A Silica Nano-Additive's Impact on the Performance and Emissions of a Diesel Engine Using DTBP Blended Low Viscous Waste Orange Peel Oil

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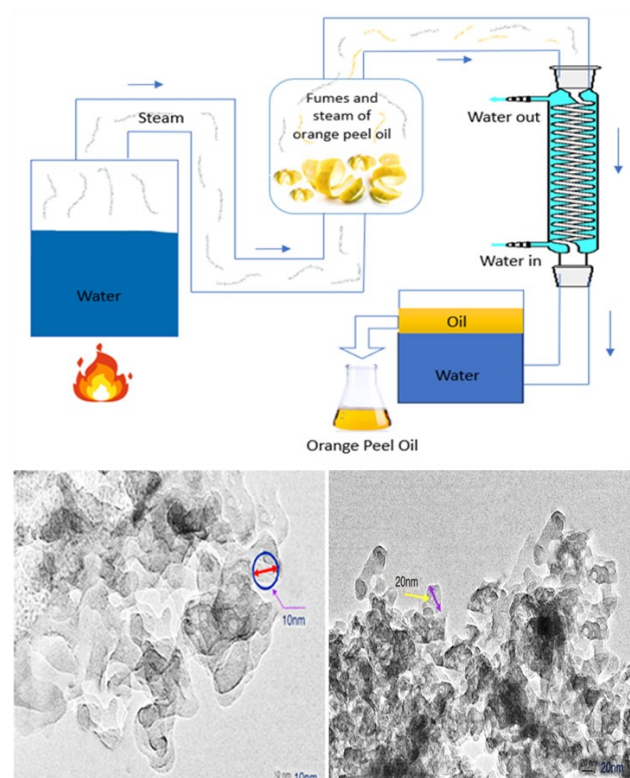
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Graphical abstract

Abstract

In the current study, the effect of silicon dioxide (SiO_2) nano-additive mixed with Orange peel oil (OPO) as Biodiesel was investigated in relation to the operation and emission characteristics of a diesel engine. Orange peel oil was extracted from the orange Peel waste by using steam distillation method. The addition of Di-tetra-butyl-peroxide (DTBP) as a cetanebooster is a novel strategy that has been attempted to improve the ignition patterns of OPO. The properties of customized fuelproduced with a varying volume percentage DTBP and SiO2in 25, 50 and 75 ppm in OPO were determined and compared to those of diesel. Uniform blending of nano-additives + DTBP with OPO is achieved by ultrasonication and isopropyl alcohol is used as a surfactant in order to stabilise the nano-additives. The physical and chemical characteristics of samples of pure and mixed fuel were identified and found in accordance with ASTM standards.Under varied loading conditions, the performance and emissions characteristics of various samples of fuel were studied. Addition of SiO_2 nano-additive + DTBP increased the brake thermal efficiency (BTE) by 3.20-8.37% while decreasing brake specific fuel consumption (BSFC) by 4.18-11.25%. Carbon monoxide (CO), hydrocarbon (HC),nitrogen oxides (NOx) and smoke emissions were reduced by 5.61-12.84%, 9.65-19.05%, 0.89-7.71%, and 10.11-19.71%, respectively, when orange peel oil is blended with SiO_2 and DTBP, and the mixture 10DTBP/90OPO -50SiO2 is found best comparable to ordinary diesel.

Keywords: Orange Peel Oil, DTBP Enhancer, nano-additive, TEM, TGA

1. Introduction

A country's technological, socioeconomic and industrial progress is dependent on the availability of affordable energy for long run. Every facet of daily life is reliant on energy, mainly fuel for commodities and people transit. Due to the dependence of the majority of transportation needs on petroleum products, the price of petroleum products has increased [Anindita Karmakara *et al.* 2012]. Biodiesel increases the combustion thereby reduces the emission of carbon monoxide, smoke and unburnt hydrocarbons.

The orange peel oil (OPO) recommended in this study had a greater inherent oxygen content, a higher heating value, a shorter carbon chain length, and a higher viscosity [Fasogbon *et al.* 2021]. OPO is extracted from orange peels by steam distillation [Kumar *et al.* 2020]. OPO has a lower flash point, boiling point, viscosity and contains more O_2 which helps the complete combustion [Rosanti *et al.* 2022]. The orange is known as the most widely across all nations. Numerous food companies produce a lot of

trash, including millions of kg of discarded orange peels [Kumar and Kumar 2019]. The fundamental reason for using OPO as a feasible alternative to traditional diesel in India, Brazil, China, Mexico, United States, and Egypt is due to its availability, advantageous and desirable qualities [Colás-Medà *et al.* 2021].

When the volume of Orange Peel Oil exceeds 30% in the blended Diesel fuel, the effects of OPO become dominant. Numerous studies have found that when diesel fuel contains more than 30% OPO, the engine exhibits poor performance and high NOx emissions. These issues are brought on by a protracted ignition delay period [Kavitha *et al.* 2019]. The cetane number determines the delay duration. The delay period is greatly shortened with a greater cetane number. As a result, a few encouraging activities are advised in order to retain the advantages of OPO, such as the inclusion of suitable nano-additives, oxygenated additives andantioxidants.The fuel's cetane index can be raised quite effectively with the ignition enhancer [LuningPrak *et al.* 2021].

Any liquid fuel must be conveniently mixed with ignition enhancers without phase separation as they are largely made of hydrogen and carbon [Nozawa-Kumada *et al.* 2020]. The preferred ignition enhancer for this application is di-tetra-butyl-peroxide (DTBP). It is a widely accessible, feasible, and affordable product [Yang *et al.* 2021]. By quickening the combustion process, which is fuelled by the free radicals found in DTBP, the delay period will be shortened [Kumar and Lata 2021]. Researchers have only looked into a small number of works using DTBP [Kumar *et al.* 2021]. By using DTBP, OPO's characteristics and combustion efficiency will be enhanced, resulting in low-temperature combustion and NOx emissions [Kumar *et al.* 2020; Çakmak and Özcan 2022].

Adzmi *et al.* [2019] looked at how 50 and 100 ppm nano-additives of silica (SiO_2)to a biodiesel blended with palm oil affected the efficiency and emissions of a diesel engine while operating under a range of operating loads and constant engine speeds.They reported a gain in BP of 43%, a decrease in CO emissions of 25%, and a decrease in NOx emissions of 4.48%.

When blending 20% biodiesel based on maize oil with diesel in the form of emulsions, Saravankumar *et al.* introduced nano-additives of silica at 50, 75, and 100 ppm to the mixture [Saravankumar *et al.* 2019]. According to test results, adding nano-additives helped to promote complete combustion by serving as a buffer for oxygen that provides adequate oxygen at greater loads, which in turn helped to reduce HC emissions.Nano additions improve the rate of evaporation and the qualities of fuel oxidation, facilitating in full combustion.

Therefore, addition of DTBP and SiO_2 with OPOis made this study. Despite conforming to standards, SiO_2 +DTBPcommercial attention was not on ignition enhancers. The objective of this study is to assess the emissions and performance of an experimental diesel engine running on various DTBP + SiO_2 and OPO fuel blends under varying power loads and to compare with

diesel fuel. This novel method of synthesizing biodiesel with nano SiO_2 particles will overcome the constraints of biodiesel.

2. Materials and Techniques

In this work waste orange peel were collected from the food industries and the oil is extracted by using distillation process. DTBP and SiO_2 nano additives were used in this current work.
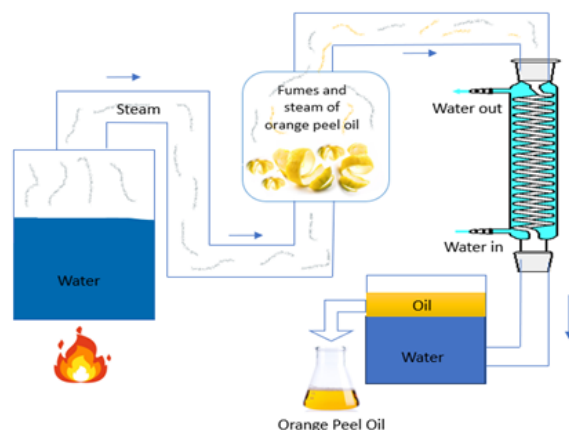
2.1. Extraction of Orange Peel Oil

Figure 1. Schematic diagram of Orange Peel Oil extraction setup.

Waste orange peelsthat had been collected and processed toextract the OPO. The extraction process is carried out using traditional steam distillation method. From the boiler, high temperature steam is forced through the processed peels. The oil from the orange peel mixes with the steam. The mixture of steam and orange oil mixture enter the condensation chamber after distillation. Water which serves as a medium for heat transmission during the condensing procedure runs through the chamber containing the steam and orange oil mixture and the steam is transformed into liquid. The condensed liquid is sent to the collecting tank and given time to settle so that density differences can cause phase separation. Water sinks to the bottom due to its larger density while OPO which is less dense, floats on top with a distinct and obvious phase separation. From the tank, the OPO is then removed and processed for additional inspection. A schematic representation of Orange Peel Oilextraction is shown in Figure 1.

2.2. Characterisation of DTBP

DTBP is a peroxide-containing chemical molecule having twin tetra-butyl groups [Yamashoji *et al.* 2020]. Due to its lack of sulphur and renewable, non-fossil energy status, it can be utilised as fuel in the engine. It decomposes anaerobically and aerobically, making DTBP large stable organic peroxide that can be used as fuel [Yamashoji *et al.* 2020]. It has the highest thermal stability of any organic peroxide. For its production, it requires only lower energy. The properties of Di-tetra-butyl-peroxide are shown in Table 1.

2.3. Silica Nano-Additive Characterization

Concurrent studies of SiO_2 nanoparticles after and before neutron irradiation were carried out on a TEM device

using 'Selected Area Electron Diffraction' (SAED). The samples were then subjected to neutron flux (2×10^{13}ncm^{-2} s^{-1}) at maximum power in the core channel of the TRIGA Mark II experimental reactor [Kling *et al.* 2008; Kling *et al.* 2006; Schamma 2008]. TEM images were taken at magnifications of up to 10 nm & 20 nm index. The TEM image of the initial nanoparticles in Figure 2 (a and b) demonstrates that, adhesion does not occur without an extramural effect. Thus, the experimental sample, which has a particle diameter of 20 nm, is selected.
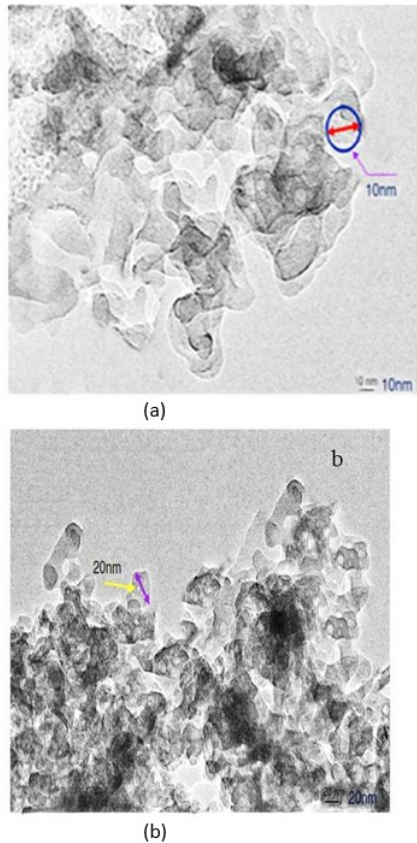

(a)

(b)

Figure 2. (a) 10 nm index and (b) 20 nm index TEM of SiO₂ nanoparticles

2.4. Preparation of the Blend

Modified fuels are prepared by varying the proportions of OPO and DTBP+SiO₂. An ultrasonicator with a mechanical agitator was used to ensure proper blending and progression [Her *et al.* 1996]. Experimental Investigation was made on OPO/DTBP/SiO₂ blends, pure OPO and dieselas test fuels. 10% DTBP by volume is blended with 90% OPO by volume to form 10DTBP/90OPO. Silicon-dioxide nanoparticles were dissolved in isopropyl alcohol at three different SiO₂ concentration levels, 25,50 and 70 ppm, to create three SiO₂ nano fuels. These three fuels were then blended with 10DTBP/90OPO blend to produce a total of three test fuels: 10DTBP/90OPO-25SiO₂, 10DTBP/90OPO-50SiO₂ and 10DTBP/90OPO-75SiO₂. Phase separation was then checked on the samples. For a week, the samples were stored in a beakerundisturbed and inspected.

Table 1. DTBP Chemical Properties

Properties	Di-tetra-butyl-peroxide
DTBP Molecular formula	$C_8H_{18}O_2$
Auto ignition temperature (°C)	165
Vapour pressure at 20 °C (mm of Hg)	40
Boiling point (°C)	111
Melting point (°C)	-40
Specific gravity	0.8
Density (g/cm³)	0.796

2.5. Physicochemical Analysis

It is essential to investigate the fuel properties of OPO as a fuel because they have a significant impact on engine combustion and performance. Table 2 illustrates the fuel characteristics such as cetane index, density, kinematic viscosity and calorific value.

Table 2. Properties of OPO with DTBP + Nano Dosed Fuel Blends

Properties	Diesel	OPO	10DTBP90 OPO-25SiO₂	10DTBP90 OPO -50SiO₂	10DTBP90 OPO -75SiO₂	Biodiesel Standard ASTM
Cetane Index Number	45	46.1	48.3	49.1	50.4	D613
Flash Point (°C)	65.5	81	79.3	78.5	78.1	D93
Fire Point (°C)	70.5	93	87.3	86.2	85.4	D97
Density@15°C (kg/m³)	830	840.3	839.5	840.7	841.1	D1298
Gross Calorific Value (kJ/ kg)	44990	43950	43952	43951	43953	D240
Kinematic Viscosity @ 40 °C	2.5	2.7	2.5	2.55	2.56	D445

The ASTM D613, D93, D97, D1298, D240 and D445 standards were used to examine important parameters such as cetane number, density, flash point, viscosity and fire point of 10DTBP/90OPO-25SiO₂, 10DTBP/90OPO-50SiO₂, and 10DTBP/90OPO-75SiO₂, pure OPO and diesel [Kaisan *et al.* 1996]. OPO has higher flash and fire point when compared with diesel which indicates its ease of handling and transportation. Blending OPO with DTBP improves its viscosity while also improving its safety. OPO has a lower calorific value than diesel and is slightly enhanced by the addition of DTBP+SiO₂.

2.6. Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) was used to investigate the thermal behaviour of OPO in an inert atmosphere. It is used to find out the thermal stability of the OPO at elevated temperatures [Thiruvenkatachari *et al.* 2021]. Mettler Toledo Simultaneous Thermal Analyzer was used to perform the thermal analysis with 30 mg of sample. Temperature was increased at a heating rate of 10°C /minutefrom room temperature to 550°C.

2.7. Experimental Setup and Testing Conditions

A single-cylinder diesel engine made by Kirloskar was used in the current investigation.Table 3 lists the engine descriptionsand Figure 3 shows the experimental setup schematically. The Engine setup has adequate instrumentation for the necessary measurements. To achieve stable testing conditions, the engine is designed to run for an hour on petroleum diesel. In order to maximize engine performance, the engine speed is fixed while the temperature of the lubricating oil and cooling water is kept constant.Following an investigation of the combustion, performance, and emissions of the diesel-powered research engine, the blended fuels, namely OPO, diesel, 10DTBP90OPO-25SiO$_2$, 10DTBP90OPO-50SiO$_2$, and 10DTBP90OPO -75SiO$_2$, were tested under identical settings. The engine's BTE, and BSFC were all measured with the aid of a computer interface and data acquisition system and the software records all the information in the system. The concentrations of CO, NOx, and HC in exhaust gases were measured using a gas analyzer. And an AVL smoke analyzer was utilized tomeasure the intensity of smoke.
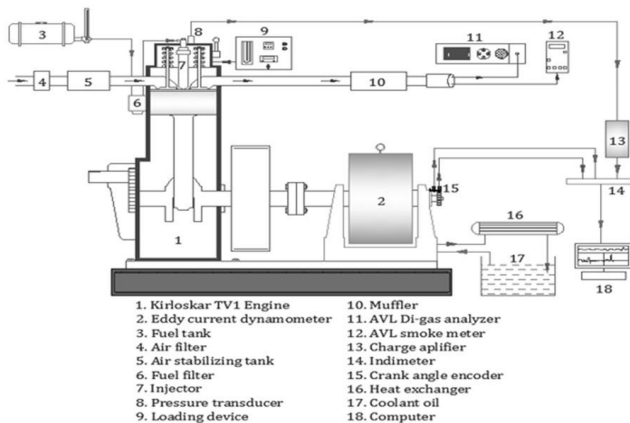

Figure 3. An experimental engine setup's schematic diagram

Table 3. Engine Specification and Terminology

Description	Specification
Engine Make	Kirloskar
Compression ratio	17.5:1
power	5.2 KW
Bore diameter (D)	87.5 mm
Cylinder	Single
Injection timing	24°bTDC
Rated speed	1500 rpm
Stroke	4
Injection pressure	210 bar
Stroke	110 mm
Load	Eddy current dynamometer
Type of cooling	Water cooling
Temperature sensor	Type K – Chromel
Pressure sensor	Kistler make piezo electric type

2.8. Uncertainty Analysis

Analysis of uncertainty is used to pinpoint possible errors during testingthat are caused by environmental factors, some of which are attributable to measuring devices [Hoseini *et al.* 2020; Fattah *et al.* 2014; Fattah *et al.* 2014].

These errors also include mistakes made by people. The accuracy and percentage of uncertainty for various parameters are shown in Table 4.

Table 4. Performance and emission parameter levels of accuracy and uncertainty

Parameters	Uncertainty (%)	Accuracy (±)
Break Thermal Efficiency (%)	±0.4	-
Break Specific Fuel Consumption (%)	±0.4	-
Break Power (kW)	±0.4	-
Carbon monoxide (%)	±0.3	±0.01%
Hydrocarbon (ppm)	±0.4	±8 ppm
Nitrogen Oxides (ppm)	±0.5	±8 ppm
Smoke meter (HSU)	±0.5	±1

3. Results and Discussion

3.1. The Influence of DTBP + Nano-Additive on Performance Parameters

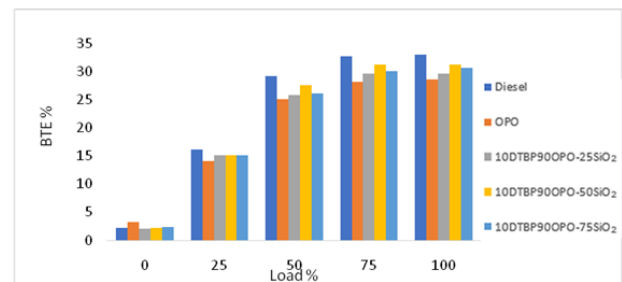#### 3.1.1. The effect of varying load conditions on Break Thermal Efficiency

Figure 4. The effect of DTBP + SiO$_2$ on BTE at different loads.

Figure 4 depicts the change in BTE as a function of load. The readings were taken for various OPO blends with DTBP + nano-additives in varied combinations. Thermal efficiency can increase by up to 9 kg of load in any combination. Then it either stabilizes or declines. In general, adding OPO reduces the ignition delay, resulting in faster combustion and higher peak pressure [Fattah *et al.* 2014; Fattah *et al.* 2014].However, the BTE reduction is significant due to biodiesel's lower heating value due to its higher density andfuel-bound oxygen. It has been observed that the inclusion of DTBP+ nano-additives improves combustion efficiency because they may be able to provide oxygen due to their lattice structure, catalyzing the combustion reaction [Najafi 2018]. They were also helpful in the reduction of ignition delay.

It was discovered that the combination of DTBP + SiO$_2$ results in improved combustion of fuel particles. As a result, blends with DTBP + SiO$_2$dose had higher BTE than OPO blends. The average value of BTE increased by3.20% for 10DTBP/90OPO -25SiO$_2$, 8.37% for10DTBP/90OPO -50SiO$_2$ and 5.17% for 10DTBP/90OPO -75SiO$_2$, at maximum load as compared to the OPO fuel blend.

3.1.2. The effect of varying load conditions on the BSFC

Figure 5 depicts the fluctuation of BSFC in relation to load and all DTBP + SiO$_2$nano additive fuel combinations. At all

loads, Diesel fuel had the least BSFC, whilst OPO had the greatest. The addition of 10DTBP of 25,50 and 75 ppm nano-additive of SiO_2 to 90OPO, on the other hand, results in lower BSFC than OPO biodiesel. As the load grows, the cylinder temperature rises as well, shortening the ignition delay period and lowering the BSFC [Hoseini *et al.* 2020]. Furthermore, with higher loads, heat loss is reduced. Because of their larger reacting surface area throughout combustion, $DTBP+SiO_2$ operate as a catalyst. [Najafi 2018; Soudagar 2020]. When a droplet is delivered into the combustion chamber, this enhances combustion and results in a lower BSFC than OPO. As a result, a 4.18% drop in BSFC was reported for 10DTBP/90OPO-25SiO_2, 11.25% reduction for 10DTBP/90OPO-50SiO_2 and a 7.48% reduction for 10DTBP90/OPO-75SiO_2 when compared to OPO. El-Seesy *et al.* [2017] found that adding multi-walled carbon nanotubes additivesto a 20% jatropha biodiesel blend reduced BSFC by up to 15% and increases BTE by up to 16%.
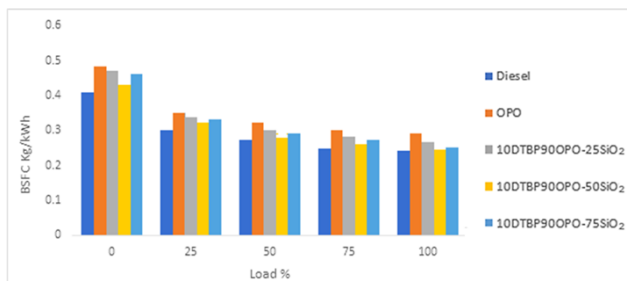

Figure 5. The effect of $DTBP+SiO_2$ on BSFC under various loads.

3.2. The Influence of DTBP + Nano-Additive on Engine Emission Parameters

3.2.1. The Influence of Variable Load Conditions on CO Emission

CO is created during combustion when an insufficient air supply is paired with a low-temperature flame [Fattah *et al.* 2014]. Figure 6 shows that as the load increased, so did the CO output. As the load advances, the volumetric efficiency continuously rises. Yet, partial combustion happens due to insufficient combustion time, resulting in CO generation. As a result, lower CO emissions for biodiesel blends turned out. As statedpreviously, oxygenated nano additives deliver oxygen molecules in the chain reactionduring combustion, resulting in complete combustion that reduces CO as opposed to baseline fuel (OPO) [Najafi 2018; Harari 2020]. When compared to other blends, 10DTBP/90OPO-50SiO_2fuel emits the least amount of CO. 10DTBP/90OPO-50SiO_2reduced CO emissions by 12.84% when compared to OPO.

3.2.2. The effect of $DTBP+SiO_2$ on HC emission at different loads

HC emissions are influenced by fuel density, engine operating conditions,fuel flow characteristics and fuel spray patterns [Imtenan *et al.* 2014; Akkoli *et al.* 2021]. It is found that HC emissions are reduced for all blends of OPO, when compared to standard diesel fuel. When compared to OPO, HC emissions were reduced by 9.65%,

19.05% and 14.12%, respectively, for10DTBP/90OPO-25SiO_2, 10DTBP/90OPO-50$SiO_2$and 10DTBP/90OPO-75SiO_2, respectively. Figure 7 in OPO mixes with or without additives, OPO has the greatest HC emissions. Its high density and viscosity lead to poor fuel atomization, which is the cause of this.
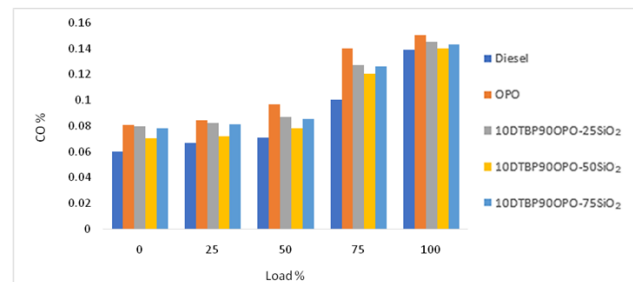

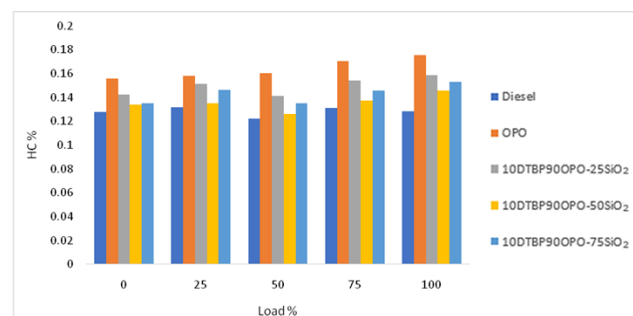**Figure 6.** The effect of $DTBP+SiO_2$ on CO emission under different loads.

Figure 7. The effect of $DTBP+SiO_2$ on hydrocarbon (HC) at different loads.

3.2.3. The Influence of Variable Load Conditions on NOx Emission
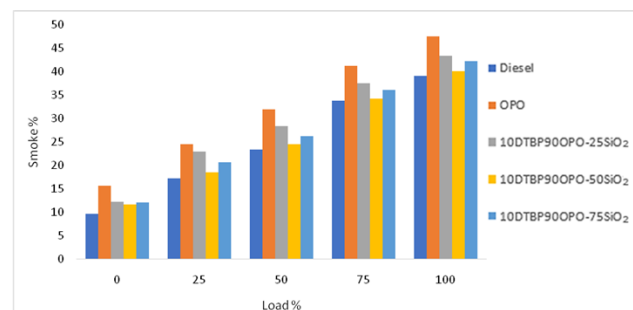

Figure 8. The effect of $DTBP+SiO_2$ on NOx at different loads.

Figure 8 depicts the NOx emissions from different biofuel blends. The plots revealed that NOx emission increased with increasing load. NOx emissions are produced at extremely high temperatures and pressures [Ming *et al.* 2018]. The complete combustion of the fuel is achieved by adding more oxygen to the fuel, which helps to deliver enough oxygen atoms to the combustion products. The use of oxygenated fuelimproves combustion and thereby decreases NOx emissions. The addition of DTBP+ SiO_2 causes a faster premixed combustion, resulting in a high internal combustion temperature and, NOx emissions was reduced when compared to baseline fuel [Najafi *et al.* 2018]. Because of the considerable cylinder temperature and pressure, all nano fuel blends emit less NOx than theOPO. When compared to OPO, NOx emissions reduced by 0.89%, 3.37% and 7.71% for 10DTBP/90OPO-25SiO_2,

10DTBP/90OPO-50SiO$_2$ and   10DTBP/90OPO-75SiO$_2$respectively.

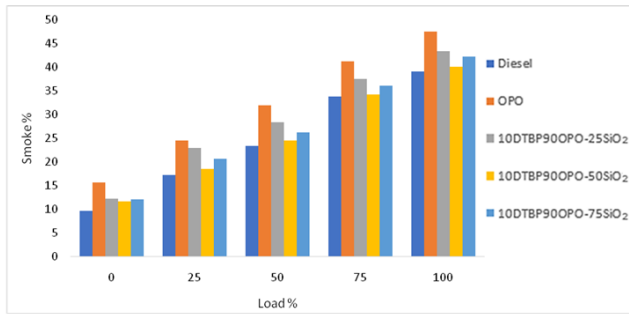### 3.2.4. The Influence of Variable Load Conditions on Smoke Emission

Figure 9. The impact of a DTBP + SiO$_2$ on smoke at various loads.

Figure 9 depicts the variation in smoke production with engine load. Smoke was shown to be significantly dependent on engine load. The capacity of smoke increases as engine loads increase [Sayin *et al.* 2009; Soudagar *et al.* 2020]. Other input factors have a smaller impact on smoke. The combustion of diesel fuel created the most smoke opacity and the addition of DTBP + SiO$_2$ results in improved combustion and, as a result, a greater combustion temperature inside the chamber. When compared with diesel fuel, the addition of DTBP + silica nano additions to OPO results in improved micro-explosion of the blend, resulting in decreased smoke opacity. Figure10 shows that the smoke emission for 10DTBP/90OPO-25SiO$_2$,   10DTBP/90OPO-50SiO$_2$and 10DTBP/90OPO-75SiO$_2$ was reduced by 10.11%, 19.71%and 14.54%, respectively, when compared to OPO.

3.2.5. Thermal Analysis (TGA)

Figure 10 displays the TGA curves for both diesel and OPO. TGA was used to measure weight changes in order to characterise the thermal stability of OPO with the increase in temperature. From the TGA curve it was found that there is no major weight loss up to 350°C. There is a slight weight loss in OPO when compared with Diesel is due to the evaporation of water particles. Beyond 350°C there is a sudden decrease in weight as the OPO start vaporising. Thermal analysis shows that the developed OPO has high thermal stability up to 350°C.
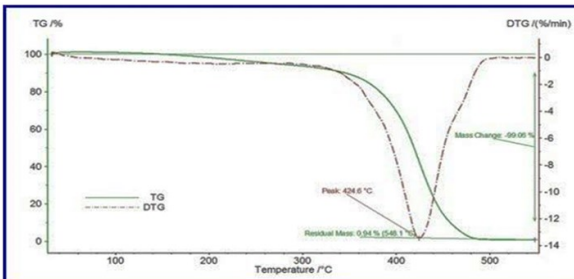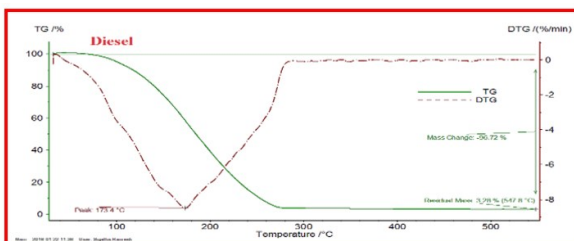

Figure 10. Thermogravimetric analysis of OPO and Diesel

4.   Conclusions

The current study focuses on the influence of DTBP + SiO$_2$ on the performance and emission parameters of a diesel engine powered by orange peel oil (OPO). In Biodiesel DTBP + silica nano-additiveoperate as a combustion trigger, strengthening the combustion phenomena and ensuring thorough combustion. This is due to an increase in net heat created inside the combustion chamber, which improves BTE while decreasing BSFC. Furthermore, the use of these nanoparticles lowers emissions such as CO$_2$, HC, NOx and smoke. Low levels of NOx were produced as a result of adding 75 ppm SiO$_2$ to the OPO+DTBP blend, which helps to deliver enough oxygen atoms to the combustion products. The addition of DTBP + SiO$_2$ nano-additives to orange peel oil raised BTE by3.20-8.37% while decreasing BSFC by 4.18-11.25%. CO, HC, NOx and smoke emissions for blends with nano additive were reduced by 5.61-12.84%, 9.65-19.05%, 0.89-7.71%, and 10.11-19.71%, respectively, as compared to OPO. Thermo Gravimetric analysis reveals that the orange peel oil has high thermal stability up to 350°C. The addition of SiO$_2$ nano additives to OPO has improved the fuel characteristics. The blend 10DTBP90OPO-50SiO$_2$ is found to be the best when compared to other diesel blends.

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