



Emission Reductions of Nitrogen Oxides, Particulate Matter and Polycyclic Aromatic Hydrocarbons by Using Microalgae Biodiesel, Butanol and Water in Diesel Engine

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ABSTRACT

The transport sector is a major consumer of fossil fuels especially petroleum diesel, which is used to power diesel engines used on-road and off-road in trucks, tractors, passenger cars as well as marine vessels. This is because the diesel engine offers various benefits compared to the spark ignition engine. The advantages include superior fuel efficiency, higher thermal efficiency, greater power output, better fuel saving, lower carbon dioxide (CO₂) emission, larger torque and greater durability. Conversely, the diesel engine is a major source of both criteria and non-criteria air pollutants, which contribute to the deteriorating air quality thereby putting the health of mankind at risk. The objective of this study was to investigate the performance of butanol- microalgae biodiesel-diesel blends in terms of energy performances and pollutants' emission reductions by comparing the brake specific fuel consumption (BSFC), brake thermal efficiency (BTE) and exhaust gases temperatures as well as the nitrogen oxides (NO_x), particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), carbon monoxide (CO) and hydrocarbons (HC) of various diesel blends and against the baseline performance of regular petroleum diesel. All diesel blends showed higher BSFCs and BTEs compared to regular petroleum diesel, whereby BT20W0.5 had the highest BSFC and BT15B2 had the best performance in terms of BTE. Among the diesel blends, only 2% microalgae added to diesel blends increased the NO_x emissions by about 2%, while for the addition of 10–20% butanol fractions and 0.5% water fractions resulted in lower NO_x emissions by about 12–28%, when compared to petroleum diesel. All the diesel blends considered in this study showed PM reductions ranging between 22.4% for B2 and 60.4% for BT15W0.5%, while reductions of PAH emissions were ranging from 6.5% for B2 to 22.76% for BT20W0.5. On the other hand, only the use of 2% microalgae biodiesel showed reductions in CO emissions of about 0.34% and 1.01% for B2 and BT20B2 blends, respectively, while other diesel blends showed increased CO emissions of about 1.72–2.94% in comparison to CO emissions of diesel fuel emissions. The addition of higher butanol fractions of 20% increased the HC emission factors by approximately 18% and 70%, while the HC emission factors for biodiesel, 10–15% butanol fractions and 0.5% water additions lead to reductions in emission by about 8–50%. According to the results of this study, more research is recommended on the economic potential of using of oxygenated additives in diesel engine especially water addition, higher alcohols and dieselhol blends to evaluate the possibility of synergetic properties of these kinds of fuels to achieve simultaneous reductions in the emissions of NO_x, PM, CO, HC, PAHs and other persistent organic pollutants (POPs).

Keywords: Microalgae; Butanol; BTE; BSFC; NO_x; PM; PAHs; Diesel engine; Emissions; Water emulsion; Energy.

INTRODUCTION

In the transport sector, the diesel engine is considered to

be as one of the greatest inventions since its inception in 1893 (Lin *et al.*, 2012) and has found a market in the light and heavy transport and agricultural industries with its application being both on-road and off-road. Diesel engines use diesel derived from petroleum which consists of mostly aliphatic alkanes and few branched alkanes composed of C₈-C₂₈ (Ribeiro *et al.*, 2007). Conversely, the current supply of fossil fuel is dwindling and it is highly associated with rising carbon dioxide (CO₂) emissions which have been a great driver of global warming (Wang *et al.*, 2014). Thus, there is a need to find sustainable and environmental friendly fuel types for application in the diesel engine.

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The diesel engine is preferred for its higher energy and power output, greater thermal efficiency, better fuel efficiency, lower CO₂ emissions, superior torque and better durability compared to the spark ignition engine which runs on gasoline (Hagos *et al.*, 2011; Alahmer, 2013; Kumar *et al.*, 2013). On the other hand, the diesel engine is a major source of both criteria and non-criteria air pollutants, which contribute to the deteriorating air quality (Pilusa *et al.*, 2012). Poor air quality is a threat to the health of mankind at risk as well as the immense contribution by greenhouse gases the climate change. The diesel engine is a major source of emissions of nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter (PM), total hydrocarbons (HC), carbon dioxide (CO₂), carbon monoxide (CO) as well as toxic chemicals such as polycyclic aromatic hydrocarbons (PAHs) (Ribeiro *et al.*, 2007; Doğan, 2011; Tsai *et al.*, 2014). The emission of these pollutants largely depends on the engine type and age, in addition to the operating conditions and the fuel type (Yao and Tsai, 2013; Popovicheva *et al.*, 2014).

These pollutant emissions pose huge risks to human health (Yao and Tsai, 2013) in form of cardiovascular disorders, respiratory diseases and lung cancer (Magara-Gomez *et al.*, 2014; Popovicheva *et al.*, 2014) especially from particulate matter and PAHs, which are mutagenic as well as carcinogenic (Lin *et al.*, 2013). As a result, many regulatory bodies have imposed very stringent rules and directives aimed at capping and reducing the amount of vehicular emissions as well as addressing the greenhouse gases problem (Rakopoulos *et al.*, 2010c; Campos-Fernández *et al.*, 2012; Kumar *et al.*, 2013; Lapuerta *et al.*, 2015).

This has prompted enactment of very stringent laws and regulations to control the emissions in order to protect the environment and the human health (Doğan, 2011). In order to comply with these regulations, various emission control methods have been put in place, which include the use of pre-combustion techniques, post-combustion or exhaust gas treatment and also fuel reformulation and use of additives as well as alternative fuels such as biodiesel and vegetable oils (Ribeiro *et al.*, 2007; Balamurugan and Nalini, 2014).

Fuel reformation involves altering fuel characteristics or substituting diesel fuels with biodiesel or vegetable oils and has been widely used as one of the viable techniques of reducing and controlling pollutant emissions from the diesel engine (Rakopoulos *et al.*, 2010b, 2011). Biodiesel blends (Ribeiro *et al.*, 2007) and dieselhols (Lin *et al.*, 2012) and diesel-water emulsions are among the most used kinds of fuel reformulations currently (Kadota and Yamasaki, 2002; Ithnin *et al.*, 2014), which are generally oxygenated additives due to their higher oxygen content in comparison to petroleum diesel (Ribeiro *et al.*, 2007; Lin *et al.*, 2012). Biodiesel blends consist of diesel and biodiesel in various fractions. On the other hand, dieselhols are made up of petroleum diesel and alcohols or diesel, alcohols and biodiesel in various suitable ratios (Lin *et al.*, 2012). The use of these types of fuel blends is to alleviate the shortcomings encountered when using biodiesel such as high viscosity, while allowing biodiesel to act as an emulsifier and binder to the alcohol-diesel interactions (Ribeiro *et al.*, 2007; Yilmaz *et al.*, 2014). This allows alcohols to lower the viscosity of

biodiesel as well as raise the octane number of biodiesel, while the biodiesel raises the cetane number of alcohols.

Biofuels as alternative fuel sources are promising especially in the transportation sector (Attia and Kulchitskiy, 2014). Various studies have focused on the use of biodiesel or vegetable derived fuels as alternative fuels, since they are more environmentally friendly and CO₂ conservative. However promising these sources of energy seem, there are few challenges that render them unattractive as the transesterification process is energy and material demanding. Additionally, concern has been raised about competition over available land between biodiesel plants and food crops considering that the global food security status not stable. Other issues include the cost of pretreatment and purification processes and secondary pollutant emanating from the transesterification processes.

Biodiesel and vegetable oil can be used in diesel engines without engine modification, since their energy contents are close to those of petroleum diesel fuel (Ribeiro *et al.*, 2007). Unfortunately, some of the drawbacks of vegetable oils and biodiesel include: incomplete combustion, deposition of particles on engine parts, cold flow plugging and poor atomization for vegetable oil. To counter these problems, the vegetable oil can be pretreated through preheating, pyrolysis, solvent addition, emulsification and transesterification processes in order to convert it to biodiesel (Ribeiro *et al.*, 2007; Rakopoulos *et al.*, 2011). Transesterification is the most widely used method for vegetable oils' pretreatment (Lin *et al.*, 2012).

Biodiesels are essentially alkyl esters of fatty acids, which are obtained when vegetable oils are reacted with suitable alcohols such as ethanol or methanol under catalytic conditions (Ribeiro *et al.*, 2007; Halim *et al.*, 2012; Tran *et al.*, 2012). Advantages of using biodiesel include reduced sulfur content, higher biodegradability, and less toxicity compared to petroleum diesel fuel (Rakopoulos *et al.*, 2011).

Microalgae has recently gained a lot of interest from researchers (Shuping *et al.*, 2010; Chen *et al.*, 2011; Halim *et al.*, 2012; Tran *et al.*, 2012; Kwon *et al.*, 2014) as a third generation biodiesel source of biofuels specifically biodiesel and bio oil, biohydrogen, bioethanol and methane (Halim *et al.*, 2012; Chen *et al.*, 2013a). Microalgae can be grown in open ponds or bioreactors and utilize CO₂ to produce proteins and lipids via photosynthesis (Yeh and Chang, 2012). Therefore, microalgae offers the advantages of sequestering CO₂ as a biological photocatalyst (Chen *et al.*, 2011; Parmar *et al.*, 2011; Wang *et al.*, 2014). In addition to being cultivated phototrophically, microalgae can be grown under heterotrophic and photoheterotrophic conditions (Yeh *et al.*, 2012; Yeh and Chang, 2012). Additionally, microalgae does not compete with food crops over arable land, since it can be grown in fresh water and marine conditions (Rawat *et al.*, 2013) without requiring a lot of inputs and high photosynthesis efficiency, higher biomass production and growth rates (Tran *et al.*, 2012; Rizzo *et al.*, 2013). To obtain microalgae biodiesel, the steps followed include culturing, harvesting, extraction, transesterification (Parmar *et al.*, 2011).

Accordingly, alcohols have been used as additives to

address the challenges posed by the use of biodiesel and vegetable oils in fuel blends as well as alternate fuels. In fact, Gong *et al.* (2014) reports that the projections done by International Energy Agency (IEA) show that the use of biofuels such as alcohols is expected to go up from 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 purpose of additives in the diesel blends is to stabilize for storage purposes, lower the viscosity as well as increase the cetane number of the fuel blends to be close to that of diesel. Alcohols have a hydroxyl group (–OH) attached on their molecular structures and form isomers depending on the position of the –OH group (Rakopoulos *et al.*, 2010c). 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_x, especially, when blended with biodiesel-diesel blends as well as reduced SO_x, since they have less sulfur content (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 the 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; Lapuerta *et al.*, 2015) 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. Alcohols with longer unbranched chain lengths offer higher lower heating values, greater densities, and increased cetane values with reduced self-ignition temperatures as well as less knock tendencies (Campos-Fernández *et al.*, 2012; Dusséaux *et al.*, 2013). Unfortunately, not much open literature is available on alcohols such as propanol, butanol or even pentanol (Karabektas and Hosoz, 2009; Rakopoulos *et al.*, 2010d; Lapuerta *et al.*, 2015).

Butanol is obtained from biomass (Rakopoulos *et al.*, 2010b, c) through the activity of *Clostridium spp.* in the Acetone-Butanol-Ethanol (ABE) fermentation process as the major product alongside ethanol and acetone (Tran *et al.*, 2010; Lin *et al.*, 2012). Compared to other lower alcohols, ethanol and methanol, that have been extensively used on diesel engine (Campos-Fernández *et al.*, 2012), butanol has been credited with several advantages. Chief among these include lower auto-ignition temperatures, lower hydrophilicity, comparatively higher heating and cetane values, less

corrosive power as well as better miscibility with diesel engine (Doğan, 2011; Lin *et al.*, 2012; Yilmaz *et al.*, 2014).

The technique of adding water to diesel fuel has been employed in diesel engine as a pollutant emission control strategy. According to (Alahmer, 2013) various ways of incorporating water in the combustion process include use of separate injectors for water and diesel, fumigation in the air intake system, mixing the fuel and water in the fuel lines prior to injection or forming emulsions. The use of water-fuel emulsions have led to remarkable reduction in pollutant emissions especially achieving NO_x-PM trade-offs (Lin *et al.*, 2010; Subramanian, 2011; Alahmer, 2013; Chang *et al.*, 2014b). Water emulsions result in micro-explosion phenomena, whereby during combustion, water evaporates faster than diesel due to differences in boiling points (Hagos *et al.*, 2011). 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_x 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.

The objective of this study was to investigate the performance of butanol- microalgae biodiesel-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), the brake thermal efficiency (BTE) and the exhaust gas temperature were the energy performance parameters utilized in this study. Additionally, the emission factors of criteria pollutants such as NO_x, PM, CO and HC as well as total PAHs and total BaP_{eq} were the emission parameters considered and compared against available Taiwan Emission Standards.

EXPERIMENTAL SECTION

Biodiesel Production from Microalgae

To obtain the microalgae biodiesel, the microalgae was isolated, cultured, harvested, extracted and transesterified according to the detailed description provided in a previous study (Mwangi *et al.*, 2015). The microalgae strain *Chlorella vulgaris*, ESP-31 and *Chlorella sorokiniana*, Mb-1 were obtained from University Center for Bioscience and Biotechnology, National Cheng Kung University, Tainan City, Taiwan, and the culture conditions is described in (Yeh *et al.*, 2012). Briefly, *Chlorella vulgaris*, ESP-31 and *Chlorella sorokiniana*, Mb-1 were isolated from open shrimp ponds located in Tainan area and inoculated in a photobioreactor and then the microalgae was cultured in a medium whose composition was as described in (Mwangi *et al.*, 2015) before being transferred to ponds, where they were cultivated for about 17 days then harvested and centrifuged to get rid of moisture. The microalgae oil was

obtained from the microalgae sludge resulting from the centrifugation process by reacting with methanol and transferred into a microwave for cell disruption then subsequently filtered using a spin drier to obtain a microalgae cake. The microalgae cake was then taken through wet extraction process and subsequent transesterification process to obtain the biodiesel according to (Mwangi *et al.*, 2015).

Diesel Engine Test

Eleven kinds of blends (D100, B2, BT5, BT10, BT15, BT5W05, BT10W05, BT15W05, BT15B2, BT20B2 and BT20B2W05) containing varying fractions of diesel, butanol, microalgae biodiesel and water were prepared as per the Table 1, whereby D, B, BT and W represent conventional diesel, microalgae biodiesel, butanol and water, respectively. The butanol used in this study was supplied by Panreac with a purity of 99.5%, while the commercial diesel was

supplied by CPC Corporation, Taiwan (CPC). The biodiesel was obtained from the extraction process described earlier and deionized water was employed. The blending process was done using a lab scale ultrasonic tank (40 kHz and 120 W power output) for 15 min after mixing using Fluko® stirring probe from Fluko Equipment Shanghai Co.

The engine used in this study was a Mitsubishi 4M40-2AT1, whose schematic representation is shown in Fig. 1. It is a direct injection and water cooled four cylinders diesel engine with a bore of 95 mm and a stroke of 100 mm. The engine has a maximum torque of 200 Nm at 3200 rpm and the rated power is 109 kWh at 3700 rpm.

The engine test procedure and instrumental analysis of the collected pollutants were done according to the method proposed and applied by previous studies done by (Chang *et al.*, 2013, 2014a, b). Before each sampling session, the engine was warmed up for 30 min and for a minimum of 3

Table 1. Diesel fuel blends.

Blend	Conventional Diesel (%)	Algae Biodiesel (%)	Butanol (%)	Water (%)
D100	100	0	0	0
B2	98	2	0	0
BT5	95	0	5	0
BT10	90	0	10	0
BT15	85	0	15	0
BT5W05	94.5	0	5	0.5
BT10W05	89.5	0	10	0.5
BT15W05	84.5	0	15	0.5
BT15B2	83	2	15	0
BT20B2	78	2	20	0
BT20B2W05	77.5	2	20	0.5



Fig. 1. Diesel engine and control system.

min between different sampling campaigns and fuel change. The sampling was undertaken for about 20 minutes in duplicate at a speed of 2200 rpm and a load of 50% giving off 12 kW at a torque of 50 Nm. 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 $< 5^{\circ}\text{C}$ 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 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^3 . The exhaust gas was passed through Belltone BE-200 gas analyzer from Belltone Technologies to detect and quantify the criteria pollutants (NO_x , CO 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 (GC/MS) set up for analysis.

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 μm). The operating conditions were an injection volume of 1 μL ; 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 $8^{\circ}\text{C}/\text{min}$ 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)

Quality control and quality assurance procedures were carried out by using serial dilution method for 21 PAHs. The range of detection limits and limit of quantification for individual PAHs were 64–768 pg/m^3 and 0.134–1.58 ng/m^3 respectively. The relative standard deviations from seven

consecutive injections of a 10 ng/L PAH standard were between 4.30–7.45% while the average recoveries ($n = 3$) for individual PAHs ranged between 81–113%. Analysis of field blanks, including glass-fiber 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) of each blend.

$$BSFC = \frac{V}{Pt} \text{ (g / kW} \cdot \text{h)} \quad (1)$$

$$BTE = \frac{Pt}{VH} \text{ (%) } \quad (2)$$

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

$$EF = CV/Pt \text{ (mass/kW} \cdot \text{h)} \quad (3)$$

RESULTS AND DISCUSSION

Brake Specific Fuel Consumption (BSFC)

Brake specific fuel consumption (BSFC) implies energy efficiency per unit mass of oil whereby the lower the BSFC value the better the energy performance in terms of cost. According to Fig. 2, compared to petroleum diesel performance, the other blends had increased BSFCs. Compared with D100, the BSFC increased by 1.23%, 0.31%, 1.69%, 3.07%, 0.13%, 2.04%, 2.90%, 3.42%, 3.88% and 4.69% for B2, BT5, BT10, BT15, BT5W05, BT10W05, BT15W05, BT15B2, BT20B2 and BT20B2W05, respectively.

Fig. 2 shows that by adding biodiesel, and butanol the resulting BSFCs were greater than those of petroleum diesel, due to the lower calorific value of microalgae biodiesel (41 MJ/kg) and butanol (35.1 MJ/kg) compared to that of petroleum diesel (46 MJ/kg), more amount of blended diesel oil required is also relatively increased in order to maintain continuous operation of the engine while maintaining the same power output.

The same observations were made by (Gill *et al.*, 2012), who observed that as fractions of rapeseed methyl ester were increased, the specific fuel consumption increased. Similar observations were also reported by (Lin *et al.*, 2008) for soy-biodiesel. In another study, Buyukkaya (2010)

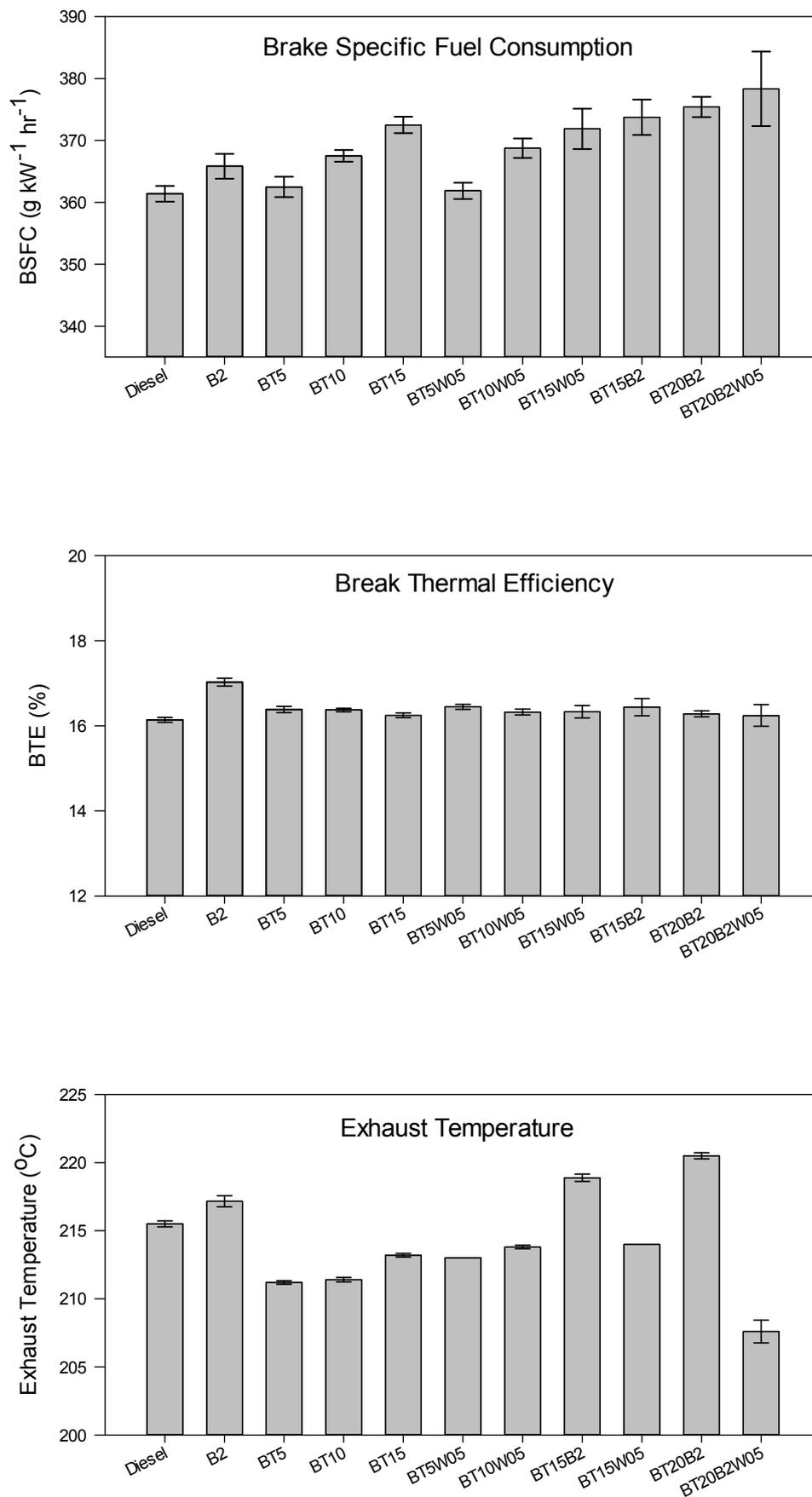


Fig. 2. Energy performances - brake specific fuel consumption, brake thermal efficiency and exhaust gas temperature.

reported BSFC increase of about 2.5%, 3.0%, 5.5% and 7.5% for rapeseed biodiesel blends of B5, B20, B70 and B100. In a recent study, by our research group, 2% microalgae biodiesel increased the BSFC by approximately 6.3% (Mwangi *et al.*, 2015). On the other hand, Labeckas and Slavinskas (2006) reported decreased BSFC at a speed of 1400 rpm by about 3.2% and 1.7% for 10% and 20% rapeseed methyl esters blends respectively, and attributed this observation to comparatively higher oxygen content in the biodiesel.

As reported for the biodiesel, Fig. 2 shows that alcohol addition to fuel blends also leads to increased BSFC compared to diesel fuel performance. Our results are similar to the observations posted by Doğan (2011), Rakopoulos *et al.* (2010d) and Rakopoulos *et al.* (2010c), who reported increased BSFCs values for butanol-diesel blends, when compared to diesel fuel. For equal engine loads, the alcohol blends exhibit higher fuel consumption due to lower heating values, which translates to lower energy content compared to fossil diesel fuel.

Similar to this study, Abu-Zaid (2004) showed that the BSFC increased with increasing water content in the emulsions. The rise in BSFC can be related to the reduced heating values of the fuel blends. The increase in BSFC in the water-emulsified fuel blends is due to the fact that less diesel is available for combustion. The available diesel is reduced by the same volume of additives in each blend when compared to the base diesel. On the other hand, Lin *et al.* (2012) observed that BSFC did not actually increase with an increase of water fractions indicating that even though reduced heating value in fuel blends is the major contributor, it may not be the only dominant factor. In some operating conditions, small amount of water added to blends may make the combustion more complete and release more amount of heat from the fuels, thus the BSFC does not necessarily increase.

Brake Thermal Efficiency (BTE)

In comparison to that of D100, the brake thermal efficiency (BTE) for B2, BT5, BT10, BT15, BT5W05, BT10W05, BT15W05, BT15B2, BT20B2 and BT20B2W05 increased by 5.51%, 1.53%, 1.46%, 0.67%, 1.92%, 1.16%, 1.19%, 1.18%, 0.90% and 0.66%, respectively as shown in Fig. 2 indicating better performance in terms of thermal efficiency than that of petroleum diesel.

As seen from the results in Fig. 2, the addition of biodiesel fraction B2 had the greatest effect on BTE compared to other blends. An increase in BTE by addition of microalgae biodiesel was also reported by the previous study (Mwangi *et al.*, 2015). Additionally, when using rapeseed methyl esters at a speed of 2000 rpm, the BTE increased by 0.47%, 0.95%, 0.47% and 0.24% for biodiesel blends containing 5%, 20%, 70% and 100% (Buyukkaya, 2010). The trends from studies by Buyukkaya (2010) and Labeckas and Slavinskas (2006) show that even though BTE increases with an increase in biodiesel contents, this trend is not infinite as the performance declines at higher fractions of biodiesel, since the temperature in the diesel engine is not high enough for the good combustion and the oxygen content

effect loses its positive influence at higher biodiesel fraction.

Compared to the effect of biodiesel addition, adding butanol increased the BTE by a lower magnitude. This observation with butanol has been reported by Rakopoulos *et al.* (2010d) and Doğan (2011), who cited the improved premixed combustion as a result of lower cetane number of alcohols. Furthermore, the higher oxygen content in the chemical structure of alcohols induces higher combustion efficiencies and reduced heat losses as well as rapid heat release due to higher ignition delays (Doğan, 2011; Campos-Fernández *et al.*, 2012; Campos-Fernández *et al.*, 2013).

A higher oxygen content provided by water content in diesel blends results in a better brake thermal efficiency in comparison to the base diesel due to a more complete combustion (Chang *et al.*, 2014b). Additionally, the BTE increases as a result of ignition delay (Subramanian, 2011; Ithnin *et al.*, 2014) and improved combustion due to the microexplosion mechanism which avails flammable gases such as CO and H₂ (Lin *et al.*, 2008). Furthermore, the ignition delay may cause more diesel to be consumed leading to increased BSFC and improved combustion and thermal efficiency.

Exhaust Gas Temperature

Previously, the exhaust gas temperature has also been employed as a criterion for the performance of various fuel blends (Utlu and Koçak, 2008; Buyukkaya, 2010; Fahd *et al.*, 2013). The results in Fig. 2 shows that using D100 as a base fuel, the exhaust temperatures in this study were lower for BT5, BT10, BT15, BT5W05, BT10W05, BT15W05, and BT20B2W05 by approximately 2.00%, 1.90%, 1.07%, 1.16%, 0.79%, 0.70%, and 3.67%. Conversely, the exhaust temperatures increased for B2, BT15B2 and BT20B2 by 0.77%, 1.57% and 2.32% respectively.

As seen from the results the addition of biodiesel resulted in higher exhaust gas temperatures. A higher oxygen content in the biodiesel may enhance combustion conditions in the combustion chamber resulting in higher exhaust gas temperatures. Similar results were posted by Buyukkaya (2010) and Acharya *et al.* (2009). Furthermore, Oberweis and Al-Shemmeri (2010) reported a 1–6% increase in exhaust temperature for B50 and B100 and attributed it to more fuel being combusted in mixing-controlled combustion and diffusion combustion phases resulting in higher temperatures as biodiesel content increases.

The addition of butanol resulted in lower temperatures with increasing butanol content compared to the petroleum diesel fuel as a result of lower energy content in butanol blends. Similarly, by using ethanol in blends, Putrasari *et al.* (2013) noted that exhaust temperature decreased with increasing amount of ethanol in blends, because of the lower energy content of ethanol compared to fossil diesel and the fact that partially oxidized OH radicals burn at lower temperatures.

The effect on exhaust gas temperatures of water addition to butanol-diesel blends was lower than that of butanol addition especially at higher butanol contents. The synergetic effect of water addition coupled with biodiesel and butanol additions resulted in higher reduction in exhaust temperatures.

Lower exhaust gas temperatures experienced with water emulsions maybe due to absorption of heat by the water content (Fahd *et al.*, 2013).

Nitrogen Oxides Emissions

According to Fig. 3, only B2 showed an increased NO_x emission, while BT5, BT10, BT15, BT5W05, BT10W05, BT15W05 and BT15B2 had reduced NO_x emissions of about 12.1%, 14.9%, 24.4%, 17.3%, 17.5%, 26.3%, 24.2%, 26.5% and 28.2% respectively.

Nitrogen oxides, NO_x, are generally formed via the Zeldovich mechanism, namely at the ambient air temperature of nitrogen and oxygen react to form NO, NO₂ and N₂O, which are collectively referred to as NO_x. Therefore the combustion temperature is a major factor affecting NO_x formation. In addition, extended ignition delay caused by oxygenated additives result in high temperatures which favor the increase of NO_x emissions.

The NO_x emissions from B2 were the highest among all the blends. Fig. 3 shows NO_x emission factor increased by about 2% for B2 compared to petroleum diesel. Similarly, Liu *et al.* (2012) reports an increase on NO_x emissions by approximately 0.38%–1.2% when using waste cooking oil biodiesel. This collaborates with other literature which report that NO_x emissions for biodiesel will increase, mainly due to higher biodiesel oxygen contents, which result in increased residence time of the fuel blends during combustion in the engine cylinder leading to a high temperature zone, and then resulting in higher NO_x emissions.

Furthermore, for varying butanol fractions in butanol-diesel fuel blends, the proportion of NO_x emissions reduction increased with increasing butanol content. This is because the butanol which has a lower heating value of approximately 35.1 MJ/kg and has a higher saturation vapor pressure, which when mixed with fossil diesel fuel lowers the calorific value of the fuel mixture as well as the vapor pressure rise, leading to a reduction in the internal temperature of the engine. Although, the cetane number is reduced by the addition of butanol and is likely to cause a longer ignition delay and more of the NO_x emissions, but overall the effect of adding butanol causing internal engine temperature to decline dominates over the impact of the ignition delay, thereby reducing emissions of NO_x (Rakopoulos *et al.*, 2010c, d).

In addition, the addition of 0.5% water to the diesel-butanol-biodiesel blends, also contributed to a reduction of NO_x emissions. This was due to the microexplosion phenomena from water emulsion that causes a cooling effect thereby reducing combustion temperature and consequently inhibiting the formation of thermal NO_x. Compared to the same proportion of water-free diesel blends, the diesel blends mixed with water further reduced the NO_x emissions by about 3–6%, which further confirms the addition of water can be conducive to the reduction of diesel emissions of NO_x.

The Taiwan Regulatory Emission Standards for NO_x are very stringent and are set at 2 g/kW/hr. Therefore a careful observation shows that the emissions in this study were an order of magnitude higher than the regulated guideline. Both fuel and engine modifications are needed to achieve the regulatory requirements.

Particulate Matter (PM)

Fig. 3 shows that the particulate matter (PM) emission factors for all the blends were greatly reduced with respect to the emission from the use of diesel fuel. For B2, BT5, BT10, BT15, BT5W05, BT10W05, BT15B2, BT15W05, BT20B2 and BT20B2W05 the respective reductions were 22.0%, 35.3%, 38.8%, 45.4%, 44.2%, 48.9%, 53.3%, 60.4%, 57.2% and 59.5%.

In general, PM formation can be divided into three phases, nucleation mode whose particle size is about 10–100 nm; the second stage accumulation or condensation process whereby the particles begin to gather and the particle size increase to about 0.1–1 μm; finally the third stage is the coalescence and agglomeration processes, whose particle size is about 1–10 μm. The second stage is the main path way for PM formation in the diesel engine exhaust.

Blended diesel containing 2% of microalgae biodiesel had its PM emission reduced by approximately 22% compared to diesel fuel, because microalgae biodiesel has a higher oxygen content of about 10–14%, which enhances the combustion process hence reduced PM formation (Yoshimoto *et al.*, 1999; Wu *et al.*, 2009). A reduction of 6.8–15% was reported by Liu *et al.* (2012), when comparing the emissions of waste cooking oil with that of diesel and attributed it to lower soot formation when using biodiesel.

With the increase in butanol content, PM reduction also increased. An increase in the alcohol content of the blends translates to higher oxygen content in the diesel fuel, which enhances combustion reaction, thereby reducing the generation of PM. In addition, the use of butanol reduces the fuel sulfur content through dilution effect thus inhibiting the formation of sulfuric acid, which according to literature increases the chances of PM formation (Lin *et al.*, 2012).

The microexplosion phenomenon is the major mechanism leading to the reduction in PM formation when using 0.5% water content in the fuel blends. The formation of secondary spray at the nozzle ensures more complete combustion, which discourages the PM formation process. Furthermore, according to Lin *et al.* (2008) and Lin *et al.* (2012), particulate matter is greatly reduced when water is added to diesel blends. This is because there is provision of the OH radicals to the fuel/air mixture during combustion, which serves to oxidize the soot being formed thus leading to a reduction in total PM. Additionally, lower cylinder temperatures translates to less pyrolysis reactions that form cenospheres.

In this study, the addition of butanol (5–20%) and 0.5% water significantly reduced PM emission factors (0.004–0.009 g/kW/hr), which are much lower than 0.03 g/kW/hr value stipulated by Taiwan regulatory emission standards for diesel engine.

Polycyclic Aromatic Hydrocarbons (PAHs)

Compared to the diesel fuel, the results in Fig. 3 shows that the reductions of PAH emissions for the fuel blends were about 6.50%, 12.7%, 15.7%, 17.5%, 14.9%, 19.2%, 20.9%, 18.1%, 19.1% and 22.8% for B2, BT5, BT10, BT15, BT5W05, BT10W05, BT15W05, BT15B2, BT20B2 and BT20B2W05, respectively. Additionally, the total

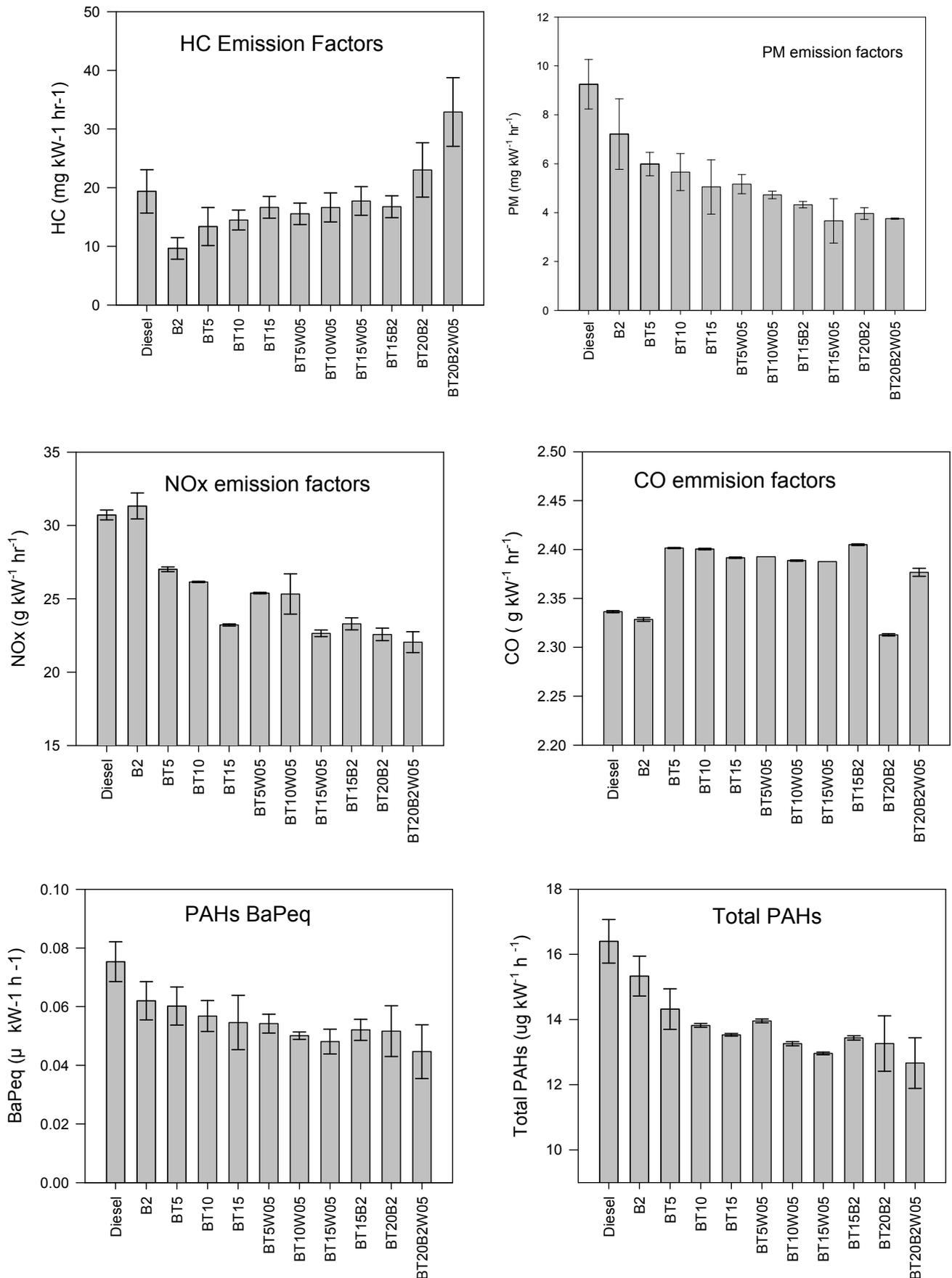


Fig. 3. Pollutant emissions from the diesel engine tests.

BaP_{eq} emission factors of B2, BT5, BT10, BT15, BT5W05, BT10W05, BT15W05, BT15B2, BT20B2 and BT20B2W05 reduced by 17.7%, 20.1%, 24.6%, 27.5%, 28.0%, 33.5%, 36.1%, 30.8%, 31.3%, and 40.6% respectively.

Polycyclic aromatic hydrocarbons (PAHs) as carcinogenic compounds are found in petroleum diesel due to the aromatic content of fossil diesel fuel (Mi *et al.*, 1998; Mi *et al.*, 2000; Lin *et al.*, 2006b, c) as well as the nature of additives (Mi *et al.*, 1998). Additionally, PAHs may also exist as result of incomplete combustion in diesel engines and arise from pyrosynthesis of aromatic compounds during fuel combustion as well as unburned fuel and lubricating oil (Borrás *et al.*, 2009). PAHs can be classified into low molecular weight (LMW), medium molecular weight (MMW) and high molecular weight (HMW). PAHs are semi-volatile organic compounds, which exist in both gas and particulate phases in the atmosphere. The low molecular weight PAHs are the major contributors of total-PAH masses, while the HMW PAHs are associated with particulate phase making them more toxic (Borrás *et al.*, 2009; Lee *et al.*, 2011).

Adding microalgae biodiesel into the diesel fuel leads to decreased PAH emissions as a consequence of dilution effect that reduces the PAHs present in the overall combusted fuel. A similar observation was reported by Liu *et al.* (2012) whereby reduction of PAH emission using waste cooking oil biodiesel ranged about 14–53%, since the PAH content in biodiesel is nearly nonexistent. Similar to this study, Mwangi *et al.* (2015) reported a reduction of 6.5% and 18% for total PAHs and total BaP_{eq} respectively when using 2% microalgae biodiesel. Recently, Tsai *et al.* (2014) reported that the addition of biodiesel reduced emissions of total PAHs by 6.13–42.5% (mean, 24.1%) and the total BaP_{eq} by 16.6–74.8% (mean, 53.2%), while Correa and Arbilla (2006), indicated that PAH emissions were reduced by approximately 2.7%, 6.3%, 17.2%, while mono aromatic hydrocarbons (MAHs) emissions were reduced by 4.2%, 8.2%, 21.1%, when using 2%, 5% and 20% biodiesel blends, respectively. Lee *et al.* (2011) attributed decreased the emissions of total PAHs and total BaP_{eq} with increasing blending of biodiesel blend due to improved combustion performance and increased oxygenation that oxidize PAH forming precursors as well as reduction in fuel PAH content due to dilution effect (Lim *et al.*, 2014). According to Borrás *et al.* (2009), reformulation of diesel fuel using biodiesel modifies the aromatic and sulfur content, which may sufficiently reduce PAH emissions.

Similar to this study, Mwangi *et al.* (2015) reported a reduction of 19% and 31% for total PAHs and total BaP_{eq} respectively when using 2% microalgae biodiesel plus 20% butanol diesel blends. Additionally, when employing ethanol-biodiesel blends, Lee *et al.* (2011) reports a 6.4–52% and 18–69% reduction for total PAHs and total BaP_{eq}, respectively. Adding butanol into the diesel fuel leads to decreased PAH emissions as a consequence of dilution effect that reduces the PAHs content in the overall volume of combusted fuel. Higher ratios of butanol addition in diesel blends resulted in reduction of lower molecular weight PAHs, thus significantly reducing the total PAHs in

addition to the increased oxygen content, which promotes complete combustion thereby retarding the formation of lower molecular PAHs (Lin *et al.*, 2012b).

Various studies report reduced PAH emission with addition of small amounts of water into the diesel fuel lead to lower PAH emissions as a consequence of competition of several mechanisms. One of these is the dilution effect that reduces the PAHs present in the overall combusted fuel (Lin *et al.*, 2006a, 2008; Lin *et al.*, 2010; Lee *et al.*, 2011; Chang *et al.*, 2013; Mwangi *et al.*, 2015). Furthermore, the addition of water causes the micro-explosion phenomena resulting in more turbulent combustion environment that enhances the air/fuel mixing. Another probable mechanism involves water dissociation into highly oxidative OH radicals as well as highly combustible H radicals, therefore, resulting in a better combustion and ignition delay. These factors combined discourage incomplete combustion, hence less PAHs are formed.

Hydrocarbons HC

According to Agarwal *et al.* (2008), unburnt hydrocarbons occur in diesel exhaust as complex mixtures of unburned and partially burnt fuel components containing hydrogen and carbon and existing in both gaseous and liquid phases/semi-volatile fractions. As per the results in Fig. 3, the hydrocarbons emissions were reduced by 50.2%, 30.9%, 25.2%, 14.0%, 19.7%, 14.1%, 8.43%, and 13.5% for B2, BT5, BT10, BT15, BT5W05, BT10W05, BT15W05 and BT15B2 while they were increased by 18.9% and 69.8% for BT20B2 and BT20B2W05.

The reductions in HC emissions were achieved due to increased oxygen content in the added biodiesel and butanol fractions. Similarly, Liu *et al.* (2012) reported decreased HC emissions by approximately 6.8–24%, when using varying amounts of waste cooking oil biodiesels as a result of improved combustion when using biodiesel. On a closer observation, when the butanol content is over 15%, a higher oxygen effect is dominated by the effect of high latent heat of the saturated butanol vapor pressure that results in a poor fuel-air mixing condition and retarded evaporation causing unstable flame and consequently inappropriate combustion conditions, hence incomplete combustion that favor increased HC emissions (Chen *et al.*, 2013b).

Similarly, adding 0.5% of water in the diesel blends, also produces higher HC emissions, this was due to the water in the combustion process will generate a cooling effect, thus reducing the combustion temperature, resulting in increased HC (Greeves *et al.*, 1977; Cui *et al.*, 2009; Ithnin *et al.*, 2014).

Addition of butanol and 0.5% water will increase HC emissions (0.009–0.033 g/kW/hr) compared to the base diesel performance, but the emission factors are still far below the regulatory emission standards in Taiwan of 0.46 g/kW/hr and HC can be removed via the use of traditional catalytic converters.

CO Emissions

The emission of carbon monoxide from diesel engines is

mainly influenced by the air-fuel ratio and is a consequence of improper and incomplete combustion processes. In this study, the performance of B2 and BT20B2 compared to base diesel fuel showed reduced CO emissions by about 0.34% and 1.01%, respectively, while the CO emissions of BT5, BT10, BT15, BT5W05, BT10W05, BT15W05, BT15B2, and BT20B2W05 increased by 2.79%, 2.74%, 2.36%, 2.41%, 2.24%, 2.20%, 2.94% and 1.72% respectively as shown in Fig. 3.

A higher cetane number of microalgae biodiesel results in a better combustion thereby enabling CO emission decline (McCarthy *et al.*, 2011). Similarly, reductions of 12%, 25%, 31% and 35% were achieved when using 5%, 20%, 70% and 100% biodiesel blends in a study done by Buyukkaya (2010), while in a prior study by our research group reported slight reductions in CO of approximately 0.34–1%, when using 2% microalgae biodiesel additions to diesel fuel (Mwangi *et al.*, 2015).

Butanol addition to petroleum diesel provides higher oxygen content that enhances oxidation of carbon content to carbon monoxide, while the lower temperatures, due to lower heating value of butanol, do not allow complete oxidation of carbon to form CO₂ thus increasing the CO emissions (Lin *et al.*, 2012). However, Rakopoulos *et al.* (2010a) and Doğan (2011) reported increased HC with addition of butanol but lower CO with equal butanol fractions and noted that higher oxygen contents could be responsible for oxidizing the formed CO to CO₂.

Similar to the addition of butanol (5–20%), the use of 0.5% water significantly increased the CO emission factors (2.33–2.40 g/kW/hr), however these values are still much lower than the Taiwan regulatory emission standards limit of 10 g/kW/hr, and may be further reduced using a combination of fuel reformation and post combustion treatment techniques. Syu *et al.* (2014) compared the emission performance of water-ethanol microemulsion (WEM) with the performance biodiesel and diesel fuel and noted that the CO emissions from the WEM were higher than that of biodiesel, but lower than those of diesel fuel as a result of larger quench layer created by higher latent heats of evaporation of water and ethanol resulting in cooling effects. Furthermore, according to Ithnin *et al.* (2014), the increased number of OH radicals from water content results in more carbon in the fuel being oxidized to CO.

CONCLUSIONS

The results show that all the blends had higher BSFCs and BTEs compared to regular petroleum diesel. The increase in BSFC ranged from 0.31% for BT5 to 4.69% for BT20W0.5, while those of BTE were about 0.67–4.18% with BT15B2 showing the best performance in terms of energy efficiency.

From the results, it is worth noting that the addition of 2% microalgae to diesel blends increased the NO_x emissions by about 2%, while for the addition of 5–20% butanol fractions and 0.5% water fractions, the NO_x emissions were reduced by about 12–28%, when compared to petroleum diesel. On the other hand, the NO_x emissions in this study

were well above the set guideline from Taiwan Regulatory Standards of 2 g/kW/hr.

All the blends considered in this study showed comparatively lower PM and PAH emissions, when compared to the diesel engine performance. The PM reductions ranged from 22.4% for B2 to 60.4% for BT15W0.5%, while those of PAHs were ranging between 6.5% for B2 and 22.76% for BT20W0.5.

When considering the CO emissions, only the use of 2% microalgae biodiesel registered reductions of about 0.34% and 1.01% for B2 and BT20B2 blends while the other blends showed increased CO emissions of about 1.72–2.94% in comparison to CO emissions of diesel fuel emissions.

A careful observation of the HC emission factors shows that the addition of higher butanol fractions of 20% increased the emission factors by approximately 18%–70%, while for the biodiesel, 5–15% butanol fractions and 0.5% water additions lead to reductions in emission of about 8–50%.

In the recent years, the simultaneous reduction of NO_x and PM has been very important area of research. Therefore, in a bid to achieve this NO_x-PM trade off, various technologies have been proposed, which majorly are based on low temperature combustion so as to control thermo formation of NO_x and particulate matter especially soot. Chief among the low temperature control strategies are the fuel modifications. It is evident that water-addition technique can successfully achieve NO_x-PM trade off. Combustion of water containing fuel results in longer ignition delay in addition to microexplosion phenomena, which reduces combustion temperatures and provides OH radicals that oxidize soot and control NO_x formation.

As can be seen from the results in this study, both CO and HC mostly increase when using fuel reformations, therefore more research is recommended on the use of oxygenated additives in diesel engine especially the water addition, and dieselhol blends. Furthermore, the possibility of synergetic properties of these kinds of fuels should be evaluated to achieve simultaneous reductions in the emissions of NO_x, PM, CO, HC, PAHs and POPs.

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