Combustion and Emission Performance of CO/NO$_x$/SO$_x$ for Green Diesel Blends in a Swirl Burner

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1. INTRODUCTION

Greenhouse gas effects, along with a thinning ozone layer, acid rain, and other adverse outcomes, are being exacerbated by higher exhaust emissions such as SO$_x$, NO$_x$, and CO$_x$ from fossil-fuel combustion in internal combustion engines. Continuous utilization of fossil-based fuels for transport systems has worsened such emissions. These air pollutants are considered to negatively affect the human health of the entire population, causing respiratory diseases, dermatology-related diseases, and other diseases related to nervous system breakdown. Consequently, numerous researchers have sighted bio-based fuel as a good substitute for fossil-based fuels to mitigate poisonous gas emission rates. Many scientific researchers have agreed that the utilization of liquid biofuel, capable of reducing the carbon monoxide (CO), soot, and carbon dioxide (CO$_2$) emissions, will help greatly in saving people’s life and the rest of the ecosystem. Biofuels are considered among the most promising, sustainable, and renewable fuels because of the availability of their feedstock and less toxic emissions. Biofuel technology is simple and affordable, and biofuels can easily be obtained from the locally produced feedstock.

Selecting the appropriate feedstock for biofuel production is important for industrial practices. Usually, edible and non-edible vegetable oil feedstock are used for biofuel production at a commercial scale. However, use of edible oils in the production of biofuel has been criticized due to the possible problems related to the competition between food and fuel in the near future. Nonedible oils, on the other hand (Jatropha curcas oil, microalgae oil, etc.), are found to be very expensive to produce, thus making the biofuel production costly; hence, they are unsuitable for biofuel production. Waste cooking oil (WCO) was found to be one of the most appropriate feedstock for the production of biofuel. WCO is the end product of frying foods using cooking oil, which contains plant or animal fats that have been processed. It has been reported that WCO is widely produced all over the world. The EU produces about 700 000−1 000 000 tons of WCO per annum, including oil used for snack foods and French fries. WCO produced in Asian countries such as China, Malaysia, Indonesia, Thailand, Hong Kong, India, etc., was estimated to be 40 000 tons per year. Improper disposal of waste cooking oil leads to environmental pollution, particularly land and water pollution, which could lead to disruption of the aquatic ecosystem. As a typical renewable raw material of green energy, WCO can be
upgraded to drop-in biofuel with the currently available technology.

Biodiesel is a nonpetroleum-based biofuel that consists of fatty acid alkyl esters (usually methyl esters, FAME) derived either by transesterification of triglycerides (TGs) or esterification of free fatty acids (FFAs), which uses low-molecular-weight alcohols (methanol) in the presence of a catalyst with heating.13,14 Undoubtedly, the use of biodiesel in commercial application has so far achieved remarkable success. However, despite the recorded success of biodiesel, it is not fully compatible with conventional diesel engines owing to the still relatively high oxygen content of the fatty acid esters.13 Thus, the produced biodiesel needs to be blended with petroleum-based fuel before it is effectively used for internal combustion engines. Even though biodiesel blends offer many advantages, Lapuerta et al. discovered that they produced higher NOX emission rates when used in engines.15,16 Similarly, Szybist et al. noted that biodiesel fuels yield between 6 and 9% higher NOX emissions when compared to green diesel.17,18 It was revealed that high NOX emission by biodiesel blends could be as a result of the high oxygen content in biodiesel.17,18 Other shortcomings related to biodiesel when compared to other biofuels include poor cold-flow properties due to a high cloud point, pour point, and cold filter plugging point.18 To overcome these issues, different routes for the production of high-quality oxygen-free biofuel derived from TGs and FFAs have been investigated.19,20 In many cases, a catalytic deoxygenation process is a popular strategy applied to convert the oxygenated species present in TGs and FFAs into oxygen-free hydrocarbon fuel known as green diesel, consisting mainly of hydrocarbons to the calorific value (CV) and the oxygen content.21,22,23 It is noteworthy to mention that general green diesel has also been proved to have a greater cetane number (85−99) than the ultra-low sulfur diesel (ULSD) standard (47−55) and biodiesel (50−65).22,23 Even though green diesel production studies from various types of feedstock have been covered by many researchers, research into green diesel and petro-diesel blends has not yet been fully reported in the literature. Accordingly, the present study explores and outlines for the first time an emission test for the blended green diesel. The detailed fuel properties of pure green diesel and blended green diesel are also investigated and reported.

2. RESULTS AND DISCUSSION

2.1. Calorific Value, Oxygen Content, and Product Distribution for Green Diesel and Blended Green Diesel. It could be proposed that the contribution of hydrocarbons to the calorific value (CV) is due to the increase in hydrocarbon chain length and the reduction in the value of O/C ratio.24 Detailed findings on the CV, oxygen content, and product distribution for G100 and blended green diesel are shown in Figure 1A. The CV of the fuel generally refers to the heat of combustion of the fuel.25 A higher unsaturation level or number of C=C double bonds increased the CV of green diesel.26 A lower CV means that the engine requires more fuel to maintain a constant speed at a particular load, and hence increased fuel consumption. The CVs of G5, G20, and G100 are 41, 46, and 47 MJ/kg, respectively (Figure 1A). It is remarkable that the CV of G20 and G100 was much higher than that of the other biofuel (biodiesel) (42 MJ/kg).27 Hence, it is firmly confirmed that rich-blended green diesel (G20, G100) has greater energy content, which transforms into high power and torque output of the engine.28 Detailed product distribution for green diesel and blended green diesel is shown in Figure 1B. Obviously, G100 and blended green diesel are mainly comprised of hydrocarbon fractions within the n-C8 to n-C20 range. Notably, the percentage of n-(C8−C20) diesel increased gradually with the increase of green diesel blends. Admittedly, a high amount of hydrocarbon fraction in the rich-blended green diesel rendered an improvement in the CV. Overall, small quantities of oxygenates such as aldehydes, ketones, alcohols, and carboxylic acids along with heavy hydrocarbon species (n-(C21−C24) were also detected. It is noteworthy to mention that the total percentage of oxygenated species for G5 was the highest (25%), while for G100 it was the lowest (1.24%). This finding is in agreement with the value of O/C ratio, whereby G100 exhibited the lowest value of O/C ratio (1.25 × 10⁻²) and G5 was found to have the highest (3.30 × 10⁻²). According to this result, low oxygen-containing green diesel (G100) will result in excellent CV characteristics, which is an advantage for heat of combustion in the engine.

2.2. Fuel Properties. The green fuel should meet the U.S. diesel standard ASTM D6751 and the European diesel standard EN 14214 to be used in diesel engine automobiles. The fuel specifications of the blend fuels G5 and G20 and the green diesel were further tested, and the results are summarized in Table 1. The flash point is the lowest temperature at which the fuel vapors will ignite in air.29,30
The green diesel should have a high flash point but still within the standard limit for its safe storage. The short chain present in the green diesel is the most important factor. This is due to the fact that a high short hydrocarbon fraction content (C<sub>n</sub>-C<sub>17</sub>) will reduce the flash point of green diesel. The results showed that the flash points of the blended green diesel (G5, G20) and pure green diesel G100 were found to be 158, 189, and 238 °C, respectively, which are superior to the range of the standard limit (101–130 °C).<sup>38</sup> Thus, the pure green diesel and blended green diesel are regarded as safer fuels. Viscosity is one of the fuel properties that is very important for fuel delivery and atomization. The impact of high viscosity is power loss because of poor combustion and coking of the injector and the fuel pump, which simultaneously lead to ignition delay and a subsequent increase in the emission of CO, CO<sub>2</sub>, and SO<sub>x</sub>.<sup>39,40</sup> It is therefore essential to lower the viscosity of green diesel to reduce poisonous gas emissions. For blended green diesel, the kinematic viscosity at 40 °C should be between 1.9 and 6.0 cSt according to ASTM specifications and 3.5–5.0 based on EN specifications.<sup>41</sup> It is important to note that the kinematic viscosity of the blended green diesel is within the ASTM recommended specifications but lower than EN specifications. Moreover, the kinematic viscosity at 40 °C was the lowest for G100 (1.8 cSt), which indicated that G20 is highly favorable in reducing the CO and SO<sub>x</sub> emissions (see Figures 4 and 5). The cold behaviors (cloud point and pour point) of fuel have become a critical consideration, especially in cold climate countries. It is noteworthy that the lowest value of the pour point but still within the standard limit for its safe storage. The short chain present in the green diesel is the most important factor. This is due to the fact that a high short hydrocarbon fraction content (C<sub>n</sub>-C<sub>17</sub>) will reduce the flash point of green diesel. The results showed that the flash points of the blended green diesel (G5, G20) and pure green diesel G100 were found to be 158, 189, and 238 °C, respectively, which are superior to the range of the standard limit (101–130 °C).<sup>38</sup> Thus, the pure green diesel and blended green diesel are regarded as safer fuels. Viscosity is one of the fuel properties that is very important for fuel delivery and atomization. The impact of high viscosity is power loss because of poor combustion and coking of the injector and the fuel pump, which simultaneously lead to ignition delay and a subsequent increase in the emission of CO, CO<sub>2</sub>, and SO<sub>x</sub>.<sup>39,40</sup> It is therefore essential to lower the viscosity of green diesel to reduce poisonous gas emissions. For blended green diesel, the kinematic viscosity at 40 °C should be between 1.9 and 6.0 cSt according to ASTM specifications and 3.5–5.0 based on EN specifications.<sup>41</sup> It is important to note that the kinematic viscosity of the blended green diesel is within the ASTM recommended specifications but lower than EN specifications. Moreover, the kinematic viscosity at 40 °C was the lowest for G100 (1.8 cSt), which indicated that G20 is highly favorable in reducing the CO and SO<sub>x</sub> emissions (see Figures 4 and 5). The cold behaviors (cloud point and pour point) of fuel have become a critical consideration, especially in cold macro-climate countries. The pour point is used to determine the lowest temperature at which the fuel will flow.<sup>42</sup> It is a very important test especially in cold climate countries. It is observed that the pour point is affected by the unsaturated compounds present in the feedstock, whereby high levels of unsaturated compounds in the oil-based green diesel lead to a low pour point.<sup>43</sup> In this study, the pour points for the G5 and G20 blended green diesel are −16 and −22 °C, respectively. The cloud points for G5, G20, and G100 are −11, −13, and −19 °C, respectively. These values are much lower than that of ASTM and EN specifications, suggesting that both blended green diesel (G5, G20) and green diesel (G100) exhibited superior cold weather performance properties. Overall, most of the blended green diesel properties are found to be superior when compared with ASTM D6751 and EN 14214 specifications. Thus, it can be concluded that the blended green diesel possesses a better fuel quality and is therefore safe to be used as a fuel.

### 2.3. Wall Temperature of the Chamber

The ratios of fuel-to-air equivalence, with respect to the process of combustion, and impact wall temperature concerning petro-diesel and green diesel blends are shown in Figure 2. Accordingly, the air-flow volume decreased with increasing fuel rate; a higher temperature value was recorded for the wall across all fuels involved in this experiment at an equivalence ratio of \( \phi = 1.2 \). A greater amount heat was generated throughout the combustion as a greater amount of fuel was burned per richer mixture and conditions.<sup>44</sup> Throughout the combustion test stage, petro-diesel was found to yield higher temperatures of the wall compared to green diesel blends. The combustion of petro-diesel yielded a maximum wall temperature of 764 °C assuming stoichiometric conditions, while G5 and G20 resulted in lowering the maximum wall temperature with values of 751 and 734 °C for the former and latter mixtures, respectively. This is attributed to the high CV of green diesel. Accordingly, petro-diesel energy content was greater when compared to that of the green diesel; as a result, this causes a simultaneous increase in the temperature of the wall. Additionally, it is important to know that the variations of temperature along the burner length could be related to the length of the flame. The higher the length of the flame, the lower the temperature, and the shorter the flame length, the higher the temperature. It is noteworthy that the lowest value of wall temperature profile was recorded for green diesel (G20), and this is attributed to the surface tension of G20 and the fact that it has the lowest viscosity. According to
Habibullah et al., these results are more effective for atomization throughout the process of combustion.  

It is important to highlight that as the equivalence ratio increases (assuming such a ratio is defined as the ratio of the real/actual air–fuel ratio to the stoichiometric air–fuel ratio), it leads to an increase in the wall temperature. Usually, higher wall temperature profiles are created in higher equivalence ratios, which suggests that a greater amount of fuel is combusted, thereby releasing a large amount of heat and subsequently yielding higher temperatures. It can also be seen that the wall temperature increased when the equivalence ratio was >1.0 and the lowest wall temperature was at an equivalence ratio of 0.8. These trends were in agreement with those reported by Huang et al., who discovered that the wall temperature increases with the increase of equivalence ratio. It can be noticed that for G20 at an equilibrium ratio >1.0, the wall temperature becomes lower than that of G5, which might be due to incomplete combustion results from richer mixtures as there is insufficient air involved in the process.

The reduction of greenhouse gaseous emission rates is the key element resulting in the green-diesel-spread scheme and stratagem. The creation rate of NOx in the combustion process of green diesel is a subject of much controversy. Figure 3 shows the NOx emission rate for all of the fuels tested at various rates of equivalence ratios. As shown in the graph, the lowest rate of emission for NOx (27 ppm) within stoichiometric contexts and settings was generated by petro-diesel (with equivalence ratio = 0.8). G20 when combusted in the same setting and circumstances generated NOx at a far greater rate of 35 ppm. Similarly, G5 showed NOx emission of 33 ppm. According to previous studies, lower NOx emission by petro-diesel is potentially due to the chamber’s mean temperature when compared with that of the green diesel combustion. Lower NOx emissions by petro-diesel could be a result of the latter’s viscosity, which is considered to be high. Viscosity enhancement could also be known as an increase in molecular length. Based on this assumption, the molecules of nitrogen are stymied in their reactions with molecules of oxygen existing in petro-diesel mixtures—because of this, a reduced amount of NOx is achieved. It is also noted that the NOx emission rates for G5 and G20 were proportionally reduced when equivalence ratio was >1. Comparing these blended fuels to green diesel with the equivalence ratio of 0.8 and to richer mixes, leaner mixtures generate higher NOx emissions, due to increased supply of air and the reactions between the oxygen and the nitrogen atoms that lead to the formation of NOx, assuming a high-temperature environment. As the temperature and access volume of air increase during combustion, so does the formation of NOx. A number of studies have reported that green diesel combustion and formation of NOx increased in the combustion of green diesel fuels others have also made a comparison between diesel combustion and NOx formation in the combustion of green diesel fuel. The lower NOx emission in the G5 blend at a fuel equivalence ratio of 1.2 could possibly be a result of a decrease in air, which subsequently leads to decreased reaction between oxygen and nitrogen that could possibly result in decreased formation of NOx in a high-temperature environment.

The CO emissions of each fuel at varied equivalence ratios are presented in Figure 4, and 80% CO reduction for G5 and 90% CO reduction for G20 have been observed. In the case of G20, a notable reduction in emission of CO suggests that as the green diesel percentage in fuel blends increases, CO emissions are reduced. Accordingly, G20 is rich in hydrocarbon-based fuels, and it can be firmly concluded that high green diesel percentage mixtures are able to simultaneously lower the oxygen content and reduce the NOx emission. As suggested by Phoon et al. and Douvartzides et al., lower green diesel percentage blends typically have a higher content of oxygenated compounds. Thus, what happens is that this might help realize higher CO combustion. Reduced CO emissions by G20 is also anticipated by the completion of the combustion process. Conclusively, lower CO emissions are obtained from higher percentage mixtures of green diesel fuels compared to that of normal petroleum-based diesel. Notably, the percentage of CO emission increases as the equivalence ratio falls (equivalence ratio = 0.8), which evinced that high oxygen content in atmospheric air may result in incomplete carbon fuel combustion, thus leading to the creation of CO, and this takes place when there is a scarcity of air, typically oxygen.

Figure 5 depicts green diesel-blend fuels’ SO2 emissions as being reduced, and this is due to a higher percentage of green diesel within the mixtures employed. The petroleum-based diesel fuel produces greater levels of SO2 emissions compared to that of green diesel mixtures. In a stoichiometric state regarding the use of both G5 and G20, 3–7 ppm level is seen, while petro-diesel yields nearly 8 ppm; potentially, this is because there is less sulfur in green diesel. Similar findings reported by Croiset and Thambimuthu and Nazri, Jaafar, and Safullah et al. concluded that petroleum products and sulfur-free green diesel mixtures result in lower SO2 emissions when compared to normal diesel. It is noteworthy that the higher the volumes of green diesel blends, the lower the SO2 emissions as a result. This is because as the blend volume of green diesel increases, the amount of sulfur decreases, resulting in lower SO2 emissions.
Overall, SO$_2$ emissions of G5 and G20 remain under the same setting for G20. Comparatively, emissions of SO$_2$ presented in Table 2.

Table 2. Percentage Volume of Green Diesel in the Employed Blends

| diesel type       | baseline | G5   | G20  |
|-------------------|----------|------|------|
| petro-diesel volume (%) | 100      | 5    | 20   |
| green diesel volume (%)   | 0        | 95   | 80   |

deoxygenation reaction under an inert N$_2$ flow over the Co$_3$O$_4$–La$_2$O$_3$-doped activated carbon catalyst were analyzed based on ASTM D6751 and ASTM D240-17 standard specifications. The aforementioned tests were carried out at the Intertake Company (Kuala Lumpur, Malaysia).

3.3. Performance Evaluation of Blended Green Diesel Combustion in an Oil Burner. An oil burner test rig was used in the experiment for evaluating the performance of the blended green diesel. It consists of an open-ended combustion chamber with mild steel of 2 mm thickness forming the combustor wall. Hy-cast cement was used as an insulator for the combustion chamber. The outer and inner diameters of the chamber were 400 and 300 mm, respectively, and the length of the chamber was 1000 mm. Nine hole openings in the combustion chamber were used to install the thermocouples. The type of burner used in this experiment was an axial swirl burner. The specifications of the burner are presented in Table 3.

Table 3. Burner Specifications (Baltur IL BT 14 G/W Light Oil Burner)

| capacity (kg/h) | fuel (°E/C) | voltage power (V) | output (kW) | thermic capacity (kW) |
|-----------------|-------------|-------------------|--------------|-----------------------|
| 7.5–14.5        | 1.5/20      | 230               | 140          | 89–172                |

The experimental setup for the oil burner is presented in Figure 6. The burner and combustion chamber are placed horizontally on a fixed structure. Air is supplied by a compressor in the Baltur burner. For all tests, a gas analyzer tube is mounted at the end of the chamber. This gas analyzer is used to measure the exhaust emissions produced during the combustion tests. The thermocouples employed are K-type, which are attached to a thermocouple reader. Tests were carried out at ambient temperature for the inlet air, and no preheating devices were used in these tests. Combustion air was supplied from the main air compressor in the laboratory. The air supply pressure was metered using an air pressure regulator. It is noteworthy that the experiment performed in a swirl burner is not totally under the same conditions as in conventional diesel engines. However, the swirl burner provided oxidation conditions similar to that of diesel engines to measure the emission rates of the greenhouse gases using different fuel blends.

3.4. Equivalence Ratio Characterization of the Blended Fuels. In combustion terms, stoichiometry relates to the amount of air (oxidizer) required to oxidize a fixed amount of fuel. The stoichiometric amount of an oxidizer required for the complete combustion of a particular amount of fuel can be determined using a formula that requires the balancing of the atoms involved in the combustion process. The air–fuel ratio can also be stated as the equivalence ratio, $\Phi$, which is used to indicate whether the fuel mixture is stoichiometric, rich, or lean. The equivalence ratio is calculated as per eq 1.
In general, during the combustion process, a specific amount of air (oxidizer) is needed to oxidize a fixed amount of fuel. The air–fuel ratio in a process in which a stoichiometric amount of air (oxidizer) is needed for the complete combustion of a specific amount of fuel is defined as the equivalence ratio ($\Phi$). The equivalence ratio of the blended fuel in this work was characterized using eq 1.

$$\Phi = \frac{(A/F)_{\text{Stoic}}}{(A/F)} = \frac{(F/A)}{(F/A)_{\text{Stoic}}}$$

If the fuel is a rich mixture, $\Phi > 1$, whereas if the fuel is a lean mixture, $\Phi < 1$.

The air–fuel ratio is the single most important factor in determining a system’s performance. To determine the amount of air required (as oxidizer) in the combustion of diesel, the stoichiometric balance of combustion was determined using the molecular composition of the diesel (blend) as reported in ref 30.

4. CONCLUSIONS

Deoxygenation process of WCO was carried out to produce renewable green diesel, an alternative to petro-diesel fuel, and the emission performance of NO$_x$, SO$_x$ and CO with respect to combustion was studied. High blend of green fuel combustion resulted in higher NO$_x$ and higher wall temperature at all tested conditions compared to diesel fuel. CO and CO$_2$ emissions were observed to be lower for the high blend samples than petroleum diesel fuel due to the super low oxygen content. This reaffirms the positive impact of the blended green diesel on the environment. The fuel properties, flash point, kinematic viscosity, pour point, and cloud point, of pure green diesel and blended green diesel are found to be complying with and superior to ASTM D671 and EN14214 standards. Thus, it can be suggested that the pure green diesel and blended green diesel possess better fuel quality and are safe to be used. Since the green diesel and blended green diesel complied with ASTM and EN standard specifications, it strongly affirmed that these fuels were highly promising for compression ignition (CI) engines. Overall, the blended green diesel is a promising drop-in fuel and is an ideal sustainable alternative to petro-diesel.

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**Notes**

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**Figure 6.** Schematic diagram of the burner test rig setup.
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