Experimental Investigation on Physicochemical Properties of Iso-Butanol Additive in Methanol-Gasoline Blends

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ABSTRACT

Alcohol fuels such as methanol are popular as an alternative fuel for internal combustion engine because of its economic and environmental advantages over fossil fuel. Blended methanol-gasoline fuels can be improved further by adding higher carbon number such as iso-butanol as they have higher energy content and are able to displace more gasoline fuel. However, the research on the addition of lower ratio iso-butanol in methanol-gasoline fuel properties is not investigated thoroughly. Therefore, this study will focus on investigating the physical and chemical properties of iso-butanol additive in methanol-gasoline blends. Different methanol-gasoline fuel blends were obtained with the addition of 5 vol%, 10 vol%, and 15 vol% iso-butanol into a lower ratio of 5 vol% methanol-gasoline blended fuel. The blended fuel properties determined are density, kinematic viscosity, lower heating value, latent heat of vaporization and Reid of vapour pressure. Characterization of the blends with iso-butanol additive was tested according to specific test standards. From the test results, improvement was recorded at density, kinematic viscosity, and latent heat of vaporization for iso-butanol additive of 5%, 10%, and 15% with 5% of the methanol-gasoline fuel blends. On the other hand, a reduction was recorded for both lower heating value and Reid vapour pressure for all blended fuels with iso-butanol additive in comparison to that of base fuel. No phase separation occurred and the blends were

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successfully blended in lower ratio volume at specific temperatures. Overall, a lower ratio of the iso-butanol additive on methanol-gasoline blends was found to improve the current existing methanol-gasoline blends.

Keywords: *Methanol, Iso-Butanol, Spark Ignition Engine, Fuel Properties*

Introduction

Interest in alternative energy sources for transportation sector has increased rapidly nowadays due to continuous energy demands and depletion of fossil fuel sources. Petroleum oil, natural gas, and coal are the examples of fossil fuel that has dominated world energy economy by taking more than 80% of the total supply of the primary energy, where about 58% are consumed by the transport sector [1, 2]. The search of alternative sources for transportation fuels has increased due to the rise of the transportation vehicle density and fuel requirement. Therefore, alternative fuels have received significant attention from the public recently due to its renewable resources, adaptation on the current transportation system and requirement of minimal modification on the fuel system.

Alcohol is considered as an alternative fuel for internal combustion engines and it has been investigated comprehensively [3-5]. Adding alcohol into gasoline or diesel allows the fuel to have a complete combustion with the presence of oxygen, which increases its combustion efficiency and reduces greenhouse gas emission [6]. Moreover, its ability to be produced from renewable resources and give better engine performance with clear emission has attracted many interests on the market [7, 8]. One of the attractive alcohol fuels for transportation sector is methanol fuels due to its abundances, as well as attractive physical and chemical properties. The presence of oxygen in methanol fuel allows soot-free combustion with a low particulate level [7]. Methanol also has a high octane number, which can reduce engine knocking. Methanol has high heat vaporization that offers fuel conversion efficiency, which cools the air entering into the engine and increases the volumetric efficiency with the power output compared to gasoline [8]. In terms of the application on internal combustion engine, methanol can be applied with little modification for material compatibility and has better engine performance compared to gasoline [9]. Besides application in engine, methanol has also been used as conversion to dimethyl ether, ingredient for biodiesel production and hydrogen for the fuel cell vehicles [10].

Some studies have been done by previous researchers regarding alcohol-gasoline blends on engine operation and exhaust emissions [11-13]. Cay *et al.* [11] theoretically investigated the effects of methanol fuel on the performance of engine and exhaust emissions. The results showed that the

CO and HC emission characteristics improved with the use of methanol compared to gasoline. This is due to the high evaporation heat of methanol when it entered engine cylinders, which significantly reduces the CO and HC emissions compared to gasoline. Altun *et al.* [12] showed that usages of methanol blends will also consume a large amount of fuel due to the stoichiometric air/fuel ratio and lower heating value to supply the same amount of energy from gasoline fuel. Methanol fuel blends with 5% and 10% are able to improve combustion and reduce unburned hydrocarbon (HC) emissions by 6.7% and 13% when compared with base gasoline [12]. An investigation carried out by Agarwal *et al.* [13] applied 10% and 20% methanol blended with gasoline in spark ignition transportation engine and the results were further compared with baseline gasoline. The results showed only minor difference in cylinder pressure and heat release rate started late for gasohol blends with peaks of heat release rate wider compared to those for gasoline. This can be explained as gasoline has numerous hydrocarbons with different boiling points, while methanol contains a single boiling point with one hydrocarbon. Moreover, methanol has oxygen in its molecular structure.

Iso-butanol has also received attention from other engine researchers who studied the performance of spark ignition engine [14, 15]. Butanol-gasoline blend of 30% butanol contents was used to measure the engine efficiency by using single-cylinder engine [14]. The results obtained implied that about 7% decrease in power was recorded when compared to the same engine fuelled with pure gasoline. The results also showed reductions in exhaust temperature and thermal efficiency compared to those with pure gasoline. Lower heating value of iso-butanol had been assumed to be the main reason for the reductions to occur. Another research done by Li *et al.* [16] showed that iso-butanol-gasoline blends were able to be blended at every ratio volume and no separation occurred in the blends. Besides that, the results also showed that lower heating value of iso-butanol slightly decreased with 33.5 MJ/kg compared to gasoline with 44.3 MJ/kg as the volume ratio of iso-butanol increased in the blends [16]. This is attributed to iso-butanol as it is an oxygenated fuel with lower stoichiometric air-fuel ratio; thus, it has the ability to give leaner combustion.

Using alcohol fuel as an alternative for spark ignition engines has started to be widely accepted as blended fuel with gasoline. However, certain properties of lower molecular weight alcohol, especially methanol fuel has made it less desirable as an alternative for gasoline fuel. One of the negative effects related to the use of methanol fuel is the lower heating value. Lower heating values of methanol are lower than gasoline, both on mass and volume basis. Therefore, this property shows that the engine will need more amount of fuel when methanol blends are used to produce the same power output in a gasoline-fuelled engine. Besides that, methanol fuel also has higher oxides of nitrogen (NO_x) and carbon dioxide (CO_2) emissions due to higher combustion temperature and complete combustion of the fuel. If the current application still insists in using methanol fuel as an alternative fuel to the gasoline fuel, a few problems such as higher fuel consumption and exhaust emissions will occur, which are still unsolved and remain a problem to the user. The initial problem of using methanol fuel can be overcome by using several methods. One of the suggested methods is by applying iso-butanol additive into the methanol–gasoline fuel blends that will eventually overcome the problems that have been mentioned before. However, not much research has been made on considering blending methanol and iso-butanol with gasoline at a specific percentage and the effect on the fuel properties. Therefore, this research will be directly focused on improving existing alternative fuel which is methanol-gasoline blends by adding an additive such as iso-butanol. By using standards and codes, the density, kinematic viscosity, lower heating value, latent heat of vaporization and Reid of vapour pressure were determined.

Material and Method

Material preparation and method of blends

Methanol and iso-butanol are obtained from the local supplier company in Selangor, Malaysia. Meanwhile, base fuel with an octane number of 95 (RON 95) is obtained from commercial fuel supplier that is available in a petrol station. Moreover, test matrix was prepared and it consisted a total of five test samples of fuel blends which were used for the fuel properties testing as presented in Table 1. These blended fuels were prepared through blending method based on volume percentages basis and mechanical mixing. For example, the blending of 5% methanol and 15% iso-butanol with 80% of the base fuel was mixed together using a shaker machine. The mixture was stirred continuously for 15 minutes at room temperature and left for another 15 minutes to reach equilibrium at room temperature before it was used for engine testing as per recommended by previous researchers [17, 18].

Table 1: Test matrix for gasoline and alcohol-gasoline blended fuel

Test Pattern	Description			Remarks
	Methanol	Iso-Butanol	Base fuel(RON95)	
Test 1	-	-	100% -> 1000ml	Base Fuel
Test 2	5% -> 50ml	-	95% -> 950ml	M5
Test 3	5% -> 50ml	5% -> 50ml	90% -> 900ml	M5B5
Test 4	5% -> 50ml	10% -> 100ml	85% -> 850ml	M5B10
Test 5	5% -> 50ml	15% -> 150ml	80% -> 800ml	M5B15

Measurement of fuel properties

In order to understand the alcohol-gasoline blends responses, the blended fuels properties need to be analyzed as it is a critical factor for consumer fulfillment, engine requirement, and industry standards. In order to have a consistent composition and quality as well as reliable engine operation, the properties of alcohol fuel must have its limit values which directly follow the available standards (EN 228). As shown in Table 2, the properties of base fuel, pure methanol, and iso-butanol are presented and it is important before presenting any results related to the additive usage.

Table 2: Properties of base fuel and blend alcohol–gasoline fuel

Property	Unit	Base fuel	Methanol	Iso-butanol
Density@ 15°C	g/cm³	0.749	0.795	0.811
Kinematic viscosity	mm²/s	0.511	0.698	4.576
Lower heating value	MJ/kg	43.92	20.10	35.69
Latent Heat of Vaporization	kJ/kg	349.00	1042.00	683.00
Reid Vapour pressure@ 37.8°C	kPa	62.77	21.10	6.60

For this study, the measurement of fuel properties that had been made are density, kinematic viscosity, lower heating value, latent heat of vaporization, and Reid of vapour pressure. All these measurements are conducted using a different set of equipment and standards as shown in Table 3 by following the test matrix in Table 1. In order to obtain an accurate data, calibration on the equipment has been done by the company before conducting the experiments. For each collected data, a set of 5 experiment results for every test was averaged.

Table 3: Set of equipment used for fuel testing properties

Properties	Test standard	Equipment	Manufacturer
Density @ 15°C	ASTM D4052	StabingerViscometer™ SVM 3000	Anton Paar's, Austria
Kinematic viscosity	ASTM D7042	StabingerViscometer™ SVM 3000	Anton Paar's, Austria
Lower heating value	ASTM D240	C200 bomb calorimeter	IKA, UK
Latent Heat of Vaporization	(N/A)	Differential scanning calorimetry	METTLER TOLEDO, UK
Reid vapour pressure @ 37.8 °C	ASTM D5191	Setavap 2 vapor pressure tester	Paragon Scientific Ltd, UK

Result and Discussion

This section presents the results of fuel properties analyses for base fuel and alcohol-gasoline blended fuel which were used for engine testing. The fuel properties provided a better understanding on the effect of the alcohol additive in the fuel and subsequently the effect on both engine performance and exhaust emission. Iso-butanol has a 4-carbon structure and it is a more complex alcohol than methanol as it only has 1-carbon structure, as given in Figure 1. The intersolubility of the iso-butanol is higher where it can blend easier with the gasoline fuel compared to methanol. This is because alcohol molecules contain alkyl and hydroxyl. The more carbon an alcohol molecule contains; the easier the alcohol can be blended into gasoline fuel [19].

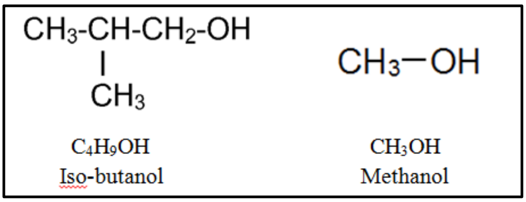

Figure 1: Iso-butanol and methanol chemical composition

Investigations on the effect of fuel properties from the alcohol additive on base fuel are performed in order to identify the characteristics of each fuel properties. The tested properties were density, kinematic viscosity, lower heating value, latent heat of vaporization, and Reid of vapour pressure. One of the alcohol additives that were used on base fuel was methanol (5%) and it was added to iso-butanol at 5%, 10%, and 15% each by volume percentage. The measurements of all fuel properties were taken based on ASTM standard methods in order to gather accurate and consistent results.

Density

Fuel density has an important effect on engine performance [20]. Generally, engine combustion characteristics and fuel efficiency of fuel atomization are affected by fuel density [21]. As shown in Figure 2, the density range was from 0.7488-0.7602 g/cm^3 for base fuel and alcohol-gasoline blends (M5, M5B5, M5B10, and M5B15). The trend of density kept increasing from base fuel until M5B15 of blended fuel with the maximum value of 0.7603g/cm^3. Furthermore, in comparison, the density between base fuel and M5B15 differed slightly by about 1.50%. It is observed that by adding alcohol into the base fuel, it will increase the density. This can be related to alcohol density is higher than base fuel and density is increasing for higher carbon number alcohol such as iso-butanol. Thus, it can explain the increase in the density of the blended fuel due to the rise of the alcohol content in the blended mixture. For engine operation, the fuel density will affect the calculating quantity and assessing ignition quality [16, 20]. Choosing an acceptable range of density for an engine operation is necessary especially in designing inlet fuel system, as well as in determining suitable flowrates of vehicle for various components in the vehicle [24].

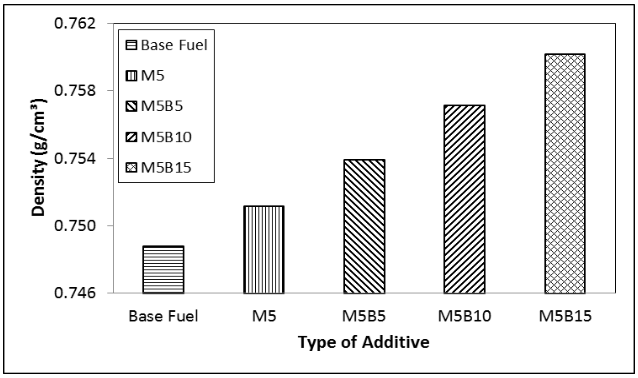

Figure 2: Effect of alcohol additives on fuel density

Kinematic viscosity

Viscosity is one of the important properties because it affects the behavior of fuel injection after an accurate amount of fuel is needed for injection [22]. Figure 3 shows the effect of iso-butanol on methanol-gasoline blends on the kinematic viscosity of the test fuel. The viscosity of base fuel and blended fuel (M5, M5B5, M5B10, and M5B15) varies in the range of 0.5103-0.6707 mm^2/s. In general, the viscosity of the blend increases with the increasing amount of iso-butanol additive in the methanol-gasoline blend. The trend of viscosity kept increasing from the base fuel until M5B15 of blended fuel with the maximum value of 0.6707 mm^2/s. The viscosity of M5B15 blend was 0.6707 mm^2/s, which is higher than that base fuel by 24.5%. The addition of iso-butanol increased the viscosity due to the longest carbon chain length possessed by iso-butanol as compared to the methanol, which is the shortest carbon chain length, as shown in Figure 1. This means that higher molecular weight alcohol, which is iso-butanol, has higher viscosity as compared to lower molecular weight alcohol, which is methanol.

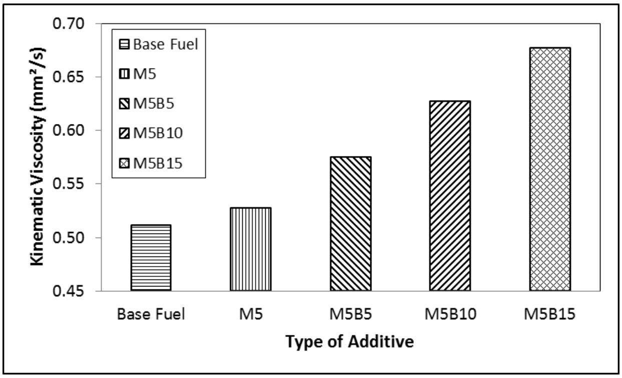

Figure 3: Effect of alcohol additives on fuel viscosity

Fuel viscosity will affect the behaviour of the fuel injection as an accurate amount of fuel is needed for injection [100]. Moreover, higher viscosity leads to degradation of fuel atomization. This will reduce the vaporization process and the injection spray angle will become smaller [23-25]. Subsequently, all these effects will increase the oil dilution and result in overall poorer combustion. This is in agreement with previous researches that also demonstrated the fuel with high kinematic viscosity caused poor atomization during fuel spraying and further resulted in engine deposits, as well as wear on the fuel system, where more energy was required to deliver fuel into engine [26, 27].

Lower heating value

The lower heating values (LHV) are known as a direct measurement of the energy content of a fuel and it is determined in terms of the quantity of heat liberated by the combustion of a unit quantity of fuel with oxygen in a standard bomb calorimeter [19, 28]. Figure 4 shows the lower heating value for base fuel and alcohol-gasoline blends. This figure shows that as the alcohol additive is increased, the lower heating value of the fuel is decreased. The maximum difference is about 5.84% at 15% of iso-butanol additive in methanol-gasoline blends compared to base fuel. This can be attributed to the pure alcohol fuels that possess lower LHV than the base fuel. In terms of relative composition of the fuel, the lower heating value for alcohol fuels rises as the carbon atom number is increased in the blends. For instance, methanol with one carbon atom has lower heating value with 20.10 MJ/kg than gasoline with 43.92 MJ/kg. In other words, the increase in carbon and hydrogen contents is related to the increase in molecular weight of alcohol fuels.

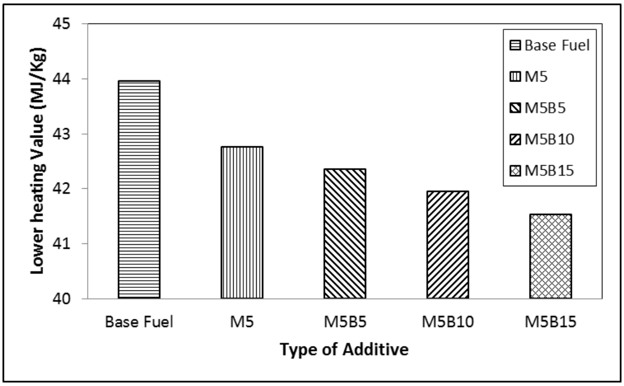

Figure 4: Effect of alcohol additives on fuel lower heating value

The lower heating value of the alcohol fuels also increases fuel consumption and reduces fuel economy. This can be explained as the usage of alcohols in spark ignition engine has twice fuel usage as compared to gasoline in order to achieve a similar heat energy output. These results are in agreement with previous studies [4, 13]. Thus, in order to overcome this situation, a few researches have suggested using alcohols with four or more carbon atoms so as to reduce fuel consumption as well as to obtain better mileage [29, 30]. This is because lower heating value of alcohol with four or more carbon atoms is closer to that of gasoline.

Latent heat of vaporization

Latent heat of vaporization is another critical factor influencing in-cylinder mixture preparation in engines. Heat of vaporization results in a temperature reduction inside the engine intake system for port fuel injection and in-cylinder for direct-injection engines since energy taken from the intake air is required to evaporate the fuel. Increased heat of vaporization is desirable particularly for direct injection engines because it can significantly reduce in-cylinder process temperatures; thus, reducing NOx emissions formation as well as knock propensity. As shown in Figure 5, the latent heat of vaporization for base fuel and alcohol-gasoline blends (M5, M5B5, M5B10, and M5B15) ranged from 349.0-440.55 kJ/kg. The figure also shows that the addition of iso-butanol into the methanol-gasoline fuels increased the latent heat of vaporization of the blended fuel. The latent heat of vaporization for M5B15 blend was 440.55 kJ/kg, which is higher than that of base fuel by about 20.7%. The results obtained can be explained from the significant difference in the chain length of alcohols. For instance, the energy needed to evaporate 1 kg of methanol is 1042 kJ, which is almost double of iso-butanol with 683 kJ. This is comparable to latent heat of vaporization for base fuel with only 349 kJ/kg.

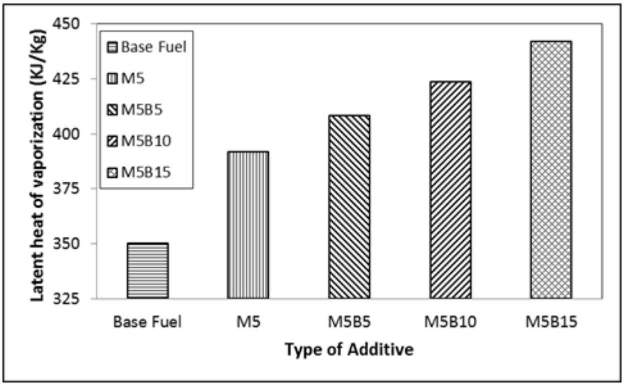

Figure 5: Effect of alcohol additives on fuel latent heat of vaporization

Furthermore, with higher latent heat of vaporization, it would be easier for alcohol fuels to vaporize in the compression stroke. This happens because as the fuel absorbs heat from the cylinder during vaporization, the air-fuel mixture is compressed more easily; thus, improving thermal efficiency for alcohol-gasoline blend than that of gasoline [31]. This result is in agreement with a previous study [32] which explains that methanol burns more efficiently under lean conditions than gasoline, besides being able to cool the air entering the engine. Thus, the volumetric efficiency is increased with power output due to its higher latent heat of evaporation.

Reid of vapour pressure

Reid vapour pressure (RVP) is a measurement to determine the ability of fuel to evaporate as it will contribute more to ozone layer which will affect the surrounding environment. Figure 6 shows the Reid vapour pressure for base fuel and alcohol-gasoline blends. The vapour pressure for base fuel is 62.77 kPa. As 5% of methanol was added, the vapour pressure increased by 10.82% to 78 kPa. However, as iso-butanol ratio increased from 5% to 15% (refer to M5B5, M5B10 and M5B15), the pressure decreased to 68.57 kPa. Therefore, it is clear that as iso-butanol additive increases, the vapour pressure of the fuels decreases. The vapour pressure of M5B15 fuel blends was still higher than that of base fuel with 8.6% difference.

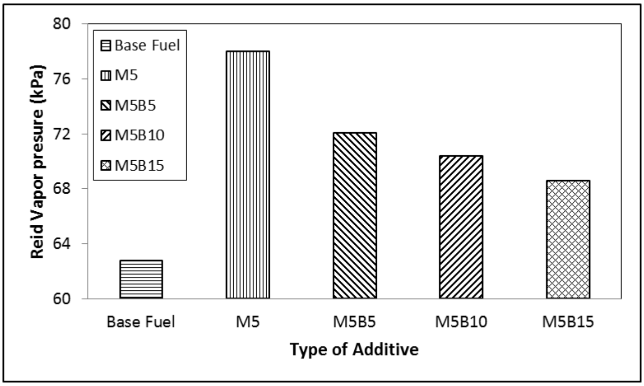

Figure 6: Effect of alcohol additives on fuel Reid vapour pressure

The volatility of alcohol fuels is decreased with the increase in carbon atom number. This means that alcohols with more than four carbon atoms have fewer tendencies on vapour lock and cavitation issues. Thus, the fuels must be adequately volatile for easier engine start and sufficient vaporization for fuel distribution between the cylinders. Vapour pressure indicates the fuel quality during engine starting and vapour lock tendency were due to absence of fuel injection, such as carburetted engines [33, 34]. Moreover, vapour pressure is an important factor in achieving the requirements of the evaporative emissions. In fact, a research conducted by Pumphrey *et al.* [35] deduced that the vapour pressure of gasoline initially increased with the addition of the alcohols, then the value began to decrease as the proportion of alcohol was increased. The total elevation and the composition of the peak affected the characteristic of the additive where it influenced engine performance and also had an impact on environment.

Conclusion

This work experimentally assessed on physicochemical properties of methanol-gasoline blends when added with iso-butanol additive at lower ratios. The measured fuel properties are density, kinematic viscosity, lower heating value, latent heat of vaporization and Reid vapour pressure. Iso-butanol additives at low ratios (5-15%) with 5% increment were used to improve the fuel properties and reduce the effect of blending on methanol-gasoline blends. Besides that, all the values obtained by the addition of alcohol (iso-butanol and methanol) into base fuel are still within the range of the standards specified (EN228). From the results revealed, significant improvement was recorded on the characteristics of fuel due to the unique properties of the alcohol additives. The density value of methanol-gasoline blends improved with the addition of iso-butanol. Improvement recorded in density of the blends was due to higher carbon atom number in alcohol (methanol and iso-butanol) than base fuel. As for kinematic viscosity, an increasing value was recorded from the base fuel until 15% additive of iso-butanol in methanol-gasoline blends. It shows that the addition of alcohol in base fuel increased its viscosity. Other than that, a significant decrease in the heating value was recorded with the increasing addition of alcohol for both methanol and iso-butanol in the base fuel. The addition of iso-butanol additives also gives moderate improvement in the latent heat of vaporization for the methanol-gasoline blends with the increasing additive ratio. However, the vapour pressure shows a decreasing trend with the addition of iso-butanol additive in methanol-gasoline blends. Based on all the obtained results, iso-butanol additive of up to 15% by volume in the methanol-gasoline blend is recommended as it improves the characterization of the fuel compared to methanol-gasoline blends and it gives better engine operation. Further research is required on feasibility and investigation on recommended alcohol additive in commercial available SI engine. More research is also required on the production of higher alcohols contents from renewable sources available in Malaysia.

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