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Research Article

Glycerol Monostearate and Distilled Cashew Nut Shell Liquid as Additives for Diesohol

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Abstract

This research involved the phase stability and fuel properties of the mixture of diesel and ethanol with GMS (glycerol monostearate) and distilled Cashew Nut Shell Liquid (DT-CNSL). The viscosity, acid value, oxidation stability and cetane index were measured in order to compare with diesel standards. Diesel engine performance and exhaust emission were investigated in terms of brake power of diesel engine, brake specific fuel consumption and exhaust gas temperature. Phase stability of diesel and ethanol blend was observed that a minimum threshold limit of 1.2 wt.% of GMS provided a homogeneous mixture. The most promising fuel blend was 85% of diesel and 15% of ethanol with 1.2 wt.% GMS and 1 vol.% DT-CNSL (DE15G1.2DT-C1). The inductive period of the fuel blends decreased with increasing concentration of DT-CNSL due to its antioxidant characteristics. As for the performance of diesel engine, at the speed of 1,500 rpm, the fuel blend has higher brake specific fuel consumption than diesel. On the other hand, the properties of fuel blend have similar the brake power of engine and exhaust gas temperature to pure diesel.

Keywords: GMS, Ethanol, Diesohol, DT-CNSL, Engine performance

Introduction

In Thailand, alternative energy sources such as ethanol, biodiesel, solar energy are undergoing intense research to reduce the amount of imported oil and strive for energy independence. A mixture between diesel and ethanol, so-called diesohol, is the one of the alternative fuels used for public transportation in Australia, USA, Denmark, and Netherlands to reduce fossil fuel consumption and harmful emissions. Blends of ethanol and diesel exhibit phase instability due to the polarity difference. Therefore, an emulsifier is generally required to stabilize the mixture. Biodiesel has been used as an emulsifier for diesohol blend, amongst many emulsifiers such as alkanols, decaglycerol mono-oleate (MO750), and alkanolamides (Fernando and Hanna, 2004). Kwanchareon et al., (2007) reported that diesohol blends containing 80 vol.% diesel, 15 vol.% biodiesel, and 5 vol.% ethanol has similar properties to that of diesel fuel. Span80 and isopropanol have been used as emulsifying agents to resolve the incompatibility between diesel and ethanol (Can et al., 2004; Cheenkachorn and Fungtammasan, 2009). Diesel engine performance has been studied in order to verify the efficiency of the fuel blends. Ali et al., (2015) studied the engine performance for the fuel blend (30% of ethanol blend with diesel and 6% of ethyl ether). It was found that the use of diesohol could lead to a slightly lower engine efficiency (4-12%) compared to the case of pure diesel due to the low calorific value of fuel blend. Praptijanto et al., (2015) investigated the effect of ethanol percentage on the brake power of diesel engine, using span 80 as emulsifier. It was found that conventional diesel exhibited a higher brake power of the engine than that of fuel blend with 2.5%-10 % ethanol, at the speed faster than 1400 rpm. This is due to the fact that ethanol has low cetane number.

The disadvantage of commercial emulsifier is the high cost because the high-quality emulsifiers are required to import from other contries (Reyes, Y., et. al. 2019) A fuel blend of 10 vol.% biodiesel in 80 vol.% diesel and 10 vol.% ethanol was stable for at least 96 hours (Park et al., 2009). However, biodiesel has a tendency to react with oxidation during storage. Oxidation degradation can lead to the formation of acids and insoluble sediments that deposit on fuel injectors (Pullen and Saeed, 2012). GMS has the glycerol head group (polar part) and the fatty acid chain (Non-polar part). Glycerol monostearate (GMS) is a non-toxic emulsifier. It has a broad range of applications such as emulsifier in food, pharmaceuticals, cosmetics, and detergents (Yu et al., 2003). GMS has a hydrophilic-lipophilic balance (HLB) of approximately 3.2, which is within the range of water-in-oil emulsions (Euston et al., 1996). GMS was used as emulsifier to prevent the separation between biodiesel and tert-butylhydroquinone (TBHQ) which is the antioxidant. It was observed that the the acid value and the iodine value of biodiesel met the standard when mix 100 ppm of GMS with TBHQ (Sutanto, H. et.al. 2018). To alleviate the problem of the unsaturated hydrocarbons, a certain amount of antioxidant can be added to the blend. Common antioxidants are phenolic compounds containing highly labile hydrogen which delays the start of the lipid oxidation reaction (Yu et al., 2003). A natural antioxidant extractable from the cashew nut industry is cardanol (Euston et al., 1996). Cardanol is a phenolic lipid and can be obtained via chemical conversion of anacardic acid, the main constituent of the oil trapped inside the cashew nut shells (cashew nut shell liquid, CNSL) (Sanjeeva et al., 2014). When heated, anacardic acid is decarboxylated to produce DT-CNSL which contains cardanol as the main component. Kubo et al., (2006) found that when cardanol was added to linoleic acid the occurrence of free radicals was reduced by 30%. The molecular structure of cardanol has both non-polar (lipophilic) and polar (hydrophilic) ends; typical characteristics for an emulsifying agent. Therefore, it is plausible that cardanol can be used to blend with diesel and ethanol to inhibit oxidation. Amongst many different surfactants, GMS/DT-CNSL have never been applied as emulsifier for diesohol. Therefore, this work dealt with the investigation on phase stability and oxidation stability of the modified diesohol by using GMS/DT-CNSL as emulsifier. Measurements of the physical and chemical properties were compared with the standards of diesel. Moreover, the effect of fuel blend on diesel engine performance in terms of brake power of the engine and brake specific fuel consumption (BSFC) was investigated and compared with the literature data.

Materials and methods

1. Materials

The cashew nut shells and diesel used in the experiments were supplied by Methee Phuket Company Limited and Bangchak Petroleum Public Company Limited. The anhydrous ethanol (99.9% purity) was supplied from MERCK.

2. Extraction of DT-CNSL

Prior to extraction of oil, the cashew nut shells (CNSL) were washed with water and dried at 80 ºC for 12 h. The shells were ground to small particles using a SK-1 model, cross-beater mill, and these were subsequently dissolved in ethanol with the ratio of 150 g CNSL: 1 L EtOH. This ratio of extraction was published in the previous research of Bangjang, et al. (2016). The solution mixture was continuously stirred at room temperature for 1 h. The mixture was then filtrated using a vacuum filter, and the filtrate containing the extracted compounds was subjected to vacuum evaporation at 180 ºC for 2 h to remove the ethanol. The extracted compound obtained was distilled technical CNSL (DT-CNSL).

3. Fuel blending

The samples of mixed fuel obtained from the different blending formulas were categorized (coded) primarily by the content of diesel (D), ethanol (E), DT-CNSL (DT-C), and GMS (G). For instance, D70E30 describes the condition that the volume ratio between diesel and ethanol is 70:30. The concentration of GMS was added to diesohol blend as weight percent of the volume of the mixture. A certain amount of GMS was mixed with diesel and ethanol using a vortex mixer for 3 minutes at room temperature. Subsequently, DT-CNSL was added to the homogeneous mixture. The solution was agitated vigorously for 10 min by vortex mixer. The samples were collected and stored in the dark. Three samples were prepared from each blending formulae, as shown in Table 3.

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4. Properties of the fuel blends

4.1 Viscosity and acid value

The viscosity and acid value were measured by Ostwald viscometer and the standard titration method according to ISO 3104.

4.2 Cetane Index

The density and mid-boiling point were used to estimate the cetane index according to ASTM D976.

4.3 Oxidation stability measurement

The oxidation stability of the fuel blends was studied according to the Rancimat method (EN 14112) for biodiesel and a modified Rancimat method (EN 15751) for the biodiesel blends. Three grams of sample was kept at a constant temperature of 110 ^{o}C, with an air flow rate of 10 L/h. The oxidation products were transferred into the distilled water in the measuring vessel by the flow of air bubbling through the sample. The conductivity of the distilled water was continuously monitored by a conductivity meter.

5. Engine performance test

The engine used in this study was a TF 90 DI-L YANMAR diesel generator. Specifications of the engine are shown in Table 1. Figure 1 represents the schematic view of diesel engine. All samples were performed at 800 rpm for 20 minutes in order to ensure the full warm-up. After that, the performance was evaluated in terms of brake power of the diesel engine, fuel consumption rate, and exhaust gas temperature at 10 rpm which provided the maximum torque (33.7 N.m). In this work, as a preliminary evaluation for the possibility of using our fuel blend, the standard engine test was performed at a fixed speed of 1,500 rpm. The load was measured by P-1.5 ANAKA-STYLE DYNAMOMETER. Different %loads were applied (25%, 50%, 75% and 100%) to the engine by using dynamometer. Once the stable load was observed, the mass of fuel consumed in 1 minute and the output torque were recorded in order to evaluate the brake power of engine and the fuel mass consumption. The exhaust gas temperature was measured by a type-K thermocouple.

Table 1 Specification of Diesel engine

Engine	TF 90 DI-L
Type	Four stroke engines
Combustion system	Direct injection
Bore x stroke	85 x 87
Cooling system	Horizontal liquid-cooled
Rate power	66 kW at 2,400 rpm
Compression ratio	16.6:1
No. of cylinders	1
Injection Pressure	200 kg/cm^3

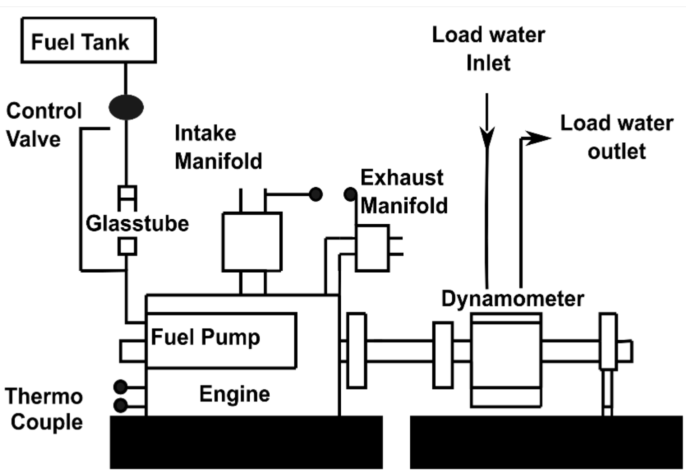

Figure 1 Schematic of diesel engine test

5.1 Brake Power and BSFC

The brake power of diesel engine calculated from equationn (1) where P is brake power of engine, W is braking load of dynamometer, L is length of dynamometer (0.716 m), N is rotation speed of power shaft and a is conversion coefficient (100 in case of kW).

$$P = \frac{2\pi WLN}{60a} \quad (1)$$

BSFC was evaluated as the ratio of fuel consumption to the brake power as shown in equation (2) where $\dot{m}_f$ is the fuel consumption (kg/h).

$$BSFC = \frac{\dot{m}_f \times 3600}{P} \quad (2)$$

Results and discussion

1. Phase stability of diesohol with GMS as additive

The physical and chemical properties of the fuel components were demonstrated in Table 2 according to the standard methods. The properties of diesel were within the ranges of diesel standard. Different states of chemical components required the screening for phase stability of fuel blends. Mixture with different compositions of GMS, diesel and ethanol were prepared and stored for over three months during which the phase separation of diesel/ethanol was visually observed. The time that each sample of the mixture became two phases was recorded. Figure 2 represents a triangle phase diagram of fuel blend. Grey circles represent the stable homogeneous blend, and black squares indicate that the separation occurred during 3 months of observation. As observed in Figure 2, in the case of D60E40 and D70E30, the diesohol was single phase for 4 wt.% and 3wt.% of GMS, respectively. When the concentration of GMS decreased to 3 wt.% and 2 wt.%, the phase separation of diesel and ethanol was observed. The required amount of GMS to obtain stable single phase was directly related to the ratio of ethanol and diesel in the mixture. For D85E15, the threshold limit of GMS content for a stable mixture was 1.2 wt.%. These results indicated that GMS can be used as emulsifying agent for diesohol. This was due to the fact that the HLB of GMS is approximately 3.8 suggesting the potential use as emulsifying agent for water-in-oil emulsion (Karbowiak et al., 2007).

2. Physical and Chemical properties of diesohol

Viscosity and cetane index of fuel blends were investigated for diesohol with different amounts of GMS according to ASTM specifications. The basic fuel properties of the blends were summarized in Table 3. The viscosity of D60E40, D70E30, D80E20, and D85E15 was within the threshold limits for high-speed diesel fuel (1.4-4.1 cSt) for all concentration of GMS. Apparently, the viscosity of fuel blend was inversely related to the ethanol portion due to the fact that ethanol has low viscosity (1.19 cSt) amongst the three individual fuel compositions used in this work. For the case of GMS, the viscosity increased with increasing amount of GMS.

Table 2 Chemical properties of the constituents

Properties	Diesel	Ethanol	GMS	Standard Diesel	Method
Color	Yellow	Colorless	White Powder		-
Density (g/cm^3) @ 15 °C	0.835	0.789	0.97	0.81-0.87	ASTM D1298
Viscosity (cSt) @ 40 °C	3.04	1.19	-	1.8-4.1	ASTM D 445
Acid value (mg KOH/g)	0.11	0.11	-	0.8 (max)	ASTM D 664
Calorific value (MJ/kg)	45.53	30.00	-	45 (min)	ASTM D 240

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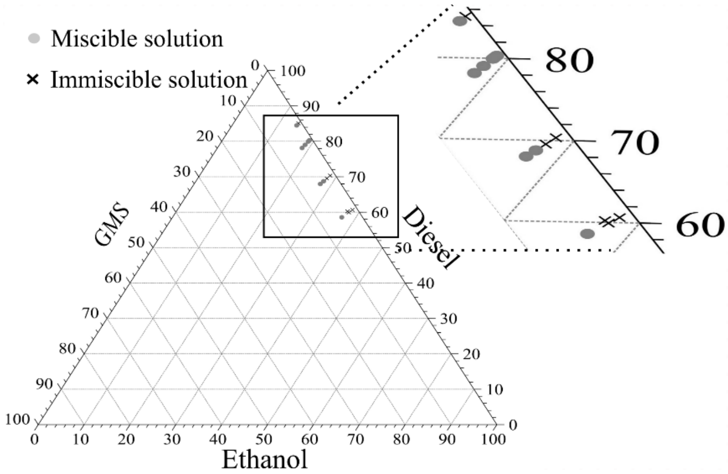

Figure 2 Phase stability of diesohol with GMS

Table 3 Properties of Diesohol

Diesel:Ethanol	%GMS	Viscosity (cSt)	Acid Value (mgKOH/g)	Cetane Index
85:15	1.2	2.62	0.11	52.21
80:20	0.6	2.40	0.11	48.85
80:20	0.8	2.49	0.11	48.82
80:20	1	2.54	0.11	48.82
80:20	2	2.60	0.11	48.85
80:20	3	2.65	0.11	48.81
70:30	3	2.38	0.11	42.69
70:30	4	2.45	0.11	42.74
60:40	4	2.02	0.11	38.75

The cetane index represents the effect of fuel on the engine start up, combustion control and engine performance (Chotwichien et al., 2009). The cetane index of both D60E40 and D70E30 did not meet the standard of diesel (minimum 45) due to the low cetane number of ethanol (Xing-Cai et al., 2004). However, the cetane index of D80E20 and D85E15 were approximately 48.8 and 52.2, which satisfied the industrial and the automotive diesel standard, respectively. The cetane index of fuel blends was in the range of 46-48; similar to those reported for diesel/biodiesel/ethanol (Kwanchareon et al., 2007). The cetane index of ethanl is lower than 8. (Hulwan, D.B. & Joshi, S.V., 2011) Increasing of amount ethanol in the mixture decrease the cetane index of the fuel blends (Chotwichien et al., 2009). In addition, the acid values of the fuel blends were studied to compare with standard values. The acid value indicates the content of fatty acids in oil, which may cause corrosion of engine and fuel tank (Shahabuddin et al., 2012). It was found that the acid values were stable at 0.11 mgKOH/g for all concentration of GMS, which meet the requirement of diesel ASTM D664 (maximum 0.5 mgKOH/g). This is due to the low acid value of GMS (less than 2 mgKOH/g) and the dilution effect of diesel/ethanol. D85E15 at 1.2 wt.% of GMS was considered to study the oxidation stability and engine performance because it was the minimum threshold of phase stability of the blend and the properties was within the diesel standard range.

3. Oxidation stability of diesohol

Oxidation stability represents the tendency of the fuel to react with oxygen. The oxidation stability of the fuel blends with GMS is shown in Figure 3. The conductivity of D85E15G1.2 increased to 67 μS/cm after

24 hours. This conductivity value shows that the oxidation reaction happened in fuel blend. It was associated with the low bond energy (94 kcal/mol) of the hydroxyl group in GMS (Blanksby and Ellison, 2003). The free radicals formed reacted with oxygen to create the carboxylic component in the solution. Therefore, 0.5, 1, 1.5% of DT-CNSL was added to fuel blend in order to delay the oxidation reaction. When the concentration of DT-CNSL was increased, there was a decrease in the conductivity of the measuring cell due to the lower bond energy of the hydroxyl group in DT-CNSL (58 kcal/mol) compared to that of GMS (Blanksby and Ellison, 2003). DT-CNSL contains labile hydrogen, so-called chain-braking antioxidant (AH). It can immediately interact with peroxyl radical (ROO·) generated from the initial step of the oxidation reaction (equation 3) (Jain and Sharma, 2010). Free radicals (I·) were formed via thermal dissociation of fatty acid substrate (RH) (Jain & Sharma, 2014). Oxygen molecules can react with carbon-based fatty acid radicals (R·) to form acid peroxide radicals (ROO·) [equations 4,5]. These radicals further react with the fatty acid chain (RH) of GMS yielding fatty acid. In the terminating step, R· combines with another radical to produce a stable product.

Initial step	$RH + I^{\cdot} \rightarrow R^{\cdot} + IH^{\cdot}$	(3)
Propagation step	$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$	(4)
	$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$	(5)
Termination step	$R^{\cdot} + R^{\cdot} \rightarrow R\text{-}R$	(6)
	$ROO^{\cdot} + ROO^{\cdot} \rightarrow$ Stable products	(7)
Antioxidant	$ROO^{\cdot} + AH \rightarrow ROOH^{\cdot} + A^{\cdot}$	(8)

Note that 1 vol.% and 1.5 vol.% resulted in similar conductivity profile possibly due to the prolonged inductive period. The composition of DT-CNSL contains cardanol, which is antioxidant and it can react with oxygen and ROO. [equation 8] (Lopes et al., 2008). The fuel blend of D85E15G1.2 at 1 vol.% of DT-CNSL was used for the engine performance test.

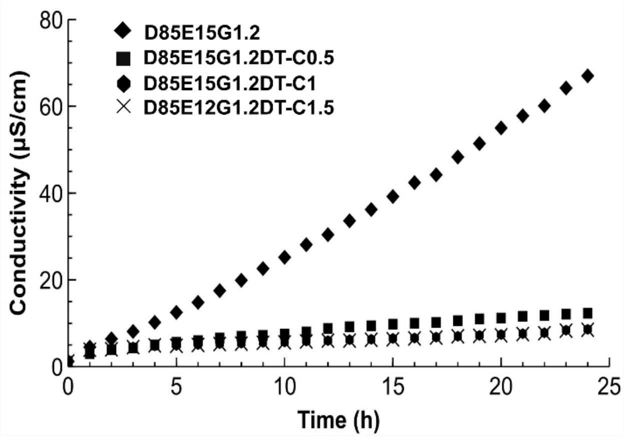

Figure 3 Oxidation stability of diesohol with GMS and DT-CNSL

4. Engine performance test

This work focuses on one speed (1500 rpm) because a relatively high torque of a similar mechanical diesel engine was obtained for diesel/ethanol blends at this speed (Freitas et al., 2022).

4.1 Brake Power of diesel engine

Figure 4 shows the brake power of engine and torque of the tested diesel engine using diesel and modified diesohol (D85E15G1.2DT-C1). For both types of fuel, the brake power of engine considerably rose with increasing percent load owing to the increased engine torque. High percent load was associated with high resistance of a crank shaft rotation motion and the engine developed the required torque as shown in Figure 4. It affects to power that engine producing. For D85E15G1.2DT-C1, it was observed that the brake power of engine at 50-100 % load was 9-14 % lower than diesel due to the lower heating value of diesel compared to diesel fuel (Karabektas and Hosoz, 2009). Our results were in line with the work by (Shahir et al., 2015), which the maximum power output of diesohol (diesel/ethanol/biodiesel) reduced approximately by 4.4-8.7% compare to pure diesel.

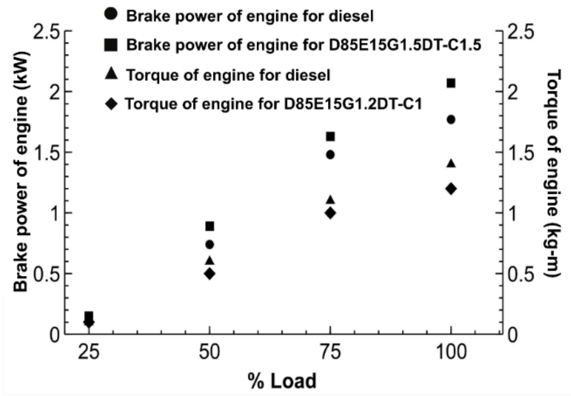

Figure 4 Brake power of engine and torque of fuel blend as a function of load

4.2 BSFC

BSFC is the rate of fuel consumed per unit brake power of engine (Shahir et al., 2015). The BSFC is shown in Figure 5(a) for the modified diesohol and diesel at 1500 rpm. BSFC of fuel blend decreased significantly with increasing percent load from 20 to 50. BSFC was relatively stable at 75-100% load. This was owing to the fact that brake power of the engine rises with an increase in the %load. In addition, BSFC was affected by fuel consumption rate as shown in Figure 5 (a). It was found that BSFC of diesel blend was higher than that of diesel by 24% and 16% at 75% and 100% load, respectively. This was also related to the low heating value of ethanol in the blend leading to higher fuel consumption of D85E15G1.2DT-C1 compared to diesel. These results were in line with the study by Subbaiah et al. (2010), which reported an increase in BSFC at high percent load for 75% of diesel, 10% of biodiesel, and 15% of ethanol. Note that the effect of ethanol on the energy content of the blends resulted in higher BSFC than that of diesel fuel for all percent load.

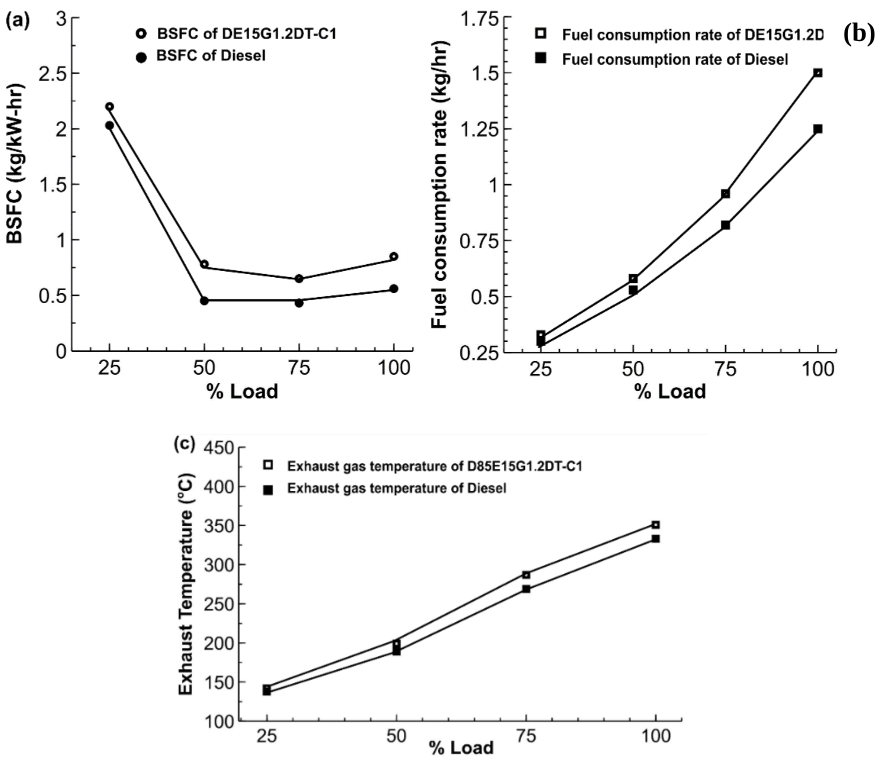

Figure 5 Effect of fuel blend on (a) Brake specific fuel consumption (BSFC), (b) fuel consumption rate of fuel blend, and (c) Exhaust gas temperature as a function of load at speed of 1,500 rpm

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4.3 Exhaust gas temperature

Exhaust gas temperature is the exact temperature of the fuel after it combusted in the engine. It is generally required that exhaust gas temperature is not to be higher than 720oC due to the possible damages of engine (Zheng et al., 2004). Exhaust gas temperature for fuel blend and diesel are shown in Figure 5(b). The exhaust gas temperature increased with increasing percent load for fuel blend and diesel. Note that the exhaust gas temperature of fuel blend is slightly higher than that of diesel. The lower cetane index of D85E15G1.2DTC-1 caused longer ignition delay leading to faster combustion, shortened combustion duration, and accumulated heat in the engine (Yilmaz et al., 2014).

5. Fuel properties

Table 4 summarizes the fuel properties of D85E15G1.2DT-C1 and diesohol blends from the literature data (with different emulsifiers). For D85E15G1.2DT-C1, the mass fraction of diesel, ethanol, GMS and DT-CNSL were 83 wt%, 14 wt%, 1.4 wt% and 1.2 wt%, respectively. Li et al., (2017); Tan, et al. (2017) studied the properties of diesel/ethanol by using SPAN80 and biodiesel as emulsifier. In the case of SPAN80, the density of our blend was similar to this blend while the viscosities of diesohol using SPAN80 and biodiesel were higher than our blend. This was because of the different portion of emulsifier. The heating value of D85E15G1.2DT-C1 was slightly higher than that of diesohol/SPAN80 while the heating value of diesohol/biodiesel was significantly higher than the other two formulas. This was owing to the low heating value of ethanol and the proportion of ethanol used in each blend. Ethanol also influenced the cetane index of the blend. The lower amount of ethanol in our blend D85E15G1.2DT-C1 resulted in higher cetane index compared to that of diesohol/SPAN80. It was slightly higher than the cetane index of diesohol/biodiesel possibly because the presence of cardanol, which has the heating value of 39.42 MJ/kg (Bangjang, et al. 2014). The minimum amount of GMS required for our blend was 1.2 wt.% (1.16 g per 100 ml of fuel blend), which was lower than other emulsifiers used for diesohol. Together with the small amount of GMS required, the inexpensive price of GMS also contributed to lower cost of the fuel blend. Note that cost of GMS (1.20 USD/kg) was relatively lower compared to that of SPAN80 and n-butanol. Therefore, GMS can be used as a low-cost emulsifier for diesel and ethanol blend.

Table 4 Properties of the fuel blend.

Properties	D85E15G1.2DT-C1	Li et al.[a]	Tan et. al.[b]	Diesel Standard
Density (g/cm^3)	0.847	0.827	0.853	0.81 - 0.87
Viscosity (cSt)	2.62	3.62	3.715	1.8 - 4.1
Calorific value (MJ/kg)	39.96	38.5	44.1	36 (min)
Cetane index	52.21	42	51.2	45 (min)
Acid value (mgKOH/g)	0.11	-	-	0.8 (max)
Retail price[c]	1.36 USD/kg	1.38 USD/kg	1.38 USD/kg	-

[a]80 ml of Diesel, 20 ml of ethanol, 0.33 g of n-butanol, 3.36 g of SPAN80
[b]80 ml of Diesel, 10 ml of ethanol, 10 ml of biodiesel
[c]Based on the price of diesel, ethanol, biodiesel, DT-CNSL, GMS, n-butanol, and SPAN80 of 1.19 USD/L, 0.81 USD/L, 1.01 USD/L, 0.64 USD/L, 1.20 USD/kg, 1.45 USD/kg, and 2.2 USD/kg, respectively.

Conclusions

GMS was applied as an emulsifier for diesel and ethanol. For phase stability of at least three months, the mixture required at least 1.2 % by weight of GMS. The properties of diesohol with GMS met the standards of diesebreakl fuel according to the Department of Energy Business, Ministry of Energy, and Thailand. For D85E15 with 1.2 wt.% GMS and 1 vol.% DT-CNSL of the mixture, the acid value, viscosity, and the cetane index were 0.11 mgKOH/g, 2.42 cSt, and 52.21, respectively. DT-CNSL was applied as an antioxidant to the diesohol in order to inhibit the oxidation of the hydrocarbon molecules in the fuel. From the engine test at the speed of 1,500 rpm, the BSFC of the fuel blend was higher while the exhaust gas temperature and brake power of diesel engine were comparable to those of diesel. Therefore, GMS can be used as an emulsifier for promoting the use of biofuel (such as ethanol and CNSL) as a substitute for diesel fuel.

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