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Real-Time Study of Noxious Gas Emissions and Combustion Efficiency of Blended Mixtures of Neem Biodiesel and Petrodiesel

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Abstract: Neem biodiesel is currently being explored as a future biofuel and was extracted chemically from the vegetable oil. Many of its properties are still under investigation and our aim was to study its noxious-gas emission profiles from blends with regular petroleum diesel. The distinct advantage of a real-time study is acquisition of *in situ* data on the combustion behavior of gas components with actual progression of time. Mixtures of neem biodiesel and petroleum diesel corresponding to neem additives of 5%, 10%, 15% and 25% were tested for combustion efficiency and emitted gases using a high-performance gas analyzer. Our study, therefore, investigated the overall efficiency of the combustion process linked to emissions of the following gases: O_2, CO_2, NO, NO_x and SO_2. The results for the 95/5% blend compared to the neat sample were most promising and showed no serious change in performance efficiency (<2%). NO/NO_x emission trends displayed maxima/minima, suggestive of interconvertible chemical reactivity. Declining CO and SO_2 emissions were consistent with rapid chemical conversion. The CO and SO_2 concentrations fell well below the toxic atmospheric limits in less than 300 s. The results are generally encouraging for blends below 10%. The potential environmental impact of the study is discussed.

Keywords: neem biodiesel; gas emissions: O_2, CO_2, NO, NO_x, SO_2; combustion efficiency

1. Introduction

Neem biodiesel is currently being developed as an alternative fuel [1,2] and its characteristic gas properties are relatively unexplored. In view of this, noxious gas emissions of blended mixtures of neem/petro-diesel were studied instrumentally (gas analyzer) and compared with neat petroleum diesel. The advantages of using a gas analyzer are broad: excellent accuracy; high sensitivity; fast gas-exchange rates; high measurement speeds and good pressure/temperature stability. The further advantage of real-time measurements is the procurement of essential information on combustion profiles of noxious-gas emissions with time. The impact of our study associated with monitoring noxious emissions from neem is linked to climate change and sustainable living. A survey of the relevant literature revealed that, in general, such emission studies of biofuels with gas analyzers have not been widely considered, and our research focused on this area of interest with particular emphasis on the comparative performance efficiency with blended mixtures; and subsequent environmental impact of toxic gases: CO, NO and SO_2.

It is well known that biodiesel can be derived from a variety of animal and vegetable oils [3–13]. The biodiesels derived from different plant oils will have slightly different toxic metal and inorganic contents due to the variation of cultivation methods, soil conditions, weather, plant parts used and processing technologies [1]. A common method to generate biodiesel involves the transesterification of the triglycerides with the help of a catalyst to produce alkyl monoesters of chained fatty acids that have comparable properties to that of conventional diesel [14–19]. Glycerol becomes a by-product of this chemical reaction that must be removed by separation processes [1]. Our biofuel was derived from neem oil using a two-step acid-base catalyzed transesterification process due to the high free fatty acid content. The neem tree is prolific in the UAE and its fruit and seeds compared to most non-edible plant species have a higher concentration of oil (30% oil content), which is generally used as insecticides, lubricants and in medicines to treat various disorders. Biodiesel production from jatropha uses a similar dual acid/base treatment; however, relatively high saponification in jatropha tends to be a drawback [20].

The aim of this paper, therefore, was to employ a high-performance instrument to study levels of CO_2, NO_x, and toxic gas-emissions (CO, NO, SO_2) in blended mixtures of neem biodiesel against commercial diesel; and to compare the overall combustion efficiency with neat diesel.

2. Experimental Methods and Conditions

### 2.1. Production of Neem Biodiesel

Neem oil was procured from local retail outlets. To extract the biodiesel the transesterification process was applied with the help of a catalyst to generate a product with comparable properties to that of conventional diesel [1].This process normally uses methanol in a basic solution (NaOH or KOH) to produce the monoester and glycerol (by-product). However, due to the high content of free fatty acids (FFA) in the vegetable oil the neem biofuel cannot be directly obtained in a one-step process [2]. Under basic conditions soap is produced which reduces the yield of the reaction and also consumes excessive alkali. This could lead to a slower reaction time and the possibility of incomplete conversion. Therefore, pre-treatment with methanol under acidic conditions is necessary to reduce the amount of

FFA by converting them to fatty acid methyl esters (FAME). A dual process: acid-catalyzed pre-treatment and base-catalyzed transesterification was thus necessary [1].

2.2. Instrumental Set-up

A schematic diagram of the experimental setup is shown in Figure 1. Experiments were conducted in a combustion unit model C492 manufactured by P.A. Hilton. Ltd. (UK). The unit consists of a 450 mm diameter by 1000 mm cylindrical water-cooled stainless steel chamber mounted on a frame on to which either an oil or gas burner can be fired. The chamber is equipped with four 100 mm diameter observation windows for visualizing the combustion process. In this investigation, the unit was fitted with a Lamborghini Calor model ECO 8 K/IR light oil burner with an output of power of 36.0 to 101.0 kW. The burner has an operating pressure of between 8 to 15 bars with a 60 degree spray angle. Fuel pump pressure is displayed using a Burdon pressure gage attached to the burner. The fuel pump pressure is adjustable using a screw mechanism, and fuel is fed to the system from a 5 L polypropylene container. A micrometrical screw device allows the adjustment of air delivery through an air flow control damper. An instrument panel integrated within the combustion unit displays inlet cooling water, outlet cooling water, and flame temperature, as well as flow rates of the inlet cooling water and fuel.

Figure 1. Schematic diagram of the experimental setup.
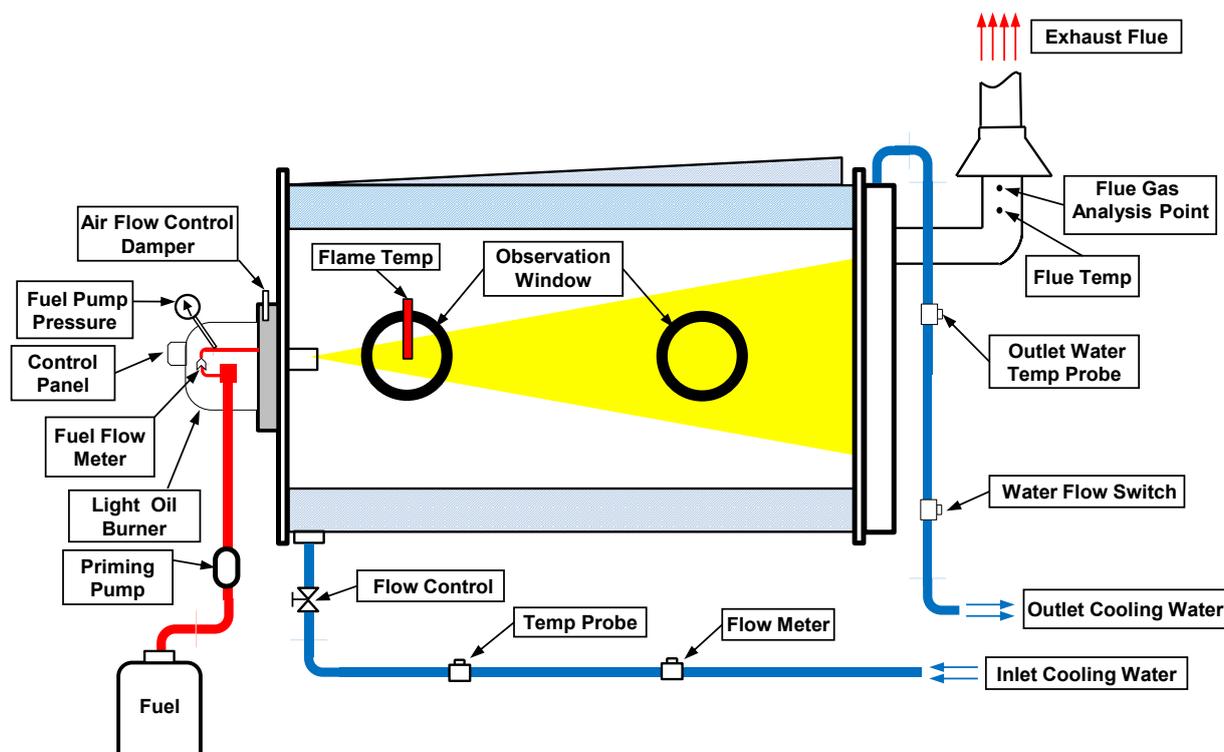
A Kane Quintox KM9106 gas analyzer was used to measure the flue gas content. The analyzer is equipped with an oxygen sensor (range 0–25%, accuracy −0.1% to +0.2%), a hydrogen compensated carbon monoxide sensor (range 0–10,000 ppm, accuracy ±20 ppm < 400ppm), an SO_2 sensor (range 0–5,000 ppm, accuracy ±5 ppm < 100 ppm), an NO sensor (range 0–5,000 ppm, accuracy ±5 ppm < 100 ppm), as well as a temperature sensor for measuring flue and ambient temperatures (±1 °C).

2.3. Analytical Procedure

The experiments were conducted by blending general green diesel with 0%, 5%, 10%, 15%, and 25% neem biodiesel. The blended fuels were stored in and fed to the burner using five separate 5 L polypropylene containers. Throughout all experiments fuel was fed to the burner at a constant flow rate of 7.7 L/h and a pressure of 1,200 kN/m^2. The burner's air flow control damper was set using the micrometrical screw device to position to obtain an average air flow rate of 15.4 L/h. The aforementioned fuel and air flow rates were selected as they resulted in the highest burning efficiency for the 100/0% blend. For each fuel blend, a total of 4 measurements (O_2, CO, SO_2, NO, flue and ambient temperatures) were taken over a 15 minute period with the exception of the 75/25% mixture, which due to the limited available quantity of the fuel blend (only 3 L), 6 measurements over a period of approximately 6 minutes were recorded. The flue gas measurements were recorded using the gas analyzer's remote handset. Inlet cooling water flow rate, fuel flow rate, and fuel pressure were manually recorded using the digital displays and mechanical gages on the combustion unit's instrument panel.

2.4. Numerical Methodology

Calculations pertaining to combustion efficiency are based upon British Standard BS 845-1:1987 [21]. In this paper we present the calculated net combustion efficiency (η_{net}) for the various blends under test as defined in Equation 1. Net efficiency calculations assume that energy contained in the water vapor that is produced during the combustion process is recovered; therefore assuming no latent heat is lost up in the flue. We define latent heat as the energy required to convert water at 100 °C into steam at 100 °C (*i.e.*, no change in temperature during the liquid/gas phase change).

$$\eta_{net} = 100\% - Loss_{dry} \tag{1}$$

where $Loss_{dry}$ are dry flue gas losses as defined by Equation 2:

$$Loss_{dry} = \frac{20.9 \times K1_{net} \times T_{net}}{K2(20.9 - \%O_2)} \tag{2}$$

where T_{net} (°C) is defined as the difference between the flue temperature and the ambient temperature measured using the gas analyzer, $\%O_2$ is the measured oxygen content (%) measured using the gas analyzer, $K2$ is the maximum theoretical CO_2 (dry basis, %) present in the fuel, and $K1_{net}$ is by defined by Equation 3:

$$K1_{net} = \frac{255 \times \%C_{fuel}}{Q_{net}} \tag{3}$$

where $\%C_{fuel}$ is the percentage of carbon in the fuel blend and Q_{net} is the net (lower) calorific value of the fuel blend (MJ/kg). Assuming a net calorific value of 44,800 kJ/kg for neat diesel and 36,080 kJ/kg for neem biodiesel, the net calorific value of the various fuel blends was estimated using Equation 4:

$$Q_{net} = (44{,}800 \times \%neat\ diesel) + (36{,}080 \times \%neem\ biodiesel) \tag{4}$$

The calculated efficiencies for the various fuel blends are discussed in the next section. Values for $\%C_{fuel}$, Q_{net}, and $K2$ for the different fuel blends are shown in Table 1. It should be noted that the maximum theoretical CO_2 percentage, or $K2$, for the 100/0% fuel mix was approximated to be 15.51%;

for the remaining fuel blends the value of *K2* was adjusted by a factor of 5% for each 5% biofuel mix. Time averaged values of *%O₂* and *T~net~* for each case was used for calculating the corresponding fuel blend net efficiencies.

Table 1. %C, net calorific values, and maximum theoretical CO_2 percentages (K2, dry basis) for various fuel blends.

Blend Ratio (Diesel/Biofuel)	$\%C_{fuel}$	Q_{net} (kJ/kg)	*K2* (%)
100.0%	86.80	44,800	15.51
95/5%	86.30	44,364	14.73
90/10%	85.80	43,928	13.96
85/15%	85.30	43,492	13.18
75/25%	84.30	42,620	11.63

In addition to the net combustion efficiency and in the absence of a CO_2 and NO_2 sensor, the CO_2 (%) and NO_x (ppm) content present in the flue gas were estimated using the measured values of O_2 (%), CO_2 (%), and NO (ppm) and Equations 5 and 6 respectively.

$$NOx = NO \ (ppm) \times (1 + assumed \ NO_2 \ percentage) \tag{5}$$

$$\%CO_2 = \frac{(20.9 - \%O_2)K2}{20.9} \tag{6}$$

3. Results and Discussion

3.1. Real-Time Study

The benefit of a real-time study is the ability to gain insight into the fluctuating profiles of noxious-gas emissions in successive time intervals. The behavior of such emitted gases over time is essential to develop an authentic picture of their toxicity and overall environmental implications. Figure 2a–f delineate the levels of the emitted gases of interest with time, and the point to underscore is that our study essentially compares blended mixtures with neat petroleum diesel.

Clearly, from Figure 2a the O_2 profiles of all samples tend to depict a stable horizontal trend line (at ~8%) following an initial short rise at the point of combustion. After about 100 s no serious differences were observed in the O_2 plots, although the 95/5% blend seemed to show reduced O_2 emission averaging out at about 7.5%. This picture contrasts sharply with Figure 2b (CO) where all samples show an erratic burst in concentration upon ignition followed by a pronounced drop with successive time intervals. The steepest drop occurs with the 75/25% blend from ~160 ppm to ~60 ppm in less than 100 s. In this particular case the high initial level could be due to the presence of concentrated neem additive.

Figure 2. Real-time measurements of gas emissions. **(a)** O_2 (%) content. **(b)** CO (ppm) content. **(c)** CO_2 (%) content. **(d)** NO (ppm) content. **(e)** NO_x (ppm) content. **(f)** SO_2 (ppm) content.
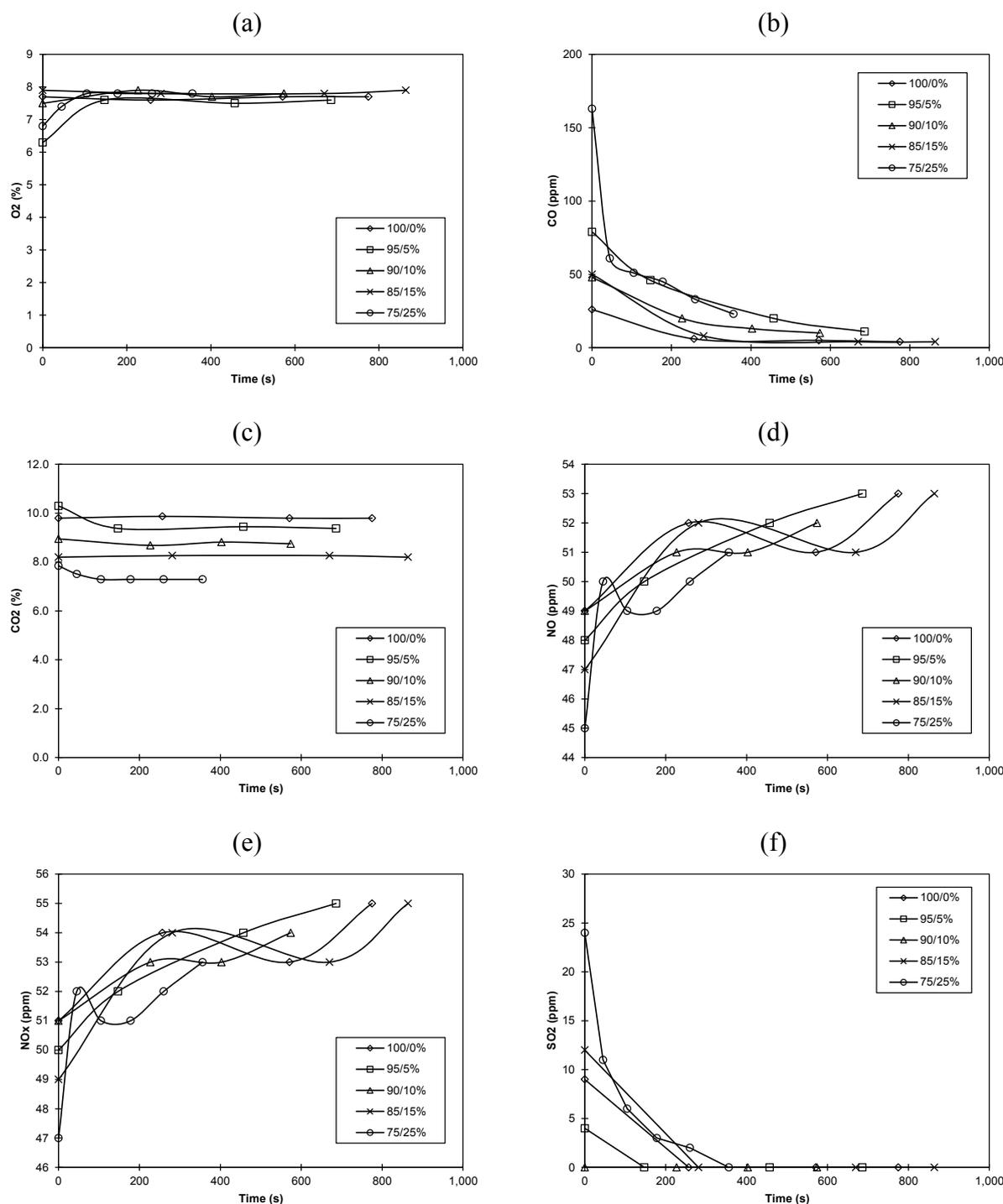

The trend is the same for the other samples but the decline from the combustion point is less accentuated, especially with neat diesel. This decreasing trend could be attributed to rapid chemical transformation of CO. After about 400 s the CO curves tend to flatten out between 0–25 ppm with no significant differences among them from this point onwards. On the other hand, the CO_2 trend, Figure 2c, shows fairly even features with the best results for the 75/25% sample at an emission level of ~7 ppm. The other samples are not far off, with emission levels between 8–10 ppm. The plots of NO and NO_x,

Figure 2d,e should be considered concurrently. In general, these figures display similar features with steep ascents followed by fluctuating behavior with the progression of time. With the exception of the 95/5% blend—which reflects a comparatively smooth rise with time—the remaining plots in both figures exhibit maxima and minima at different time intervals. The presence of maxima could be attributed to slow combustion to achieve the appropriate activation energy. The minima could be due to chemical conversion and subsequent reverse conversion. The lack of maxima/minima in the 95/5% blend is suggestive of a balance between possible exothermicity and energy absorption leading to a smooth curve that seems to peter off at ~53 ppm and ~55 ppm for NO and NO_x, respectively. The plots for SO_2, Figure 2f, adopt a fixed trend—sharply descending (due to chemical conversion) and reaching the baseline after ~300 s. The 95/5% and 90/10% samples are the most promising, showing comparatively reduced emission levels at time zero.

3.2. Combustion Efficiency/Temperature Considerations

The combustion efficiencies for the neat and blended samples appear in Figure 3a. It is evident from these results that the 95/5% mixture produces comparable efficiency to the pure petroleum diesel (63.3% and 64.9%, respectively). As the fraction of the neem biodiesel component increases in the blended mixture the performance efficiency—relative to the neat sample—deteriorates progressively by ~6%, ~11% and ~19% for the 90/10%, 85/15% and 75/25% blends, respectively. This deterioration is particularly appreciable and lends credence to the view that the properties of the blended mixtures change dramatically with increasing biofuel additive. Therefore, from the perspective of combustion efficiency the 95/5% mixture is the most promising and closest to the behavior of regular petroleum diesel.

Figure 3. Efficiency and temperature considerations. **(a)** Combustion efficiency performance for various fuel blends. **(b)** Flame temperature.
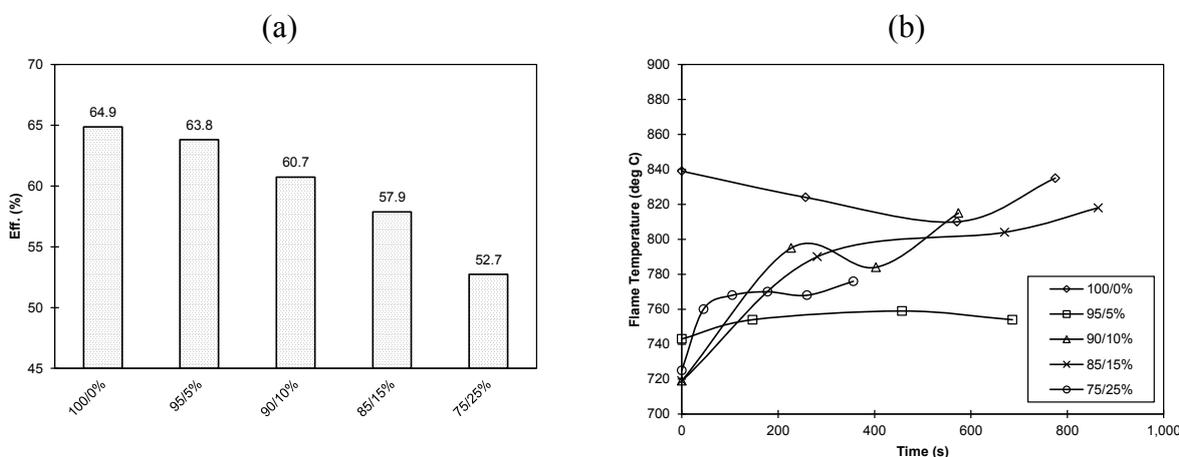
The variation of temperature within the flame, Figure 3b, relays significant information with respect to the internal behavior of the sample. In Figure 3b, the neat sample shows the highest initial combustion point (840 °C), which drops smoothly and increases again after 600 s. This purports initial cooling of the flame followed by exothermicity, possibly from chemical conversion. The remaining plots (except for the 95/5% blend) display maxima and minima, and here again, the implication is

absorption of heat from the flame during combustion with ensuing exothermicity associated with chemical conversions leading to continued production of the original gas component and restoration of the flame temperature. With particular regard to the 95/5% blend, exothermicity and energy absorption probably reach a balance in this sample, thus the absence of maxima and minima.

3.3. Potential Environmental Implications

To fully appreciate the environmental implications of our study minute scrutiny of the plots in Figure 2a–f is necessary. With regard to carbon monoxide (CO) it can be essentially produced in the presence of carbon, oxygen and carbon dioxide but quickly converts to carbon dioxide and soot (Figure 2b) via the Boudouard reaction ($2\ CO \leftrightarrow CO_2 + C$) [22]. The atmospheric limits of CO is ~50 ppm [23] and its biochemical effects on the human body is serious leading to displacement of oxygen in haemoglobin and producing loss of awareness and judgment. Figure 2b shows that production of CO in the 95/5% blend drops to acceptable levels (< 50 ppm) after about 3 minutes. The permissible atmospheric limit for NO is ~25 ppm [23]. During combustion nitrogen in fuel is converted to NO and NO_2.The reactions leading to formation of NO and NO_2: $N_2 + O_2 \leftrightarrow 2\ NO$; $2\ NO + O_2 \leftrightarrow 2\ NO_2$ are interconvertible, consistent with maxima and minima observed in Figures 2d,e. Nitric oxide (NO) resembles CO and also affects haemoglobin in the blood. Figure 2d does not present a promising picture of NO toxicity in the blended mixtures showing elevated levels (>25 ppm) compared to the admissible atmospheric limit. Perhaps, introduction of an innocuous chemical additive to the blended mixtures to inhibit NO production could be the subject of a future study. Since fuel contains sulphur compounds, combustion leads to production of sulphur dioxide (SO_2). The SO_2 is quickly converted to other compounds, hence the sharp decline observed for plots in Figure 2(f). The health effects of sulphur dioxide (SO_2) are associated mainly with respiratory disorders. Its atmospheric limit is ~2 ppm [23]. The results reflected in Figure 2f are favorable for diminished SO_2 production indicating that levels <5 ppm are attained within 200 s. More details linked to environmental effects appear in our earlier paper entitled: Engine Emissions and Performances with Alternative Biodiesels: A Review [24].

4. Conclusions

The primary advantage of real-time measurements of noxious gas emissions is the ability to develop a clear image of the combustion behavior of gas components as time progresses. This produces essential information on the need for chemical inhibitors (and other means of refinement) to suppress levels of undesirable emissions. In this study we found that the 95/5% blend compared reasonably well with pure petroleum diesel, in terms of combustion efficiency. The principal drawback is the elevated production of NO and NO_x—which is a drawback in the neat sample as well. From the environmental perspective, CO and SO_2 levels are diminished in all blends after about 200 s. With further refinement, neem biodiesel could be a possible candidate for blending with regular petroleum diesel.

Acknowledgments

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