Experimental studies on the effect of Carbon nanotube additives with Calophyllum Inophyllum biodiesel in CI engine

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Abstract: The rapid depletion of Non-renewable fuel sources coupled with environmental degradation, has led us further into the exploration of alternate energy resources. Biodiesels originating from non-edible feedstocks have garnered much attention in a span of few years. The current study focuses on the addition of Carbon Nanotubes in Tamanu oil biodiesel in a Diesel engine. In this study, parameters such as brake thermal efficiency, unburned hydrocarbon, carbon monoxide, and NOx emissions have been studied. The performance of these biodiesel-diesel blends were charted and results are compared with diesel. It is noted that the inclusion of nano-additives in dosages of 30 and 60 ppm enhances brake thermal efficiency, the drawback being increased specific fuel consumption. The emissions of HC, NOx and emissions show a favorable trend with addition of CNT but CO2 emissions were observed to be on the higher side. Also graphs were plotted revealing the relevant combustion characteristics of the test fuels. They are further discussed in detail and a comprehensive conclusion was made.

Keywords: Biodiesel, Calophyllum inophyllum, tamanu oil, transesterification, Carbon Nanotubes performance, Combustion, Emissions, NOx emissions, CI engine.

1. Introduction

The inadequacy of fossil fuels and stringent emission laws has driven us to look towards viable alternatives for the conventional petroleum based fuels. In 1985, petroleum consumption was 2807 million tons, but in 2008, figures indicate 3928 million tons [1], with an average annual growth rate of almost 1.5%. Since then there has been a steady incline in these figures owing to rapid industrialization and to support various sectors like transportation, construction etc. Transportation sector alone consumes massive amount of fossil reserves and are responsible for One-fifth of global CO2 emissions[2]. Hence it is imperative to come with a solution to the ongoing energy crisis in order to safeguard the future generation from adversity. Biodiesels have been gaining widespread attention in recent years owing to a multitude of favorable properties. They are renewable, can be domestically produced and are better for the environment[3]. At present, biodiesel is mainly produced from conventionally grown edible oils such as sunflower, palm, soybean, and rapeseed. Commercialization is hampered largely due to the huge costs involved in obtaining and further processing of these food crops ,also many developing countries tackle with food shortage issues. These concerns have forced researchers to produce biodiesel from non-edible feedstock[4]. Some of the non-edible sources widely used for biodiesel production are Jatropha, Mahua, Karanja, cotton, Ricinus Communis, Calophyllum Inophyllum(tamanu) .

Calophyllum inophyllum is a medium-large sized evergreen tree, which is native to east Africa, India, south Asia and Australia [5]. Calophyllum inophyllum kernels have considerably high oil content (75%) with an average oil yield is 11.7 kg-oil/tree or 4680 kg-oil/ha [6]. Moreover, the physiochemical properties are comparable to diesel, having high values of viscosity and flash point when compared to other non-edible oils [7]. Habibullah et al. [8] studied the friction and wear characteristics and concluded that calophyllum inophyllum biodiesel blends displayed better lubrication and wear characteristics when compared to pure diesel. One major hurdle with using CI biodiesel is its very high Free Fatty Acid content (FFA). The percentage and type of Fatty acids are an important factor while choosing the biodiesel feedstock. In order to produce biodiesel from a feedstock having high acid value (high FFA content), multi-step esterification process is required. Venkanna and Venkataramana Reddy [9] adopted a three-stage production technique involving acid esterification, alkali transesterification and post treatment for obtaining biodiesel from calophyllum inophyllum linn. They found that post acid esterification, for the biodiesel production for 8:1 M ratio methanol to oil with 1.25wt% KOH at 60 ± 1°C for 2h produced the optimum yield. In recent years researchers have tried different additives and optimizing various parameters to improve the performance and suitability of CI biodiesel. Ramesh et al. [10] carried out tests on blends of CI biodiesel and diesel with n-hexanol as additive. Findings from their study indicates that addition of hexanol has improved the BTE with significant decline in BsFC and BSEC values. Apart from the addition of higher alcohols, Nano particle emulsions and antioxidants have been quite popular choices in the recent past.

FTIR assessment of CI biodiesel laced with 1000 ppm TBHQ, a synthetic antioxidant, reveals superior Oxidation, thermal and storage stability when compared to pure biodiesel thereby improving their shelf life significantly [11]. In recent years due to the advent of new technologies the ability to produce nanoparticles have greatly improved, as a result the usage of nanoparticles, in particular metal-oxide Nano emulsions, have emerged as suitable additives. Özgür et al. [12] used two different Nanoparticles- MgO and SiO₂ and their study revealed that addition of nanoparticles resulted in slight improvement of torque and brake power at higher engine speeds. Exhaust emission data shows that CO and NOx emissions reduced with a slight increase in CO₂. Tamilvanan et al. [13] incorporated copper nanoparticles into Tamanu oil biodiesel to map the performance, emissions followed by combustion characteristics of a diesel engine. The Cu nanoparticles were prepared from deposition of aqueous CuSO₄ solution. In terms of performance, addition of nano-copper particles improved BTE and lower values of BsFC was observed. The combined effect of shorter ignition delay and large surface area to volume ratio of nano-particles aided in reducing the emissions of NOx, CO and HC.

Since their inception, Nanotubes have been garnering a lot of attention due to their superior physical and chemical properties. High tensile strength, low density, high thermal conductivity coupled with excellent chemical stability makes them the ideal material for an array of domains. Medicine and electronics are few industries that could potentially benefit from their inclusion. Some of the inherent drawbacks associated with the usage of biodiesels can be refined by the addition of nanoparticles. The research regarding addition of Nanotubes and their influence on various parameters is still in its nascent stages with a lot of grey areas. Experiments carried out by Sadhik Basha and Anand [14] revealed noticeable improvement in Brake thermal efficiency and reduction in emissions of NOx and smoke using CNT blended emulsion fuels. Here Carbon nanotubes were employed to overcome the drawbacks of emulsion fuels. They noticed reduction in heat release rate of CNT dosed fuels compared to neat biodiesel, biodiesel-emulsions. Prajwal Tewari et al. [15] used Honge oil biodiesel in conjugation with multi-walled Carbon nanotubes. The inclusion of carbon nanotubes marginally improved the Brake thermal efficiency when compared to the test without any additive. This improvement is testimonial to the catalytic nature of MWCNT which facilitated an improvement in combustion characteristics. The smoke opacity, HC and CO emissions too followed a similar trend. Addition of CNT acted as cetane improvers, thereby reducing the ignition delay. The NOx emissions showed lower values for HOME when compared with other blends.
2. Materials and Methodology

2.1 Biodiesel preparation

Tamanu oil is sourced from local entities and commercially available MWCNT's and diesel are used for preparing the blends. The details of above mentioned are represented in table 1. Transesterification is done to overcome the drawbacks associated with biodiesels such as, high viscosity and low volatility, leading to poor atomization, pumping problems followed by plugging of injectors. Transesterification is an organic reaction involving the conversion of Triglycerides into their corresponding Methyl Ester (biodiesel), catalyst are usually present to improve the reaction rate. Tamanu oil extraction is followed by a 3 step purification process, this is adopted due to its high Free Fatty Acid content (FFA). The first step involved, is for bringing down the acid value of the oil. Acid value is designated as the amount or quantity of KOH required for neutralization of the natural acids present. In acid catalyzed esterification, the solution of Calophyllum Inophyllum oil and methanol is heated along with sulphuric acid for a duration of 120 minutes at 60 °C. Then alkali catalyzed reaction is done to reduce the FFA content which makes it suitable for engine operation. In this step, the oil-methanol mixture is treated with potassium hydroxide at 60 °C accompanied with constant stirring. Then the whole solution is let to settle and the glycerin gets sedimented at the bottom. The final step involves washing the solution to remove the excess glycerin and separate the ester. Figure 1 shows the oil undergoing transesterification process.

Table 1. Details of Nano-particles

| Chemical name | MWCNT |
|---------------|-------|
| Manufactured by | Shilpent Enterprises |
| Purity | 99% |
| Diameter | 5-20 nm |
| Length | 10µm |
| Appearance | Black, Fine particles |

Figure 1. Esterification of Biodiesel

Figure 2. Ultrasonication of CNT
2.2 Blending and CNT addition

In our study three blends of B20 (20% biodiesel and 80% diesel) are prepared as shown in figure 2. The CNT particles are then weighed at 30 and 60 ppm using precise weighing apparatus. In order to create a homogenous nanofluid, an ultrasonicator is used. The required quantity of Nanotubes are then dispersed into the blend in the ultrasonicator, where they are agitated for 20 minutes in order to create a stable fluid. The details of the blended samples are provided in table 2.

**Table 2.** Properties of fuel

| Fuel Property | Diesel | B20  | B20C30 | B20C60 |
|---------------|--------|------|--------|--------|
| Density (kg/m³) | 833.1  | 847  | 861    | 872    |
| Kinematic Viscosity (mm²/s) at 40°C | 3.556  | 4    | 4.11   | 4.13   |
| Gross Calorific Value (KJ/kg) | 44664  | 40920| 41530  | 42011  |

3. Experimental Setup

The engine used to carry out our evaluations, shown in figure 3, is a four stroke, kirloskar made single cylinder engine, having a compression ratio of 17.5:1. The set up is coupled to an eddy current loading device for various loading conditions. Moreover it is equipped with necessary instruments for calculating combustion pressure and crank-angle. A standalone panel is provided which comprises of fuel tank, air box, fuel measurement gauges which are used for measuring various parameters. Table 3 shows the engine specification. The details of the Eddy current dynamometer employed is shown in table 4.

![Figure 3. Engine set-up](image-url)
Table 3. Engine Specifications

| Specifications   | Value                   |
|------------------|-------------------------|
| Make             | Kirloskar               |
| No. of cylinder  | 1                       |
| No. of strokes   | 4                       |
| Fuel             | Diesel                  |
| Rated Power      | 5.2 kW@ 1500 rpm        |
| Compression Ratio| 17.5:1                  |
| Cylinder diameter| 87.5mm                  |
| Stroke length    | 110mm                   |

Table 4. Dynamometer details

| Specifications          | Value   |
|-------------------------|---------|
| Make                    | Techno Mech |
| Model                   | TMEC-10 |
| Rated Power             | 7.5KW   |
| RPM                     | 1500-6000 |
| Dynamometer Arm length  | 185mm   |

4. Results and Discussion

The present work aims to study the influence of CNT additives at 30 and 60 ppm with biodiesel produced from Calophyllum Inophyllum feedstock. Initially Diesel is run as base fuel and then the blends are tested for combustion, emission and performance parameters. At an injection pressure of 200 bar with 23° bTDC. The blends were tested at a constant engine speed of 1500rpm with varying loads of no load, 25%, 50%, 75% and 100%.

4.1 Effect of Crank angle

4.1.1 Variation of Cylinder pressure with Crank angle

The maximum in-cylinder pressure of biodiesel blends without CNT is lower to that of diesel, as it is evident from the graph, due to the combination of various factors such as higher viscosity, lower volatility and calorific value. The peak pressure for diesel was observed to be 71 bar and 64 bar for B20, from figure 4. The rise in peak pressure indicates that inclusion of Nanotubes improved the combustion reaction. As a result the peak pressures for B20C60 and B20C30 were found to be 69 and 67 bar respectively with B20C60 blend faring better than diesel. The nanoparticles along with the superior physiochemical properties they also act as cetane improvers and also increase the heat transfer rate by providing a large surface area for reactions to take place. The combined effect of these factors aided in increasing the peak pressure of those blends.
4.1.2 HRR Vs Crank angle

The Heat release rate analysis can provide crucial insights on how combustion proceeds inside the chamber and also the operating conditions of the engine. Figure 5 shows how Heat release rate values changes in response to changes in Crank angle. Ignition delay is a crucial factor for determining the peak values of heat release rate. A higher ignition delay ensures that more fuel molecules combine with air and once the required temperature is achieved it results in large amount of heat being released. The viscous nature of biodiesel blends lead to improper mixing and poor atomization thereby having a low HRR value. Diesel showed highest HRR value followed by blends having CNT additives. The addition of carbon nanotubes significantly improved the HRR values due to its superior catalytic and ignition properties. The addition of CNT’s offsets the higher viscosity associated with biodiesel-diesel blends with B20C60 showing the maximum HRR value among the biodiesel samples.
4.2. Performance Attributes
Brake thermal efficiency and the fuel consumption are calculated to ascertain the performance parameters.

4.2.1 Variation of BTE with BMEP

The Brake Thermal efficiency indicates how efficiently the energy produced during the combustion of fuels (chemical energy) is converted into useful mechanical work. The above graph shows the BTE for different blends at different loads. We could see that BTE is increasing with increase in load condition. This is because at peak load condition more fuel is being supplied to support combustion leading to increased power output. Also at higher loads the increased temperature improves the rate of evaporation resulting in a higher thermal efficiency.

The biodiesel -diesel blend, B20, showed the lowest thermal efficiency with diesel offering the highest. The BTE of B20 was observed to be 31.47% compared to the 33.2% offered by neat diesel. Biodiesel blends dosed with CNT showed improvement in BTE over B20 blend with B20C30 AND B20C60 having efficiency of 31.92% and 32.14% respectively. The improvement in efficiency can be attributed to the better flow properties of CNT dosed fuels, which leads to improved combustion.

4.2.2 Brake Specific Fuel Consumption

For any fuel, generally lower values of fuel consumption are desired. Figure 7 shows the variation of fuel consumed while using biodiesel blends and diesel with BMeP. Diesel due to its low viscosity, high volatility showed the lowest BsFC value whereas B20 due to its inherently low heating value combined with inferior flow properties resulted in elevated BsFC value. The Higher values of BsFC for biodiesels and its blends
can be related to their higher density, resulting in more amount of fuel to be consumed. B20C60 performed better in comparison to B20 and B20C30 and obtained 2-4% reduction in fuel consumption values. This improvement is brought about by the catalytic nature of nanotubes along with increase in thermal efficiency. Addition of 30 ppm of CNT did not produce any noticeable changes on the fuel consumption compared to 60 ppm.

![Figure 7. BsFC VS BMeP](image)

4.3 Emission Analysis

4.3.1 Oxides of Nitrogen

Figure 8 shows the variation of NOx emissions of Diesel, B20, B20C30 and B20C60 with BMeP. Among the various oxides of nitrogen, NO being the most dominant followed by nitrogen dioxide. One of the major drawbacks of using biodiesels was the increased NOx emissions associated with it but from the figure it is evident that at lower load conditions, biodiesel blends produced lower NOx compared to neat diesel. This can be attributed to reduced heat release during the premixed phase leading to lower temperature. NOx formation is a highly temperature dependent mechanism and the lower temperatures associated with biodiesel blends help reducing it. A maximum reduction of 30.95% was obtained by using B20C60 blend at intermediate load condition. However at higher loads the NOx emissions of biodiesel blends increased significantly and were almost similar to diesel. This increase is mainly due to the improvement in combustion brought about by the addition of CNT’s which in turn leads to drastic increase in pressure and temperature.
4.3.2 CO Emission

Figure 8. Oxides of Nitrogen Vs BMeP

Figure 9. Carbon monoxide emissions Vs BMeP
The variation of Carbon monoxide for diesel and the biodiesel blends are shown in figure 9. The tested fuels with and without additives showed lower values of CO than neat diesel. CO emissions are generally lower for biodiesels compared to the petroleum fuels due to their higher oxygen content. The higher CO values at lower loads is due to formation of locally rich mixtures combined with improper mixing.

Experimental results show that addition of CNT reduced CO emissions compared to diesel at all load conditions. The fuel blend containing 60 ppm of CNT achieved 55% reduction at peak load condition compared to neat diesel. This is because carbon nanotubes act as cetane improvers and the presence of more oxygen molecules help in conversion of CO to CO$_2$. The CO emissions at peak load was 0.18%, 0.11%, 0.09%, 0.08% for Diesel, B20, B20C30 and B20C60 respectively.

### 4.3.3 Unburnt Hydrocarbon Emission

Figure 10. Unburnt hydrocarbons Vs BMeP

Figure 10 shows the unburnt hydrocarbon emissions of the tested fuels. It is found that neat diesel produced more HC emissions compared to Biodiesel-diesel blends. This is due to the higher oxygen content of biodiesels which leads to complete combustion. HC emissions arise mainly due to insufficient oxygen available for combustion. HC emissions follow a similar trend to CO where both show higher values at lower loads and gradually decrease with increasing load condition. This can be attributed to the over-leaning of mixture in the initial stage combined with lower wall temperature. This results in partial oxidation leading to increased HC emissions. The blends containing Calophyllum Inophyllum performed better in comparison to neat diesel. B20C60 showed the lowest emissions among the tested samples with a 20% reduction at peak load conditions. The increasing value of HC observed at peak loads is due to the availability of more amount of fuel leading to the formation of rich mixtures. Addition of CNT further helped in reducing the ignition delay leading to lower values of HC.
4.3.4 Smoke Opacity

Figure 11 shows the variation of smoke opacity of Diesel, B20, B20C30 and B20C60 with brake mean effective pressure. It is visible that smoke opacity increases with a subsequent increase in load, since more amount of fuel needs to be injected at higher load conditions. Neat diesel presents higher smoke opacity at all tested conditions compared to biodiesel blends. Biodiesel samples usually portray lower values of smoke opacity due to their superior oxygen content and addition of CNT improved emissions marginally. This can be attributed to their catalytic nature which promotes combustion which in turn inhibits soot formation to a certain extent. At peak load conditions Diesel,B20,B20C30 and B20C60 presented values of 63.1%,62.9%,61.7% and 60.8% respectfully.

![Figure 11. Smoke opacity Vs BmeP](image)

4.3.5 Carbon Dioxide Emission

Generally Biodiesels produce more CO2 compared to neat diesel to their oxygenated nature. As can be seen from figure12 , CO2 emissions steadily rise with increase in load condition .At peak load B20 produced highest CO2 emission at11.2% but addition of CNT showed slight decrease in C02 compared to B20. CO2 emissions of biodiesel blends with CNT are higher compared to neat diesel due to their large surface area to volume ratio which promotes better heat transfer leading to better combustion. This trend is further backed by the decrement in CO emission observed earlier. Diesel,B20C30 and B20C60 presented values of 10.9%,11.1%, and 10.9% respectively, with both diesel and the biodiesel blend dosed with 60 ppm CNT showed the lowest CO2 values at maximum load condition.
5. Conclusion

The following conclusions can be drawn from the results obtained:

- Addition of CNT improved the BTE with regards to B20 blend. Maximum BTE was observed to be 32.14% for B20C60, 31.9% for B20C30 and 31% for B20.
- In general, the Nano size particles have high surface area and this property ensures better combustions of the blends. Addition of MWCNTS significantly reduced the Nox emissions by a maximum of 30.95%. At higher loads NOx emissions increased as a result of increase in heat release rate and reduced ignition delay which resulted in higher peak temperatures.
- The unburnt hydrocarbons were reduced for B20C60 blends due to a combination of factors such as, increased reactivity, reduced ignition delay and the superior oxygen content of biodiesel fuels.
- This shows that addition of MWCNT’s led to more complete combustion
- The smoke emitted by biodiesel was comparatively lower. The CO2 emissions increases because of the higher oxygen content of biofuels which facilitated complete combustion.

Abbreviations

BTE- Brake Thermal Efficiency
BsFC- Brake specific fuel consumption
CNT- Carbon Nanotubes
CI- Calophyllum Inophyllum
B20- 20% biodiesel, 80% diesel
B20C30 - 20% biodiesel, 80% diesel, 30ppm Carbon Nanotubes

B20C60 - 20% biodiesel, 80% diesel, 60ppm Carbon Nanotubes

HC - Hydrocarbon
NOx - Oxides of nitrogen
CO2 - Carbon dioxide
CO - Carbon monoxide
FFA - Free fatty acid
Nm - Nanometer
NaOH - Sodium hydroxide
ppm - parts per million

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