



## Evaluation of TiO<sub>2</sub> Nanoparticles as an Additive in Diesel-n-Butanol - Bombax Ceiba Biodiesel Blends for Enhance Performance and Emissions Control of a CI Engine

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### ABSTRACT

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*bombax ceiba oil methyl ester, TiO<sub>2</sub> nanoparticles, engine performance, emission control, stability of nano particles*

In this study, additions of Titanium dioxide nanoparticles into diesel- Bombax ceiba methyl ester (BCME) and n-butanol (C<sub>4</sub>H<sub>9</sub>OH) and the impact of nano particles on the emission and performance characteristics of a diesel engine were studied experimentally. The n-butanol in fuel samples significantly influenced the physicochemical properties of the blends. The TiO<sub>2</sub> nanoparticles were added at different concentrations of 30, 60, and 90 ppm. The ratio of 1:4 TiO<sub>2</sub>: QPAN 80 was observed to deliver maximum possible stability in biodiesel. In addition, more oxygen in n-butanol and nano additives minimize environmental air pollution. The experiments employed Diesel, B20, B20Bu10, B20Bu10T30, B20Bu10T60, and B20Bu10T90 blends using the four-stroke, direct injection diesel engine with single-cylinder. The experimental results showed that adding 60 ppm TiO<sub>2</sub> nano particles in B20Bu10 improved thermal efficiency by 8.36% and reduced the brake-specific fuel consumption by 21.6% compared to B20Bu10. The B20Bu10T60 blend reduced the carbon monoxide (CO) and unburned Hydrocarbon (UHC) emissions by 22.91% and 12% correspondingly compared with other blends. The above results demonstrated the optimal improvement in whole engine performance characteristics and fewer environmental pollutants at a dosage level of 60 ppm TiO<sub>2</sub> nano particles.

## 1. INTRODUCTION

Due to the enhanced durability and reliability, diesel engines were extensively employed in the transport sector for public transportation worldwide. However, the transportation sector produces approximately 30% of global greenhouse gas emissions, contributing to global warming [1]. Exhaust gases such as carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>), which lead to global warming, produce greenhouse effects in the atmosphere. As reported in various research studies, particulate matter (PM) emissions have been linked to degenerative disorders and diseases [2]. Several automotive production communities have already investigated resources to reduce emissions emitted by vehicles to fulfill potential mitigation standards. Moreover, renewable, and alternative fuels, including alcohol, natural gas, biodiesel and dimethyl ether (DME), are witnessed to be a viable way of reducing emissions of NO<sub>x</sub>, greenhouse gas and PM emissions [3].

Biodiesel is made from non-edible seeds of plants such as Pongamia, Mahua, castor, jatropha, and others. The non-edible oils come under second-generation feedstock, and they can be cultivated in areas of less rainfall as they require less water [4, 5]. Furthermore, n-butanol surpasses ethanol and methanol in terms of improved thermal capacity, diesel fuel derivatives, and water solubility [6]. Due to the above rationales, n-butanol

was chosen for this research work.

Butanol is a kind of primary alcohol that is better than methanol and ethanol as an alternative fuel for IC engines. Since the properties of butanol are closer to Diesel [7, 8]. Nevertheless, there was a rise in BSFC and NO<sub>x</sub> emissions, decreased with butanol. Both butanol and biodiesel have a lower energy content, which reduces engine performance. Practically, various additives were available, which helped the biodiesel meet some quality requirements. Metal-based, oxygenated, antioxidant, and cetane number improving additives boost fuel efficiency.

Furthermore, adding alcohol to biodiesel lowers the viscosity of the fuel [8]. According to the previous survey results, alcohol acted as an oxygenated additive and improved engine efficiency. Concurrently, nanoparticle addition to alcohol-biodiesel blends was proved as a promising method for significantly improving engine performance [9].

Based on the literature review, n-butanol and biodiesel blends were used in diesel engines to enhance performance and reduce emissions and the use of TiO<sub>2</sub> Nano Particles was done separately. The present research aims to blend with diesel and n-butanol and evaluate the effects of TiO<sub>2</sub> nano particles as an additive. Nonetheless, the authors state that no previous research has been done on using TiO<sub>2</sub> nano additives in a diesel-n-butanol- Bombax ceiba methyl esters as the modified fuel.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Bombax ceiba seed oil was Purchased from Tamil Nādu. TiO<sub>2</sub> nanoparticles were purchased from Platonic Nanotech Private Limited-Kachwa Chowk, Dist: Godda, Jharkhand, with an average size of below 30-50 nm and found in milky white color. QPAN 80 is used as the surfactant. The surfactants are AR grade and the chemicals purchased are of GR grade. Procured from M/s Sigma Aldrich India Pvt. Limited.

### 2.2 Surface modification

The surfactant (QPAN 80) mixes the nano-fluid with base fuel. To reduce the surface tension between the B20Bu10 and TiO<sub>2</sub> nano particles, the surfactant (QPAN 80) was used in the five combinations (1:1, 1:2, 1:3, 1:4, and 1:5). The most appropriate ratio between TiO<sub>2</sub> and QPAN 80 in liter blend was determined by testing five combinations. The most significant results were obtained with a TiO<sub>2</sub> nano particles-to-surfactant ratio was 1:4 because the dispersion was steady, homogeneous, and consistent. The ultrasonic approach for dispersing nanoparticles into a basic fluid is the best since the possible nanoparticle agglomeration back into a nanometer range is facilitated. The diagrammatic representation of the ultrasound aided B20Bu10 and TiO<sub>2</sub> nano particles preparation is shown in Figure 1.

### 2.3 Characterization of TiO<sub>2</sub> nanoparticle and biodiesel blends

The Field emission scanning electron microscope (FESEM) is used to study the morphology of TiO<sub>2</sub> nanoparticles. The analysis was performed using Model: FEI- Apreo LoVac. FESEM images at different magnification levels are shown in Figure 2(a). Figure 2(b) shows the FE-SEM images of TiO<sub>2</sub> at 100,000x of nanoparticles. These images show that TiO<sub>2</sub> nano-fluid is clustered, spherical shaped with a smooth surface with an average particle size of 35 nm. Figure 3 shows the Fourier transform infrared spectra of TiO<sub>2</sub> nanoparticles (FT-IR). The strong bond was shown at a spectrum of 1100 cm<sup>-1</sup>. The broad absorption at 3350 cm<sup>-1</sup>-3750 cm<sup>-1</sup> corresponds to O-H vibrations associated with in-plane deformations at 1620 cm<sup>-1</sup>.

### 2.4 Preparation of TiO<sub>2</sub> nano-fluid

TiO<sub>2</sub> nano-fluid enhances the catalytic effect and possesses high oxygen content during combustion. The large volume to surface ratio of TiO<sub>2</sub> nano-fluid also offers high surface energy, which expedites the combustion process. Initially, a B20 blend was prepared, involving 20% of BCME and 80% of diesel. In the second step, B20Bu10 was prepared, containing 20% of BCME, 10% of butanol, and the remaining 70% diesel. In the third step, TiO<sub>2</sub> is blended with B20Bu10 in the various proportions of 30, 60, and 90 ppm with the help of an ultrasonicator. The samples are stored in test tubes under static conditions to analyze their stability. The typical investigations showed that they were stable for more than two weeks. According to the ASTM standards, the physio-chemical characteristics of diesel, B20, B20Bu10, B20Bu10T30, B20Bu10T60 and B20Bu10T90 fuel are shown in Table 1.

The preparation of TiO<sub>2</sub> nanoparticles with the concentrations of 30, 60 and 90 ppm in B20Bu10 is shown in Figure 4.

### 2.5 Biodiesel production

Bombax ceiba is native to India, Sri Lanka belongs to the Malvaceous family [10-12]. It grows in sub-humid and humid tropical regions. The plants are drought-resistant, and the seed pods are fibrous, spherical, and dangling shells [13]. The seeds are dark brown and each fruit contains about 25-28% of oil. Traditionally, Bombax ceiba fibers are used to stuff pillows [14].



Figure 1. The schematic diagram of ultrasound-assisted BCME-TiO<sub>2</sub> biodiesel blends production unit

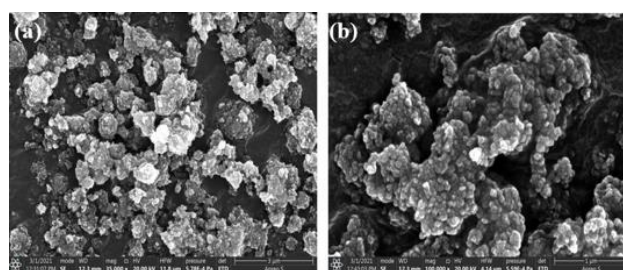


Figure 2. (a) FE-SEM images of TiO<sub>2</sub> at 35,000x magnification level: (b) FE-SEM images of TiO<sub>2</sub> at 100,000x

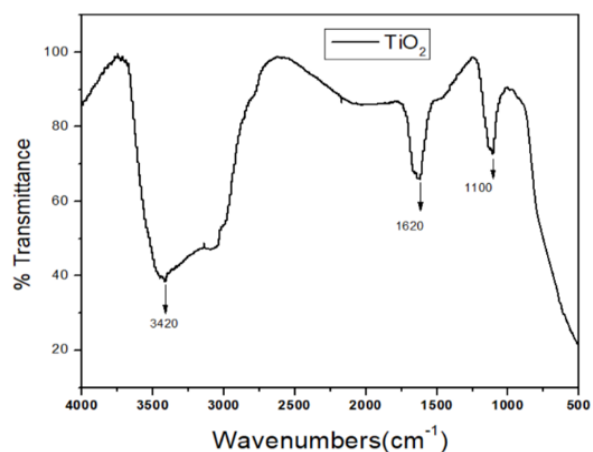


Figure 3. Fourier transform infrared spectroscopy (FT-IR) spectroscopy of TiO<sub>2</sub> nanoparticle



Figure 4. Represents various B20Bu10 blends with different concentrations of nano-fluids

## 2.6 Transesterification process

The transesterification process is done in two-step processes [5]. The acid treatment is done using sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in the initial stage. In stage -II, the solution added alkaline sodium hydroxide (NaOH) at a 6:1 molar ratio. The oil after the two-step process is water washed to remove the impurities. The water-washed oil was purified using a rotary evaporator to remove the water from biodiesel completely. Figure 5 shows a diagram of the biodiesel plant.

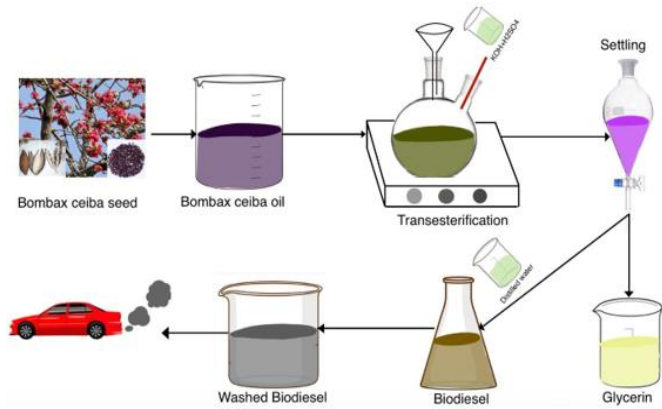


Figure 5. Schematic diagram of the biodiesel plant

## 3. EXPERIMENT DESIGN AND EQUIPMENT

This investigation utilized a four-stroke, single-cylinder, water-cooled, direct injection, diesel engine with no technological changes with a compression ratio of 18, at a constant pressure of 200 bar, and a constant speed of 1500 rpm for all samples. Table 2 shows the technical characteristics of the test engine. The complete layout of the experimental setup is illustrated in Figure 6. The tests were conducted under atmospheric conditions of 25°C in the laboratory. The engine was experimented with diesel for reference data and compared to other samples. Then it was run for remaining blends such as B20, B20Bu10, B20Bu10T30, B20Bu10T60, B20Bu10T90. The performance and emissions characteristics were noted from the engine at steady-state condition.

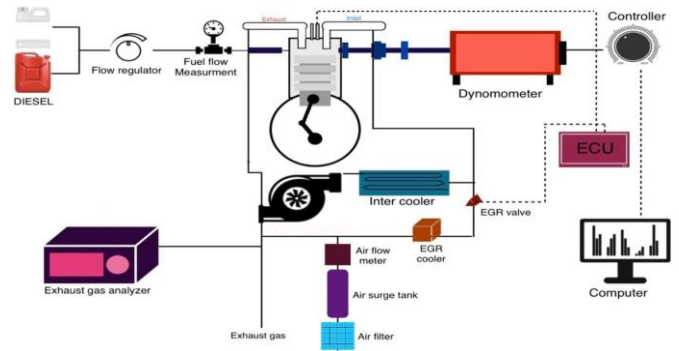


Figure 6. Schematic layout of the experimental setup

The engine was run with standard diesel with no load condition at an idle speed of 1000 rpm before each subsequent test to prevent thermal cracking and ensure that the engine fuel system was clear of the previous residual fuel. Multiple experiments for all fuel tests were done to prevent mistakes and obtain further accurate findings.

Every sensor and instrument was calibrated before the engine testing. Table 3 presents uncertainties in several measured parameters.

### 3.1 Uncertainty analysis

An experiment using common instruments yielded varying levels of accuracy depending on the manufacturers. The parameters measured and the values estimated in this research have been used to assure the correctness of the values achieved by the equipment. There are many ways to cause errors and uncertainties in an instrument, such as environmental conditions, empirical observations, instrument calibration, operational conditions, and instrument accuracy. Experiments were repeated five times and the average values were used to ascertain the level of uncertainty in this study. An experiment's total percentage uncertainty was calculated using the square root approach that many researchers and scientists generally recommended. The uncertainty of the observed and computed values is given in Table 3. The experiment's uncertainty was estimated using the following variables, including BP, BTE, BSFC, HC, CO, NO<sub>x</sub>, and smoke. The total percentage uncertainty was given in the following equation.

$$= \sqrt{(THERu)^2 + (BSFCu)^2 + (UHCu)^2 + (COu)^2 + (NOu)^2 + (EGTu)^2 + (BPu)^2 + (Nu)^2}$$

$$= \sqrt{(0.6)^2 + (0.4)^2 + (0.06)^2 + (1.2)^2 + (1.5)^2 + (0.5)^2 + (0.2)^2 + (1.15)^2}$$

Table 1. Physio-chemical Properties of standard Diesel, B20, B20Bu10-diesel blends with and without the addition of TiO<sub>2</sub>

Properties	ASTM standards	Test limit	Diesel	B20	B20Bu10	B20Bu10T30	B20Bu10T60	B20Bu10T90
		ASTM D6751-15c						
Density kg/m <sup>3</sup> at 15°C	ASTM D4052	815–835	833.6	836.3	835.9	835.7	835.3	835.5
Calorific value kJ/kg	ASTM D5865	Min. 35,000	42,450	40,759	40,955	40,865	41,090	40,950
Kinematic Viscosity cSt at 40°C	ASTM D445	1.8–4.2	2.57	3.8	3.61	3.69	3.3	3.38
Cetane Number	ASTM D613	Min. 40	44.58	47	48.2	54.6	54.52	53.81
Flash Point °C	ASTM D93	Min. 92	81	134	133.7	133.4	133.3	133.4
Pour Point °C	ASTM D97-12	-15 to 17	-3	4.57	4.59	4.72	4.53	4.62
Copper strip corrosion	ASTM D130	Max. 3	1	1	-	-	-	-



**Table 2.** Technical specification of the test engine

Parameters	Values
Engine Make	Kirloskar
Type / No. of Cylinders	Single-cylinder/Four-stroke
Various loads at a constant speed	1500 rpm
Variable compression ratio	16 to 18
Rated power	5.2 kW @ 1500 rpm
Injection point variation	23°BTDC
Cylinder diameter	87.5 mm
Stroke length	110 mm
Orifice diameter	20 mm
Connecting rod length	234 mm
Dynamometer arm length	185 mm
Loading	Eddy current dynamometer
Lubricating system	Forced feed system
Type of cooling	Water-cooled direct injection

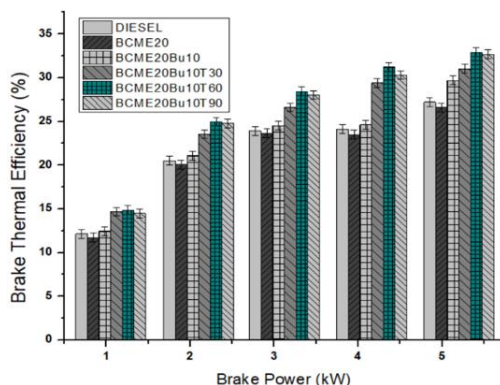
**Table 3.** Uncertainties in the parameters measured

Examined Parameters	% Uncertainty
BTE	0.6
BSFC	0.4
UHC	1.2
CO	0.06
NO	1.5
EGT	0.5
BP	0.2
Speed (N)	0.15

Total percentage uncertainty of this experiment = ± 2.52

#### 4. PERFORMANCE AND EMISSION ANALYSIS

The following sections have examined several performances and emission parameters, including BTE, BSFC, CO, UHC, and NO.



**Figure 7.** BTE vs. BP

#### 4.1 Brake thermal efficiency

The relationship between brake thermal efficiency (BTE) and brake power (BP) for diesel, B20, B20Bu10, and B20Bu10 emulsions containing TiO<sub>2</sub> at different concentration levels of 30, 60, and 90 ppm were presented in Figure 7. It was noticed from the figure that increasing engine load improves brake thermal efficiency for all fuels utilized. BTE improved when engine load increased due to increased braking power and a corresponding rise in fuel supply. The addition of TiO<sub>2</sub> nanoparticles in B20Bu blends enhanced BTE significantly, and B20Bu10+60 ppm had considerably higher BTE than other nano fuel blends. The higher O<sub>2</sub> content from TiO<sub>2</sub> nanoparticles in the fuel increased the combustion

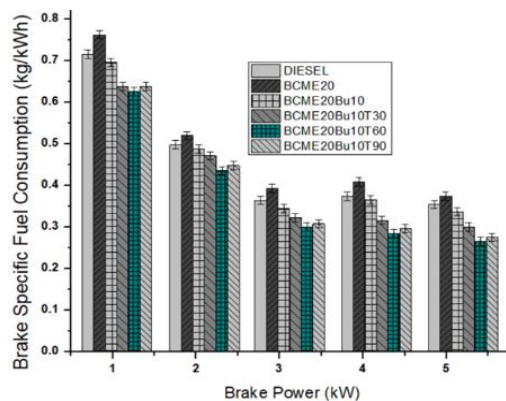
and increased the heat release rate by achieving higher thermal efficiency [15].

It was observed that all B20Bu10 nanoparticle blends had shown better BTE than B20Bu10 at all engine loads. BTE for B20Bu10+60 ppm blend was increased by 10.73% than B20Bu10 blend with no inclusion of nanoparticles at maximum load. This is mainly because of properties of fuel samples such as higher calorific value, cetane number, and catalytic effect and the surface-area-to-volume ratio of nanoparticles, superior atomization due to the addition of n-butanol, thus decreasing the viscosity of the blends, which results in faster evaporation, thus leading to higher BTE [16-21].

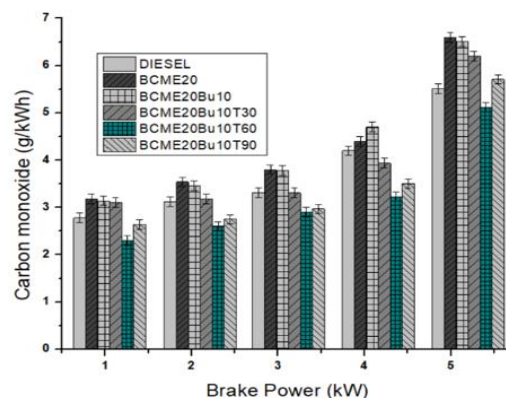
#### 4.2 Brake specific fuel consumption

The effects of brake-specific fuel consumption with the variation of brake power for all fuels are represented in Figure 8. An increased quantity of fuel is provided with increasing load to maintain the combustion process, leading to higher power output and reduced BSFC. The addition of TiO<sub>2</sub> nanoparticles in B20Bu10 blends effect greatly on BSFC. It is observed from the graph that the B20Bu10+60ppm blend showed a lower BSFC. The maximum reduction in BSFC is observed for B20Bu10+60ppm as 21.2% compared to the B20Bu10 blend. The reduction in BSFC is due to the addition of n-butanol and TiO<sub>2</sub> nano particles, which serve as oxygen enhancers, thus leading to complete combustion and reducing ignition delay period. Nevertheless, finer atomization of fuel particles prevents accumulation, thus improving the combustion rate and reducing BSFC [17-19].

#### 4.3 Carbon monoxide (CO)



**Figure 8.** BSFC vs. LOAD



**Figure 9.** CO vs. BP

Figure 9 illustrates the CO emission under different loads for various blends. It is noticed from the graph that CO emissions are increased when the increasing load for all fuel samples increases. CI engines are operated better with lean and stoichiometric mixtures, while partial combustion takes place with rich mixtures/very high equivalence ratios, thus leading to CO emissions. It also depends on fuel properties, lower flame temperature, and longer ignition delay [19-21].

It is observed that CO emissions are reduced with the inclusion of TiO<sub>2</sub> nano particles in the B20Bu10 blend rather than other blends. The natural oxygen content in the biodiesel and n-butanol leads to complete combustion and the catalytic effect of TiO<sub>2</sub> additives leads to better heat transfer during the combustion process [19, 22]. The CO emissions were greatly reduced by 21.19% for the B20Bu10+60ppm blend than other nano blended fuels.

#### 4.4 UHC emissions

The variations of HC emissions under various loads are represented in Figure 10. It illustrates that the HC emissions increase as the load increases for all fuel blends. It is clear from the graph that the TiO<sub>2</sub> nano fuel blends resulted from lower HC emissions than standard diesel, B20 and B20Bu10 samples. The HC emissions were reduced by 13.30% for the blend of B20Bu10T60ppm blend than other samples, which was attributed to the higher levels of oxygen in the biodiesel and butanol, and additional oxygen content is supplied by TiO<sub>2</sub> nano particles, which leads to better combustion [15, 19, 21]

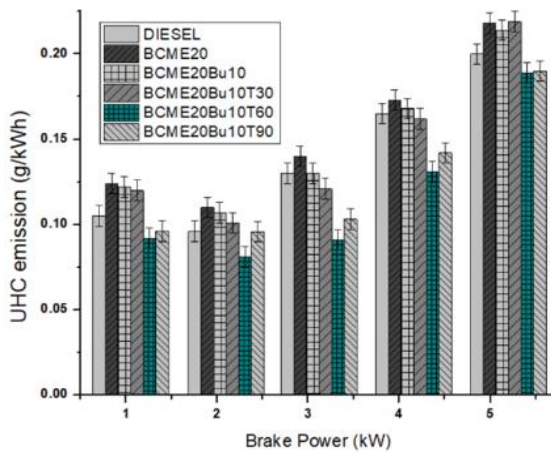


Figure 10. UHC vs. BP

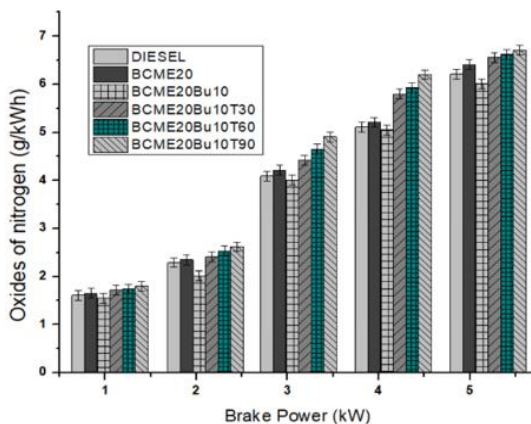


Figure 11. NO<sub>x</sub> vs. BP

#### 4.5 NO<sub>x</sub> emission

NO<sub>x</sub> emissions for all blends under varying loads are represented in Figure 11. The increases in NO<sub>x</sub> emissions are observed as 8.51%, 19.14%, 21.99% and 22.20% for B20, B20Bu10+30ppm, B20Bu10+60ppm, B20Bu10+90ppm blends respectively while, NO<sub>x</sub> emission is reduced by 2.17% for B20Bu10 sample. It is usually known that NO<sub>x</sub> production is mostly based on the Zeldovich phenomenon in diesel engines [23].

The major parameters determining NO<sub>x</sub> emissions are flame temperature, residence duration and oxygen content. As the latent heat of vaporization of fuel blend is greatly improved with the inclusion of n-butanol, the flame temperature at local zones is less than the biodiesel [19]. Nevertheless, the samples' high-temperature durations/reaction durations are shortened due to enhancement in combustion that reduces the formation of NO<sub>x</sub> for the B20Bu10 blend [24].

The increase in NO<sub>x</sub> emissions owing to high cetane number, availability of oxygen in the fuel blends, and TiO<sub>2</sub> additives, thus improving the combustion process and increasing the cylinder pressure and temperature, thus resulting in higher values of NO<sub>x</sub>.

#### 5. CONCLUSION

In this research work, biodiesel from Bombax ceiba oil is produced and blended with standard diesel, n-butanol and TiO<sub>2</sub> nanoparticles. Physical and chemical properties of all fuel blends were determined, such as density, pour point, cloud point, cold filter plugging point, flash point and kinematic viscosity. The performance and emission parameters were evaluated using a single direct injection diesel engine. The following conclusions were reached based on the results observed in this study:

- The results evidenced that TiO<sub>2</sub> nano particles improved physio-chemical properties such as cetane number and calorific value. In contrast, n-butanol improved fuel properties such as density, kinematic viscosity, flash point, pour point, and cloud point.
- The blend B20Bu10+60ppm enhanced BTE by 8.36% and reduced BSFC by 21.6% compared to other blends. It is concluded that the addition of TiO<sub>2</sub> served as the catalyst, and n-butanol and biodiesel supplied additional oxygen for effective combustion, which leads to higher BTE and lowers BSFC.
- The addition of n-butanol and TiO<sub>2</sub> nano additives reduced CO and HC emissions due to high oxygen content, whereas NO<sub>x</sub> emissions are increased for all blends except B20Bu10. The latent heat of vaporization is improved with n-butanol in the B20 sample, which suppresses the flame temperature at local zones, thus reducing the NO<sub>x</sub> emissions.
- With the afore mentioned results, it is concluded that the prepared blends containing biodiesel (from Bombax ceiba oil), standard diesel, n-butanol and TiO<sub>2</sub> nanoparticles are treated as potential alternative fuels in diesel engines. With the addition of TiO<sub>2</sub> nanoparticles, BTE is significantly improved and BFSC is reduced. Nevertheless, it also greatly improved the combustion process greatly such that emissions such as CO and HC are reduced whereas n-butanol

affected the reduction of NO<sub>x</sub> emission.

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BCME	Bombax ceiba oil methyl ester
B20	Biodiesel-20% and diesel 80%
B20Bu10	Biodiesel-20%, n-butanol-10% and diesel 70%
B20Bu10T30	Biodiesel-20%, n-butanol-10%, diesel 70% and titanium dioxide 30 PPM
B20Bu10T60	Biodiesel-20%, n-butanol-10%, diesel 70% and titanium dioxide 60 PPM
B20Bu10T90	Biodiesel-20%, n-butanol-10%, diesel 70% and titanium dioxide 90 PPM
BTE	brake thermal efficiency
BP	brake power
BSFC	brake specific fuel consumption
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
EGT	Exhaust Gas Temperature
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier transform infrared
N	speed
NaOH	sodium hydroxide
NO	nitric oxide
H <sub>2</sub> SO <sub>4</sub>	sulfuric acid
TiO <sub>2</sub>	titanium dioxide
UHC	unburned Hydrocarbon

## NOMENCLATURE

ASTM            American Society for Testing and Materials