

Full Length Article

The role of molecule cluster on the azeotrope and boiling points of isooctane-ethanol blend

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ABSTRACT

This study aims to assess the fraction of the isooctane-ethanol blend which has azeotrope condition. Isooctane was selected as a conventional fuel. Isooctane-ethanol blend with various mixture fractions is given the heat to obtain the distillation temperature curve and the fuel vapor. The blended fraction is varied from 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100% v/v ethanol to predict the condition (near) azeotrope fuel blend. Molecular analysis was used to verify the predicted azeotrope mixture of isooctane-ethanol. The results show that the isooctane ethanol blend has an azeotrope mixture at exactly on the ethanol fraction of 41.48% v/v. In this fraction blended, two polar molecules of ethanol induce a nonpolar molecule of isooctane to form a molecular cluster.

1. Introduction

Increased energy demand has an impact on rising fuel prices, and air pollution. Several studies from different countries concentrate on developing and finding alternative energy sources to reduce dependence on fossil fuels [1] and harmful emissions into the air [2]. Investigations of alternative fuels behavior for substitute fossil fuels are needed to the adjustment of the existing fuel system. Combustion of fuel is the fastest way to generate energy from primary energy sources [3]. One of the important properties of fuel for SI engines is the vapor pressure [4,5]. The vapor pressure is a degree of the volatility of the fuel. Reid vapor pressure (RVP) is the vapor pressure of the fuel at a temperature of 100 °F (37.8 °C) in a container with a composition ratio of the liquid phase and gas phase by 4:1 with a specific measurement [4]. So, RVP relates directly to the fuel distillation temperature. Under ideal mix conditions, the vapor pressure of a mixture is formulated by the Raoult's law as shown in Eq. (1) [4].

$$P = \sum P_n X_n \quad (1)$$

P is the vapor pressure of the blend, P_i is the vapor pressure of substance n, and X_n is the mole fraction of substance n. While, under non-ideal mix conditions, the pressure will deviate from Eq. (1). The deviation is corrected by the blended activation coefficient γ so that the blend pressure becomes Eq. (2).

$$P = \sum \gamma \cdot P_n X_n \quad (2)$$

In a blend, the activation coefficient (γ) is the unique number of the mixture composition of the constituent. The activation coefficient of the mixture is determined by the composition of the constituent and is obtained empirically.

Alcohol is one of the future alternative fuels to modern engines especially for light duty vehicles [6]. The advantages of alcohol as fuel for SI Engine is a high octane rating [7], high oxygenated fuel, wide flammability limit, and small hydrogen-carbon ratio [8]. Another advantage is high laminar flame propagation speed and high evaporation enthalpy thus providing a better cooling effect [9] and a thermal efficiency [10]. Methanol and ethanol are the groups of short-chain alcohols that are the most widely used to replace fossil fuels because it has some physical and combustion properties similar to gasoline [8]. Methanol and ethanol also have a boiling temperature of 78.29 °C and 64.7 °C, respectively, while gasoline has a boiling temperature of 40 °C [11]. Gasoline is a multi-substance (C₄–C₁₂) that has a multi boiling point between 27 and 225 °C [7]. Therefore, it will have an impact on the uncertainty of the composition of the ratio of air fuel during the combustion process on the SI engine.

Many researchers studied alcohol as an SI Engine fuel as a blended and full-dedicated fuel. Most studies of alcohol as an SI engine fuel focus on reduction in exhaust emissions and engine performance impacts [2,7–29]. Some researchers agree that the addition of alcohol in gasoline gives a positive impact such as reducing harmful emissions [17,26], improving thermal efficiency and volumetric [30,31] and produce a complete combustion. However, addition of more alcohol

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Table 1
Properties of test fuels.

Properties	Isooctane	Ethanol
Purity (%)	99.5	99.7
Chemical formula	C ₈ H ₁₈	C ₂ H ₅ OH
Boiling Temperature (°C)	98–100	78.3 [4]
Enthalpy of evaporations at 25 °C (kJ kg ⁻¹) [35]	308	924.2
H/C ratio	2.25	3
O/C ratio	0.5	0
Low heating value (MJ kg ⁻¹)	44.4	26.83
Molecular Weight (g mol ⁻¹)	114.23	46.07
Density @ 20 °C (kg L ⁻¹)	0.691–0.696	0.789–0.792
Acidity	0.0003	0.0006
Vapor pressure at 20 °C (kPa) [36]	5.5	5.95
Oxygen content (wt%) [36]	0	34.73

content tends to have a negative impact, especially on a cold start and cold idle conditions [32]. This condition is caused by the fact that addition of high levels of alcohol reduces fuel vapor pressure. It leads to the lean fuel-air mixture, that result in incomplete combustion.

Until recently, study to investigate the properties of alcohol-gasoline blend changes still rare. Isooctane is a single substance of hydrocarbon that represent gasoline because of some of its important properties [33]. Isooctane, 2,2,4-trimethylpentane is an octane isomer (C₈H₁₈) that has a molecular weight of 114.23 and a boiling point 98–99 °C. Isooctane is an important substance in gasoline because it was used in a relatively large proportion to upturn the knock resistance of the fuel. Ethanol has a very low RVP of gasoline, so it has adverse effects especially on cold start and cold idle running [34]. The ethanol-gasoline blend has a non-linear RVP to the mixed fraction (Eq. (1)). The previous study of alcohol-gasoline blends showed that the (near) azeotrope mixture condition occurred in the composition of between 5 and 10% v/v [4,5]. In this mixed fraction, the vapor pressure of the gasoline-alcohol mixture is higher than the vapor pressure of all the constituents. The boiling temperature is correlated with its vapor pressure so that under such conditions the gasoline-alcohol mixture has the lowest boiling temperature.

However, until now the phenomenon of deviation vapor pressure on alcohol and hydrocarbon fuel blend has been no satisfactory scientific explanation [35]. Until recently, studies of alternative fuels to get the fuel equivalent to fossil fuels are still rare. A related study on an alcohol-gasoline blend, Andersen et al. (2010), clarify that alcohol and

gasoline forms a nonideal mixture with the vapor pressure higher than ideal mixture expected [4]. This condition happens because alcohol is a polar substance and hydrocarbons in gasoline are nonpolar substance. In an alcohol-hydrocarbon fuel blend, polar molecule of alcohol induces some nonpolar hydrocarbon molecules around it, so that the dipole moment of hydrocarbon molecules becomes higher than ever. Therefore, it will form a molecule cluster of an hydrocarbon-ethanol fuel blend.

These studies reveal the abnormalities phenomenon vapor pressure of isooctane-ethanol blend. The vapor pressure of isooctane-ethanol blend was represented by the distillation temperature of the isooctane-ethanol blend. This research uses a simple distillation system to form temperature distillation and evaporation of fuel blends curve so that the predicted mixture of the (near) azeotrope can be determined. The study also analyzed the molecular interactions of isooctane-ethanol mixtures to determine the azeotrope point of the isooctane-ethanol blends.

2. Experiments

2.1. Fuel blends preparation

This study used isooctane (2,2,4-Trimethylpentane) and ethanol analytical reagent grade with a molar weight (MW) of 114.23 and 46.07 g mol⁻¹ and purity 99.5% and 99.7% respectively. Isooctane was supplied by Merck, Germany and ethanol were supplied by Smart-Lab, Indonesia. Both fuels were used without additional purification. The detailed fuel properties used in this study were presented in Table 1.

The blend used in this study was I100E00, I95E05, and I90E10, up to I00E100. The Ixx Eyy fuel code means that the fuel blend contains isooctane and ethanol xx% and yy% v/v respectively. Isooctane was blended with ethanol manually. The volume of the isooctane and ethanol blend used in this study is 50 centimeters cubic (cm³) for each data retrieval. The fuel heating at each test was carried out until it reached the boiling temperature and was stopped before the fuel in the flask was completely evaporated. It was done to avoid the outbreak of the fuel container due to overheating.

2.2. Experimental apparatus

This experiment was conducted to obtain the distillation temperature and the fuel vapor curve of the ethanol-isooctane blend at various blended fractions. This analysis was conducted by placing an isooctane-ethanol blend on a 500-cc flask. An electric heating mantle was used to

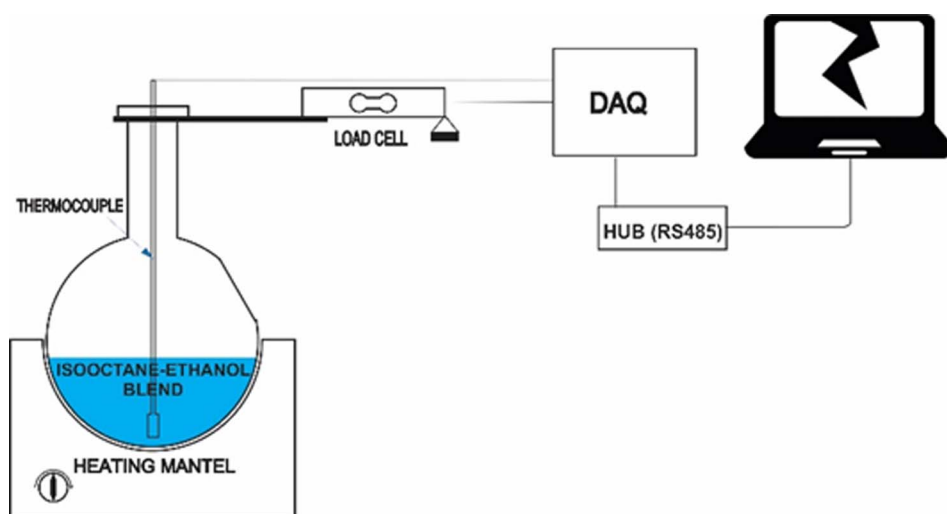


Fig. 1. The experiment setup.

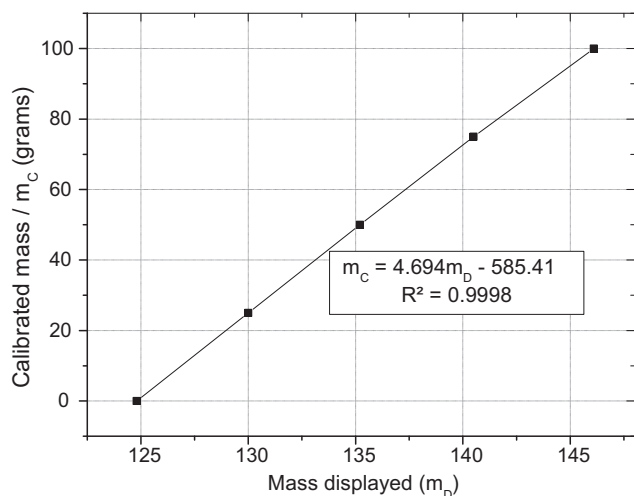


Fig. 2. Mass calibration graph and equation.

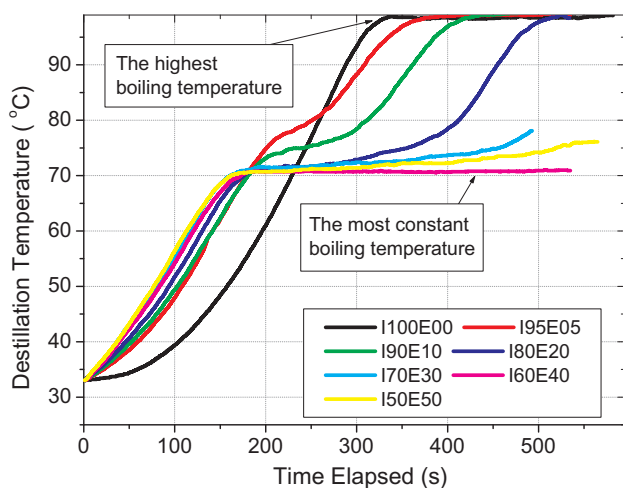


Fig. 3. Temperature distillation curve of 0–50% v/v ethanol fraction.

supply heat energy to the fuel blend. K type of thermocouple was used to record temperature changes during the heating process. A load cell was used to detect the mass change of isooctane-alcohol blends in the

fuel flask. Therefore, boiling flask must be hung on a load cell to detect a reduction in fuel blend lifetime. The experimental setup was presented in Fig. 1. The evaporation rate in this study was defined by the decrease in mass per unit time.

This experiment was conducted at room temperature and pressure of 26 °C and 1 atm respectively. The initial temperature of the fuel blend of each data retrieval in this study was 33 °C for all various blends. The heat energy supply from the heating to the fuel was about 30 W.

2.3. Data acquisition

Fig. 2 shows that thermocouple express temperature changes due to heating of fuel blends, while load cell signals show mass changes due to the evaporation process of fuel blends. Evolution of temperature and mass of fuel blend were converted to millivolt signals by thermocouple and load-cell. Both signals are processed by TM4-N2RB to be transformed into digital signals. The digital signal is connected to a personal computer through RS 485 Autronics SCM-US481. Test data is displayed and stored in a personal computer using DAQ Master V1.6.3 software. Calibration data was performed to evaluate mass measurement results using a load cell. Mass calibration was performed using five standard weights 0, 25, 50, 75, and 100 g. The measured mass was displayed on personal computers versus mass calibrated as shown in Fig. 2. That shows the calibration equation was acceptable because it has $R^2 = 0.9998$.

3. Result and discussion

3.1. The distillation temperature of isooctane ethanol blend

The distillation temperature is a description evolution of temperature and fuel state change due to a heating process. The azeotrope mixture is associated to its distillation temperature curve since the fuel blend looks like a single substance. The mixture under azeotrope conditions has a vapor mixture composition equal to the composition of the liquid mixture [37]. So that the azeotrope condition of the fuel mixture is an important fuel property to produce a stable and consistent combustion result.

Fig. 3 shows the distillation temperature of ethanol fractions of 0%, 5%, 10%, 20%, 30%, 40% and 50% volume base. It shows that blend of 5%, 10% and 20% v/v ethanol have two boiling temperatures as shown in Fig. 4.

Fig. 3 shows the rate of distillation temperature increase estimated from the slope of the heating process in Fig. 4 especially for 5%, 10% and 20% v/v ethanol fraction. So, the rising curve in Figs. 4 and 5

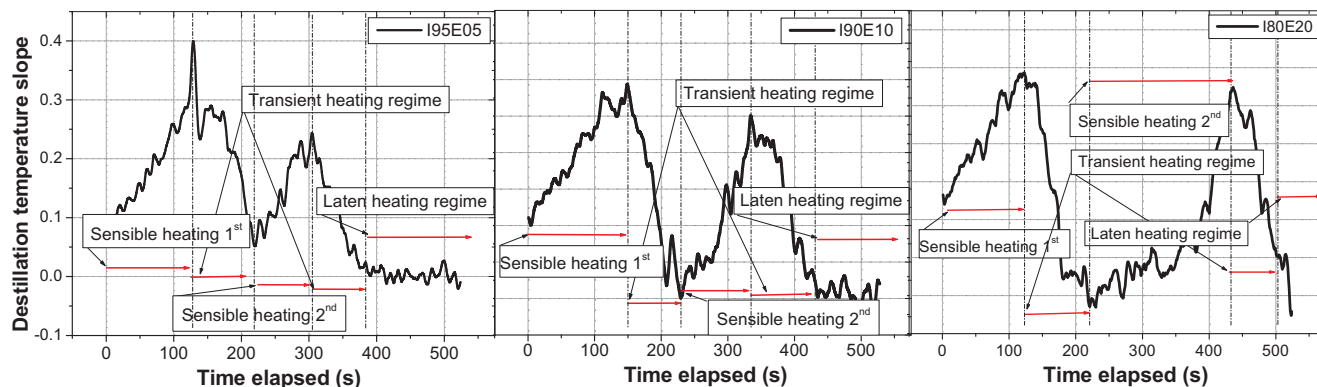


Fig. 4. Temperature distillation slope curve of 5%, 10%, and 20% v/v ethanol fraction.

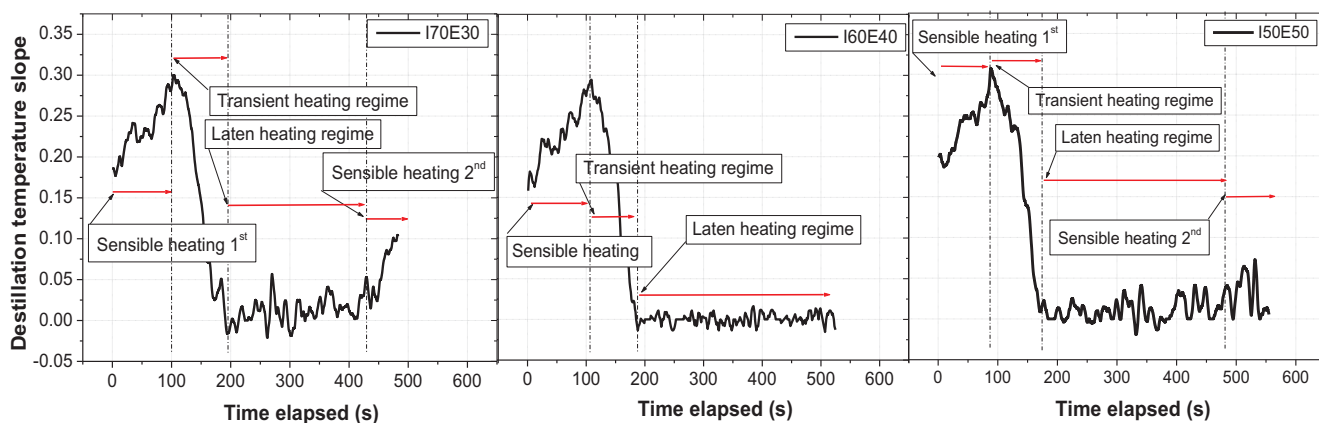


Fig. 5. Temperature distillation slope curve of 30%, 40%, and 50% v/v ethanol fraction.

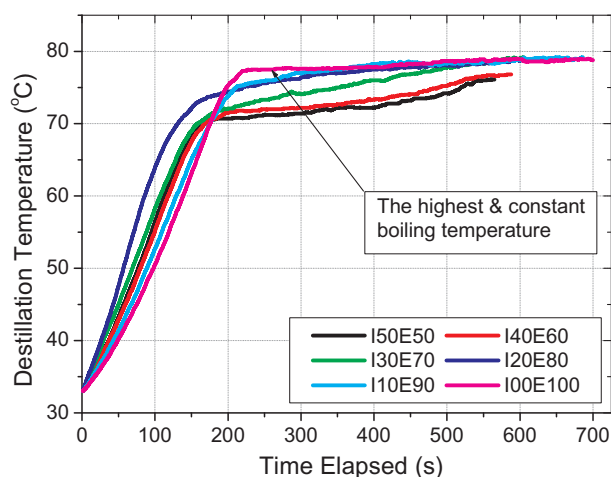


Fig. 6. Temperature distillation slope curve of 50%, 60%, 70%, 80%, 90%, and 100% v/v ethanol fraction.

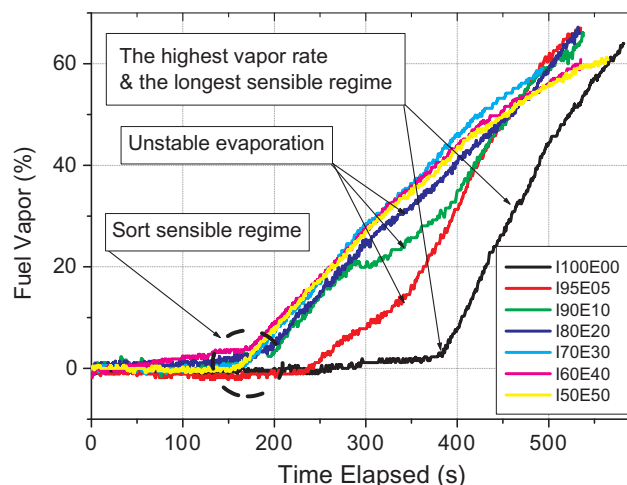


Fig. 7. Fuel vapor curve of 0%, 5%, 10%, 20%, 30%, 40% & 50% v/v ethanol fraction.

means a sensible heating process; the downward curve is a transition from sensible to latent heating; while the zero or horizontal curve around zero is a latent heating regime (boiling process). Fig. 4 also shows the incidence of two stages of the sensible heating, transient heating, and latent heating process during the distillation period of the fuel blend.

These facts (Fig. 4) indicate that the mixture of ethanol up to 20% is not constant boiling temperature (Zeotrope). While the rate of distillation temperature increases for the ethanol fraction mixture of 30%, 40%, and 50% shown in Fig. 5 exhibit azeotrope condition. This is due to the fact that they have low boiling temperatures and do not perform two stages of sensible heating. However, in the ethanol mixture fraction of 30% and 50% the heating process depart from latent to sensible heating at the end of the distillation.

As shown clearly at Fig. 5 only 40% ethanol blend fraction has only one sensible heating stage. So, it can be concluded that the mixed fraction of 40% v/v is the closest to the azeotrope conditions.

Distillation temperatures for high-grade ethanol fractions (50%,

60%, 70%, 80%, 90% & 100%) are presented in Fig. 6, which explains that a high concentration of ethanol blends is seen in the azeotrope effect phenomenon of all mixed fractions.

However, there is no evidence of a constant boiling temperature and increased boiling temperature of the mixture as the ethanol fraction increases. At this high concentration of ethanol boiling temperature does not constant though two boiling stages does not appear. There is seems a multi-stage boiling temperature (Fig. 6) so that the high concentration of ethanol mixture is not a constant boiling temperature blend.

From the distillation temperature curve of isooctane ethanol blend it is seen that the ethanol fraction of 40% v/v has low and most constant boiling temperature (Fig. 3), so it seems that this mixed fraction is an azeotrope condition. This fact is in line with the research of Jeuland (2004), which states that azeotrope mixture of two or more substances resulting in low and constant boiling temperatures [9]. However, the ethanol-isooctane mixture fraction above 40% v/v (high concentration)

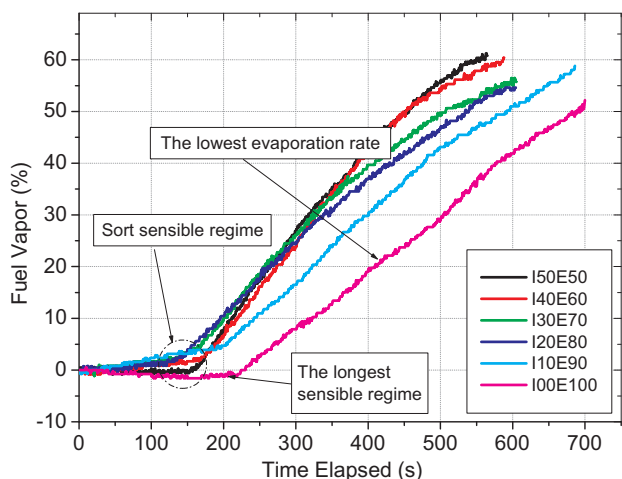


Fig. 8. Fuel vapor curve of 50%, 60%, 70%, 80%, 90% & 100% v/v ethanol fraction.

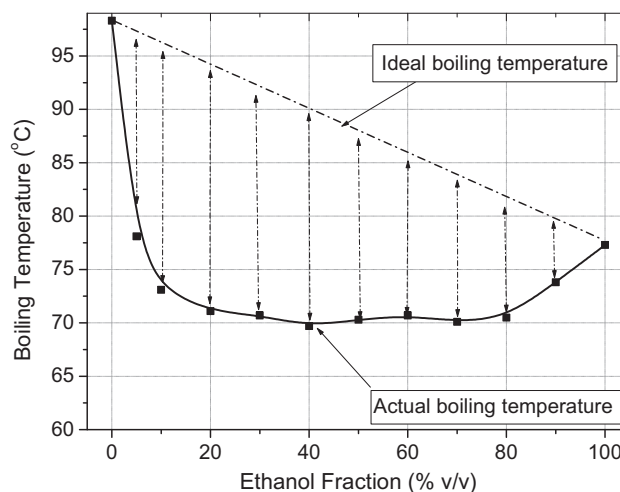


Fig. 10. Boiling temperature of various isooctane ethanol blended fractions.

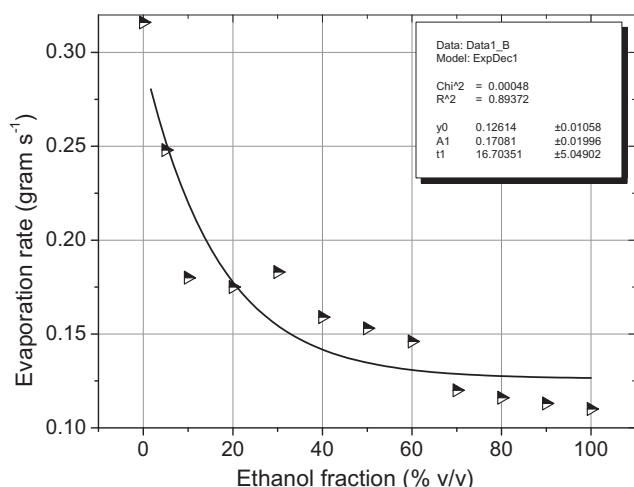


Fig. 9. Fuel evaporation rate at various ethanol fraction.

has a boiling temperature that tends to rise in proportion to the increase in the ethanol fraction.

3.2. The fuel vapor of isooctane ethanol blend

Evaporation occurs due to losing bonding between molecules interaction in a liquid. The bond strength between molecules of a liquid is determined by the type of molecular interaction bond. The fuel vapor curve of isooctane ethanol blend is grouped into poor and rich fraction ethanol mixture, i.e., 0–50% v/v and 50–100% v/v. The poor fraction ethanol is presented in Fig. 7 whereas the rich one is presented in Fig. 8.

Fig. 7 shows that pure iso-octane has the widest sensible heating regime and the highest evaporation rate because it is correlated with the boiling temperature and the evaporation enthalpy of the fuel mixture (Table 1). Addition of polar ethanol of 10%–50% v/v to non-polar isooctane shortens the sensible heating regime, but tends to decrease the rate of fuel evaporation. The unstable evaporation occurs at

addition of ethanol of 20% v/v, 30% and 50% v/v. The 40% ethanol blend fraction has the most stable evaporation during the distillation process. This condition corresponds to the distillation temperature curve (Fig. 5) that is the 40% ethanol blend fraction represents the most constant boiling temperature.

Fig. 8 shows that pure ethanol produces the lowest evaporation rate because ethanol has a high evaporation enthalpy 924.2 kJ kg^{-1} (Table 1) while that of isooctane is 308 kJ kg^{-1} . Fig. 8 also shows that the isooctane-ethanol blend shortens the sensible heating regime for all mixture fractions. The rate of evaporation for all these rich fractions blends also shows unstable evaporation. So, this corresponds to Fig. 6 which shows that the multi-stage boiling temperature occurs at concentration of high ethanol (rich).

From Figs. 7 and 8 it can be seen that the evaporation rate of the blend is directly proportional to the ethanol fraction. The evaporation rate of the fuel mixture is the average of the evaporation rate from the boiling point to the end of the distillation process. The fuel evaporation rate at various ethanol fractions is shown in Fig. 9.

Fig. 9 shows that the evaporation rate drops when isooctane is added ethanol up to a 20% v/v ethanol blend fraction. The evaporation rate decreases slightly gradually at high concentrations of ethanol above 40% v/v.

3.3. Boiling temperature of various isooctane ethanol blended fractions

The isooctane boiling point corresponding to water is presented at Eq. (3) [38].

$$T_{iso} = -16.0924 + 1.044559 \cdot T_w + 0.00108698 \cdot T_w^2 \quad (3)$$

T_{iso} and T_w are temperatures of isooctane and water, respectively under the same ambient conditions. Eq. (3) gives $T_{iso} = 99.2 \text{ }^\circ\text{C}$ while the test result is $98.5 \text{ }^\circ\text{C}$. Therefore, the accuracy of temperature measurement is 99.3%. The boiling temperature of various isooctane-ethanol blends is determined when there is a drastic change in the fuel vapor curve (Figs. 7 and 8). The boiling temperature of various isooctane ethanol blended fractions shown in Fig. 10. Blending of ethanol to isooctane up to 20% indicates a very significant effect of decreased boiling

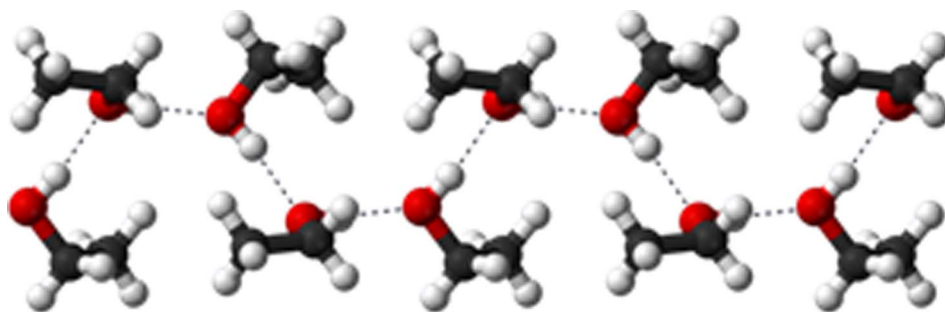


Fig. 11. The ethanol intermolecular hydrogen bond.

Table 2
Atom properties of ethanol.

	Type	Element	Valence	Formal charge	Partial charge
Atom 1	C3	C	4	0	-0.042
Atom 2	C3	C	4	0	0.041
Atom 3	HC	H	1	0	0.025
Atom 4	HC	H	1	0	0.025
Atom 5	HC	H	1	0	0.025
Atom 6	O3	O	2	0	-0.395
Atom 7	HC	H	1	0	0.550
Atom 8	HC	H	1	0	0.550
Atom 9	HO	H	1	0	0.209

Table 3
Atom properties of isooctane.

	Type	Element	Valence	Formal charge	Partial charge
Atom 1	C3	C	4	0	0.060
Atom 2	C3	C	4	0	-0.037
Atom 3	HC	H	1	0	0.023
Atom 4	CH	H	1	0	0.023
Atom 5	HC	H	1	0	0.023
Atom 6	C3	C	4	0	-0.046
Atom 7	C3	C	4	0	-0.046
Atom 8	HC	H	1	0	0.027
Atom 9	HC	H	1	0	0.027
Atom 10	C3	C	4	0	-0.063
Atom 11	HC	H	1	0	0.023
Atom 12	HC	H	1	0	0.023
Atom 13	HC	H	1	0	0.023
Atom 14	C3	C	4	0	-0.060
Atom 15	HC	H	1	0	0.023
Atom 16	HC	H	1	0	0.023
Atom 17	HC	H	1	0	0.023
Atom 18	C3	C	4	0	-0.060
Atom 19	HC	H	1	0	0.023
Atom 20	HC	H	1	0	0.023
Atom 21	HC	H	1	0	0.023
Atom 22	C3	C3	4	0	-0.063
Atom 23	HC	H	H	0	0.030
Atom 24	HC	H	H	0	0.023
Atom 25	HC	H	H	0	0.023
Atom 26	HC	H	H	0	0.023

temperatures. This fact is in line with the results of Oktavian et al. (2013) and Anderson et al. (2010) which show that the isooctane vapor pressure rises significantly with the addition of ethanol [2,36].

Fig. 10 illustrates Raoult's Law (Eq. (1)) invalidity for a polar

ethanol blend in non-polar isooctane. Fig. 10 also shows that the largest deviation of the ideal mixed temperature occurs in 10–20% v/v ethanol blend. This result is slightly offset by the findings of Andersen et al. (2010) about the vapor pressure of the mixture which states that the largest deviation occurs at a mixed concentration of about 50% [4]. However, this is harmonized with Chen & Stone (2014) who reported that the largest deviation of temperature drops when mixing ethanol in isooctane occurred in the ethanol fraction 15–20% v/v [35]. This deviation occurs because Andersen et al. (2010) use gasoline-ethanol blends. Nevertheless, Fig. 11 shows the lowest temperature occurring in the ethanol blend fraction of 40% v/v., while gasoline is a multi-substance liquid, so it has the wide boiling temperature.

3.4. The role of molecular interaction on boiling point of isooctane-ethanol blend

Molecular interactions are strongly influenced by the attractive or repulsive force between molecules. Ethanol is an ethyl group connected to a hydroxyl group, so it has a higher boiling temperature than ethyl. Ethanol molecule has nine pieces of atoms with partial charge is presented in Table 2. This partial charge was calculated using Avogadro software version 1.0.1. As shown in Table 2 the largest partial charge emerges in the hydrogen and oxygen atoms which is $\delta^+ = 0.209$ and $\delta^- = -0.395$ respectively. Therefore, this hydroxyl group causes ethanol to be polar which creates hydrogen bonds between molecules of ethanol as presented in Fig. 11.

The isooctane molecule has twenty-six atoms with partial charge spread evenly across the entire atom as shown in Table 3. Consequently, isooctane is a nonpolar group of long-chain hydrocarbons (2,2,4-Trimethylpentane) because it has a small partial charge difference in all atoms. High boiling temperatures of isooctane is due to its long chain (C_8) creating great van der Waal's force that attract each other molecules as illustrated in Fig. 12. However, Table 3 shows that isooctane has a large potential partial charge ($\delta^+ = 0.429$ and $\delta^- = -0.435$) derived from the sum of each positive and negative partial charge. This large potential partial charge could emerge when isooctane is strongly induced by molecules that have a great dipole moment.

Ethanol is one molecule that has a great dipole moment because it has an hydroxyl group (Table 2). However, charge of one ethanol molecule has not been able to induce all the partial distributions of the isooctane partial charge. Ethanol has only a partial charge of $\delta^+ = 0.209$ and $\delta^- = -0.395$ while the partial potential charge of isooctane is $\delta^+ = 0.429$ and $\delta^- = -0.435$. So, isooctane requires two molecules of ethanol to induce all their potential partial charges. Based on Table 1, the molecular weight of isooctane and ethanol are 114.23 and 46.07 g mol⁻¹ respectively. It means that the volume ratio of two molecules ethanol to one molecule isooctane is 41.48%. The modeling

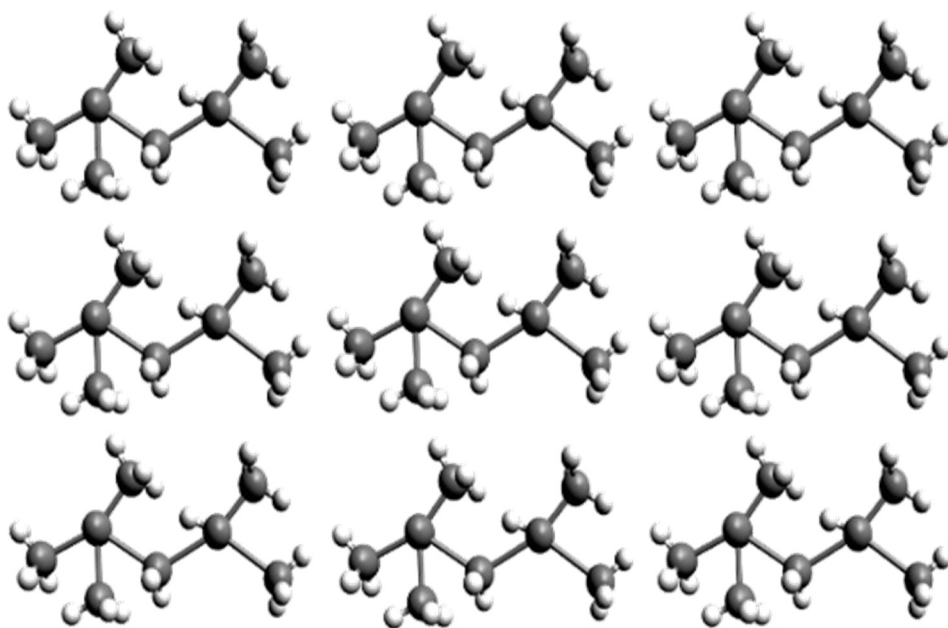


Fig. 12. The isooctane molecular interaction.

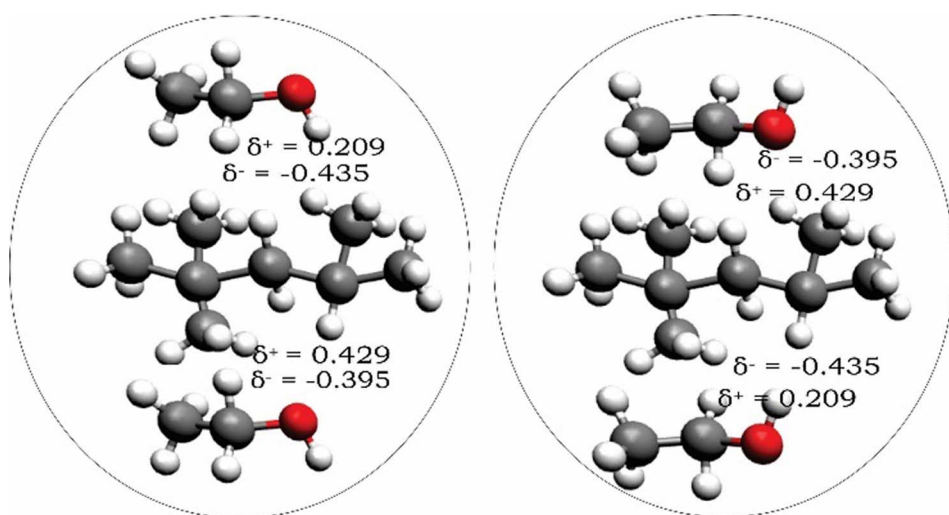


Fig. 13. The isooctane-ethanol cluster model for 41.48% v/v ethanol fraction.

of molecular fuel clusters in the ethanol blend fraction of 41.48% v/v is presented in Fig. 13.

The modeling of molecular fuel clusters in Fig. 13 notifies that the fraction of ethanol mixture of 40% v/v in this experiment is still in the condition of the (near) azeotrope. The isooctane-ethanol molecular stack model for 41.48% v/v ethanol fraction is shown in Fig. 14.

The formation of the molecular clusters of the isooctane-ethanol blend at 41.48% v/v shown in Fig. 14 breaks the hydrogen bond between molecules of ethanol and separates the van der Waal's force between isooctane molecules. Consequently, the fuel mixture has a low and constant boiling temperature. For ethanol and gasoline blended applications, a more detailed molecular interaction analysis between ethanol and all the gasoline compounds is required.

4. Conclusions

A simple distillation method was used in this study to determine the temperature curve of various distillation fractions of the isooctane-ethanol blend. The load-cell sensor successfully records the weight reduction of the fuel mixture during the heating process. Molecular analysis was used to verify the predicted azeotrope mixture of isooctane-ethanol. The results showed that the dipole induction of two molecules of ethanol transformed a non-polar isooctane molecule into a polar molecule. These two molecules of ethanol and an induced isooctane molecule bind very strongly in a cluster of molecules so that it becomes like a single substance. This study yielded important findings that the isooctane-ethanol azeotrope mixture occurred in the ethanol

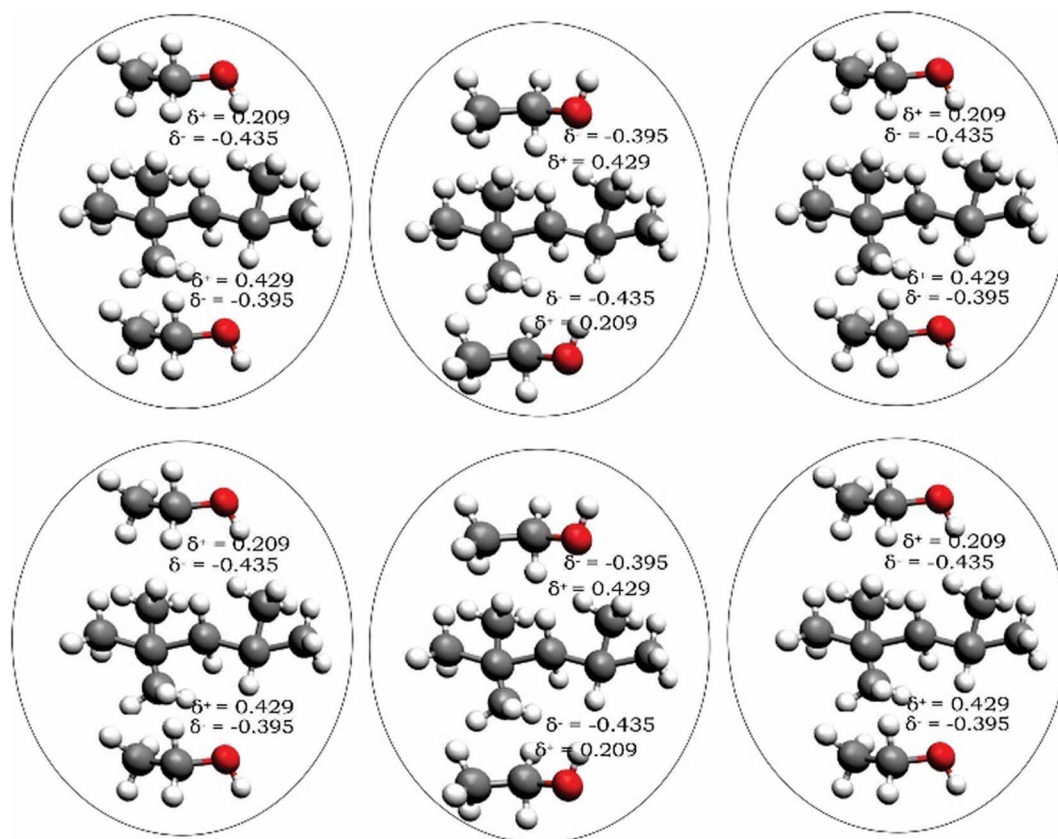


Fig. 14. The isooctane-ethanol molecular stack model for 41.48% v/v ethanol fraction.

fraction 41.48% v/v. This finding is very useful to be applied to SI Engine to produce more stable and consistent combustion as well as improved performance of alternative fuels.

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