Microalgae Oil: Algae Cultivation and Harvest, Algae Residue Torrefaction and Diesel Engine Emissions Tests

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ABSTRACT

Microalgae can be used as a biological photocatalyst to reduce the CO_2 levels in the atmosphere, with the advantage of not competing with food crops for arable land, and thus offer a potential method for limiting climate change. Microalgae have also been proposed as a sustainable fuel source. This study investigated the microalgae harvest yields, the thermogravimetric behavior of both microalgae oil and microalgae residue, the torrefaction of microalgae residue, and diesel engine tests using diesel-microalgae biodiesel blends. The mean annual harvest rate of microalgae oil in open ponds was found to be 4355 kg per 10000 m^2. Compared with conventional diesel, the fuel blends - B2 (2% microalgae biodiesel + 98% conventional diesel), B2-But20 (B2 + 20% Butanol) and B2-But20-W0.5 (B2-But20 + 0.5% water) showed a reduction of 22.0%, 57.2%, and 59.5% in PM emissions, and a decrease of 17.7%, 31.4% and 40.7% in BaPeq emissions, while B2-But20 and B2-But20-W0.5 had reduced NO_x emissions, of approximately 25.0% and 28.2%, respectively, but B2 showed a 2.0% increase in NO_x emissions. Conversely, the addition of water and butanol fractions in diesel increases HC and CO emissions, although these can be easily removed using tailpipe catalysts and absorbers. In addition, torrefaction of microalgae residue results in solid, liquid and gas products. This study is the first of its kind to report the liquid compositions from the torrefaction of microalgae residue. The condensate liquid products contained glucose molecules like 1,4:3,6-Dianhydro-α-d-glucopyranose, and furfural, limonene, pyridine, levoglucosan, and aziridine, among others. These compounds can be utilized as microalgae value added products, and applied in specialty industries as pharmaceutical, cosmetic, or solvent raw materials. Briefly, microalgae not only offer benefits in reducing CO_2 from the atmosphere or providing raw materials for biodiesel production, but microalgae residue can also be treated via torrefaction to produce biochar. Based on the results of this study, more research is recommended on the economic potential of using both solid and liquid products from microalgae torrefaction.

Keywords: Energy; Biomass; Microalgae; Torrefaction; Diesel; Engine; Emission; PAHs; NO_x; PM; CO_2.

INTRODUCTION

Traditionally fossil fuels such as coal, petroleum have been the main energy sources and even have been noted as the key drivers of industrialization. However, the reserves of energy sources are being depleted as a result of the high energy demand that is currently being experienced due to the world wide population explosion which results in increased need for transportation and housing, spiraling urbanization and ever rising industrialization. Moreover coal and petroleum are not renewable. The oil crisis of 1970 was a wakeup call of the dire situation facing the world over in terms of its fuel demands (Sadeghinezhad *et al.*, 2013). The impact is far much felt by the non-oil producing nations in terms of ever rising fuel prices (Popovicheva *et al.*, 2013). Hence there is a unanimous agreement and concerted efforts among the governments, research bodies and international

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organizations geared towards availing alternative energy sources to the markets and masses (Rakopoulos *et al.*, 2011; Tüccar *et al.*, 2014). In addition to receding energy reserves fossil fuels are associated with high pollution levels of carbon monoxide (CO_2), hydrocarbons (HCs) and volatile organic hydrocarbons (VOCs), and particulate matter (PM) which are associated with health problems and emission of greenhouse gasses (carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and hydroflourocarbons (HFCs)) that cause global warming at a rate of 2°C yearly. For example the carbon dioxide emissions in the world are rising by 2.23% per annum (Parmar *et al.*, 2011; Wu *et al.*, 2012; Show and Lee, 2014) as a result of the prevailing overdependence on fossil fuels.

Among the renewable energies options available with the current technology are: solar, wind, geothermal, hydroelectric and marine and biomass. Apparently biomass, ranks fourth among most available primary energy sources (Wu *et al.*, 2012) and is increasingly being exploited worldwide in the form of wood, energy crops, aquatic plants, agricultural plants and their wastes, municipal-, animal-wastes and more recently microalgae (Kwon *et al.*, 2014). Biofuel from biomass is projected to reduce the overreliance of fossil fuels as well as reduce the amount of emissions as well as the detrimental consequences arising from those emissions (Popovicheva *et al.*, 2013).

Biodiesel is obtained from plants or biomass through fermentation or transesterification process. There are first, second and third generation biodiesels sources. First generation sources include food crops such as soybean, sunflower, rapeseed, castor and palm from which bioethanol can be produced with a risk of creating food shortages. On the other hand, the second generation sources are essentially from non-edible parts of the crops such as rice husks, corn cobs, corn straws as well as nonfood based energy crops include fuel from jatropha, jojoba, tobacco seed, salmon oil and sea mango. Microalgae are in the third generation category alongside waste cooking oil and animal fat. (Rawat *et al.*, 2013) Among the sources of biodiesel, microalgae have been proposed as a promising source especially for biodiesel production. Algae has a few the advantages over conventional plants such as soybean, sunflower, castor by the fact that it does not compete over available land with food crops as other energy sources do. In addition to that fact there is also the issue of high growth rates i.e., the biomass weight doubles every 24 hours (Murphy and Allen, 2011; Rawat *et al.*, 2013), short maturity period of about 8 to 10 days, high biomass production rates of about 60 ton per hectare annually (Rizzo *et al.*, 2013) including rapid lipid accumulation of up to 30–70% coupled with low environmental impacts (Chen *et al.*, 2011; Halim *et al.*, 2012; Rawat *et al.*, 2013). There are myriad of other uses for microalgae principally among them is fuel production through fermentation processes to produce acetone-butanol-ethanol (ABE) solution, organic fertilizers, anti-oxidant cosmetics, pharmaceuticals and drug production (Parmar, *et al.*, 2011). Furthermore biogas, bio-oil and syngas can ultimately be obtained from microalgae biomass depending on the treatment method employed (Wen *et al.*, 2011). In addition, thermochemical processes

can be applied directly on the microalgae especially pyrolysis and gasification as energy recovery strategies for low lipid strains (Kwon *et al.*, 2014).

Microalgae cover cyanobacteria and also eukaryotic algae and largely depend on photosynthesis by utilizing sunlight, water and carbon dioxide to synthesize lipids and proteins (Wen *et al.*, 2011). Therefore microalgae offer an option of a biological photocatalyst for reducing the CO_2 levels in the atmosphere offering a solution to retarding climate change (Wang *et al.*, 2013). It is estimated that a kilogram of microalgae biomass can help reduce CO_2 emission by approximately 1.83 kilograms (Brennan and Owende, 2010). Additionally some strains are facultative in that they use organic sources of carbon and others heterotrophically use free carbon as carbon sources (Leite *et al.*, 2013). Among the few challenges faced in microalgae cultivation and exploitation is finding a strain with optimum lipid output, finding ways to effectively and economically cultivate microalgae and subsequent cost friendly harvesting and separation techniques (Chen *et al.*, 2011; Ho *et al.*, 2014).

Cultivation of microalgae usually occurs in in open ponds, closed bioreactors, or as immobilized cultures (Suali and Sarbatly, 2012). Open pond method is most popular due to its perceived low costs and ease of setup alongside the maintenance costs. Various types of open pond systems include unstirred ponds, raceway systems and circular ponds (Razzak *et al.*, 2013). Even though it is popular, the open pond method is faced with various challenges such large scale production, culture integrity, environment control, contamination and scavenging, poor mixing in efficient use of carbon dioxide, evaporation losses that alter the ionic composition of the growth cultures and temperature variations (Christenson and Sims, 2011; Rawat *et al.*, 2013; Costa and de Morais, 2014). Consumption of algae by zooplanktons and protozoa also presents a devastating problem to successful microalgae cultivation as the destruction rate of whole cultures are within days (Rawat *et al.*, 2013). Being photosynthetic (Rizzo *et al.*, 2013), they can survive in both fresh water and marine environments. Just as any other crop or microorganism, the microalgae cultivation process is subject to various factors that determine and dictate the final content and amount of lipids. These factors include sunlight, atmospheric carbon dioxide, light conditions, light intensity, effective nitrogen and climate conditions (Suali and Sarbatly, 2012). There are various challenges facing microalgae cultivation via open pond including finding suitable land, infrastructure costs (depending on the type of cultivation method), harvesting, dewatering, extraction and separation.

On their part, the closed bioreactors ensure reduced setbacks experienced in open pond method as they offer optimum growing conditions. The closed bioreactors are more flexible in that the growth conditions can be tuned to suit the particular strain and intended end products. Thus, it is possible to alter the pH, the nutrient concentrations, light intensity, and CO_2 concentration to achieve maximum output (Lam and Lee, 2014). Incidentally, it is easy to selectively bio-engineer the microalgae for enhanced microalgae oil production via enhanced cell growth and lipid accumulation

(Chen *et al.*, 2013). Closed bioreactors come in various forms such as tubular, plastic bag, airlift and flat plate bioreactors (Razzak *et al.*, 2013).

When it comes to immobilized cultures, the microalgae is attached to particles in packed or fluidized bed reactors. This method of culturing is constrained by low production scales and high cost of the immobilizing matrix although it offers advantages in form of low land and water requirements and higher culture densities (Christenson and Sims, 2011). The microalgae can be attached to polymeric matrix or biofilms or on surfaces of rotating biodiscs. These types of immobilized cultures have found a niche in waste water treatment schemes (Hoffmann, 1998).

Harvesting of microalgae for fuel extraction presents one of the great challenges when it comes to using microalgae for large-scale production and exploitation. Centrifugation, sedimentation, filtration and flocculation (Parmar *et al.*, 2011; Show and Lee, 2014) are a few techniques that are employed to harvest microalgae in addition to electrophoresis, electrofloatation and ultrasound. After harvesting the microalgae the lipids or oil is extracted from the biomass and there remains the residues using pressing technique (mechanical crushing), ultrasonic and microwave extraction and Soxhlet extraction (Suali and Sarbatly, 2012; Rawat *et al.*, 2013). After extraction of the oil, transesterification is used to convert the microalgae oil with high fatty acid content to fatty acid alkyl esters which can be used as biodiesel in diesel engines as will be discussed later.

Since their inception, the diesel engines are popular as both on road and off road use in trucks due to their comparative higher thermal efficiency, higher power output, fuel economy, durability and lower carbon monoxide and hydrocarbon emissions compared to gasoline engines (Lee *et al.*, 2011; Lam and Lee, 2014; Ithnin *et al.*, 2015; Öztürk, 2015). For these reasons they are preferentially used in heavy transport and agricultural sectors (Tüccar and Aydın, 2013). Conversely, the diesel engine due to its high usage is also a major source of nitrogen oxides, sulfur dioxide and particulate matter which acts as a carrier for other toxic and carcinogenic species such as polyaromatic hydrocarbons (PAHs) volatile organic carbon (VOCs), polychlorinated dibenzo dioxins and dibenzofurans (PCDD/Fs) as well as brominated contaminants (PBDEs) (Alahmer, 2013; Tsai *et al.*, 2014). Particulate matter, particularly, the $PM_{2.5}$ is linked with serious respiratory and cardiovascular health concerns due to their uncertain physiochemical and toxicological characteristics (Popovicheva *et al.*, 2013; Magara-Gomez *et al.*, 2014). Yao and Tsai (2013) notes that high vehicle related pollution levels in the urban areas cause about 80,000 premature deaths in the world with a majority of this happening in Asia.

Various studies have investigated various methods to reduce the pollutant emissions from the diesel engine including water addition (Lee *et al.*, 2011; Chang *et al.*, 2013, 2014a, b; Ithnin *et al.*, 2015), exhaust gas recirculation, selective catalytic reduction (SCR) for NO_x reduction (Ithnin *et al.*, 2015) use of particulate trap and particle filters for PM reduction (Magara-Gomez *et al.*, 2014), plasma enhanced combustion for PAH and greenhouse gases

reduction (Lin *et al.*, 2013) and replacement of conventional fossil based diesel with alternative fuels (Rakopoulos *et al.*, 2010). Fuel substitution involves completely changing the fuel to a different kind or altering the fuel characteristics. Biodiesel has been used as a diesel's substitute in its neat form or as dieselhols which are essentially blends between base diesel and biodiesel on various proportions (Rakopoulos *et al.*, 2011).

Biodiesel is produced from biomass via transesterification either direct acid catalyzed transesterification of vegetable oil or animal fats oil in presence of methanol or in a step wise process whereby the first step involves base catalyzed with alcohol to fatty acids followed by conversion to methyl esters via acid catalysis (Sadeghinezhad *et al.*, 2013). The benefits offered by biodiesel include reduction in overdependence on oil imports and reduced exhaust emissions (Rakopoulos *et al.*, 2011). According to (Öztürk, 2015) the most important characteristics are cold flow properties, iodine value, viscosity and oxidation stability and storage stability all which depend on the fatty acid composition of the biodiesel. Even though many a study has pointed out that biodiesel can adequately substitute diesel with any modifications on the engine, the use of biodiesel in diesel engines is not devoid of some drawbacks especially where it concerns the compatibility with the diesel engine. Biodiesel presents problems of clogging during cold weather due to its higher cold filter plugging point (CFPP). Moreover due engines using biodiesel experience poor fuel atomization owing to its high kinematic viscosity (Chen *et al.*, 2012). To overcome these disadvantages biodiesel is blended with normal diesel in various fractions.

Solvents and additives like acetone, ethanol and butanol have been added to fortify these blends by minimizing the problems experienced with straight biodiesel (Chang *et al.*, 2014a; Tüccar *et al.*, 2014; Öztürk, 2015). Additionally, these blends tend to decrease the emissions from the internal combustion engines (Doğan, 2011). Acetone, butanol and ethanol are produced in the Acetone –Butanol-Ethanol (ABE) fermentation process which was developed during the World War I by Chaim Weizmann (Ni and Sun, 2009). This process occurs in two stages of acidogenesis and solventogenesis. Aceric and butyric acids are the main products of acidogenesis while the solventogenesis process gives acetone, butanol and ethanol (Chang, 2010). Ethanol has previously been used in diesel engines but poses challenges such as low cetane number, reduced viscosity and calorific value of its blends (Rakopoulos *et al.*, 2011). Butanol is the main product of the ABE process and apparently in contrast to other alcohols has superior qualities that make an easy pick for blending with diesel such as less hydrophilicity, easy miscibility, higher cetane value, less volatile, higher heating values and its energy density is similar to gasoline's (Wen *et al.*, 2014). Furthermore butanol apart from being as a fuel it is used in the food, plastic and specialty industries (Tran *et al.*, 2010). ABE fermentation process depends on cellulosic sources as substrates. Initially, the substrates included carbohydrate rich feedstock such as bagasse, rice straw, cassava, molasses, palm fiber, maize, potatoes, beets or even domestic wastes (Claassen *et al.*, 2000; Ponthein and Cheirsilp, 2011; Wen *et al.*, 2014). The solventogenic

activity of anaerobic *Clostridium* bacteria strains drives the ABE fermentation process (Maddox *et al.*, 1995).

Other researchers have also reported that use of a small amount of water in the biodiesel blends helps create a trade of between reduction of PM, CO and also reduction in NO_x contrary to using straight biodiesel that lead to increased NO_x emissions (Liu *et al.*, 2012; Chang *et al.*, 2013; Chang *et al.*, 2014b). According to the report of (Alahmer, 2013) the presence of small amounts of water in the fuel has a significant effect on the physical and chemical kinetics of combustion where by it reduces combustion temperatures and providing OH radicals in the combustion environment. The OH radicals act to control NO_x formation and to oxidize soot resulting in reducing both NO_x and PM. In addition, the micro-explosion action of water droplets has been proposed as the major mechanism that results in a better turbulence of fuel and oxidants, causing more complete combustion and consequently a significant reduction of criteria pollutants emissions when using water-containing fuels.

Apart from being exploited for liquid fuel or biofuel, biomass and more so the waste material after biodiesel extraction has the potential to be treated via thermochemical processes such as torrefaction to harness more energy. Torrefaction is basically mild pyrolysis whereby biomass is treated under inert conditions mostly nitrogen flow at temperatures in the range of 200 to 300°C. Important to note is that torrefaction is a pretreatment process to augment biomass characteristic for easier and efficient handling in downstream process such as gasification or pelletisation (Wu *et al.*, 2014). In addition whereas pyrolysis occurs at high temperatures thus being energy intensive, torrefaction due to its operating low temperatures is not as energy intensive. Biomass generally has a high water content, poor grindability and decreased storage life in its original form thus torrefaction process helps to alleviate these shortcomings by making the biomass more hygroscopic, more homogeneous and less bulky. Examples of materials that have been torrefied include oil palm wastes (Uemura *et al.*, 2011) corncobs (Zheng *et al.*, 2013) rice husks and sugarcane residues (Wang *et al.*, 2012) and even microalgae (Wu *et al.*, 2012). Bondioli *et al.* (2012) observed that microalgae fuel is far more costly than petrodiesel hence cannot compete favorably for day to day usage. Thus more efforts have to be put in place to find ways to make microalgae more sustainable in order to cut a niche in the fuel industry (Parmar *et al.*, 2011). In an effort to maximally exploit the microalgae several process can be employed to treat the residues to make them useful or to harness the remaining energy in form of carbon and proteins. These various processes include thermochemical processes such as pyrolysis, gasification (Rizzo *et al.*, 2013) and torrefaction. The process of torrefaction primarily results in solid products while pyrolysis gives off liquids containing acids, alcohols, aldehydes, esters, ketones sugars phenols, furans and gasification produces gases such as CO, CO_2, H_2 and CH_4 (Khoo *et al.*, 2013). In addition to biodiesel production the algae residue can be treated via torrefaction and used as a source of energy. Wu *et al.* (2012) studied torrefaction of microalgae residue under various temperatures and

residence times and noted an increased heating value at higher temperatures and improved Hardgrove Grindability Index with decreased moisture content up to 1% which was superior to that of bituminous coal.

The purpose of this study is to investigate the torrefaction characteristics of both microalgae oil and microalgae residues with a special interest in the qualitative analysis of the liquid fraction collected from the microalgae residues torrefaction at various temperatures. Another objective of this article was to investigate the performance of microalgae fuel blends in a diesel engine in relation to pollutant emission reduction and energy saving.

EXPERIMENTAL SECTION

Culture Cultivation

The microalgae strain *Chlorella vulgaris*, ESP-31 (Fig. 1) and *Chlorella sorokiniana*, Mb-1 (Fig. 2) were obtained from University Center for Bioscience and Biotechnology, National Cheng Kung University, Tainan, 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.

From the isolated samples, a 20 mg/L seed cultures of *Chlorella vulgaris,* ESP-31 and *Chlorella sorokiniana*, Mb-1 Muli-01 were inoculated in a photobioreactor respectively, which was a 1-L glass vessel (15.5 cm in length and 9.5 cm in diameter) equipped with an external light source (14 W fluorescent light (TL5)) mounted on both sides 20-cm from the photobioreactor with the light intensity on the photobioreactor fixed at ca. 60 mol/m^2.s. The microalgae was cultured in a medium with following composition in terms of (g/L): glucose, 10; $NaNO_3$, 0.75; KH_2PO_4, 0.175; K_2HPO_4, 0.075; $MgSO_4·7H_2O$, 0.075; $CaCl_2·2H_2O$, 0.025; NaCl, 0.025; $FeCl_3·6H2O$, 5.0×10^{-3}; $ZnSO_4·7H_2O$, 2.87×10^{-4}; $MnSO_4·H_2O$, 1.69×10^{-4}; H_3BO_3, 6.1×10^{-5}; $CuSO_4·5H_2O$, 2.5×10^{-6}; $(NH_4)_6Mo_7O_{24}·7H_2O$, 1.24×10^{-6}. The temperature of the culture medium was kept at 25°C while the pH was 6.5 and the culture was agitated at 300 rpm. Organic carbon sources for the growing microalgae were supplied in form of glucose, fructose, sucrose, glycerol, sodium acetate and acetic acid. After culturing, the microalga was transferred to cultivation ponds.

Two open ponds both with 4 m inner diameter and 50 cm depth and mixing by using 100−150 rpm rotating circulation mixer were used for microalgae cultivation. During the experimental periods, the ambient air temperatures around the cultivating ponds were between 30−34°C, while the water temperature in ponds ranged from 33 to 38°C.

After cultivating for an average of 17 days, the microalgae were harvested for biodiesel production. To remove the surface water of microalgae, a continuous flow centrifuge was applied at 13500 rpm to produce microalgae sludge. The sludge contained approximately 70−80% moisture content and the oil content was about 26% by weight of dry biomass.

Microalgae Oil Production

Thereafter, the microalgae sludge was pretreated in a lab scale set up. About 100 g of sludge was placed in a 500 mL
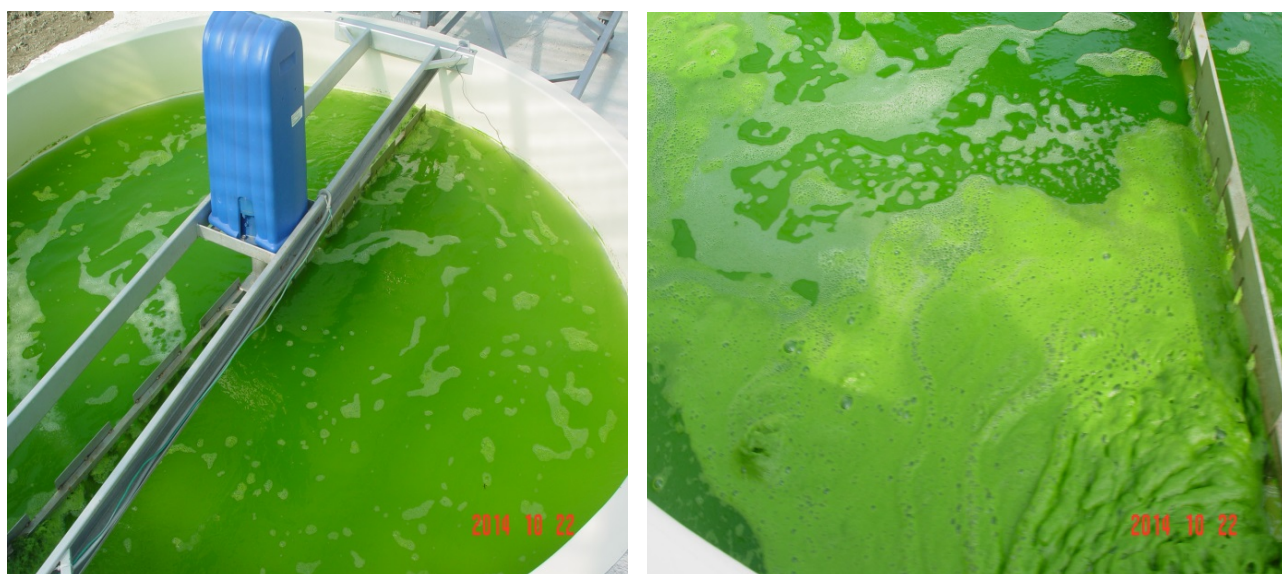
Fig. 1. Microalgae (*Chlorella vulgaris*, ESP-31) after one day of cultivation.
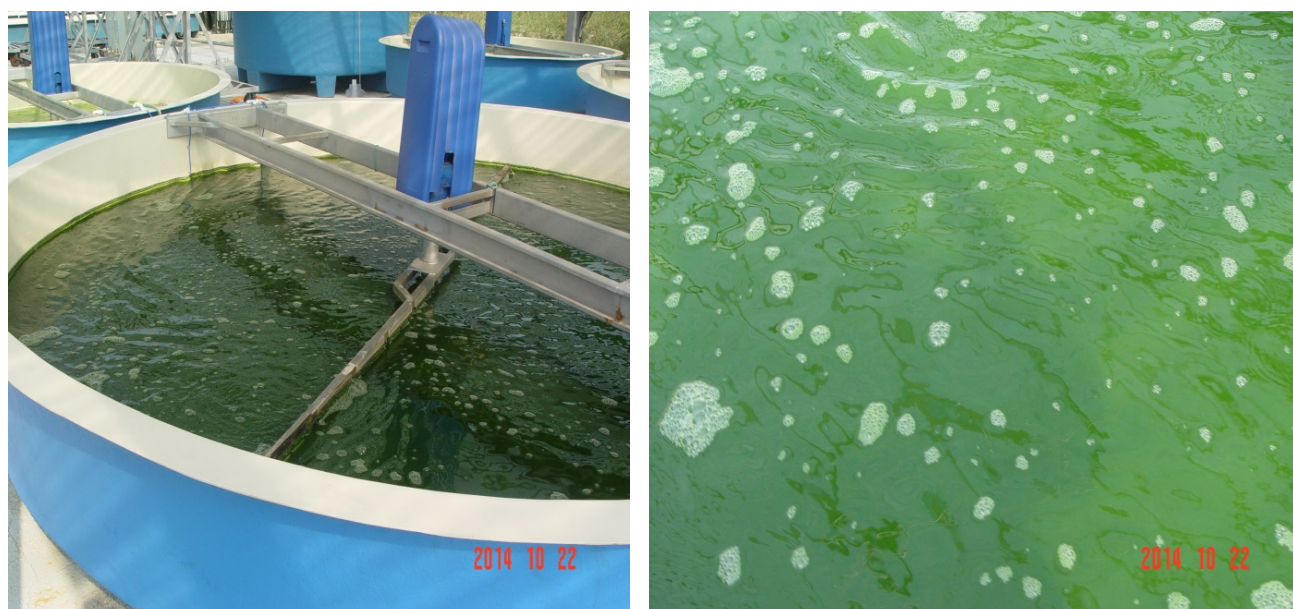
Fig. 2. Microalgae (*Chlorella sorokiniana*, Mb-1) after five days of cultivation.

serum bottle and mixed with 300 mL methanol at 400 rpm for 20 minutes using a magnetic stirring bar. The bottle was then transferred into a microwave oven operated at 350 W for 10 min to achieve cell disruption. After that, the mixture was poured into a commercial filtration bag which was centrifuged with a spin dryer to removal liquid from the mixture to yield a microalgae cake.

Wet oil extraction was performed by placing 5 g of the microalgae cake was place in a 100 mL serum bottle. The oil was extracted by subjecting the cake to the following conditions the wet oil extraction from the microalgae cake were extraction time, 80 min; extraction temperature, 45°C; the hexane/methanol ratio, 3:1. After stirring at 600 rpm under the above-mentioned conditions, the mixture was centrifuged at 6000 rpm for 3 min to achieve the separation of oil phase, water phase, and microalgae residue. Then, the oil phase including microalgae oil and hexane was preserved in another 100 mL serum bottle. After extraction the oil phase was transesterified to produce biodiesel.

The next step was transesterification whereby methanol containing 0.5 wt% NaOH was added to the microalgae oil-containing hexane solution from the wet oil extraction in a ratio of hexane/methanol ratio, 6:1. The transesterification process was carried out for 15 minutes at a temperature of 45°C. After that, the mixture was centrifuged at 6000 rpm for 3 min and then the hexane solution passed through the vacuum distillation to yield pure biodiesel and recover pure hexane. The lab scale process described above was scaled up for a pilot plant for mass production of microalgae oil and biodiesel.

Torrefaction and Thermogravimetry Analysis of the Microalgae Residue and Oil

The composition of microalgae was determined using the ASTM E870 standard methods for biomass fuel analysis. The microalgae oil was weighed in crucibles. The samples were first heated at 105°C for one hour to extract the moisture then heated up to 800°C for 2 hours. The weights of the empty crucibles, crucibles with samples, weight after heating at 105°C and weight after heating at 800°C were noted in order to calculate the moisture, combustibles and the ash contents. Similarly elemental analysis of the residues was done according to ASTM E870 method for wood fuels analysis using ELEMENTAR Elemental analyzer from the National Cheng Kung University Instrument Center. The heating values of the microalgae oil and microalgae residues were determined using a bomb calorimeter (IKA C2000 Basic).

Thermogravimetry analysis (TGA) was done in a non-isothermal fashion using a PerkiElmer Pyris 1 Thermogravimetry Analyzer from Tainan University Biomass Laboratory. Due to the ease of evaporation and rapid mass loss, the microalgae oil was torrefied by first setting the initial temperature to about 45°C and increased at a heating rate of 20 °C/minute from 45°C to 800°C. Nitrogen gas was used as the carrier gas at a flow rate of 100 mL/min. On the other hand the microalgae residues samples were held at 50°C for one minute then the temperature was increased to 105°C at a rate of 20°C per minute. This temperature was held for 5 minutes before heating up to 800°C at 20°C per minute. About ten milligrams of microalgae oil and microalgae residues was used for TGA.

As for torrefaction process, about 10 grams of microalgae residues were weighted and placed in a laboratory scale fixed bed furnace made of quartz glass with the dimensions of 45 mm inner diameter, 80 mm outer diameter and a length of 470 mm. The torrefaction process is carried out at inert atmosphere on nitrogen gas. The nitrogen gas was passed through the furnace at a flow rate of 100 cc/min. A furnace with a temperature controller was used to provide the heating.

The residues were heated at 105°C for 30 minutes before the temperature is raised to 200, 225, 250, 275 or 300°C at 20 °C/min intervals. The residues were torrefied at the mentioned temperatures for approximately 60 minutes. The initial and final weight of the raw microalgae residues and the torrefied end products were recorded for calculation of energy yield. During torrefaction the liquid part was cooled down and collected in sample bottles and the weight of the liquid part was recorded. After torrefaction the heating values of the torrefied products were determined as mentioned before.

The liquid product from the torrrefaction of microalgae residue was further subjected to qualitative analysis using gas chromatography coupled with mass spectrometry (GC/MS) to determine the organic molecules present using the JEOL JMS-700 and SHIMADU QP2010 (Japan) gas chromatography from Instrument Center, National Cheng Kung University. The GC/MS was operated on split mode with a split ratio of 5.0. The carrier gas used in this process was helium at a flow rate of 3.0 mL/min using a DB-5 ms column whose specifications are as follows, 5% polydiphenyl, 95% dimethylpolysiloxane, 30 × 0.25 mm i.d., and 0.25 μm film thickness. The following temperature program was used: the oven temperature was initially set at 40°C and held at this point for 4 min then was raised to 230°C at a rate of 10 °C/min and held for 7 min. From 230°C the temperature was raised to 280°C at a rate of 3 °C/min. The pressure was maintained at 71 kPa while the column flow rate was 1.30 mL/min resulting in a linear velocity of 41.2 cm/sec.

Diesel Engine Test

Four kinds of blends were prepared as per the Table 1 where D, B, But 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 suing 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 specifications of the engine used for the engine test in this study are as shown in the Table 2 while Fig. 3 is the schematic representation showing the various components of the engine test set up. The engine test procedure and instrumental analysis of the collected pollutants were done according to the method proposed and applied by similar studies done previously by Chang *et al.* (2013, 2014a, b).

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 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

Table 1. Diesel Fuel Blends.

Diesel Blend	Diesel (%)	Algae Oil (%)	Butanol (%)	Water (%)
Base Diesel	100			
B2	98	2		
B2-But20	78	2	20	
B2-But20-W0.5	77.5	2	20	0.5

Table 2. Specifications of Test Engine.

Item	Specification
Manufacturer	MITSUBISHI 4M40-2AT1
Bore (mm) × Stroke	95 × 100 (mm)
Stroke	100
No. of Cylinders	4
Injection System	Direct Injection
Cooling System	Water cooled
Fuel	Diesel
Compression Ratio	20.1:1
Rated Power	109 kWh at 3700 rpm
Maximum Torque	200Nm at 3200 rpm

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^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, CO_2 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.

The GC/MS (Agilent 5890A and Agilent 5975) used for subsequent PAH identification was equipped with a capillary column (HP Ultra 2, 50 m × 0.32 mm × 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 °C/min
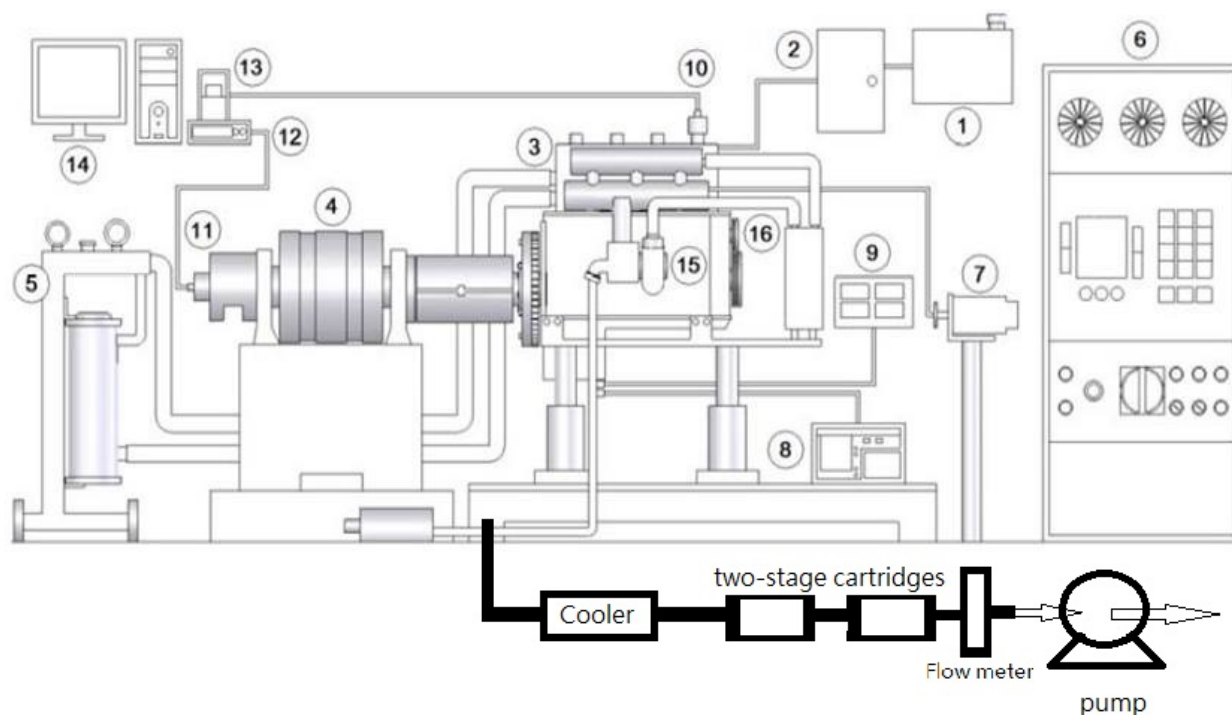
Notes:
1. Fuel tank, 2. Volumetric fuel consumption meter, 3. Diesel Engine
4. Engine dynamometer, 5. Heat exchanger, 6. Dynamometer control box
7. Jet pump throttle opening degree controller, 8. Exhaust gas analyzer
9. Exhaust temperature measurement device, 10.Pressure transducer
11. Decoder, 12. Signal converter, 13. Voltage signal amplifier
14. Cylinder pressure data processing computer, 15. Turbocharger
16. Intercooler, 17. Air flow meter, 18. Air flow meter power supply and display header

Fig. 3. Schematic configuration of the diesel engine.

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 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.

RESULTS AND DISCUSSION

Microalgae Harvest

After being cultivated for 15–20 days (with an average periods of 17 days per run), the amount of microalgae harvest were between 5–8 kg (wet weight) with water content around 80–90%. Therefore, the mean dry weight of microalgae harvest was approximately 1.2–2.0 kg (with an average value of 1.5 kg) per run. The oil content in dry microalgae (zero water content) was found to be between 22% to 35% and averaged 26%. Therefore, the mean production rate of microalgae oil in this study was 0.67 kg per m^2 of cultivation pond. Assuming the working space for microalgae cultivation field was designed to be 30% and 40% for each pond, respectively, the harvest rate for microalgae oil will be 4690 and 4020 kg per 10000 m^2, yearly and averaged at 4355 kg per 10000 m^2.

As mentioned earlier the oil yields on dry weight basis can be in the range of 30–70% but this study reports lower yields of 26% owing to the fact that controlled environments in the laboratory bioreactors may give higher theoretical oil yields. On the other hand uncontrolled conditions in the open field may yield lower oil yields. As is with any biological system, there exists a large difference in performance in controlled environments with uncontrolled environments. Additionally growth conditions as well as the species and strain types have a major effect on the productivities. This fact is well documented in Chen *et al.* (2011) and Christi (2007) whereby different smicroalagae speies and different culture conditions result in varying oil yields. In fact the yields from this study are higher than the values reported by Rodolfi *et al.* (2009) for *Chlorella sorokiniana* IAM-212 (19.3% oil yield on dry weight basis) and *Chlorella sp.* F&M-M48 (18.7% oil yield on dry weight basis).

Proximate and Elemental Analysis

The results of the proximate and elemental analysis were presented in Table 3. According to Table 3, it is evident that the microalgae oil generally has a higher combustible fraction, moisture, carbon and hydrogen contents than the residues. The microalgae residues on the other side they contain greater amount of nitrogen and ash. In agreement with (Chen *et al.*, 2014) this study found out that the ash content in the residues was also high. The knowledge of the ash content is essential in the design of the downstream processes especially in the ash removal mechanisms. The microalgae residue has a lower heating value when compared to that of the microalgae oil as a result of the higher oxygen content. The presence of noncombustible ash in the solid residue decreases the overall combustibility of the residue hence it has a comparatively lower heating value (Wu *et al.*, 2012). Due to their higher carbon content, the microalgae oil results in a higher heating value. Microalgae are composed of carbohydrates, lipids, and proteins. When the oil is extracted mostly the lipids and the carbohydrates are removed thus leaving behind the proteins. This can be confirmed by the higher amount of nitrogen in the residues. There is no significant difference in the amount of fixed carbon and volatile matter between the two microalgae products.

Thermogravimetry Analysis

Figs. 4(a) and 4(b) shows the thermogravimetry analysis and derivative thermogravimetry analysis of both the microalgae oil and residue. The Fig. 4(a) shows that microalgae oil is more severely thermo decomposed in the temperature range of 40°C to 800°C compared to the residues Fig. 4(b). This can be attributed to the high amount of volatile matter in the oil than the residues. Moreover the oil is decomposed at lower temperature range of 200 to

**Table 3.** Proximate and elemental analysis of *Chlorella vulgaris* ESP-31.

Proximate Analysis (wt %)	Microalgae residue[a]	Microalgae oil[b]
Combustibles (Volatile Matter and Fixed Carbon)	88.10	89.51
Moisture	3.80	10.45
Ash	7.90	0.04
Elemental Analysis (wt %)		
C	45.07	74.24
H	7.64	13.11
N	3.88	0.58
O	35.52	12.07
Chemical Formula	$CH_{2.03}O_{0.59}N_{0.07}$	$CH_{2.104}O_{0.122}N_{0.007}$
Heating value (MJ/kg)	16.46[b]	38.96

Notes: [a]: cited from (Chen *et al.*, 2014); [b]: determined in this study.
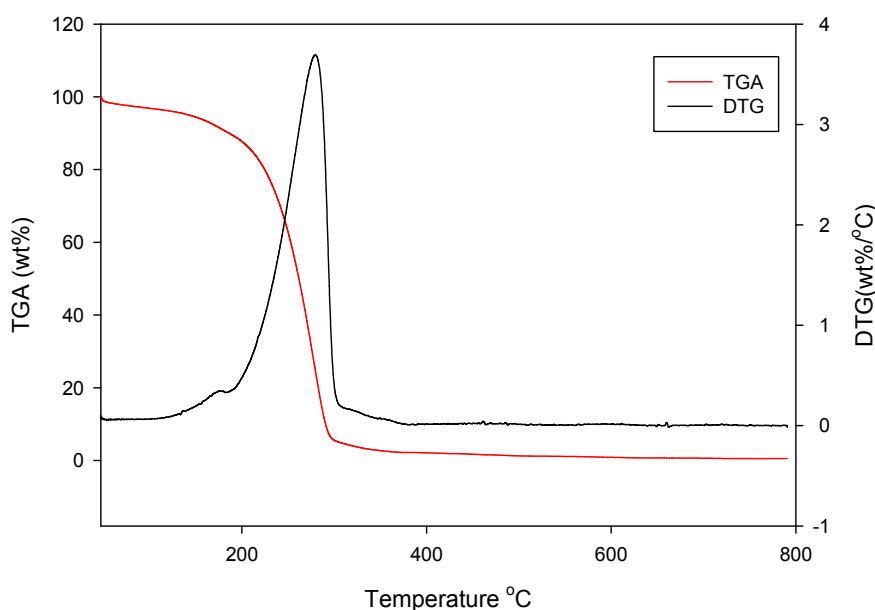
Fig. 4(a). TGA and DTG curves for the microalgae oil.
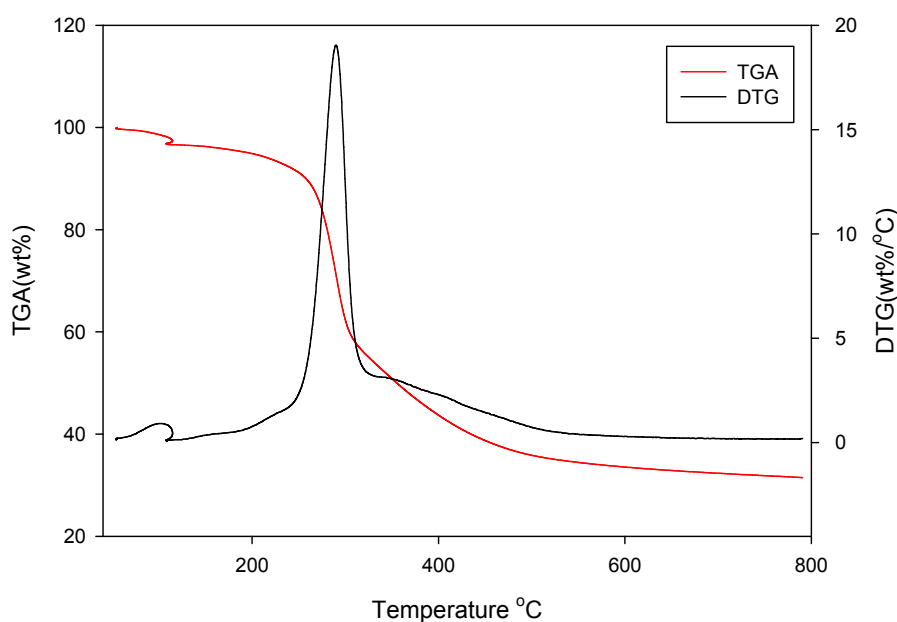
Fig. 4(b). TGA and DTG curves for the microalgae residues.

300°C corresponding to the high gradient region of the TGA curve while the greatest decomposition for the residue happens at the temperature range between 300 to 350°C with even lower weight loss per temperature rise. Microalgae oil consists of mostly fatty acids a larger fraction of which are poly unsaturated fatty acids with more than nine carbon atoms in a molecule. Polyunsaturated fatty acids are basically a mixture of long chain hydrocarbons which includes compounds such as tridecanoic acid, myristic acid, palmitic acid, hexadecenoic acid, heptadecanoic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, eicosanoic acid. The other fractions are fatty acid methyl esters, ketones and aldehydes (Shuping *et al.*, 2010; Dong *et al.*, 2013).

From the TGA analysis it is clear that there exist a three stage thermal decomposition of the polyunsaturated fatty acids. The first stage there is minimal losses in weight as the temperature is below 200°C. But the second region shows that major decomposition of polysaturated fatty acids occurred between temperatures of 200°C and 300°C characterized by great weight loss. The degradation after 300°C corresponds to oxidation of polyunsaturated fatty acids and the resulting thermal decomposition. The microalgae oil has more than 50% volatiles; hence in this analysis the starting temperature was about 40°C as compared to usual TGA procedures whereby the initial temperature is about 105°C which serves to drive off moisture.

The energy yield and weight loss were calculated using the Eqs. (1) and (2) from (Chen *et al.*, 2012). Fig. 5 shows that the calorific values of the torrefied products increased with temperatures indicating that energy densification increased with rising temperatures although the energy yields dropped. Additionally an evaluation of the input/output energy ratio resulted to ratios between 1.1–2.0 when considering energy losses from 10% to 50%. This reveals that more energy is applied in the torrefaction than is recovered especially due moisture evaporation severe mass loss. But this is surpassed by the advantages of the properties imparted on torrefied products especially when used in subsequent energy intensive processes such as grinding, pelletisation and gasification whereby less energy is needed to handle the biomass. Additionally in large scale set ups the hot gases and water vapor can be harnessed and used to provide heating in downstream processes.

$$Energy\ Yield(\%) =$$
$$\frac{Weight\ of\ torrefied \times HHV\ torrefied\ product}{Weight\ of\ raw\ residues \times HHV\ raw\ residues} \times 100\% \tag{1}$$

$$Weight\ Loss(\%) =$$
$$\frac{(Raw\ residue\ weight - Torrefied\ residue\ weight)}{Raw\ residue\ weight} \times 100\% \tag{2}$$

The Fig. 6 shows that the weight loss of the residues increases with an increase of temperature. This can be seen by evaluating the weight loss between 200 and 250°C is not severe. This region corresponds to the light torrefaction. While between 250 and 275°C is s the mild torrefaction region with weigh loss less than 50%. Above 275°C there exists the severe torrefaction zone whereby the weight loss exceeds the energy densification even though the heating values are higher. The gradient of the in agreement with (Chen *et al.*, 2014) it is recommended that torrefaction of the residues should be carried out at temperatures below 250°C as there is less weight loss and comparatively higher energy densification. Thus 250°C was identified as the optimum temperature with an energy yield of 71%, solid yield of 53.7%, liquid yield of 12.3% and gas yield of 34.0%.

To calculate the solid, liquid and gas yields, the initial weight of the microalgae residue and the final solid were noted. The solid yield was determined as the difference between the initial weight of the microalgae residue and the final solid product at each temperature. The liquid weight was determined from the weight of the collected liquid while the gaseous product was calculated by using the mass balance. From the Fig. 6 showing the product yields, it is clear that as the microalgae residue degraded the solid yields decreased as the liquid and gas yields increased with temperature. At 220°C The solid, liquid and gas yields in this study were 73.4%, 4.0%, 22.6% respectively while at 225°C the solid, liquid and gas yields were

69.2%, 5.3%, 25.6% respectively. Further on at 250°C the solid, liquid and gas yields were 53.7%, 12.3%, 34.0% respectively while for 275°C they were 46.0%, 16.2%, 37.8% respectively. Finally at 300°C the solid, liquid and gas yields were 39.8%, 16.8% and 43.4% respectively. Previously (Khoo *et al.*, 2013) reported a 78.82%, 18.44%, 6.74% solid, bio-oil and gas yields at 330°C while (Rizzo *et al.*, 2013) pyrolized *Chlorella* spp and performed non isothermal TGA and reported a solid (char) yield of 29 wt%, liquid yield (34%) and 37% wt gas yield at 450°C.

Khoo *et al.*, (2013) reports higher solid yields even at higher temperatures principally because unlike this study. They evaluated the product yields on the basis of dry weight while this study did not factor the contribution of moisture content in the original microalgae residue. The apparent differences between this study and the report by (Rizzo *et al.*, 2013) arise from the conditions of thermotreatment. Rizzo *et al.* (2013) carried out thermo-pyrolisis while this study torrefied the microalgae residue. Thermo-pyrolisis is more severe than torrefaction, while the latter is considered as a mild pyrolisis resulting in a lower thermodegradation. Hence, it has a higher solid yield than the pyrolisis process.

As the temperature increases the macromolecules that form the solid structure of the microalgae residues are cleaved into simple molecules that combine to form liquids and gases resulting in a lower solid yield and higher both liquid and gas yields. When the temperature is further raised, both the macromolecules in the solid and liquid state are further fragmented into even simpler micromolecules that exist in gaseous form hence higher gas yields.

Qualitative Analysis for the Liquid Composition

Considering the moisture content of the microalgae residue is about 3.8% (see Table 3) then water forms the highest percentage of the condensable liquid product. In fact, Tumuluru *et al.* (2012), identified water as the major condensable product of biomass torrefaction processes. The sources of water are evaporation of freely bound water and as a reaction product of chemical dehydration and condensation reactions. It should be noted that characterization of the liquid product is not entirely conclusive as it is difficult to handle since it was mixed with the aqueous phase and treated as one. Apart from water the other condensation products identified via GC/MS from microalgae residue torrefaction are as depicted in the Table 4. Esters and organic acids formed a majority of identified compounds and they are ultimate products of cellulose and hemicellulose decomposition. At lower temperatures the condensate liquid product contained glucose molecules like 1,4:3,6-Dianhydro-α-d-glucopyranose which were not destroyed due to low temperatures. Furthermore other molecules detected included furfural, limonene, pyridine, levoglucosan, aziridine among others. These molecules can be used in specialty industries. For example limonene can be used in pharmaceuticals and cosmetics products as well as a solvent. Furfural can be further derived and used as pesticides. Meanwhile aniline acts as a precursor in production of the indigo dye which is widely used in the dying of blue jeans. Levoglucosan has been used as an indicatory compound for biomass burning
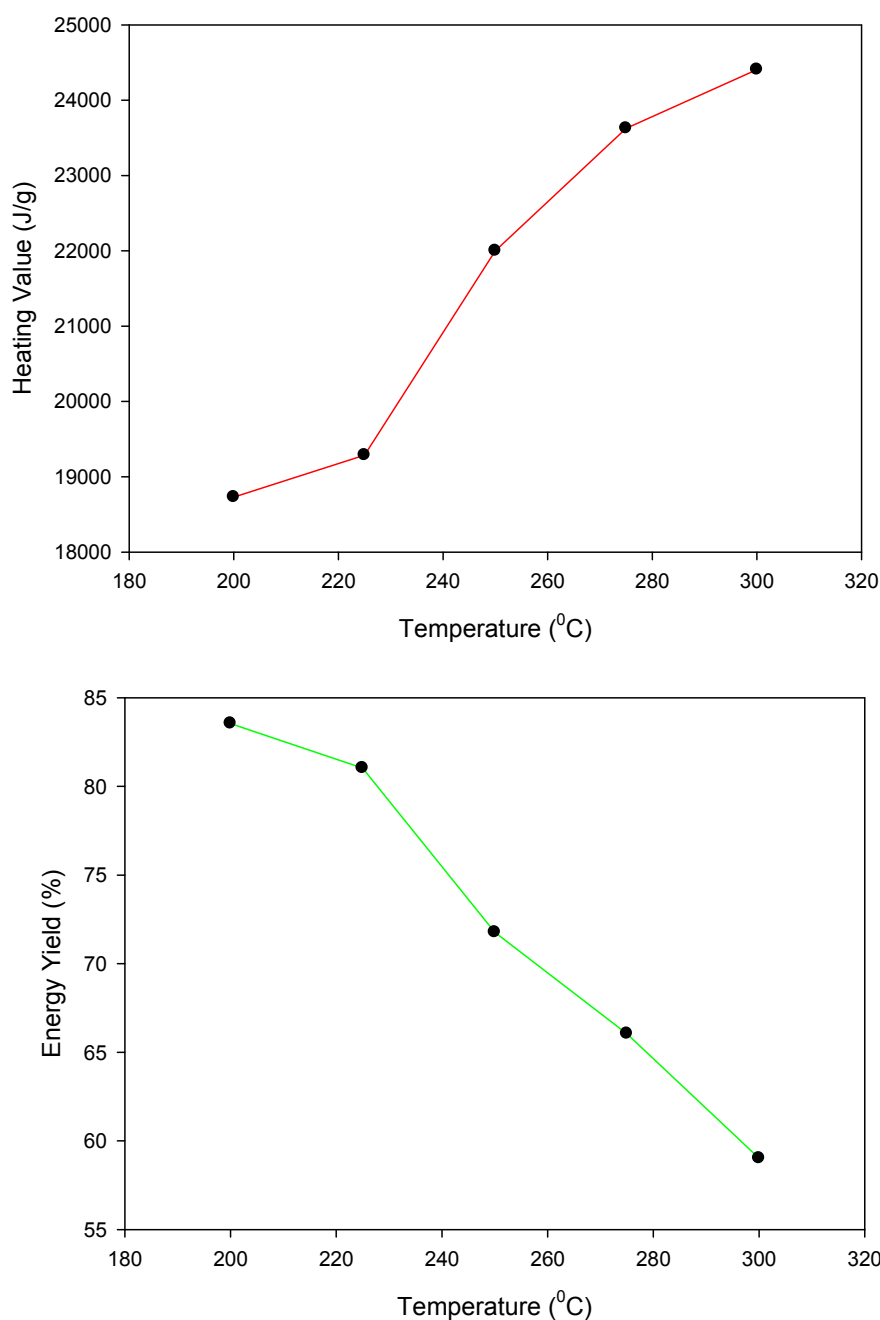
Fig. 5. Variation of heating value and energy yield of torrefied residues with temperature.

(Sang *et al.*, 2011) and its presence can be explained by the carbohydrate content of the microalgae residue. Microalgae residue contains high nitrogen due to the presence of proteins and this can be confirmed by the identification of nitrogen containing compounds such as urea, aniline and aziridine Similar to other studies referenced in (Tumuluru *et al.*, 2012) this study identified furfural in the liquid condensate from torrefaction process. Contrary to other studies, there was no acetic acid detected in the liquid condensate from this study. This can be attributed to the difference in the type of torrefied material. Woody materials which are commonly torrefied contain hemicellulose and cellulose in their structures that contain methoxy- and acetoxy- groups that are

precursors for acetic acid formation. Microalgae have low content of cellulose and hemicellose thus the condensable torrefaction products are devoid of acetic acid. Furthermore since it lacks lignin there is no phenolic compounds detected compared to other lignocelullosic materials in (Verhoeff *et al.*, 2011). A report by Nocquet *et al.* (2014) identified water, formaldehyde, acetic acid, methanol furfural and formic acid as the main compounds from the liquid condensate from wood torrefaction.

The information obtained from qualitative analysis of the liquid condensate of the torrefaction process can potentially shed light on other useful constituents that can be obtained from microalgae. Specialty chemicals in form of
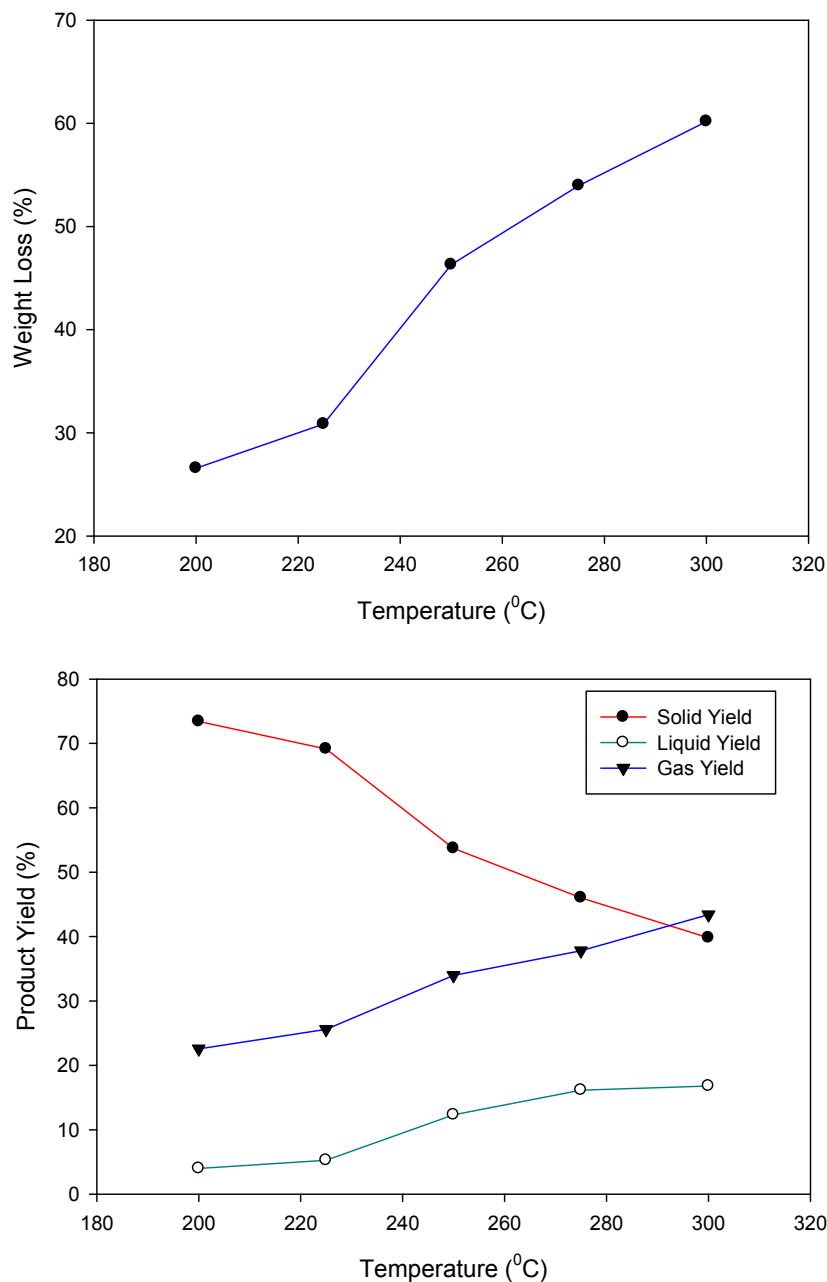
Fig. 6. Variation of weight loss and product yields (solid-, liquid-, and gas-yield) of torrefied residues with temperature.

organic molecules in the liquid phase from thermochemical conversions can potentially make microalgae torrefaction more economically feasible and recover the overall production cost.

Engine Performance

The Break Specific Fuel Consumption (BSFC), Break 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 Eq. 3 and Eq. 4 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 of each blend.

$$BSFC = \frac{V}{Pt} \ (g \, / \, kW \cdot h) \tag{3}$$

$$BTE = \frac{Pt}{VH} \ (\%) \tag{4}$$

Considering Fig. 7 and evaluating the BSFC and BTE using the normal diesel as a base it is evident that the biodiesel blends had a higher BSFC and BTE. Break specific fuel consumption is used to evaluate the engine

Table 4. Organic compounds analyzed in the liquid condensate of torrefied microalgae residue.

Urea	Aziridine
2,2,3-Trimethylbutane	2(5H)-Furanone
2,2-Dimethylpentane	2-Propenoic acid
Methylcyclopentane	2-Hexene
2-Methyl-1-pentene	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose
Butylcyclobutane	Aniline
2-Amino-1,3-propanediol	2-Propenoic acid,
Formic acid hydrazide	2-ethylbutyl ester
Pyridine	Pyrimidine-4,6-diol
2-Pyridinecarboxaldehyde	levoglucosan
2-Butenoic acid	5-Methyl-2-furaldehyde
Pyrrolidin-4-ol-2-carboxylic acid	Furfural
Heptanal,	Limonene
4-Methylpentyl acrylate	
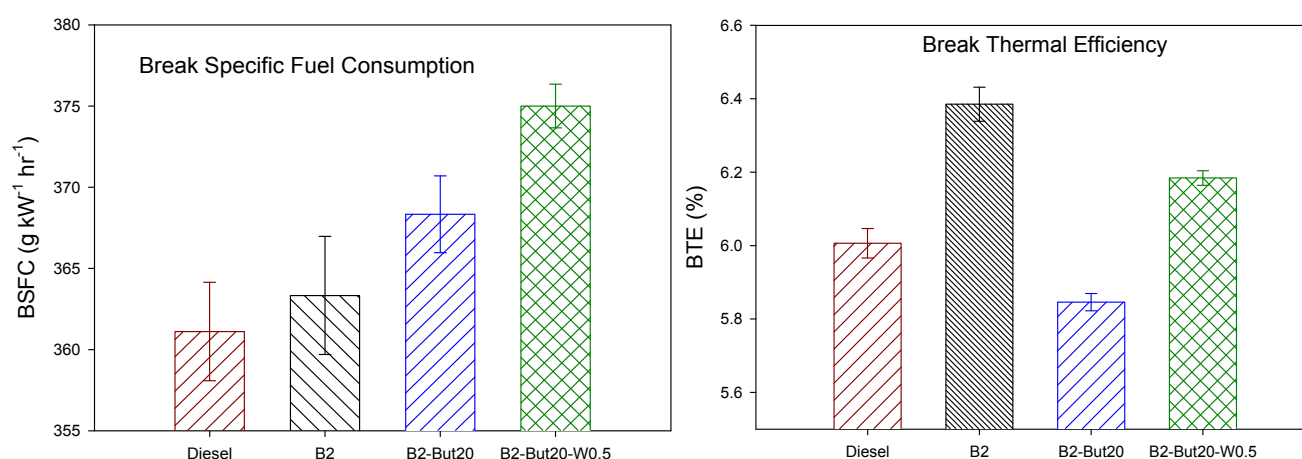
Fig. 7. Energy Performance -Break Specific Fuel Consumption (BSFC) and Break Thermal Efficiency (BTE).

performance in terms of fuel consumption. In this study BSFC increased by about 0.62–3.85% while the B2 had an overall increase in break thermal efficiency of 6.31% while B2-But20 decreased by 2.67% and B2-But20-W0.5 increased by 2.96%. B2-But20 had the least break thermal efficiency which was even lower than base diesel. Addition of water to the butanol blends enhanced the energy performance of the blends as there is a significant increase in BTE with B2-But20-W0.5. The rise in BSFC can be related to the reduced heating values of the fuel blends. The increase in BSFC in the B2, B2-But20 and B2-But20-W0.5 is due to the fact that less conventional 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 (Popovicheva *et al.*, 2013) and the blends offer a comparatively less calorific value (Ithnin *et al.*, 2015). The higher break thermal efficiency offered by the blends in comparison to the base diesel is as a result of the higher oxygen content which offers a more complete combustion as opposed to base diesel translating to increased energy efficiency (Chang *et al.*, 2014). On the other hand, the BTE increases as a result of ignition delay and improved combustion due to the microexplosion mechanism. Furthermore the ignition delay may cause more diesel to be consumed leading to increased

BSFC and improved combustion and thermal efficiency.

Pollutant Emissions

Fig. 8 illustrates the variation in pollutant emission factors for diesel, B2, B2-But20 and B2-But20-W0.5for the criteria pollutants HC, CO, NO_x and PM as well as PAHs. The emission factors for CO_2 were not presented in this study as they were not significant enough owing to the fact that the amount of biodiesel added was only about 2%. The emission factors were determined as per the Eq. (5), where C is the concentrations of each pollutant (mass/Nm^3), V denotes the total exhaust volume 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.

$$EF = CV/Pt \quad (mass/kW·h) \tag{5}$$

Hydrocarbon emissions from B2 decreased by 50.2% while that of B2-But20 and B2-But20-W0.5 increased by 18.9% and 69.8% when compared to base diesel emissions. Only B2-But20-W0.5 showed an increase of 1.72% in relation to CO emission when compared to base diesel but B2 and B2-But20 had a reduction of 0.34% and 1.01% respectively. CO emissions from diesel engines are
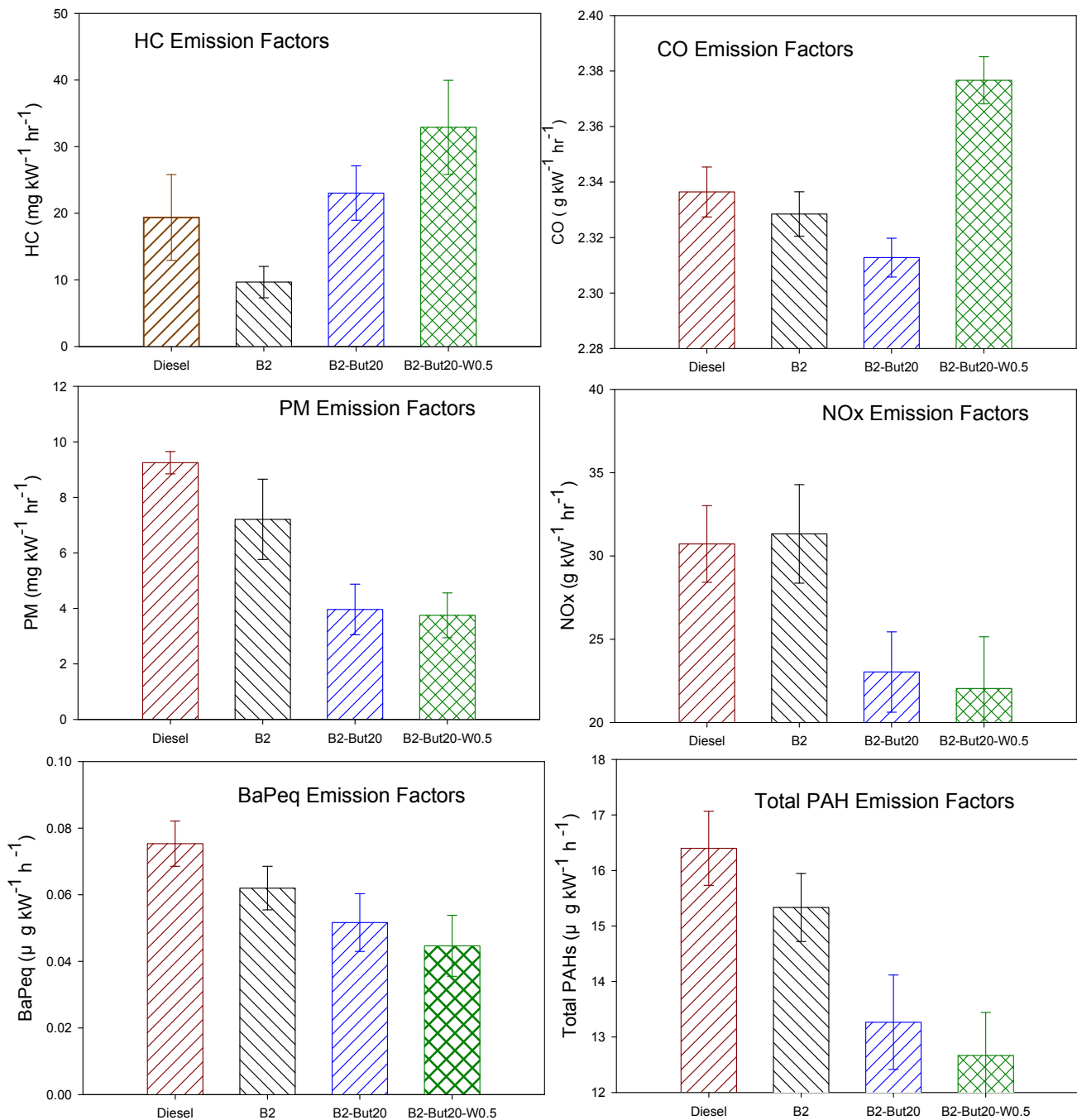
Fig. 8. Pollutant emissions from the diesel engine test.

characteristically high due to the incomplete combustion of carbon in fuel to form CO_2. The lower temperatures due to water addition means less complete combustion of the fuel hence as B2 and B2-But20 lead to decreased CO emission the B2-But20-W0.5 registered a slight increase in CO emissions (Lee *et al.*, 2011). On the other hand B2 had decreased HC emissions while B2-But20 and B2-But20-W0.5 had an increased HC emission compared to base diesel. The lower BTE of the blends may lead to higher HC and CO emissions but this can be solve this problem countered using tailpipe catalysts and absorbers (Pilusa *et al.*, 2012). Actually, Yilmaz *et al.* (2014) in their recent study noted that

addition of butanol fractions to fuel lead to increased HC emissions because butanol has a low cetane number that favors incomplete combustion resulting from delayed ignition and short combustion periods. Previously (Tüccar and Aydın, 2013) reported a decrease 3.8% for CO at 2200rpm using microalgae biodiesel. Makarevičienė *et al.* (2014) recently did a study using fuel containing microalgae methyl esters at a ratio of 30% biodiesel 70% base diesel and reported that HC emissions decreased at a range of 12–15% while CO emissions decreased by about 10% when running a diesel engine using the biodiesel blend.

All fuel blends had excellent PM reduction with 22.0–

59.5% reduction rates. Particulate matter in engine is as a result of soot nucleation, hydrocarbons condensation and from sulfates formation. Addition of microalgae biodiesel to normal diesel reduces the amount of sulfur in the fuel through the effect of dilution as well as the higher oxygen content of the biodiesel lead to lower unburnt hydrocarbons. These factors contribute to reduce particulate matter (PM) formation as there are fewer nuclei and aromatic rings formed which act as PM precursors. In addition, the existence of water during fuel combustion provides oxidizing species such as OH· that react to reduce soot formation (Yahaya Khan *et al.*, 2014).

B2 showed a slight increase in NO_x emission (2.0%) while B2-But20 and B2-But20-W0.5 had reduced NO_x emissions with about 25% and 28% respectively. Chang *et al.* (2013) and Chang *et al.* (2014A) reported that a trade-off between NO_x and PM occurs when water is added to the biodiesel and biodiesel-diesel blends. The study attributed the NO_x and PM reduction lowered temperatures that lead to reduced thermal formation of NO_x. Water that is added has a greater latent heat that induces a cooling effect resulting in reduced combustion temperatures in the engine hence lower thermal NO_x compared to base diesel. Similarly butanol which is an organic alcohol additive has been shown to have a higher heat of vaporization that offers a cooling effect hence reduced temperatures and consequently decreased the level of thermal NO_x emission. Furthermore, a higher oxygen content ensures oxidation of soot which otherwise may raise the internal temperatures by heat radiation since they acts as black bodies. In terms of NO_x reduction, the B2-But20 and B2-But20-W0.5 performed reasonably as the ABE solution with about 25% used in (Chang *et al.*, 2014A). In their recent study (Chang *et al.*, 2013) reported 5.82–61.6% reduction for NO_x, and 3.69–16.4% reduction for PM when compared to normal diesel emissions for 0.5% water content in ABE diesel blend. Similarly (Tüccar and Aydin, 2013) reported a reduction in NO_x emissions with about 10% at 2200 rpm using microalgae biodiesel. The study attributed the reduction in NO_x albeit the high oxygen content to less air is being drawn into the cylinder during combustion of microalgae biodiesel and lower combustion temperatures due to low calorific value. The slight increase in NO_x observed in this study when using the B2 blend maybe caused by the increased nitrogen content that is responsible for the formation of fuel prompt NO_x and which when reduced by the dilution effect of adding butanol and water fractions leads to reduced levels of NO_x in subsequent blends of B2-But20 and B2-But20-W0.5.

As for the PAHs the total PAHs represents the emission factors in terms of mass concentration while the BaPeq represents the overall toxicity. The overall mass concentration of total-PAHs reduced in all blends when compared to base diesel. There was a 6.50%, 19.1%, and 22.8% reduction for B2, B2-But20 and B2-But20-W0.5 respectively. In terms of toxicity levels (BaPeq), the decrease registered was 17.7%, 31.4%, and 40.7% for B2, B2-But20 and B2-But20-W0.5 respectively. Diesel fuel contains aromatic compounds such as PAHs and there are two mechanisms through which the PAHs may appear in the exhaust gases. The first mechanism

is known as the survival method whereby the PAHs present in the fuel are not destroyed in the combustion process and the other is fuel fragments may combine to synthesize PAHs (Rhead and Hardy, 2003). The reduction of PAH emission can be explained by the lower aromatic content in the biodiesel as there is dilution effect from biodiesel and butanol and water additives. Additionally, a higher oxygen content of the biodiesel fractions and the butanol fractions ensures a greater combustion potential that lead to decreased PAH formation. The microexplosion mechanism initiated by the water vaporization during combustion also provides an atomization effect that ensures more complete oxidation of PAHs. Lin *et al.* (2012) in their earlier works reported a reduction of 7.78% to about 20.4% when using 0.5% wt water content in butanol diesel blends.

Generally, addition of microalgae biodiesel to diesel fuel leads to increased NO_x emissions, but this can be countered by water and butanol addition which offers combined reduction of NO_x, PM and PAHs. Conversely, the addition of water and butanol fractions in diesel has an increasing effect on HC and CO emissions which can be easily removed using tailpipe catalysts and absorbers.

CONCLUSIONS

The mean dry weight of the microalgae harvested from the cultivation ponds averaged at about 1.5 kg per run (17 days) and the average oil content was 26%. Generally the open ponds can produce 4355 kg of microalgae oil per 10000 m^2 of cultivation area annually.

Considering the thermal degradation behavior, microalgae oil is severely affected by thermodegradation process due to the high content of volatile matter which results to high weight loss. On the other hand, the recommended temperature range for torrefaction of microalgae residue is between 200°C to 250°C. The optimum temperature was 250°C with an energy -, solid-, liquid-, gas yield of 71%, 53.7%, 12.3% and 34.0% respectively.

The liquid condensate from microalgae residue torrefaction contained compounds such as furfural, limonene, pyridine, levoglucosan, aziridine that can be ultimately be used specialty chemicals such as pharmaceuticals and other industries.

In this study BSFC increased by about 0.62–3.85% for all the blends while the BTE increased by 6.31% and 2.96% for B2 and B2-But20-W0.5 respectively and dropped by 2.67% for B2-But20.

Compared to base diesel, the HC emissions from B2 decreased by 50.2% while that of B2-But20 and B2-But20-W0.5 increased by 18.9% and 69.8%. The diesel fuel blends - B2, B2-But20 and B2-But20-W0.5 showed a reduction of 22.0%, 57.2%, and 59.5% in PM emission, and a decrease of 17.7%, 31.4% and 40.7% in BaPeq emission, while B2-But20 and B2-But20-W0.5 had reduced NO_x emissions with approximately 25.0% and 28.2% respectively but B2 showed a 2.0% increase in NO_x emissions. There was a remarkable decrease in PAH emissions in the range of 22.0–59.5% when using all the fuel blends

Among the fuel blends that were considered B2 has a

better performance when compared to base diesel except a slight increase in NO_x emissions. B2-But20 had a lower break thermal efficiency than base diesel but also showed decreased pollutant emissions. B2-But20-W0.5 revealed a higher CO and HC emissions, but lower NO_x and PM emissions. Similarly, it had higher BSFC and BTE values than base diesel. All blends showed a remarkable decrease in PAHs emissions when compared to neat diesel.

ACKNOWLEDGMENTS

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