

Impact of Carbon Nano Tubes on the Performance and Emissions of a Diesel Engine Fuelled with Pongamia Oil Biodiesel

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Abstract

Biodiesel is considered an immediate substitute for the fossil diesel as the fuel properties, such as calorific value, density, ash content and acid value are comparable to the diesel. In India, pongamia oil has considerable potential for the biodiesel production. The pongamia oil biodiesel has lower volatility and slightly higher viscosity than the diesel. Hence the pongamia oil biodiesel fuelled diesel engine results in lower thermal efficiency as compared to the diesel. The carbon nanotubes (CNTs) were used in this work as additive to the pongamia oil biodiesel, to enhance the atomization and to reduce the ignition delay of the pongamia oil biodiesel. The CNTs were added to the pongamia oil biodiesel with different dosages and subjected to ultrasonication for 60 min, to prepare homogenous mixture. The engine tests were conducted on a single cylinder diesel engine without making any modifications in the fuel injection system. The addition of CNTs to the pongamia oil biodiesel resulted in higher brake thermal efficiency at higher loads between 75 to 100 % of the full load. From the engine tests, it was observed that the CNTs improves the engine thermal efficiency and reduces the CO, HC and smoke emissions of the diesel engine depends upon the CNT dosage. This is due to shorten ignition delay caused by the CNTs which improves the combustion of the pongamia oil biodiesel. The optimum CNT dosage of 50 mg/l results in 4% increase in thermal efficiency and reduces the CO, HC and smoke emissions by 20.33, 25 and 12.5% respectively at full load.

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1. Introduction

Most of the countries worry about the recent increase in air pollution which causes environmental degradation. The increase in number of diesel vehicles will increase air pollution issues. The energy demand of the globe increases due to industrialization and fossil fuels supply the current energy requirements (Geetesh et al 2021). The energy sources greatly affect the country's economic growth and hence the energy sources should be affordable, accessible and environmentally friendly. It is reported that the energy demand of countries which are not members of the organization for economic co-operation and development Asian region is projected to increase during the period of 2015 to 2040 (eia., 2017). Over the past four decades, the world's rapid growth in energy demand has mainly been satisfied by fossil fuels. Oil, coal, natural gas, hydroelectric, nuclear energy, and renewables accounted for 33.6, 27.2, 23.9, 6.8, 4.4 and 4% of the world's primary energy consumption in 2018, respectively. On the other hand, fossil fuels accounted for 84.7% of world primary energy consumption in 2018 (BP 2019). The global social, economic, political, environmental and technological changes create a fundamentally different outlook for the international energy markets. It is expected that a different future would be characterized by shale oil and shale gas revolution (Ghasemian et al., 2020). It is estimated that the

world's oil demand will increase to 105.4 MMbpd in 2030 from the 96.9 MMbpd recorded in 2018 and hence alternative energy sources will be utilized to meet the energy demand of the world (Josiah et al 2020). The biodiesel is suggested as renewable replacement to diesel (Sameh et al., 2018) and is produced by transesterification reaction (GeeteshGoga, 2018). The biodiesel does not have sulphur, and thus results in lower sulfur dioxide emission as compared to diesel (Ajay et al., 2014).

In Asia, India is one of the largest energy consumers (Anindita et al., 2016) and India's biofuel policy encourages biodiesel production from non-edible oils to reduce the demand of fossil diesel (Mnre., 2018). This policy aims to ensure availability of minimum quantity of biofuels in the market (Gain., 2017). It reduces the oil import and to meet the regional energy demand by using non-food feed stocks (Gain., 2016). The production cost of biodiesel is high and hence newer technologies are being developed (Kapilan et al., 2014). The ultrasound assisted biodiesel production method results in higher biodiesel yield and reduces reaction time (Ibrahim et al., 2020). The biodiesel derived from rice bran oil can be blended with n-butanol, and thus can be used as a fuel in compression ignition engine (GeeteshGoga, 2019). In dual fuel mode, mass flowrate of biogas must be optimized (GeeteshGoga, 2020).

The ignition delay period of the biodiesel is higher than the diesel (Balaji et al., 2015) and hence the additives can be added with biodiesel to reduce the ignition delay period which enhances the combustion of the fuel. The diethyl

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ether can be used as oxygenated additive to enhance the ignition by decreasing the ignition delay of fuel in the compression ignition engine (Mohanan et al., 2003).

The addition of alumina nanoparticles to the biodiesel diesel blend increases the brake thermal efficiency and reduces the CO and HC emissions of the engine (Seyyed et al., 2017). The use of graphene oxide as additive in *ailanthus altissima* biodiesel results in higher power and reduces the CO and HC emissions (Hoseini et al., 2018). The addition of graphene nano-platelets to the *Jatropha* biodiesel diesel blend increases thermal efficiency of the engine as compared to biodiesel blend (Ahmed et al., 2018). The engine tests conducted on a variable speed compression ignition engine with CNTs added emulsion of water and diesel shows enhancement in thermal efficiency and reduction in smoke emission (Sadhik and Anand., 2011). It is reported that the CNTs improves the homogenization of mixture of fuel and air and reduces the emission levels of blends of biodiesel and diesel fuelled C.I. engine (Vivek and Kriplani 2016).

The cost of the CNTs varies between US \$ 15 to 35 per g, depends upon purity. The addition of CNTs to the biodiesel is in mg and hence a marginal increase in the operating cost. This cost is almost similar to the cost of higher alcohols or gaseous fuels. The fire hazards related to alcohols and gaseous fuels are very high and additional retrofitting are required to supply these fuels to the combustion chamber which increases investment cost. Hence, in recent years, researchers are using nanoparticles to enhance the performance of the fuel. From the literature, it is observed that biodiesel has lower volatility and higher viscosity. A small dosage of nanoparticles results in improvement in the properties and combustion of the biodiesel. It is also observed from the literature that, no work has been carried out to study the effect of CNT on the performance of constant speed diesel engine fuelled with biodiesel, without making any modification in the engine's injection timing and injection pressure. Hence in this work, an attempt was made to understand the effect of CNT on the performance and emissions of biodiesel fuelled constant speed engine which is most widely used in agricultural purpose. It is reported that the optimum multi walled carbon nanotubes dosage for the biodiesel blend is 30 mg/l for the variable speed engine (Ahmed et al 2016.). In this work, biodiesel was used as the fuel and hence higher dosages such as 40, 50 and 60 mg/l were considered.

The pongamia is a tree that grows to about 15 to 25 m height with a large canopy. It does not need much maintenance and grows in dry areas. The flowering generally starts after 3 to 4 years and the brown seed pods appear immediately after flowering. The pods are thick, and they contain one or two bean like brownish red seeds. Figure 1 shows the seeds.



Figure 1. Pongamia Seeds

Generally non-edible oils are used as raw material for the production of biodiesel (Kapilan et al., 2011) and non-

edible pongamia oil is cheap and has considerable potential for biodiesel production compared to waste cooking oil, eucalyptus oil, and linseed oil..etc. The pongamia oil biodiesel can be used as fuel in compression ignition engine without making any modifications in the fuel injection system (Noel et al., 2016). The volatility of the biodiesel can be enhanced with the addition of ethanol, and it is suggested that 5 to 10% of ethanol can be added with biodiesel which results in acceptable engine performance (Al-Hassan et al., 2012). The stability of the biodiesel diesel blend can be increased with ultrasonic treatment (Dong et al., 2019).

The pongamia oil biodiesel fuelled diesel engine results in lower thermal efficiency due to lower volatility and slightly higher viscosity of the biodiesel, and thus it is necessary to improve the performance of pongamia oil biodiesel fuelled engine. The nanoparticle which has better thermal and physical properties can be used to increase the properties of the biodiesel. The CNT has higher surface area to volume ratio and higher thermal conductivity and hence it was used as additive in this work. Also, we have optimized the dosage of CNT required for the biodiesel based on better thermal efficiency and lower emissions.

2. Materials and Methodology

The pongamia oil was used as raw materials to produce biodiesel using a two step transesterification process as the acid value of the pongamia oil was high. Methanol was used as the alcohol and the molar ratio of oil to methanol considered in this work was 1:6. The sulfuric acid was used as catalyst in the esterification reaction which is the first step to reduce the acid value of the pongamia oil to less than 1 and the reaction was carried out for 90 min. This treated pongamia oil was converted into biodiesel in transesterification reaction using potassium hydroxide as the catalyst and the reaction was carried out for 90 min. This method results in the biodiesel yield of 91 %. The fatty acid composition of pongamia oil biodiesel was determined using gas chromatography and it shows that this biodiesel contains oleic acid (36%), palmitic acid (10%), stearic acid (7%), behenic acid (6%), linoleic acid (19%) and arachidonic acid (1%). Table 1 shows the details of the chemicals used for the biodiesel production.

Table 1. Chemicals used for biodiesel production

Name of the Chemical	Manufacturer	Purity
Methanol	Merck	99 %
Sulfuric acid	Merck	98 %
Potassium hydroxide	Merck	99%

The CNTs were procured from NITK, Surathkal, India. The CNTs of 40, 50 and 60 mg were mixed in one litre of pongamia oil biodiesel and subjected to ultrasonication for 60 min using ultrasonic bath to prepare the homogenous mixture and is shown in the figure 2. The CNTs with the dosage of 40, 50 and 60 mg/l are represented in this work as BDCN40, BDCN50 and BDCN60. The properties of the diesel, biodiesel and biodiesel with different concentrations of CNTs were determined as per the ASTM procedures. A redwood viscometer was used to measure the kinematic viscosity (ASTM D 445-03) of the pongamia oil biodiesel. The calorific value (ASTM D 240-03) and density (ASTM D4052-96) of the pongamia oil biodiesel was determined using bomb calorimeter and relative density bottle,

respectively. A Cleveland open cup tester was used to measure the flash point of the biodiesel (ASTM D92-18).



Figure 2. Biodiesel subjected to ultrasonication

3. Engine experimental setup

A diesel engine which is most widely used for agricultural purpose was modified to work as an experimental setup. Figure 3 shows the engine used for the experiments. The diesel engine used in this work is a direct injection, water cooled, naturally aspirated compression ignition engine and its technical specifications details are given in the Table 2. The engine load is the force which resists the power produced by the engine. The load on the engine was varied using eddy current dynamometer as it significantly affects the thermal efficiency and engine emissions (Man et al., 2016). An eddy current dynamometer was attached to the engine using coupling. A load cell was attached to the dynamometer to measure the engine load. A rotameter was used to control the flow rate of water supplied to the engine. The engine was retrofitted with air box, fuel tank, manometer, fuel measuring unit, transmitters for fuel flow measurement and process indicator. The exhaust gas temperature was measured using K-Type thermocouple. The engine is naturally aspirated. The engine governor varies the fuel injected into the engine by adjusting fuel pump to meet the required load. All the engine tests were carried out on the same day. The engine brake power and brake thermal efficiency were determined using the equation I and II.

Table 2. Engine details

Engine	1 cylinder, 4 stroke, naturally aspirated, direct injection C.I engine
Make and model	Kirloskar; model TV1
Displacement (cc)	661
Maximum brake power (kW)	5.2 at 1500 rpm
Compression ratio of the engine	17.5 : 1
Engine bore (mm)	87.5
Engine stroke (mm)	110
Fuel injection time of engine	23 degree bTDC
Injector nozzle opening pressure (bar)	200



Figure 3. Engine experimental setup

$$\text{Brake Thermal Efficiency in \%} = \frac{\text{Brake Power}}{m_f \cdot C.V} \times 100 \quad (1)$$

$$\text{Brake Power in kW} = \frac{2 \pi N T}{60} \quad (2)$$

Where, m_f – Mass of fuel consumed, kg/s

C.V – Calorific Value of the fuel, kJ/kg

N – Engine speed, rpm

T – Torque on the engine, kN-m

4. Engine Tests Procedure

The engine tests were carried out with pongamia oil biodiesel to obtain baseline data and the engine tests were carried out at constant speed. The natural aspiration system is used in this engine. The schematic view of engine setup is shown in Figure 4. The emissions of the engine were measured using a gas analyzer and smoke meter and details are given in Table 3. The leak test and purging were carried out before emission test. The gas analyzer's probe was placed into the engine's exhaust tube to measure the emission level.

The engine tests were carried out with pure biodiesel (B100) to get baseline data at steady state condition. The engine was started by manual cranking and after reaching steady state condition, important observations were recorded at no load condition. Then the engine load was increased to 25% of the full load using eddy current dynamometer and important observations were recorded. Then the engine load was increased to 50, 75 and 100 % of full load and the observations were recorded. After the engine tests, the B100 was drained from the fuel tank and fuel filter. Then the BDCN40 was filled in the fuel tank and fuel nozzle was removed. The hand cranking of the engine results in discharge of BDCN40 in the fuel injector and it was collected to remove the traces of biodiesel. Then the fuel injector was fixed into its original position and engine was started with BDCN40 and run for 15 min. The important observations and emissions were recorded at steady state condition. Similar procedure was followed for BDCN50 and BDCN60.

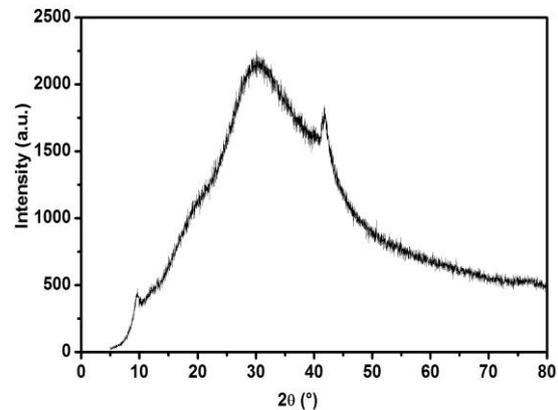
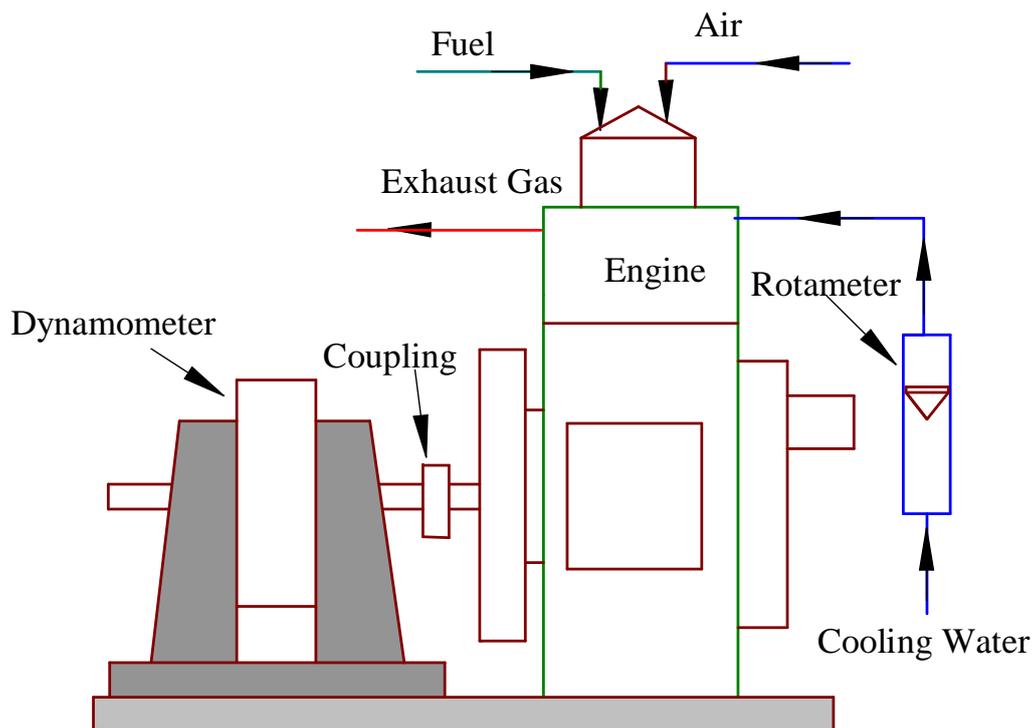
Table 3. Details of Engine Exhaust Gas Analyser

Make and model	AVL India; Digas 444 N		
Type of emission	Range	Accuracy	Uncertainty
CO emission (% vol)	0 to 15	±0.01	1.0
HC emission (ppm)	0 to 20000	±10.00	0.5
NOx emission (ppm)	0 to 5000	±50.00	1.0
Smoke meter			
Make and model	AVL; 437C		
Range (%)	0 to 100 %	±1.00	1.0

5. Results and Discussions

The biodiesel was produced from pongamia oil and CNTs were added with this biodiesel to study its effect on engine performance and emissions. Table 4 shows the properties of the diesel, biodiesel and biodiesel added with CNTs. Each property was measured three times and the average value was considered. This table shows that the addition of CNTs to the biodiesel affects the properties of the pongamia oil biodiesel. The flash point of the biodiesel decreases with the addition of CNTs. The calorific value of the biodiesel increases with the addition of CNTs. The structural properties of the CNT were measured using X-ray

diffraction. Figure 5 shows the X-ray diffraction image of the CNT. The XRD pattern of CNTs is close to those of graphite as CNTs is intrinsic in nature. The lower part of the X-ray diffraction peaks become broader as compared to graphite, due to crystallinity in carbon materials.

**Figure 5.** X-ray diffraction image of the CNT (Zahra et al. 2017)**Figure 4.** Schematic of the engine experimental setup**Table 4.** Comparison of fuel properties

S.No	Property	Diesel	B100	BDCN40	BDCN50	BDCN60	ASTM*
1	Flash Point of fuel (° C)	68	142	140	139	138	>130
2	Density of fuel (kg/m ³)	841	872	874	875	877	900
3	Viscosity of fuel at 40 ° C(mm ² /s)	2.7	4.8	4.83	4.86	4.88	1.9-6
4	Calorific Value of fuel (MJ/kg)	42.9	37.1	37.3	37.4	37.6	>33000

* Geetesh et al, 2019.

6. Fuel Droplet Size

When the fuel is injected into the combustion chamber, it is atomized and then fuel spray formation takes place. It is reported that the mean fuel droplet size of diesel and biodiesel are about 21 and 76 μm respectively. It shows that the biodiesel droplet size is about three times higher than the diesel. This is due to higher kinematic viscosity and surface tension of the biodiesel (Tizane et al., 2013). This large difference in fuel droplet size affects the fuel spread angle and spray penetration, which affects the mixing of fuel and air, fuel evaporation and combustion (Pawel&Róbert, 2018).

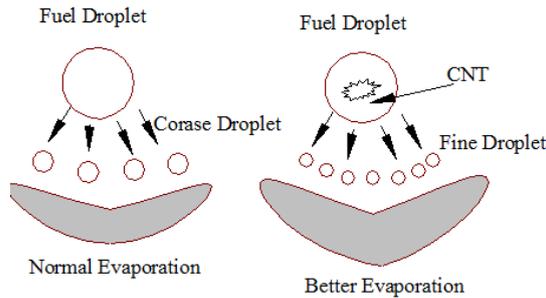


Figure 5. Schematic of fuel droplet breaking and evaporation

The fuel spray formation is affected by the surface tension and viscosity of the fuel. Figure 5 shows the schematic of fuel droplet breaking in the combustion chamber and evaporation of the tiny fuel droplets which form the fine spray. The biodiesel has higher viscosity, intermolecular bonding and surface tension and the addition of CNT reduces the intermolecular bonding and breaks the fuel droplets into tiny particles which increases the evaporation and causes better spray formation (Nikhil et al., 2020).

The engine tests were carried out without making any modifications in the fuel injection system. The effect of CNTs on the engine performance is discussed in the following paragraphs. The effect of CNTs on the brake thermal efficiency of the engine at different loads is shown in the figure 6. From the figure, it is observed that the brake thermal efficiency increases with increase in load. This is due to reduction in friction losses with increase in load. The viscosity and intermolecular attraction of the pongamia oil biodiesel is higher than diesel. This results in higher ignition delay and hence pongamia oil biodiesel has lower premixed combustion phase and higher diffusive combustion phase. The addition of highly reactive CNTs to the pongamia oil biodiesel helps to break the biodiesel droplets into small molecule which results in better evaporation and combustion of the fuel (Tizane et al., 2013). However, the CNT dosage affects the brake thermal efficiency, and it has to be optimized. The CNTs dosage with biodiesel, BDCN50, results in higher BTE as compared to the biodiesel and other CNT dosages at higher loads. The optimized dosage provides higher surface to volume ratio which enhances the heat transfer between the fuel droplets and improves the fuel droplet atomization and the combustion process. The higher dosage of CNT, BDCN60, affects the fuel atomization and spray formation. This phenomenon increases the ignition delay and affects the preflame reaction, cylinder pressure and heat release rate. It is reported in the literature (Pankaj et al., 2021 and Harish et al., 2020) that the higher dosage of nanoparticle results poor combustion which results in higher ignition delay, lower cylinder pressure and lower heat release rate as compared to

other dosages. Paramashivaiah et al reported that the higher dosage of graphene nanoparticle reduces the thermal efficiency of Simarouba biodiesel fuelled diesel engine due to poor atomization which increases fuel consumption and reduces the brake thermal efficiency.

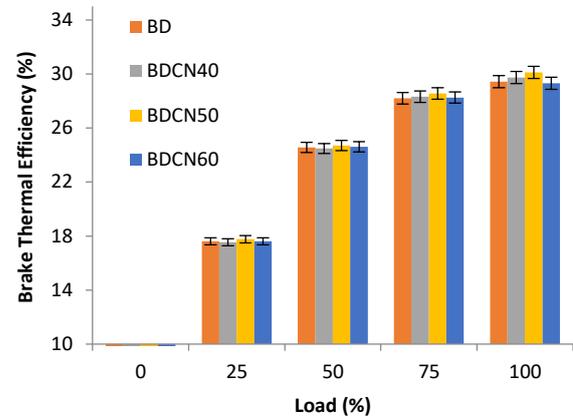


Figure 6. Brake Thermal Efficiency Vs Load

Figure 7 depicts the variation in exhaust gas temperature (EGT) of the engine at different loads with different dosages of CNTs. The exhaust gas temperature was measured at the outlet of the engine. From the figure, we observe that the exhaust gas temperature value increases with increase in engine load due to consumption of higher amount of fuel by the engine at higher loads. The exhaust gas temperature of BDCT60 is lower than the BDCT40 and BDCT50 at higher loads. This is due to poor atomization and spray formation (Brandão and Suarez, 2018). The exhaust gas temperature of BDCN50 is higher than other dosages due to reduction in ignition delay and improvement in premixed combustion which results in better combustion and higher combustion temperature. The higher combustion temperature results in higher exhaust gas temperature. In literature (Sadhik Basha J and R B Anand, 2011), it is reported that the addition of CNT reduces the ignition delay period of the fuel.

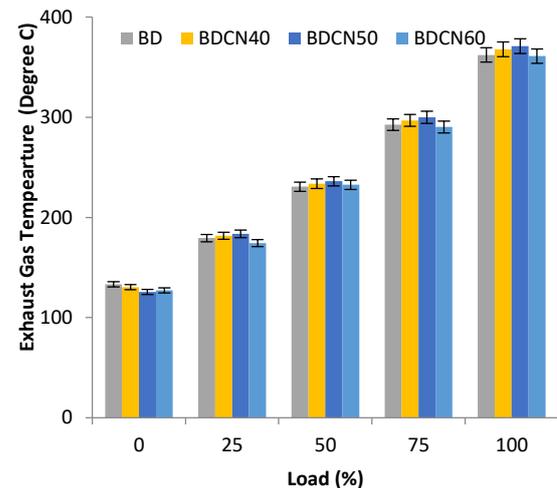


Figure 7. Exhaust Gas Temperature Vs Load

The poor mixing of fuel and air, locally rich zone and incomplete combustion of fuel results in higher carbon monoxide (CO) emission of the engine. The carbon monoxide also indicates poor combustion. The variation in carbon monoxide emission of the pongamia oil biodiesel fuelled engine with different CNTs dosage is represented in the Figure 8. It is observed that the carbon monoxide

emission of the engine increases from part load to full load due to reduction in air to fuel ratio. The compression ignition engine emits higher carbon monoxide with pongamia oil biodiesel at all loads as compared to other fuels. The addition of CNT to the pongamia oil biodiesel results in improvement in premixed and diffusion combustion phases. This results in lower carbon monoxide level (Balaji et al., 2015). The addition of CNT with the dosage of 50 mg/l, to the biodiesel reduces the carbon monoxide emission significantly as compared to other CNT dosages. This optimum CNT dosage results in reduction in ignition delay and enhanced fuel to air mixing which improves the premixed combustion. This phenomenon results in lower carbon monoxide level as compared to other dosages. The BDCT40 results in lower carbon monoxide level as compared to BDCT60 as the higher dosage causes poor atomization which results in incomplete combustion of fuel and higher CO emission (Paramashivaiah et al. 2018)

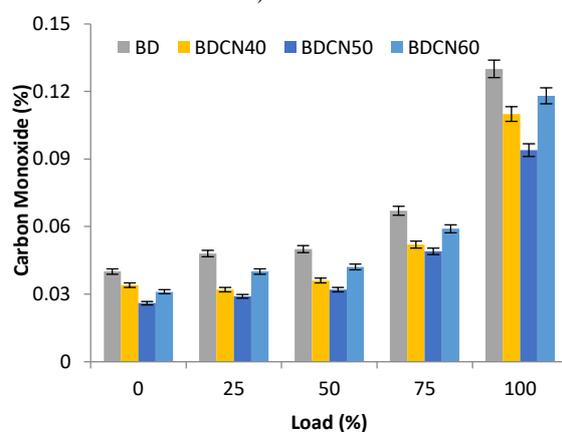


Figure 8. Carbon monoxide Vs Load

The incomplete combustion of the fuel causes the formation of unburned hydrocarbon (HC) emission in the compression ignition engine. Figure 9 depicts the HC emission of the engine with biodiesel, and biodiesel added with different dosages of CNTs, and it is observed that the hydrocarbon emission of the engine increases with load due to consumption of higher amount of fuel by the compression ignition engine. The addition of CNTs to the biodiesel reduces the hydrocarbon emission of the compression ignition engine. The higher viscosity of the biodiesel causes lower premixed combustion phase and higher diffusive combustion phase. The addition of highly reactive CNTs to biodiesel breaks the biodiesel droplets into small molecule and causes better mixing of fuel and air. This process improves evaporation of fuel and improves the premixed combustion. The improvement in the fuel evaporation and premixed combustion results in better combustion and reduces the hydrocarbon emission level. This behavior is similar to work done by Tizane et al., 2013. The BDCN50 results in lower hydrocarbon emission as compared to other CNT dosages due to its ability to improve the pre-mixed combustion as compared to other CNT dosages. The BDCN60 results in higher hydrocarbon emission due to poor combustion and this result is comparable to similar type of work reported in literature (Seyyed et al. 2017).

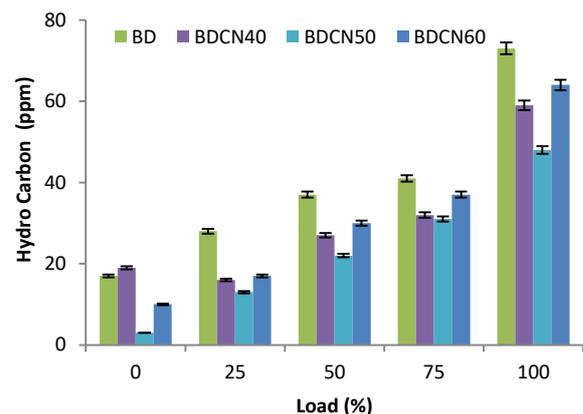


Figure 9. Hydro Carbon Vs Load

Figure 10 depicts the oxides of nitrogen (NOx) emission of the C.I. engine at various loads with pongamia oil biodiesel and pongamia oil biodiesel added with various dosages of the CNTs. The oxides of nitrogen emission is formed during the premixed combustion phase of the fuel. The improvement in premixed combustion causes better combustion and higher combustion temperature. The oxides of nitrogen emission level is low at lower loads due to lower combustion temperature. However as the load increases, the fuel consumption increases which result in higher combustion temperature and higher oxides of nitrogen emission level (Ahmet Uyumaz et al., 2020, Álvaro et al., 2019). The addition of CNTs to the biodiesel increases the oxides of nitrogen emission. The CNTs improve the fuel and air mixing and premixed combustion which results in better combustion and higher combustion temperature. This results in higher oxides of nitrogen emission. However, the oxides of nitrogen emission vary with the CNT dosage. The increase in CNT dosage increases the oxides of nitrogen level. The oxides of nitrogen emission of BDCN50 is higher than the other dosages due to better combustion of biodiesel which results in higher oxides of nitrogen emission. The BDCN60 results in lower oxides of nitrogen emission as compared to other dosages at higher loads.

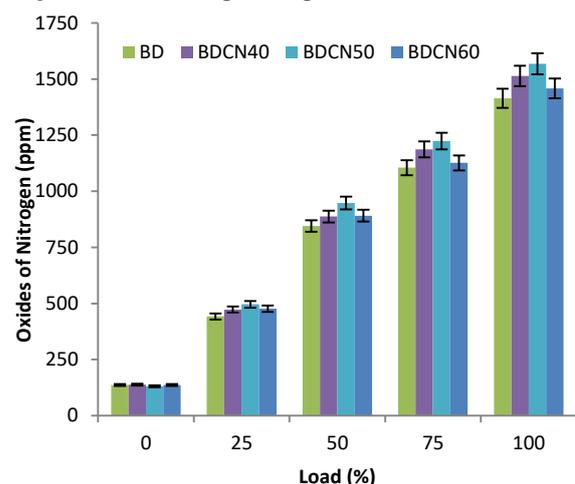


Figure 10. Oxides of Nitrogen Vs Load

The smoke opacity of the diesel engine with biodiesel and biodiesel added with different dosages of CNTs and at different loads is shown in the Figure 11. It is observed from the figure that the smoke emission increases with increase in load for all the fuels due to consumption of higher amount of fuel at higher loads. The CNT dosage impacts the smoke

emission. The BDCN60 results in higher smoke emission as compared to other CNT dosages at higher loads. The BDCN50 results in lower smoke emission due to improved heat transfer between the biodiesel particles due to higher surface area to volume ratio and higher chemical reactivity which increases molecule breakup during injection and ignition characteristics of the fuel (Gad&Jayaraj, 2020). The improved biodiesel oxidation and quick flame propagation reduces the engine smoke (Prabu et al., 2018). The higher dosage of CNT, BDCN60, results in higher smoke opacity and similar type of results were reported in literature (Ahmed et al 2016, Paramashivaiah et al 2018, SadhikBasha et al 2011)

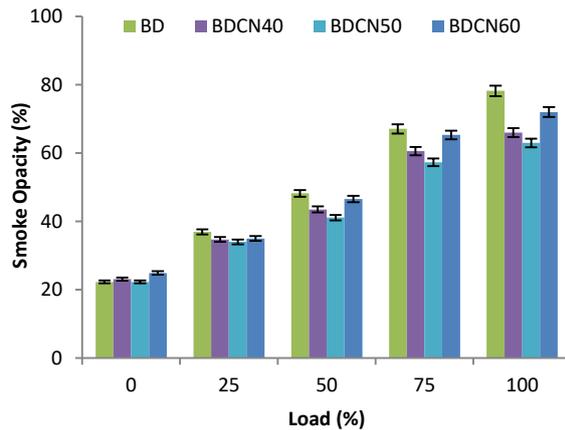


Figure 11. Smoke Opacity Vs Load

Conclusion

In this work, biodiesel was produced from non-edible pongamia oil using a two-step transesterification method. The pongamia oil biodiesel has lower volatility and slightly viscous and hence CNTs were added to the biodiesel. From the property analysis, it was observed that the addition of CNTs to the pongamia oil biodiesel improves the fuel properties of the biodiesel such as flash point and calorific value. The engine tests were carried out with biodiesel and biodiesel added with different dosage of CNTs. The CNTs dosage of 50 mg/l results in higher thermal efficiency and lower smoke, hydrocarbon and carbon monoxide emissions. The compression ignition engine emits higher hydrocarbon, carbon monoxide and smoke emissions at higher loads and the addition of CNT reduces these emissions significantly. However, these emissions were lower at lower loads. The cost of the biodiesel may be increased due to the addition of CNTs, however the reduction in hydrocarbon, carbon monoxide and smoke emission is significant. From this work, it is concluded that the CNTs can be added with the pongamia oil biodiesel to improve its properties and to enhance the performance of the diesel engine.

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