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# 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 ($C_4$–$C_{12}$) 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 | $C_8H_{18}$ | $C_2H_5OH$ |
| 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 | 0.789–0792 |
| 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 ($C_8H_{18}$) 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 ($cm^3$) 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

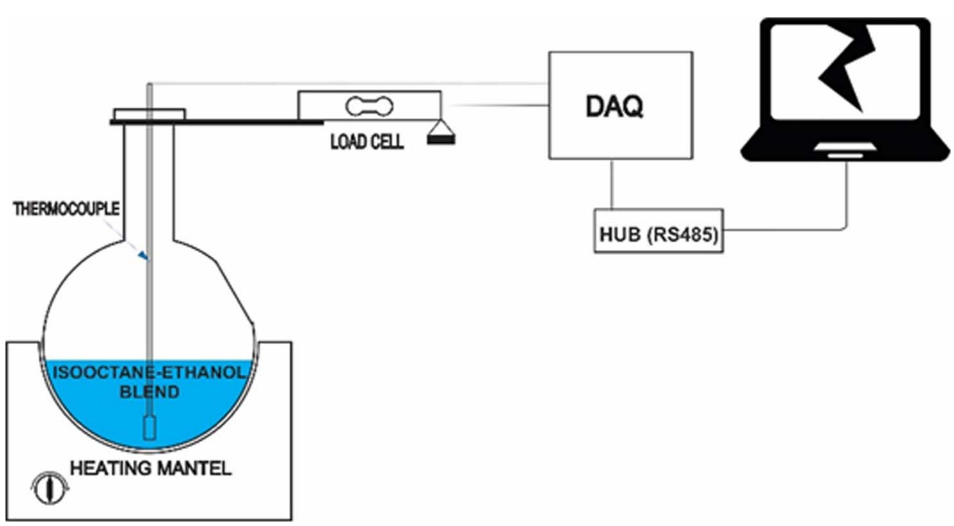


**Fig. 1.** The experiment setup.