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# Energy Saving and Pollution Reduction by Adding Water Containing *Iso*-Butanol and *Iso*-Propyl Alcohol in a Diesel Engine

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# **ABSTRACT**

In this study, two diesel blends with different iso-butanol and isopropyl alcohol ratios, 5% iso-propanol with 15% isobutanol and 1% iso-propanol and 19% iso-butanol, were used and compared against the performance of petroleum diesel as a base fuel. Additionally, water addition strategy was included for further comparison. Brake specific fuel consumption (BSFC) increased with increasing ratios of iso-butanol and water fractions, since the heating value decreased resulting in more fuel being combusted to maintain the same power output. On the other hand, brake thermal efficiency (BTE) increased with increasing water content. Specifically, P5B15W1 had a higher BTE than regular diesel at low engine loads (12 kW and 25 kW-LS). Compared to the regular diesel, the results show that in-cylinder pressures slightly increased while HRR had longer ignition delay with higher iso-butanol and water content. For the two different ratios of blended diesel, P1B19 registered NO<sub>x</sub> emission reductions factors by about 12–35% compared regular diesel due to its low heating value and combustion temperature, while those for P5B15 were reduced 8-33% in comparison to regular diesel. For CO and PM emission factors, P5B15 had better performance than P1B19 which showed 13-37% and 37-50% lower than regular diesel, respectively. However, HC emission factors were all greater than those of regular diesel with the highest increase being from P1B19. This diesel blend, P1B19 showed 6-30% and 3-10% higher HC emission factors than regular diesel and P5B15, respectively. For water containing blends, NO<sub>x</sub> emission factors decreased with an increase in water content. The trends for CO and PM emission factors were similar to those of non-water containing diesel blends. P5B15W1 had largest decrease which showed 5-17% and 7-26% lower CO and PM than regular diesel, respectively. Notably, the CO and PM emission factors are all higher than non-water contain blended diesel. As for HC, P5B15W1 had an increase of about 26-51%. Moreover, the total-PAHs emission factors between two different ratios of blended diesel were compared whereby P5B15 had 12-22% lower than P1B19. Besides, total-BaPeq emission factors are similar to total-PAHs emission, which P5B15 had largest reduction by 28-44%. In summary, P5B15 would be a best choice in terms of PM reduction, while the best choice for NOx control would be P1B19W0.5 blend. Ultimately, further economic feasibility studies are recommended for an overall performance evaluation.

*Keywords:* Water emulsified diesel; BSFC; Heat release rate; Green fuels; NO<sub>x</sub>; PM; PAHs.

## INTRODUCTION

In the last few decades, alcohols have been used as additives and alternative fuels in the diesel engine

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(Agarwal, 2007; Campos-Fernández *et al.*, 2012; Fraioli *et al.*, 2014; Tüccar *et al.*, 2014) to address the challenges of emissions of particulate matter (PM), total hydrocarbons (HC), nitrogen oxides (NO<sub>x</sub>) carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO) as well as toxic chemicals such as polycyclic aromatic hydrocarbons (PAHs) (Doğan, 2011; Popovicheva *et al.*, 2014; Tsai *et al.*, 2014). These exhaust pollutant emissions pose huge risks to human health in form of cardiovascular disorders, respiratory diseases and lung cancer especially PAHs, which are carcinogenic as well as mutagenic (Lin *et al.*, 2013). In fact, Gong *et al.* (2014) reports that the International Energy Agency projects the use of biofuels such as alcohols is expected to go up from

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3% in 2010 to about 27% by 2050. Alcohols can be easily distilled from the abundantly available biomass resources which are also renewable (Saeed and Henein, 1989; Kumar *et al.*, 2013).

The role of additives in the blends is to stabilize for storage purposes, lower the viscosity as well as increase the cetane number of the fuel blends closer to that of diesel. Alcohols have a hydroxyl group attached on their molecular structures and form isomers depending on the position of the -OH group (Rakopoulos et al., 2010b). The -OH group offers the same advantages as the oxygen content in biodiesel in terms of combustion efficiency. In addition, the alcohol additives decrease the formation of NO<sub>x</sub> especially when blended with biodiesel -diesel blends as well as reduced SO<sub>x</sub> since they have lower sulfur content (Lin and Huang, 2003; Doğan, 2011). Furthermore, alcohols are used as octane number boosters in diesel, because they possess a higher octane number than the petroleum fuels. The application of alcohols in diesel engine is not without its drawbacks which include reduced lower heating values, stability and miscibility problems in blended fuels, lower cetane number and poor lubricity (Campos-Fernández et al., 2012).

Ethanol and methanol are the two most studied alcohols in the diesel engine (Campos-Fernández et al., 2012) but not much literature is available for alcohols with longer chain lengths. In fact methanol and ethanol have been in use since 1970 according to (Kumar et al., 2013) due to their accessibility, low cost, high oxygen content and ease of use in diesel engines without modifications. Even though ethanol has been noted to be superior to methanol in performance, its main disadvantages are high heat of vaporization, high auto-ignition temperatures and low lubricity (Yilmaz and Vigil, 2014). These disadvantages can be overcome by use of long chain alcohols whose properties are near those of gasoline than the short chain alcohols. Unfortunately not much open literature is available on alcohols such as isopropyl alcohol, butanol or even pentanol (Karabektas and Hosoz, 2009; Rakopoulos et al., 2010a; Magara-Gomez et al., 2014; Tsai et al., 2014; Lapuerta et al., 2015). Alcohols with longer unbranched chain lengths offer higher lower heating values greater densities, and increased cetane values with reduced self-ignition temperatures as well less knock tendencies (Campos-Fernández et al., 2012; Dusséaux *et al.*, 2013).

Isopropyl alcohol CH<sub>3</sub>CH(OH)CH<sub>3</sub>, a common fuel in catalytic air freshening diffusers (Geiss *et al.*, 2014), is one of the two isomers of propanol while the other is 1-propyl alcohol with the formula CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH. Isopropyl is conventionally produced via hydration reaction involving propene and water or via hydrogenation of acetone. From biomass, isopropyl alcohol can be produced via fermentation process using microbes such as cyanobacteria such as *Clostridium beijerinckii*, *Escherichia coli and Synechococcus elongates* (Dusséaux *et al.*, 2013; Kusakabe *et al.*, 2013; Hirokawa *et al.*, 2015). Even though there are not so many research studies on iso-propanol, its use in engines has been studied as early as 1989 in compression ignition engines (Saeed and Henein, 1989) and recently in gasoline

and spark ignition engines (Gong et al., 2014). Recently, (Balamurugan and Nalini, 2014) in their paper investigated the performance of 1- propyl alcohol when blended with diesel fuels and reported reduced break specific energy, reduced engine operating temperatures which translates to increased engine life, as well as reduced CO and  $NO_x$  emissions.

On its part, iso-butanol (used in this study) is one of the isomers of butanol (C<sub>4</sub>H<sub>9</sub>OH). The isomers include normal (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH), secondary butanol (CH<sub>3</sub>CH<sub>2</sub>CHOHCH<sub>3</sub>), iso-butanol ((CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CHOH and finally tert-butanol ((CH<sub>3</sub>)<sub>3</sub>COH). Butanol in general can be generated from fermentation of cellulosic biomass (Doğan, 2011) and anaerobic fermentation of glycerol from biodeiesel production (Kumar et al., 2013). Nonetheless, it is worth noting that the specific manufacturing methods of each isomer are different so are their physiochemical properties such as density, boiling points, water solubility and flash points (Kumar et al., 2013). Iso-butanol can be produced from both petroleum and non-petroleum resources such as agricultural crops (Karabektas and Hosoz, 2009) and it has advantages over ethanol such as lower hygroscopicity, hence it can easily mix with diesel fuel with no phase separation as well as latent heat of vaporization and specific gravity which are comparable to those of diesel fuel. Additionally, isopropyl alcohol can be used as a co-solvent to stabilize water and oil mixing phases (Tsai et al., 2014).

Iso-butanol and diesel blends of 10, 20, 30 and 40% have been investigated before by Al-Hasan and Al-Momany (2008) resulting in increased engine speeds, higher exhaust temperatures, as well as greater brake power and brake specific fuel consumption (BSFC) but a lower brake thermal efficiency (BTE) when compared to neat diesel. In review by (Kumar et al., 2013), a comparison between isobutanol and n-butanol reveals that n-butanol additives result in increased BTE and BSFC and decreased exhaust temperatures while iso-butanol -diesel blends result in increased BSFC but lower BTE, engine power and exhaust gas temperatures when compared to diesel fuel. Furthermore both n-butanol and iso-butanol cause lower NOx, CO and smoke emissions but increased HC (Karabektas and Hosoz, 2009). Recently (Tsai et al., 2014) revealed that adding one percent of isopropyl alcohol to waste-edible oil-acetonediesel blends lowered the particulate elemental carbon emissions by 4.8-5.7% in addition to reduced particulate organic carbon, total PAHs and total BaPeq.

Additionally, water addition to fuel is one of the techniques of emission control in the diesel engine. Different ways can be used to introduce water into the engine and they include (i) mixing water in form of steam with air at inlet, (ii) injecting water and diesel coincidentally (iii) forming water and diesel emulsions which can be stabilized or not be stabilized with surfactants or co-solvents. Water emulsions result in micro-explosion phenomena where by during combustion, water evaporates faster than diesel due to differences in boiling points (Hagos *et al.*, 2011; Lin *et al.*, 2012; Chang *et al.*, 2013; Chang *et al.*, 2014). When water reaches its superheated stage earlier than diesel it creates a vapor expansion break up causing micro-explosion

whereby droplets disintegrate into smaller droplets in a kind of secondary atomization. This secondary atomization enhances air and fuel mixing which is advantageous in emission reduction (Kadota and Yamasaki, 2002). According to Ithnin *et al.* (2014) water in diesel emulsions can reduce NO<sub>x</sub> and PM concurrently as well as induce improved combustion efficiency without engine modifications. What is more is that water presence increases amount of OH radicals which act to reduce soot formation by oxidizing the soot precursors (Mwangi *et al.*, 2015a, b).

The objective of this study was to investigate the performance of *iso*-butanol-*iso*-propyl alcohol-diesel blends in terms of energy performance and emission reduction by comparing against the baseline performance of regular diesel. The brake specific fuel consumption (BSFC) and the brake thermal efficiency (BTE) are the energy performance parameters utilized, while the criteria pollutants such as NO<sub>x</sub>, CO, PM and HC as well as total PAHs and total BaPeq were the emission parameters considered in this study.

#### EXPERIMENTAL SECTION

# Fuel Preparation and Stability Tests

The diesel used in this study was purchased from Chinese Petroleum Company with a 2% biodiesel content. The heating value of this D98%B2% is nearly the same as that of D100% with about 0.15% discrepancy. The physiochemical properties of the diesel are shown in Table 1. The isopropyl and iso-butanol alcohols were obtained from Pancreac and their properties are also listed alongside those of diesel in Table 1. The blending process was carried out using labscale ultrasonic tank (40 kHz and 120 W power output and a capacity of 5 litres) for 15 min after mixing using Fluko® stirring probe which was operated at 3000 rpm for 15 minutes. The diesel, iso-butanol and iso-propanol were mixed with water at three different ratios which are D79P5B15W1 (79% Diesel, 5% isopropyl alcohol, 15% iso-butanol, and 1% water), D79.5P5B15W0.5, and D79.5P1B19W0.5, respectively as shown in Table 2.

After the blending process, the blended fuels were subjected to stability tests were carried out via gravitational and centrifugal processes. The fuel blends were subjected to standing tests for 30 days for the gravitational test. The longer storage stability was validated by a centrifugal test for 15 min at 5,000 rpm, referring to the previous study (Lin *et al.*, 2012). The results of the two stability tests, was evaluated using four levels of the phase appearances of the blended fuels forming an empirical index of stabilities: (a) one-phase clear liquid; (b) one-phase liquid crystalline; (c) two-phase liquid crystalline; (d) two-phase clear liquid. Whereby the order of stability will be evaluated as (a) > (b) > (c) > (d), so that an unstable blend will transform its appearance from (a) to (d) over the 30 days' time period or after a high speed centrifugation.

### Engine Test and Exhaust Gas Monitoring

Stable blends obtained from the stability tests were selected for further engine tests. The operation specifications of the diesel engine testing facility are laid down in Table 3 and Fig. A1 (appendix). In this study the various test load were automatically controlled using a computer module and a generator. The operating conditions were as follows: idle operation, 75% (150 Nm with 2220 rpm), 50% (100 Nm with 2405 rpm and 108 Nm with 2035 rpm), and 25% (50 Nm with 2220 rpm), which were achieved by changing the torque and speed to give outputs of 0kW (idle), 12 kW, 25 kW, and 35 kW generator loads, respectively.

The exhaust gas from the engine was analyzed is using by the BE-2000 Exhaust Emission Analyzer, whose specifications are outlined in Table 4. The carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and hydrocarbon (HC) were analyzed by Non-dispersive Infrared (NDIR) detector while the nitrogen oxides (NO<sub>x</sub>) were detected by an electrochemical sensor. The sampling flow rate was 2–4 L min<sup>-1</sup>. The detection range of CO, CO<sub>2</sub>, HC, and NO<sub>x</sub> were 0–10%v, 0–20%v, 0–15,000 ppmv, and 0–2,000 ppmv, respectively (as shown in Table 4)

Properties	Diesel	Isopropyl alcohol a	Iso-butanol <sup>b</sup>
Heating value (MJ kg <sup>-1</sup> )	43.5	30.4	33.0
Latent heat of vaporization (kJ kg <sup>-1</sup> )	250	750	578
Cetane number	55	13	Below 15
Flash point (°C)	> 55°C	12	28
Vapor pressure @ 20°C (mmHg)	2	32.4	8.8

**Table 1.** Properties of diesel, isopropyl alcohol, and iso-butanol.

Table 2. Diesel Fuel Blends.

Diesel	Blending ratios (%)			Heating Value	
Blends	Diesel	Isopropyl alcohol	Iso-butanol	Water	$(MJ kg^{-1})$
D100	100.0%	0%	0%	0.0%	46.035
P5B15	80.0%	5%	15%	0.0%	44.375
P5B15W05	79.5%	5%	15%	0.5%	43.76
P5B15W1	79.0%	5%	15%	1.0%	42.911
P1B19	80.0%	1%	19%	0.0%	43.887
P1B19W05	79.5%	1%	19%	0.5%	43.92

<sup>&</sup>lt;sup>a</sup> (Karabektas and Hosoz, 2009); <sup>b</sup>(Mishra *et al.*, 2015).

-	•	
Item	Specification	
Manufacturer	MITSUBISHI 4M40-2AT1	
Bore (mm) $\times$ Stroke	$95 \times 100  (mm)$	
Stroke	100	
No. of Cylinders	4	
Injection System	Direct Injection	
Cooling System	Water cooled	
Fuel	Diesel	
Compression Ratio	20.1:1	

**Table 3.** Specifications of Test Engine.

**Table 4.** Specifications of gas analyzer.

Target species	Detection Range	Resolution	Precision
СО	0–10%v	0.001%v	± 0.02 or 3% (select larger one)
$CO_2$	0–20%v	0.01%v	$\pm$ 0.3% or 3% (select larger one)
HC	0–15,000 ppmv	0.1 ppmv	$\pm$ 4 ppm or 3% (select larger one)
$NO_x$	0–2,000 ppmv	1 ppmv	- · · · · · · · · · · · · · · · · · · ·

## PAH Sample Pretreatment and Analysis

Rated Power

Maximum Torque

Before each sampling, the engine was warmed up for 30 min and for a minimum of 3 min between different sampling campaigns and fuel change. The sampling was undertaken for about 20 minutes in duplicates for all the sampling conditions mentioned earlier. The exhaust of the diesel engine was sampled directly and isokinetically during the entire testing cycle by a sampling system that consists of a glass fiber filter, a flow meter, a condenser, two-stage glass cartridges and a pump.

Particulate phase PAHs were collected by a glass fiber filter which were pretreated by placing in an oven to get rid of all organic compounds. A condenser located before the two-stage glass cartridges was used to lower the exhaust temperature to < 5°C and to remove the water content from the exhaust. The gaseous-phase PAHs were then collected by the two-stage glass cartridges. Specifically, the cartridges were packed with 5.0 cm (approximately 20 g) of XAD-2 resin sandwiched between two 2.5 cm polyurethane foam plugs. The cartridges had been pretreated by Soxhlet extraction in with methanol, dichloromethane, and n-hexane for a period of 24 hours in each solvent. The sampled flue gas volumes were normalized to the condition of 760 mmHg and 273 K and denoted as Nm<sup>3</sup>. The exhaust gas was passed through Belltone BE-200 gas analyzer from Belltone Technologies to detect and quantify the criteria pollutants  $(NO_x, CO, CO_2 \text{ and } HC).$ 

After sampling the glass fiber filters were weighed to determine the amount of particulate matter (PM) after being placed overnight in a dehumidifier to remove any moisture. Thereafter the glass fibers were treated in a similar manner as the PUF/resin cartridges for extraction processes. The Soxhlet extraction process was carried out using a mixed solvent composed n-hexane/dichloromethane in a 1:1 volume ratio for a period of 24 hours. For the glass filter containing particulate phase PAH were extracted using 250 mL of the solvent while the cartridges were treated to

a 750 mL solvent volume. The extract was then purged with ultra-pure nitrogen to 2 mL and passed through the cleanup column packed with silica. The eluents were then re-concentrated by purging with nitrogen to exactly 1 mL in vials which were transferred to gas chromatography/mass spectrometer set up for analysis.

109 kWh at 3700 rpm

200Nm at 3200 rpm

The GC/MS (Agilent 5890A and Agilent 5975) used for subsequent PAH identification was equipped with a capillary column (HP Ultra 2, 50 m  $\times$  0.32 mm  $\times$  0.17  $\mu$ m). 21 PAHs considered in this study were Naphthalene (Nap), Acenaphthylene (AcPy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Cyclopenta[c,d]pyrene (CYC), Benz[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[e]pyrene (BeP), Benzo[a]pyrene (BaP), Perylene (PER), Indeno(1,2,3-cd)pyrene (IND), Dibenzo(a,h)anthracene Benzo[b]chrysene, (DBA), Benzo(ghi)perylene (BghiP), and Coronene (COR).

The operating conditions were an injection volume of 1  $\mu$ L; splitless injection at 300°C; ion source temperature at 310°C; oven temperature held at 45°C for 1 min, ramped from 45 to 100°C in 5 min, ramped from 100 to 320°C at 8 °C min<sup>-1</sup> and held at 320°C for 15 min. The masses of the primary and secondary PAH ions were determined by using the scan mode for pure PAH standards. The PAHs were qualified by using the selected ion monitoring (SIM) mode.

# Quality Assurance and Quality Control (QA/QC)

The detection limit (DL) estimated using a serial diluted standard solution of 21 PAHs was 64–768 pg. The limit of quantification (LOQ) is defined as the detection limit divided by the sampling volume, and it was in the range of 0.131–1.59 ng m<sup>-3</sup> for individual PAH compounds in the current study. Seven consecutive injections of a 10 ng L<sup>-1</sup> PAH standard yielded relative standard deviations (RSD) between 3.70–7.95% of the GC/MSD integration area. The

 $R^2$  of calibration lines of the 21 PAH compounds were over 0.996. Additionally, the results showed the average recovery (n = 3) of individual PAHs by NIEA A730.70C was 77–109%. Analysis of field blanks, including glassfiber filters and cartridges, showed all PAH levels were less than the detection limit.

## Data Analysis

The brake specific fuel consumption (BSFC), brake thermal efficiency (BTE) and emission factors (EF) were calculated for the engine operating at a load of 25% (2200 rpm and 50 Nm torque) as per the equations provided in the earlier works by (Chang *et al.*, 2013, 2014a, b). The BSFC and BTE were determined according to Eqs. (1) and (2) where V represents the volume of fuel consumed in each sampling run (g), P is the power generated in (kW), and t represents the sampling time (h) and H represents the heating value (kJ g<sup>-1</sup>) of each blend.

$$BSFC = \frac{V}{Pt} \left( g \ kw^{-1} \ h^{-1} \right) \tag{1}$$

$$BTE = \frac{Pt}{VH} \, (\%) \tag{2}$$

The emission factors were determined as per the Eq. (3), where C is the concentrations of each pollutant (mass Nm<sup>-3</sup>), V denotes the total exhaust volume collected from the stack during the sampling period at standard conditions (Nm<sup>3</sup>), P represents the power output in (kW), and t stands for the sampling time in hours.

$$EF = CV/Pt (mass kW^{-1} h^{-1})$$
(3)

In addition, in cylinder is measured by a piezoelectric pressure transducer and recorded in AVL INDICOM 1.5. The in-cylinder pressure was recorded for 200 cycle per test and averaged. The crank angle position was measured by encoder (h-25). The in-cylinder pressure was used to calculate heat release rate which was determined by the adiabatic energy balance (Ren *et al.*, 2008; Chang *et al.*, 2014;). Thermodynamic model is applied to calculate heat release rate, the model neglects the leakage through the cylinder, and thus the energy conservation in cylinder. The heat release equation is given by:

$$\frac{dQ_B}{d\varphi} - \frac{dQ_w}{d\varphi} = \frac{d(mu)}{d\varphi} + p\frac{dV}{d\varphi} = mC_v \frac{dT}{d\varphi} + mT\frac{dC_v}{d\varphi} + p\frac{dV}{d\varphi}$$
(4)

where gas state equation is

$$pV = mRT (5)$$

Differentiate the gas state equation with respect to the crank angle and get the following equation:

$$p\frac{dV}{d\varphi} + V\frac{dp}{d\varphi} = mR\frac{dT}{d\varphi} \tag{6}$$

And the heat release rate,  $(dQ_B/d\varphi)$ , can be derived from (1) and (3) which is given by:

$$\frac{dQ_B}{d\varphi} = p \cdot \frac{C_p}{R} \frac{dV}{d\varphi} + \frac{C_v V}{R} \frac{dp}{d\varphi} + mT \frac{dC_v}{d\varphi} + \frac{dQ_w}{d\varphi}$$
(7)

where heat transfer rate is given by:

$$\frac{dQ_w}{d\varphi} = h_c \cdot A \cdot (T - T_w) \tag{8}$$

Heat transfer coefficient  $h_c$  was used the Woschni's correlation formula.  $C_p$  and  $C_v$  are temperature-dependent parameters and their formulae are given in literature (Heywood, 1988).

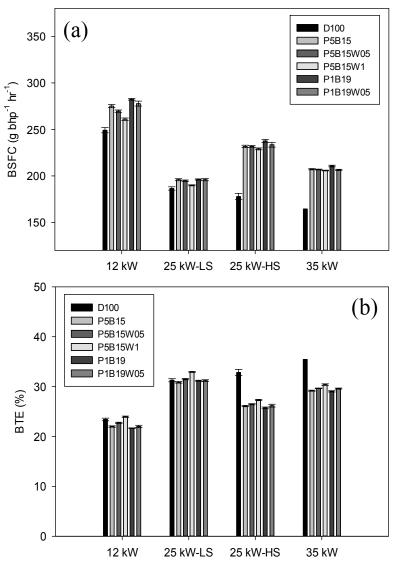
## RESULTS AND DISCUSSION

## Energy Performance by Using Various Diesel Blends Brake Specific Fuel Consumption

Brake specific fuel consumption (BSFC, g bhp<sup>-1</sup> hr<sup>-1</sup>) is shown in Fig. 1(a) BSFC is a scale which represents engine performance, whereby the higher BSFC means comparatively lower engine performance. For blended diesel, all of them have higher BSFC than regular diesel due to the heating value of blended value were lower than regular diesel, which correspond to the previous studies (Mohammadi *et al.*, 2012). From the Fig. 1(a), it is clear that the BSFC was higher at low engine load and high engine speed than high engine load and low engine speed. This result indicates that higher engine loads will cause higher combustion temperature, which improves the engine combustion efficiency. Besides, the BSFC was also higher at engine speed of 25 kW-HS than at 25 kW-LS. This was because engine at higher speed has shorter residence times; resulting in less complete combustion, decrease in spray atomization and more friction loss.

When using alcohol blended diesel, the BSFC significant increased at all loads. Comparing different P/B ratio of alcohol blended diesel, P5B15 has higher BSFC than P1B19. The BSFC of P5B15 increased by 1.6%, 1.5%, 1.2%, and 0.3% at 12 kW, 25 kW-LS, 25 kW-HS, and 35 kW than P1B19, respectively. Higher fractions of *iso*-butanol added into blended diesel may increase BSFC. This observation is reasonable because the engine would consume more fuel to generate the same output power considering the lower energy content of the alcohol blends compared to the conventional diesel fuel, hence the increase in BSFC (Al-Hasan and Al-Momany, 2008).

To investigate the effect of water containing blended diesel, the 0.5% and 1% water additions were compared with the performance of other blends. As the water fractions increased in the blended diesel, the BSFC slightly decreased. The reduction in BSFC with water addition is caused by (1) secondary atomization because of the water-in-oil emulsion, a micro-explosion effect, (2) decrease the combustion temperature and a less luminous flame due to cooling effect, (3) longer ignition delay due to larger



**Fig. 1.** (a) BSFC and (b) BTE for different blended diesel at various loads.

premixed combustion (Yoshimoto *et al.*, 1999). The BSFCs of P5B15W1 and P5B15W05 were 5% and 7% higher than those of D100 at 12 kW; 2% and 4% at 25 kW-LS; 29% and 30% at 25 kW-HS; 25% and 26% at 35 kW. Therefore, adding small amount of water into blended diesel significantly decreased BSFC at low engine load and slightly decreased BSFC at highest engine speed load among all blended diesel.

# Brake Thermal Efficiency

In thermodynamics, the brake thermal efficiency (BTE,%) is a dimensionless performance measure of a device, such as an internal combustion engine, especially. It is indicates how well energy transfer process is accomplished. From Fig. 1(b), the alcohol blended diesel has decreased BTE at various loads. Besides, when the engine loads or engine speeds were increased, the BTE decreased indicating lower engine performance. Compared to D100, all kinds of blended diesel had lower BTE performance in the range of 17–22%.

On the other hand, water added in blended diesel results in micro explosion and secondary atomization which can improve combustion and lead to increase of BTE. High vapors of water could also increase in expansion work and reduction in compression work which lead to increase BTE (Kannan and Udayakumar, 2009; Yahaya Khan *et al.*, 2014). From Fig. 1(b) 1% it is clear that the water additions improved the BTE performance of the blended fuels by greater than 0.5% at various loads. Notably, P5B15W1 had a slight increase in BTE at low engine load due to microexplosion which improved BTE performance, compared to D100. However, more *iso*-butanol in blended diesel didn't show much difference at various loads, which is as a result of a combination of lower heating value and higher BSFC of blended diesel.

# In-Cylinder Pressure

The in-cylinder pressure is a measure of the effect of various blended diesel on combustion phenomenon. In addition, using in-cylinder pressure one can further determine heat release rate. The Figs. 2(a)–2(d) shows the in-cylinder pressure of all blended diesel at different loads.

Normally, in-cylinder pressure increase with increase of engine load. D100 registered the highest in cylinder pressures at all loads. When more *iso*-butanol or water is added to blended diesel, the high latent heat of evaporation of water and low cetane number of *iso*-butanol reduces the in-cylinder pressure. But 1% water content displays higher pressure than 0.5% water content because of micro-explosion phenomena which improves combustion leading to increased pressure at low loads. However, the high engine loads or high speeds didn't show this trend due to the counteracting effect between low latent of evaporation of the blends and micro-explosion phenomena (Cui *et al.*, 2009).

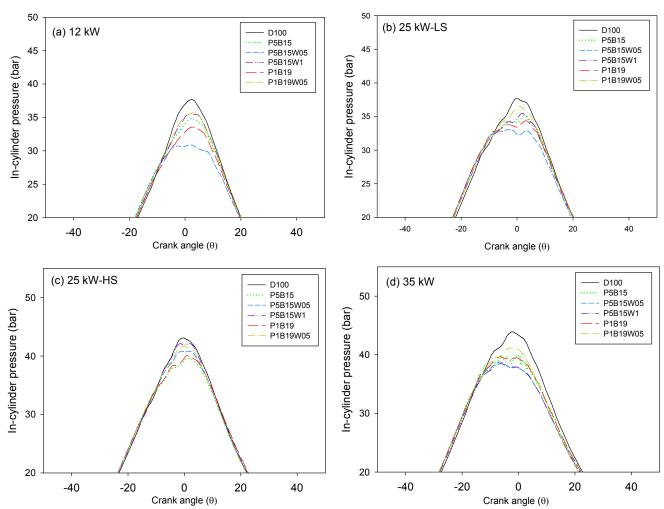
## Heat Release Rate (HRR)

According to Buyukkaya (2010), the heat release rate is a criterion for identifying the onset of combustion process, the fraction of fuel burned in premixed mode and differences in combustion rates of fuels. It is obtained by analyzing the cylinder pressures and using the first thermodynamic law to calculate (Qi *et al.*, 2010). Some undesirable combustion products, such as smoke, CO, CO<sub>2</sub>, NO<sub>x</sub>, HC, and PAHs

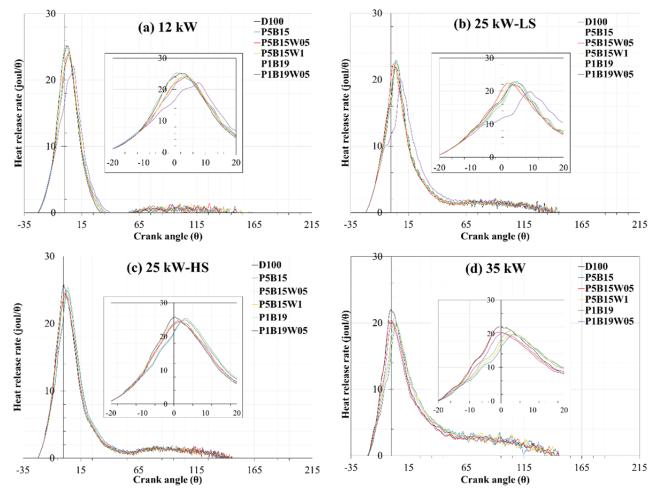
would increase with HRR increase. Based on a study by Lyn (1963), the injection rate and burning rate can be dividedly into three types: (a) fuel injection across the chamber with substantial momentum; (b) fuel deposition on the combustion chamber walls; (c) fuel distributed near the wall. Using above mechanisms, the combustion situation in the cylinder can be analyzed for different blends of diesel.

From Figs. 3(a)–3(d) which shows the HRR for various blends, all blended diesel showed ignition delay at different loads. When comparing the HRR for the blends at constant engine loads with different engine speed, higher engine speeds did not show any significant changes among all the diesel blends. These results are due to high absolute burning rate by increasing engine speed (Lyn, 1963). Although D100 did not reflect the high pressure on the high heat release rate, this is probably because of counteracting effect of later combustion in a lower temperature (Rakopoulos *et al.*, 2011).

It is clear that high water content or high *iso*-butanol fractions had longer ignition delay at various loads. With higher *iso*-butanol content, the lower cetane number of *iso*-butanol could cause the increase of ignition delay (Rakopoulos *et al.*, 2010b). Aside from *iso*-butanol, water



**Fig. 2.** In-cylinder pressure versus crank angle for different blended diesel: (a) 12 kW; (b) 25 kW-LS; (c) 25 kW-HS; (d) 35 kW.



**Fig. 3.** Heat release rate versus crank angle for different blended diesel: (a) 12 kW; (b) 25 kW-LS; (c) 25 kW-HS; (d) 35 kW.

content is another factor to cause longer ignition delay which its high latent heat of evaporation and low cetane number (Cui *et al.*, 2009). Compared to D100, P1B19W05 showed the longest ignition delay at low engine load and speed which is as a result of its low heating value and water content.

## Traditional Pollutant Emissions by Using Diesel Blends Nitrogen Oxide Emissions

In the diesel engines, the thermal NO<sub>x</sub> formation mechanism, also called Zeldovich mechanism, dominates as the main formation processes which is controlled primarily by the combustion temperature. Although all blended diesel have longer ignition delay, the low temperature have the dominant influence, which is against the opposing effect of lower cetane number of *iso*-butanol causing high temperature combustion (Rakopoulos *et al.*, 2010b).

From Fig. 4(a) P5B15W1 had lowest  $NO_x$  emission because of the higher water content which led to lower exhaust temperature as shown in Fig. 4(b). The reductions were 38%, 32%, 28%, and 21% at 12 kW, 25 kW-LS, 25 kW-HS, and 35 kW, respectively. Besides, 1% water-contain had  $NO_x$  reductions of about 4%-12% compared to 0.5% water-content and while compared to no water-

content the  $NO_x$  reductions ranged about 9%-14%. Lin *et al.* (2010) showed that increased water in blended diesel reduced the  $NO_x$  emission. In their study, by adding 3% water content to blended diesel; the reductions were about 2.4–6.5% for different loads. These observations can be explained by the resulting low heating value and the high latent heat of water which results in a cooling effect.

To investigate the effect of different P/B ratios, P5B15 and P1B19 were compared. With the decrease the P/B ratio, NO<sub>x</sub> emission factors decreased by 8–33% and 12–35% for P5B15 and P1B19 compared to the D100 at various loads, respectively. The isopropyl alcohol and *iso*-butanol have low cetane and heating value that cause lower combustion temperature (Karabektas and Hosoz, 2009). From Table 2, the P1B19 has lower heating value than P5B15 which more easily leads to lower combustion temperature. Although the NO<sub>x</sub> emission was also effected by the ignition delay, lower heating value and cetane number were enough to reduce the NO<sub>x</sub> emission.

# Carbon Monoxide Emissions

Generally, the formation of CO is mainly due to the incomplete combustion. Higher torque can lead to improved combustion condition which can reduce the CO emission

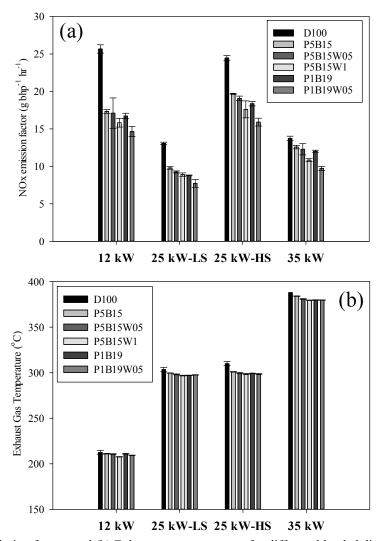


Fig. 4. (a) NO<sub>x</sub> emission factors and (b) Exhaust gas temperature for different blended diesel at various loads.

(Ithnin *et al.*, 2014). The presence of isopropyl alcohol and *iso*-butanol provides more oxygen content which could lead to better combustion reaction. Fig. 5(a) shows that compared to D100, all the diesel blends recorded decreased CO emission factor at various loads. CO emission factors decreased significantly at 35 kW whereby reductions were 28%, 40%, and 32% for P5B15W1, P5B15W05, and P1B19W05, respectively. This was due to the fact that higher engine loads provide higher exhaust temperature and improve combustion.

From the results, alcohol diesel blends with same P/B ratios had decreased CO emission factors when water-content decrease. Compared to the P5B15, the reduction were 0.2–10% and 10–19% for 0.5% and 1% water content at various loads, respectively. Similarly, the P1B19 had 10–15% than P1B19W05 at various loads. The results were because increasing water content in diesel caused cooling effect which lead to lower temperature. When the combustion temperature drops, it makes combustion reaction more incomplete and cause higher CO emission (Cui *et al.*, 2009).

CO emission factors increased by 3-13% with higher fractions of iso-butanol blended in diesel. This is caused

by the lower heating value and further decrease in the temperature. High temperature may provide better combustion environment which improve the CO reduction. P1B19 has higher heating value than P5B15 which induce the higher CO emission. In addition, engine running effectively is lean which the aspirated air mass is still same, and *iso*butanol provides more fuel-bound oxygen in the rich zones during the combustion (Rakopoulos *et al.*, 2010a).

## Unburned Hydrocarbon Emissions

Hydrocarbon (HC) is one of well-known air pollutant which comes from petroleum, pesticides or other toxic organic matter. Especially HC emission from petroleum, people is exposed to petroleum in many ways directly, such as vehicles on the road. HC generally formed when fuel do not burn or burn partially. Compared to the regular diesel, all kinds of blended diesel had higher HC emission at various loads according to Fig. 5(b). At 12 kW, the HC emission was higher than other three loads due to low combustion temperature.

From Fig. 5(b), it is observed that the HC emission factors increase with increase of water under same ratio of

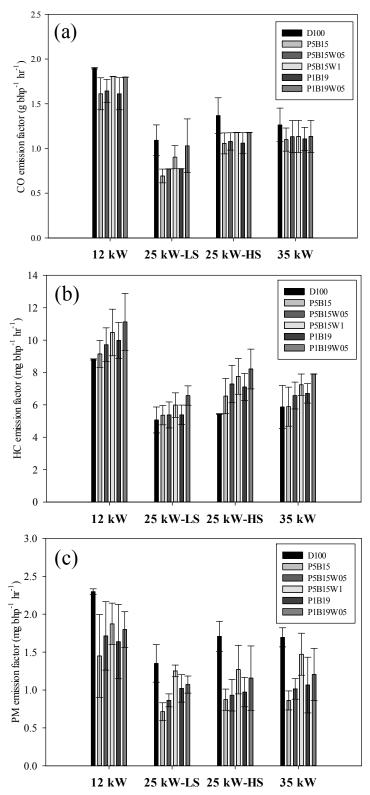


Fig. 5. (a) CO and (b) HC and (c) PM emission factor for different blended diesel at various loads.

P/B blended diesel condition. Many researches have showed that water in diesel will increase HC emission due to longer ignition delay (Greeves *et al.*, 1977; Cui *et al.*, 2009; Ithnin *et al.*, 2014). The high heat of vaporization of water will decrease temperature and reduce fuel-air mixture. The

long burning period, low fuel-air mixture temperature would contribute to higher HC emission (Özcan and Söylemez, 2005). The HC emission factors of P5B15W1 increased by 12–23% and 6–11% at various loads to the P5B15 and P5B15W05, respectively.

In this study, all kinds of alcohol diesel blends resulted in increased HC emission factors compared to petroleum diesel. Among these three alcohol blended diesel, P1B19W05 had the largest increase at all loads. Compared to the D100, the alcohol diesel blends diesel increased the HC emissions by 26%, 30%, 51%, and 35% at 12 kW, 25 kW-LS, 25 kW-HS, and 35 kW respectively. The higher isobutanol in blended diesel resulted in higher HC emission. This is caused by the low cetane number of iso-butanol which affects the self-ignition characteristics of the blended diesel and quenching effect. Also the low density and viscosity of iso-butanol lead to smaller size of fuel droplet which is easier and closer to the section of the cylinder walls and cause quenching effect and unburned fuels (Karabektas and Hosoz, 2009). Although HC emission factors for all blended diesel were higher than D100, they were much lower than The Environmental Protection Administration of Taiwan (TWEPA) regulation standards (< 0.46 g bhp<sup>-1</sup> hr<sup>-1</sup>). The HC can be easily removed by current catalytic converters.

#### Particulate Matter Emissions

Generally, the formation of particulate matter occurs via three steps: (1) nucleation mode (10–100 nm); (2) accumulation/condensation process (1–10 µm); and (3) coalescence and agglomeration process (1–10 µm). Many studies have shown that the increase of particle in exhaust gas of diesel engine is mainly due to accumulation mode (Maricq et al., 2002). From Fig. 5(c), the PM emission factors of all blended diesels are lower than those of D100 for all engine loads and speeds. These results could be due to the decreasing sulfur content of regular diesel when adding more sulfur-free additive (iso-propanol and iso-butanol) would inhibit the formation of sulfuric acid. The sulfuric acid has been reported to form PM by accumulating or condensing process on the soot or metallic ash in the exhaust gas at lower temperature (Lyyränen et al., 2002; Maricq et al., 2002; Vogt et al., 2003; Lu et al., 2013; Shukla et al., 2014). Additionally, high oxygen content in alcohol blended diesel which enhance the oxidation reaction and further reducing the PM formation (Lapuerta et al., 2009).

Fig. 5(c) shows that same ratio of P/B blended diesel increase with PM emission factor when increase water from 05% to 1%. This is caused by the cooling effect which enhances the condensation process for PM formation and hinders soot oxidation (Chang *et al.*, 2013). P5B15W05 reduce 9–31% at four different loads, compare to P5B15W1.

For different fraction of P/B, the P1B19 has higher PM emission factor. The *iso*-propanol alcohol has higher vapor pressure than *iso*-butanol which means *iso*-propanol alcohol is easier to turn into gas. When engine sprayed fuel into cylinder, the fuel was not totally vaporized at all and then caused incomplete combustion. The P5B15 reduce 10–30% PM emission factor, which compare to the P1B19, because of the higher vapor pressure than P1B19.

# PAHs and BaP<sub>eq</sub> Emissions Improvement

Generally, PAHs are mainly caused by incomplete combustion and the aromatic content in fuel (Mi *et al.*, 2000). According to Fig. 6(a), all diesel blends diesel had

reduced total-PAHs emission and decreased total-PAHs emissions factors with higher engine loads, compared to the regular diesel. When engine loads increased, the high temperature would lead to more complete combustion and reduce the total-PAHs emission.

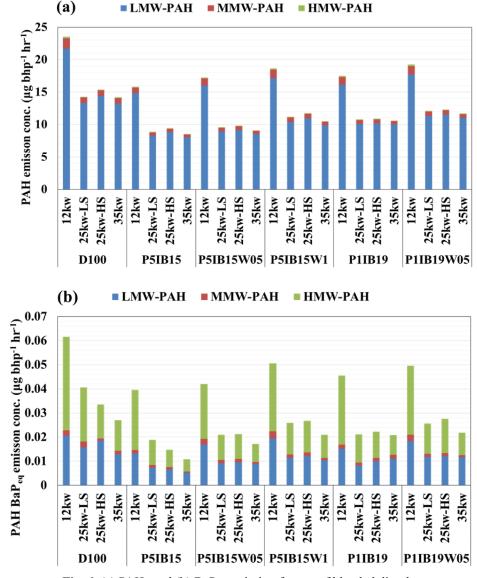
P5B15 and P1B19 were two diesel blends with varying P/B ratios whose total-PAHs emission factors increased with increase of *iso*-butanol. As previously explained, the P5B15 provide better combustion due to its high heating value than P1B19. Nevertheless, the higher volatility of IPA provided better premixing with air during ignition delay time and leaded to a faster and more complete combustion than those of IBA. Therefore, P5B15 reduce total-PAHs emission by 12–22% from using P1B19 at different loads.

To investigate the effect of water, P5B15W05 has better reduction than P5B15W1. It may be caused by the incomplete combustion which similar to the CO and PM emissions. With more water add into blended diesel, it leads to cooling effect which reduce the temperature and further retard the combustion process. As temperature decrease, it is easier to lead to incomplete combustion and high CO and PAHs emission (Levendis, 1998). The emissions of total PAHs for P5B15W1were increased by 8–20% at different loads, compared to those of P5B15W05. Fortunately, both of emissions them were significantly lower than those from the regular diesel, and could be considered more about their NO<sub>x</sub> reduction.

Molecular PAHs (LM-PAHs) have major contribution of total-PAHs and have shown the similar trend with total-PAHs as shown in Fig. 6(b). In contrast, Medium Molecular- (MM-) and High Molecular (HM-) PAH emissions are much lower than LM-PAHs. The above result indicates that the internal combustion engine has good performance and form less amount of toxic PAH contents (HM-PAHs) by using either regular diesel or testing diesel blends. As shown Fig. 6, P5B15 still have lowest emission among all blended diesel which reduction are 31-40%, 38-47%, and 21-45% for LM-PAHs, MM-PAHs, and HM-PAHs at various loads. PAH BaPeq is an index of measuring the toxicity of PAH carcinogenic potency. Although LM-PAH dominated total-PAHs emission, the TEF of LM-PAHs (TEF = 0.001) was relatively low in comparison to the MM-PAHs (TEF = 0.01) and HM-PAHs (TEF = 0.1-1). Therefore, the HM-PAH showed obviously higher BaP<sub>eq</sub> contribution in Fig. 6. The most efficient way to reduce the BaPeq is reduce HM-PAHs emission. From Fig. 6(e), P5B15 reduced 28–44% BaPeq which shows the same trend with total-PAHs emission. As mentioned before, higher water content or increased iso-butanol content will result in increased LM-PAHs, MM-PAHs, and HM-PAHs, and their BaP<sub>eq</sub> to incomplete combustion.

## **CONCLUSIONS**

In the current study, a series of diesel, iso-butanol, iso-propyl alcohol, and water emulsions were found to be stable with specific blending ratios. In summary, the current engine exhaust control technologies focus majorly on the  $NO_x$  and PM emissions. Unfortunately, simultaneous control



**Fig. 6.** (a) PAHs and (b) BaP<sub>eq</sub> emission factors of blended diesels.

of these two kinds of pollutants is not easily attained without engine modifications. The results of the study can be summarized as follows:

- 1. The BSFC increased with increasing iso-butanol or water content because of low heating value of blended diesel. The BTE of all blended diesel also increase with more water addition at various loads. Specifically, the BTE for P5B15W1 increased by 1% compared to D100 at low engine loads.
- 2. In-cylinder pressures were found to be lower than D100 for all blended diesel at various loads. Additionally, the in-cylinder pressures of 1% water-content were observed to be higher than those of 0.5% water-content at certain loads. The reason can be explained by the micro-explosion phenomenon which would lead to better combustion reaction.
- The HRR results show that all diesel blends had ignition delay at various loads. The ignition delay was caused by the low cetane number of blended diesel and high latent

- heat of evaporation of water. Although there were ignition delays for all the blends, the  $NO_x$  emission factors still reduced because of counteracting between ignition delay and low combustion temperature.
- 4. For the two different P/B ratios of blended diesel, the  $NO_x$ , CO, and PM emissions were all lower than D100 except HC which was higher than D100. Also, lower heating value of blended diesel would lead to lower combustion temperatures which lead to low  $NO_x$  emission but high CO, PM, and HC emission.
- 5. With water addition, the results were similar to the non-water containing diesel blends. It was observed that NO<sub>x</sub> emission decreased with increasing water content, but CO, PM, and HC emissions increased due to the cooling effect, as a result of low heating value and high latent heat of water.
- Total-PAHs and total-BaPeq emissions for all blended diesel were lower than those of D100 at various loads. On the other hand, the total-PAHs and total-BaPeq increased

- with increasing water and isobutanol content due to the resulting low combustion temperature.
- 7. In summary, in this study, lower iso-butanol and water content had showed better engine performance and lower exhaust gas emission. Particularly, P5B15 would be a best choice in terms of PM reduction among all other blends in this research. Although P5B15 had highest NO<sub>x</sub> emission among all blended diesel, it can be removed by equipping with catalytic converters. On the other hand, the best choice for NO<sub>x</sub> control would be P1B19W0.5 which could be combined with the use of diesel particulate filters for PM control. Overall, a future economic feasibility study on the best fuel blend is suggested.

## SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aagr.org.

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