



## Review

# Characteristics of CO and NO<sub>x</sub> emissions from combustion of transmethylated palm kernel oil-based biodiesel blends in a compression ignition engine

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## ABSTRACT

This study assessed hazardous emissions from transesterified Palm Kernel Oil-based (PKO-based) biodiesel blends in a Compression Ignition Engine (CIE). Automotive Gas Oil (AGO) was blended with the PKO-methyl esters in the ratios 1:9; 2:8; 3:7; ...; 9:1. The various blends were thereafter fired in a CIE. Besides, 100% AGO and 100% PKO-methyl esters were also burnt in the CIE. Results showed that as the concentration of the PKO biodiesel increased in the blends, carbon monoxide (CO) emissions reduced. There was about 35% significant reduction in the lethal CO emissions as the concentration of methyl esters increased in the blends at 99.9% confidence ( $p \ll 0.001$ ). At 90% confidence, there were no significant changes in NO<sub>x</sub> emissions as a result of change in blend ratios ( $p > 0.01$ ). There exists a degree of association between NO<sub>x</sub> and gas temperature in agreement with Zeldovich mechanism.

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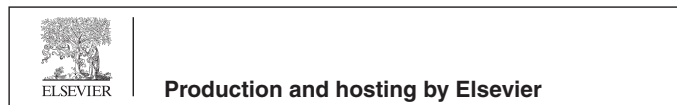
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## 1. Introduction

Habitable environment is key to healthy existence of humanity. The ever increasing population gives rise to increase in energy demand across the nations of the world. Environmental concern of pollution and greenhouse gas effect are some of the propelling factors for research into renewable eco-friendly fuel substitute for internal combustion engine (ICE). Various types of oils have been used to synthesize biofuels. However, the environmental friendliness of these oils needs to be examined for maximum optimization and conservation of our biodiversity. Therefore, the use of 'clean energy' is inevitable as the climate is gradually changing due to discharges from the combustion of fossil fuels and other harmful pollutants from stationary and mobile sources.

The level of pollution and emission arising from the use of fossil fuels are wrecking a lot of havoc on our environment. One of the focal points of the recently held United Nations climate summit (7th–18th Nov., 2016) in Marrakesh focused on the need to reduce the greenhouse gas emissions and conserve our environment. Hence, we cannot be complacent about the increasing trend of environmental pollution. Pollution is "the introduction by man into the environment, substances or energy liable to cause hazards to human health, harm to living resources and ecological system, damage to structures or amenity, or interference with legitimate uses of the environment" (Holdgate, 1979). Carbon monoxide emission is well known for its injurious activities in the blood stream (Fig. 1). The cut down of these extremely dangerous gaseous emissions containing CO and NO<sub>x</sub> being discharged into the atmosphere is imperative. One of the solutions proposed by the Climate Summit was the use of eco-friendly clean/low carbon energy substitutes.

Biodiesel, an attractive alternative fuel for diesel engine, is at present receiving great attention. It is both renewable and environmentally friendly. Several types of fat and vegetable oils used for the production of biodiesel include Rapeseed (Saka and Dadan, 2001), Soybean (Aransiola et al., 2010), Karanji (Dorado et al., 2002), Sunflower (Antolin et al., 2002), Jatropha (Bagby et al., 1987), Tallow (Chung et al., 2009).

Palm Kernel Oil (PKO) is one of the many alternatives 'green energy' options that have the potential to reduce dependence on fossil fuels and its associated hazardous emissions. It is a major

oil palm product. Previous study showed that the oil can be used to produce methyl esters (Shote et al., 2009).

Automobile companies are making tremendous effort to design compression ignition engine (CIE) that is capable of firing 100% pure vegetable oil without major challenges. Elsbett from Germany has designed specially the combustion chamber of a CIE to give excellent running by pure vegetable oils of different composition and grades (Meher et al., 2006); (Halder et al., 2009) and (Jeschke, 2009). Although, some oils have been blended with diesel without being chemically modified, reports showed that only limited amount of the pure oil can be blended with diesel. However, emission problem may not be reduced significantly by this method. Halder et al. (2009) showed that maximum of 30% blend of Putranjiva oil can be used as an alternative fuel in diesel engine. Up to 50% neat Jatropha oil can be substituted for diesel in CIE without major problem (Pramanik, 2003). Soybean oil blends with diesel could be used as fuel extender in low concentration without modification (Engelman et al., 1978). Blending biodiesel with petro-diesel may run better in CIE since their properties are similar.

It is very important for us to take cognizance of the extent of pollution, its causes, the substances involved, their biological and environmental effects, and methods of controlling and curbing pollution. Hence, we cannot overemphasize the menace of environmental pollution looking at the instances where 'chemical time bombs' have wrecked dramatic ecological effects, such as in the forests of Central Europe where many years of inputs of SO<sub>2</sub> and other atmospheric pollutants eventually led to a widespread die-back in conifers (Alloway and Ayres, 1993).

Common industrial pollutions, depending on their concentrations, can have acute effects on human health and environmental quality. Lead emissions, for instance, are linked to mental and physical impairments in children and adults (El-Mahallawy and Habik, 2002).

Oxides of nitrogen (NO<sub>x</sub>) emissions are also one of the major pollutants beside carbon monoxide (CO). However, Temperature could be the major contributor for increase in NO<sub>x</sub> emissions. Nitrogen and oxygen combine to form NO<sub>x</sub> in 3-ways (Prather and Logan, 1994). 'Thermal NO<sub>x</sub>' is very sensitive to temperature because the 'N–N' bond in molecular Nitrogen is very strong. Zeldovich or Thermal Mechanism better predicts NO level from combustion processes.

NO<sub>x</sub> is one of the major causes of photochemical smog (a brownish gray haze) which causes irritation of the eyes, nose, throat, coughing, breathing difficulties, chest tightness, headaches, and damages to agricultural crops as well as reduced driving visibility. The burning of fossil fuels (coal, petroleum and gas) and the recent biomass (such as savannas, forest, vegetable oils and agricultural waste) lead majorly to global alteration in the composition of the atmosphere and the depletion of the ozone layer, greenhouse effect and the level of stratospheric oxidants.

It was pointed out (Prather and Logan, 1994) that the consequence of greenhouse warming leads to two important phenomena: firstly, sea levels will rise as a result of expansion of the water body as temperatures increase, and also of its enhancement by melting South Polar ice causing backing up of rivers leading to flooding. Secondly, in the UK the southeast will become drier and growth of arable crops would tend towards the west to secure water supplies. Also, the African desert would move northward and areas of Spain, Italy and Greece may become deserts.

This increase in NO<sub>x</sub> will contribute to disruption of ozone balance by producing 'ground level ozone' also known as photochemical smog, which is venomous, and destroys naturally occurring ozone in the stratosphere (15,000–50,000 m above the earth surface), where it is beneficial. This is a serious problem in the urban areas (Glarborg et al., 1994). Thus, in the troposphere the problem

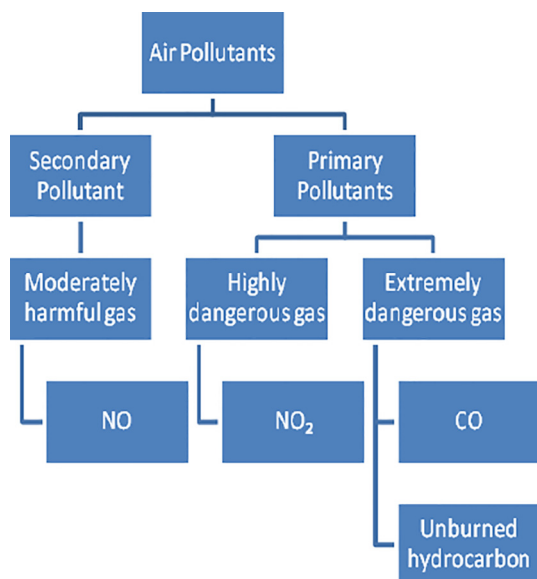


Fig. 1. Classification of air pollutants according to type and the degree of danger posed by the pollutants. Source: Adapted from El-Mahallawy and Habik (2002).

is the production of O<sub>3</sub>, which is destructive to organisms. Ozone (O<sub>3</sub>) at 10 to 15 ppmv can kill mammals. Smog (about 0.08 ppm) can damage cells in the lung's air tracks, causing inflammation; 3 ppmv can create O<sub>3</sub> alert.

The greater recognition of the imminent environmental consequences of combustion of fossil fuels and the merit biodiesel has for the reduction of noxious emissions have necessitated the use of PKO as a viable substitute for sustainable production of renewable Internal Combustion Engine (ICE) fuel. Biofuel is also key to energy security. Hence, this study presented the characteristics of hazardous carbon monoxide (CO), nitric oxides (NO), nitrogen dioxide (NO<sub>2</sub>) and the generic oxides of nitrogen (NO<sub>x</sub>) emissions of PKO-based methyl esters blends from its combustion in a CIE. The aim of this paper is to establish detailed environmental suitability of these emissions from the combustion of PKO-based biodiesel blends.

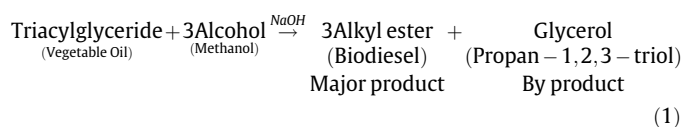
## 2. Experimental section

### 2.1. Background

The combustion of fossil fuel removes O<sub>2</sub> from the atmosphere and gives out equivalent amount of H<sub>2</sub>O; CO<sub>2</sub>; with numerous hydrocarbons (such as CO, nitrogen oxides (NO, N<sub>2</sub>O), CH<sub>4</sub>, CH<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, and CHO); reduced nitrogen compounds (NH<sub>3</sub> and HCN); sulphur gases (SO<sub>2</sub>, OCS, CS<sub>2</sub>); halo-carbons (CHCl and CH<sub>3</sub>Br) and particles (El-Mahallawy and Habik, 2002). A review of the atmospheric budgets of these emissions shows that combustion of fossil fuels besides biomass has led to global alterations in the composition of our atmosphere (Prather and Logan, 1994). Chemical modification of agric-renewable source of fuel substitute particularly in ICE is a dependable panacea to this problem.

### 2.2. Alcoholysis process for the production of PKO biodiesel

The chemical equation employed for the production of PKO methyl esters is shown Eq. (1). Vegetable oil (PKO) was combined with methanol in the presence of sodium hydroxide catalyst to accelerate the reaction to products (biodiesel and glycerine). Biodiesel can also be produced through non-catalytic supercritical alcoholysis (Da Silva and Oliveira, 2014). Details of the PKO methyl esters production procedure are in Shote et al. (2009).

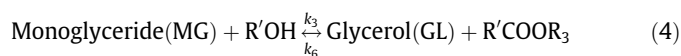
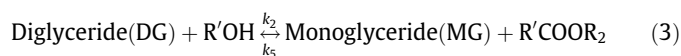
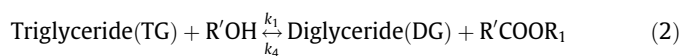


#### 2.2.1. Alcoholysis mechanism kinetics

Tranesterification reaction is a reversible reaction and proceeds essentially to right for quick formation of the products (biodiesel and glycerine) in the presence of a strong catalyst (NaOH). Shote et al. (2009) recommended production variables for the synthesis of PKO methyl esters and glycerine. The glycerine settled down at the bottom of the separating chamber.

In the transesterification schemes, diglyceride and monoglyceride are the intermediates. In the presence of excess methanol, the forward reaction is pseudo-first order and the reverse reaction

is second order (Meher et al., 2006). The schemes for the transesterification are described in Eqs. 2–4.



Noureddini and Zhu (1997) suggested values for kinetics parameter  $k_x$  at 50 °C in Table 1.

### 2.3. Fuels properties measurement

The physical and chemical properties of PKO-biodiesel were determined and tabulated in Table 2. More detailed characteristics can also be found in Shote et al. (2009). The characteristics of this biodiesel were determined along with the convectonal diesel fuel obtained for blending.

Pensky Martens closed cup tester was used for the determination of the flash point as recommended by American Society for Testing and Materials norms. The pour and cloud points were also measured according to ASTM. The viscosities of the various experimental oil-fuels were measured with Canon Fensky Viscometers. Specific gravity bottle was used for the determination of specific gravity.

### 2.4. Emissions assessments

Specific assessment of toxic CO NO<sub>2</sub> and NO emissions from PKO-biodiesel blends combustion are measured in a CIE. To quantify these emissions, an EGA4 Flue Gas Analyzer (FGA) manufactured by Eclipse Company was used. It is also capable of measuring ambient parameter indicator (temperature). The CIE used was a conventional diesel engine of model 165F, power output of 3.23 kW at rated speed of 2600 rpm. This engine was manufactured by Bhokyjson and Co. Nigeria Plc. And has a net weight of 44 kg. AGO was blended with the PKO-biodiesel in the ratios 1:9; 2:8; 3:7; to 9:1 respectively. The resulting blends, including 100% AGO and 100% PKO-biodiesel were burnt in CIE in succession. NO, NO<sub>2</sub>, NO<sub>x</sub> and CO emissions and flue gas temperature (T<sub>g</sub>) were taken concurrently with the aid of the FGA. However, for convenience these blend ratios are sometimes represented by 'Bxx'. The 'B' represents the biodiesel and the 'xx' denotes the percentage of the biodiesel in the blend. A tachometer was used for the determination of the engine speed. The speed was varied as 600, 700 and 800 rpm. Each of these various speeds were kept and CO, NO, NO<sub>2</sub> and NO<sub>x</sub> emissions assessed all through the blends.

## 3. Discussion of results

### 3.1. Characterization of the PKO methyl esters

Table 2 shows the results of the properties of PKO-biodiesel and that of the conventional diesel in addition to the appropriate standard associated with them. All parameters complied with the limits established by the international norms related to both biodiesel and AGO qualities. These properties duly fulfill the qualities desired for an environmentally friendly CIE fuels.

### 3.2. CO assessment

In line with Kyoto Protocol, it is pertinent that any fuel substitute for ICE must be environmentally friendly. The Kyoto Protocol

**Table 1**  
Values for kinematics parameter  $k$ .

Kinematics parameter	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$	$k_6$
Value	0.049	0.102	0.218	1.280	0.239	0.007

**Table 2**  
PKO methyl esters and conventional diesel.

Characteristics	PKO biodiesel	Requirement for biodiesel fuel	AGO <sup>†</sup>	Requirement for AGO
Kinematic Viscosity @ 40 °C (cSt)	3.3674	1.9–6.0 <sup>1</sup>	3.0730	2.0–7.5
Kinematic Viscosity @ 100 °C (cSt)	1.3070	–	–	–
Specific Gravity @ 15 °C	0.8732	0.87–0.9 <sup>2</sup>	0.8599	–
Cloud Point (°C)	3	Summer 4.0; winter – 1.0 <sup>3</sup>	–12	–
Pour Point (°C)	–3	Summer: Max. 0; Winter: Max. < –15 <sup>4</sup>	–16	Max. 6
Flash Point (°C)	100	≥100 <sup>5</sup>	72	Min. 38
ASTM Colour	Yellow	–	Red	–
Water Content (% vol.)	Nil	–	Nil	0.05

<sup>†</sup> IS: 1460–1974.

<sup>1</sup> ASTM D-445.

<sup>2</sup> BIS.

<sup>3</sup> ASTM D-2500.

<sup>4</sup> ASTM D IP-309; ASTM D-97.

<sup>5</sup> ASTM D-93; UNI (Italy) and ON (Australia).

is a United Nations binding international treaty on climate change adopted in Kyoto, Japan on the 11th of December, 1999.

Parameters leading to the behavioural patterns of the profiles of CO emissions through the various blends were itemized and discussed.

The profiles (Fig. 2) of CO emissions shows a gradual reduction in emission trend as PKO-biodiesel concentration increases in the blends with respect to various speed variations (600, 700 and 800 rpm). Biodiesel is noted to be oxygenated (Barnwal and Sharma, 2005). This oxygen, coupled with the oxygen (21% by mole) in the atmospheric air was helpful in the combustion process for the downward trends of CO emissions. Indeed, this oxygen is playing a positive role in the pulling down of this venomous emission. At 100% biodiesel, CO has a range of about 30 to 46% reduction in the emissions emanating from the exhaust of the CIE. This is a significant reduction in malicious CO emissions. PKO-Biodiesel also has a merit of sustainability over fossil fuel which is finite.

Analysis of variance also showed that at 99.9% confidence, there is a significant reduction in CO emission as a result of increase in the concentration of PKO-methyl esters in the blends ( $p \ll 0.001$ ). Besides, there was no significant change at 90% confidence as a result of variation in the speeds as variance analysis suggested ( $p > 0.01$ ). Hence, discussing one of the profiles of CO emissions suffices.

### 3.3. $\text{NO}_x$ assessment

The main parameters relevant to the formation reactions of  $\text{NO}_x$  are combustion temperature, oxidant concentration or its partial pressure, and length of time spent in the high temperature region. Any reduction of these leads to reduction of  $\text{NO}_x$  formation (El-Mahallawy and Habik, 2002).

Figs. 3–5 show the profiles for NO,  $\text{NO}_2$ ,  $\text{NO}_x$  and CO for various blends assessed.  $\text{NO}_x$  does not show any major increase in emissions save in Fig. 5 where there is slight increase in  $\text{NO}_x$ . In Fig. 5, there is no significant change in the  $\text{NO}_2$  emission through the blends. This suggests that, environmental damage from NO does not appear to occur directly, but rather through the subsequent conversion to  $\text{NO}_2$  by the reaction of NO with ozone.  $\text{NO}_2$  has a more serious effect on the respiratory system than NO. It affects the blood hemoglobin, thus depriving body tissue of oxygen, thus, causing oxygen starvation. Ozone ( $\text{O}_3$ ) is regulated by ozone-precursors such as  $\text{NO}_x$  and volatile organic compounds (HCs). Ozone exists at 15,000–30,000 m above earth acting as ultraviolet filter (Annamalai and Puri, 2007). It is typically formed around the equator and transported to Polar Regions by wind. Ozone could also be formed at lower altitudes owing to reactions between NO and volatile organic compounds. The affinity that ozone has for NO means a reduction in the protection that the former has against ultraviolet light. In addition to this, Ultraviolet

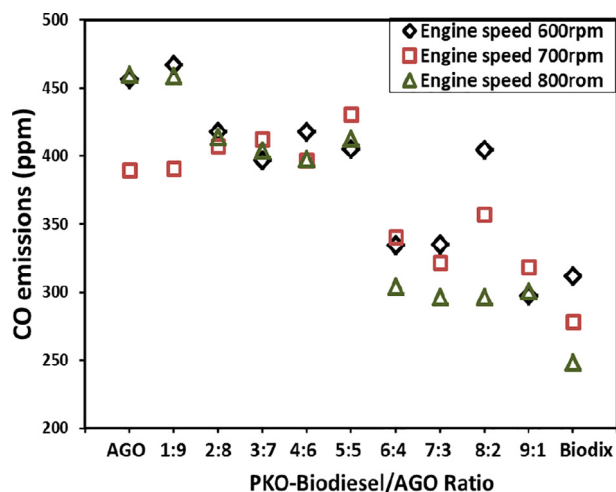


Fig. 2. CO Emissions (ppm) against biodiesel/AGO blends.

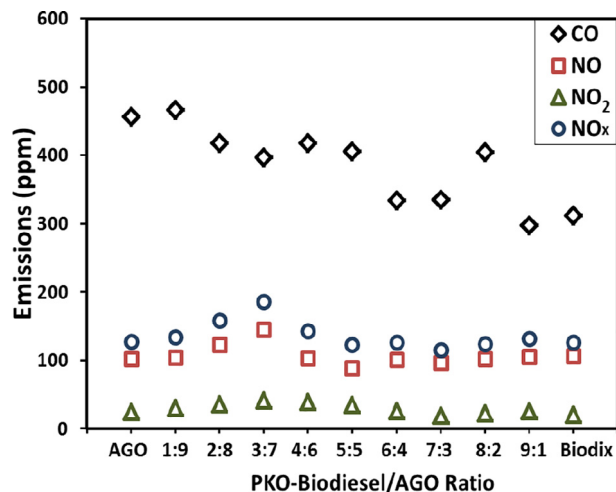


Fig. 3. Emissions (ppm) from biodiesel/AGO blends at speed 600 rpm.

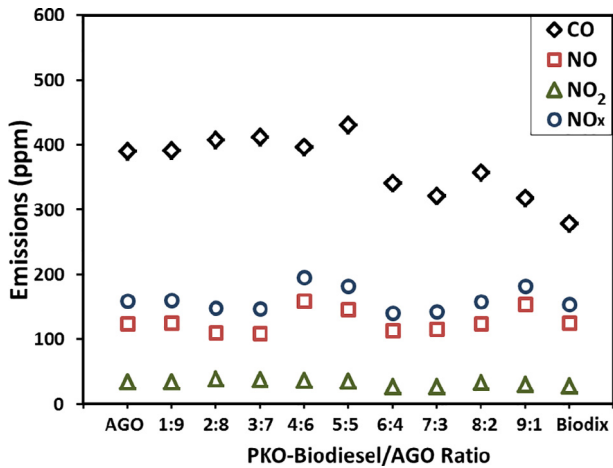


Fig. 4. Emissions (ppm) from biodiesel/AGO blends at speed 700 rpm.

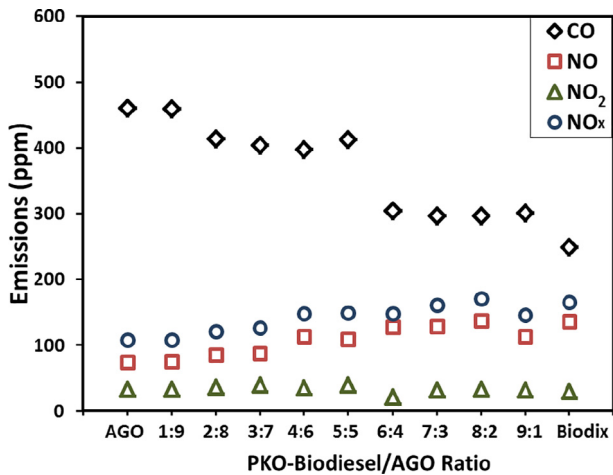


Fig. 5. Emissions (ppm) from biodiesel/AGO blends at speed 800 rpm.

light causes skin cancer in human and the increase penetration of the light to the earth surface means an increase in human skin cancer.

However, Figs. 6–8 establish the type of correlation (R) that exist between NO<sub>x</sub> and Flue gas temperature (T<sub>g</sub>). Specifically, in Fig. 6, there is correlation between NO<sub>x</sub> and flue gas temperature since the reliability between the two variables is less than 0.01 at speed 600 rpm. Hence, with 99% confidence, there is degree of association between NO<sub>x</sub> and temperature. Variation in NO<sub>x</sub> depends particularly on CIE combustion chamber temperature and/or flue gas temperature. From Fig. 6, 83.3% of the total variation in NO<sub>x</sub> can be accounted for by the variation in flue gas temperature. This variation is predicted by Zeldovich mechanism. Therefore, the control of temperature will be sufficient to control NO<sub>x</sub> formation at 600 rpm. Prompt NO<sub>x</sub> (Fenimore mechanism) and fuel NO<sub>x</sub> were possibly responsible for the remaining 16.7%. Eqs. 5–7 predict the NO<sub>x</sub> formation at various speeds.

$$NO_x(\text{ppm}) = 2.464x(T_g) + 101.74_{\text{at speed 600rpm}} \quad (5)$$

$$NO_x(\text{ppm}) = 0.7475x(T_g) + 83.585_{\text{at speed 700rpm}} \quad (6)$$

$$NO_x(\text{ppm}) = -2.1116x(T_g) + 372.82_{\text{at speed 800rpm}} \quad (7)$$

Fig. 7 shows that at 99% confidence,  $p \gg 0.01$ . This implies that there is no degree of association between the two variables. 3.7% of

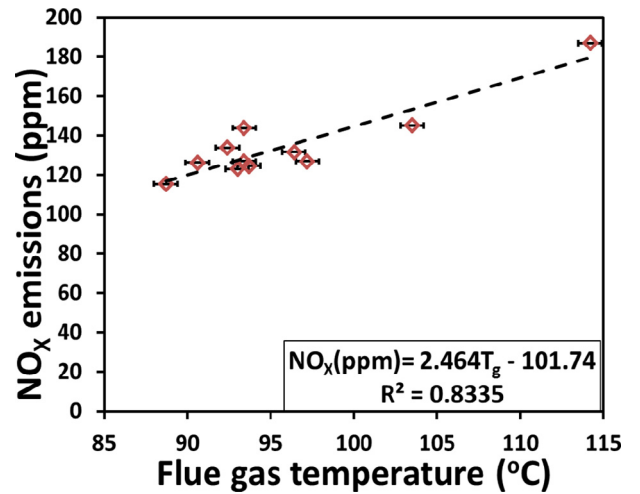


Fig. 6. Correlation (R) of NO<sub>x</sub> (ppm) and flue gas temperature (°C) at engine speed 600 rpm.

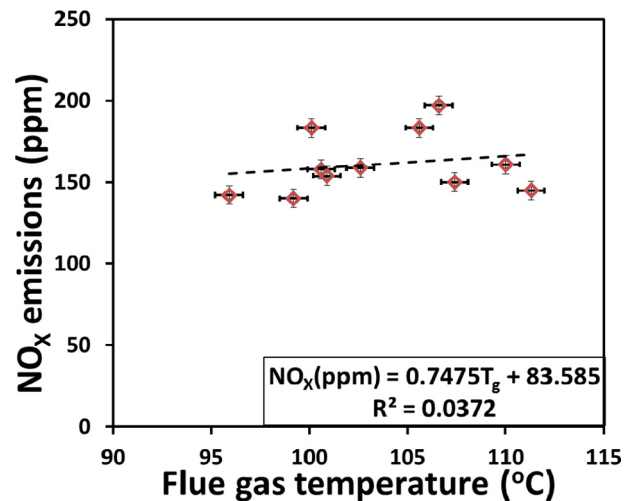


Fig. 7. Correlation (R) of NO<sub>x</sub> (ppm) and flue gas temperature (°C) at engine speed 700 rpm.

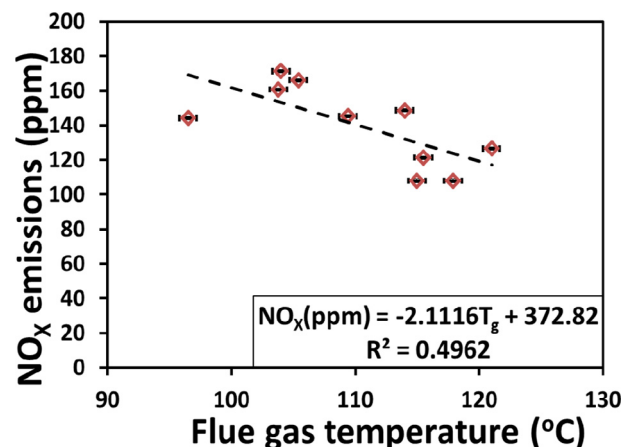


Fig. 8. Correlation (r) of NO<sub>x</sub> (ppm) and flue gas temperature (°C) at engine speed 800 rpm.

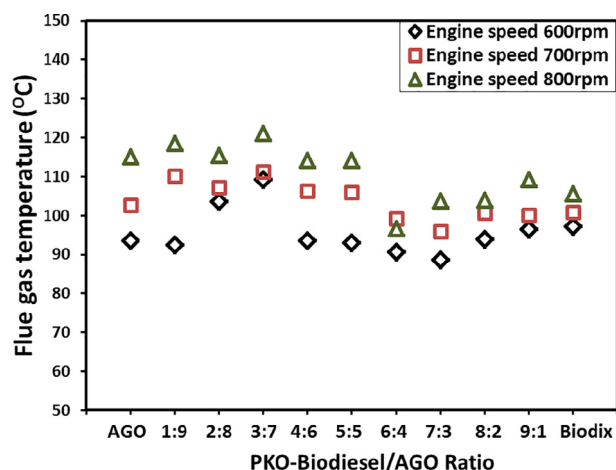


Fig. 9. Flue gas temperature (°C) against biodiesel/AGO blends.

the  $\text{NO}_x$  can only be accounted for by variation in temperature. Hence, prompt and fuel  $\text{NO}_x$  mechanisms were responsible for  $\text{NO}_x$  synthesis. Also Fig. 8 shows a good but negative correlation. At 99% confidence,  $p > 0.01$ , approx. imately 50% of the  $\text{NO}_x$  can be accounted for by the temperature of the hot exhaust gas. Thermal, fuel and prompt  $\text{NO}_x$  formation mechanisms have played parallel roles in this  $\text{NO}_x$  formation. Previous studies Banweiss et al. (2007); Halder et al. (2009), show that  $\text{NO}_x$  emissions could either increase or reduce. This depends on specifically the combustion chamber temperature and the calorific values of the various blends of the methyl esters and the automotive gas oil (AGO). There is no significant change in  $\text{NO}_x$  emissions as a result of blend variations at 90% confidence ( $p > 0.01$ ). Also speed variations do not have significant effect on  $\text{NO}_x$  emissions at 97.5% confidence ( $p > 0.025$ ).

### 3.4. Flue gas temperature

Fig. 9 shows variations in the exhaust gas temperature as a result of the differences in the calorific values and specific fuel consumptions of the various fuel blends. Friction and combustion were significantly responsible for rise in temperature. It is also evidence that increase in PKO-based biodiesel blend slightly reduced the temperature of the exhaust discharge. Hence, the temperature of the Internal Combustion Engine (ICE) would have been reduced. Viscosity of the biodiesel (Table 2) which is higher than that of the fossil diesel is responsible for this slight reduction in temperature.

At 90% confidence, there is a difference in flue gas temperature as a result of speed variations ( $p \ll 0.001$ ). In other words, there is tendency for flue gas temperature to increase as the speed of the engine increases.

## 4. Conclusions

The conclusions arrived at from this study are: Higher concentration of PKO-biodiesel in the blends gives lower CO emissions. This is justified by the fact that biodiesel is oxygenated. The increase in the oxygen in the combustion system aided a more complete combustion process thereby forcing the quantity of hazardous CO on a downward trend as PKO-biodiesel increased in the

blend. At 99.9% confidence, there is about 35% reduction in carbon monoxide (CO) with 100% biodiesel blend.

Over 80% of  $\text{NO}_x$  variation can be accounted for by the variation in flue gas temperature at 99% confidence.  $\text{NO}_x$  formation is associated with temperature. Controlling the temperature suffices controlling the oxides of nitrogen emissions.

Therefore, the use of PKO-biodiesel as a fuel substitute in CIE will reduce the environmental impact of conventional diesel fuel. However, characteristics of other vegetable oils can also be looked into and compared with fossil diesel.

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