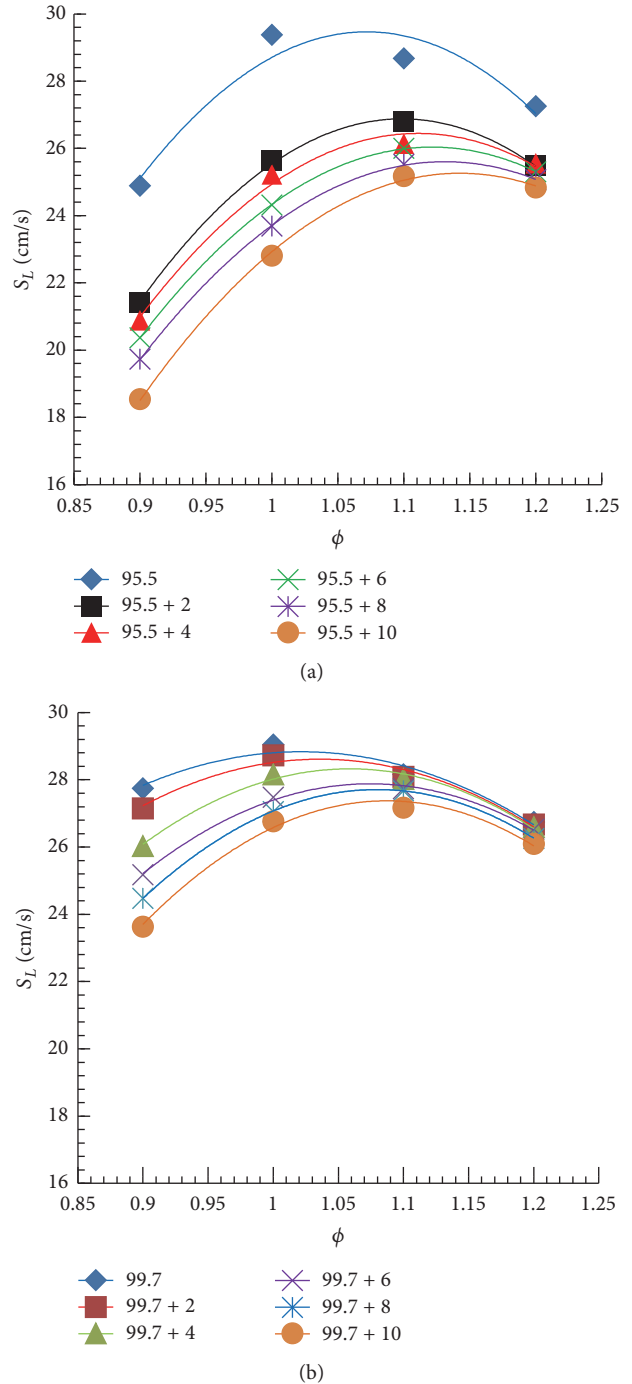

(a)

(b)

FIGURE 8: Laminar burning velocity of ethanol and its mixture with n-heptane. (a) Hydrous ethanol; (b) anhydrous ethanol.

are 26 ethanol molecules that have calorific value with four water molecules that do not have calorific value. The azeotropic characteristic with centered oxygenate is very disrupted by the presence of n-heptane. Meanwhile, at the anhydrous ethanol added with 8% of n-heptane (Figure 11), there are 29 ethanol molecules and one n-heptane molecule. Besides the larger number of ethanol molecules, the same molecule structure causes the decrease of velocity to be
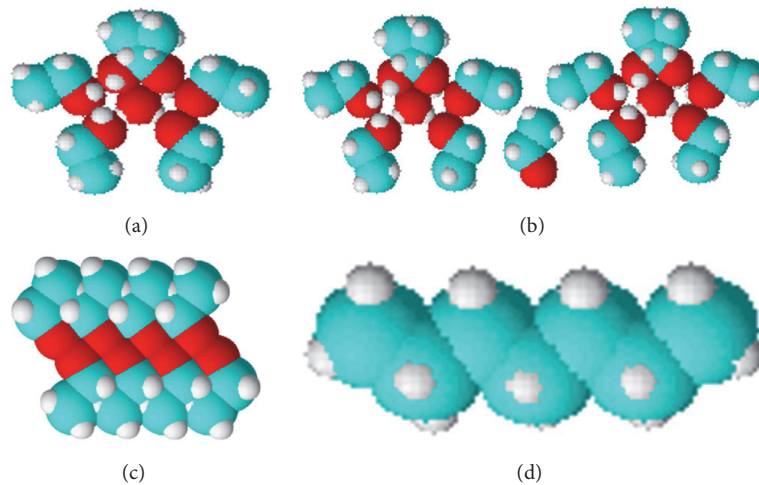
FIGURE 9: The molecular structure of (a) azeotropic ethanol; (b) ethanol of 95.5% v; (c) anhydrous ethanol; (d) n-heptane.
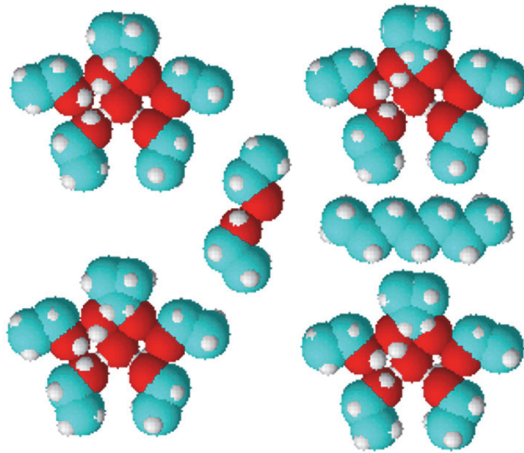

FIGURE 10: The molecular structure of ethanol 95.5% v being added with 8% v n-heptane.
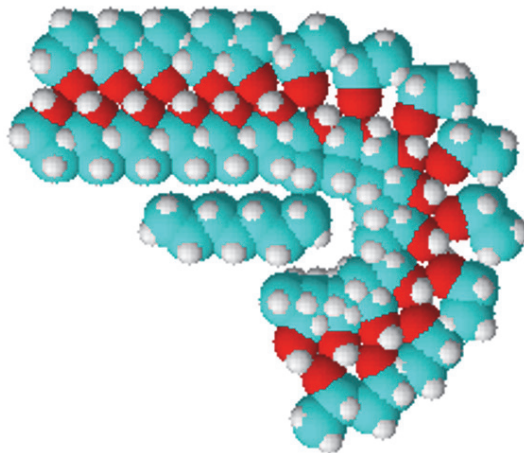

FIGURE 11: Molecular structure of anhydrous ethanol being added with 8% v of n-heptane.

between the burning velocities of each fuel. Or it decreases proportionally to the addition of the volume of n-heptane.

6. Conclusion

From the comparison between premixed combustion of hydrous ethanol with n-heptane and that of anhydrous ethanol with n-heptane, there are some conclusions gathered as follows:

(i) Without the addition of n-heptane, the burning velocity of hydrous ethanol is higher than anhydrous ethanol and n-heptane.

(ii) The burning velocity of hydrous ethanol decreases drastically with the addition of n-heptane.

(iii) The burning velocity of anhydrous ethanol with n-heptane is between the velocities of each fuel, depending on the composition.

(iv) Hydrous ethanol is better to be used as pure fuel so that its azeotropic molecular structure is not disrupted.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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