Effect of nanofluids in waste cooking oil biodiesel fuel: An experimental investigation on diesel engine characteristics

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Abstract. The diminishing crude oil source and the environmental effluence created by the fossil fuels have forced the researchers to search for an alternative source of energy. Many researchers found that Waste cooking oil biodiesel (WCOB) derived from waste cooking oil (WCO) could be an economic source of fuel for diesel engines because some of the properties of WCOB were found similar to diesel. Disposing of WCO in sewage has been a great concern for many countries. Instead of disposing, converting WCO into WCOB, using them in diesel engines could be the best choice of utilizing energy. In this context, WCOB was selected as a basic fuel. In the first phase, experimentation was carried out using WCOB. Single-cylinder, water-cooled diesel engine with full set up was used for experimentation. Then, Zinc Oxide (ZnO) nanofluid was prepared by a wet chemical method in two mass proportions of 50ppm and 100ppm and blended with WCOB and considered fuels as WCOBZ50 and WCOBZ100. These fuels were tested and readings were measured. The experimental results showed that the engine characteristics were found better for WCOBZ100 compared to neat WCOB. In the second phase, ZnO with Copper Oxide (CuO) mixed nanofluid was prepared in two mass proportions of 50ppm and 100ppm and considered fuels as WCOBZC50 and WCOBZC100. Then these fuels were tested and results were evaluated with previous results. Finally, it was found that greater improvement in engine output characteristics and extreme drop in emission gases for WCOBZC100 compared to other nano blends and neat WCOB.

1. Introduction

Diesel engines are the power supplying machines for medium and heavy automotive vehicles. Due to rise in population and energy demand, large quantities of petroleum products are consumed by many countries in the world exclusively by internal combustion engines and emit lots of harmful gases and contaminating the atmosphere. These pollutants affect the air quality, further it affects the human health. To solve this problem, many researchers focused their research on finding a new biofuel. So, some inventors found that
biodiesel derived from WCO was the reliable source of fuel for diesel engine. The following research articles are the findings related to WCOB and their performance in diesel engines.

Nantha Gopal et al. [1] derived waste cooking oil methyl ester (WCME) from WCO and investigated the WCME and their blends with diesel. The authors discovered that WCME produced lesser performance, lesser emissions of Carbon monoxide (CO), Hydro Carbon (HC) and smoke than diesel. But oxides of nitrogen (NOx) was found higher. Can Ozer [2] conducted experiments using two types of WCOB and its blends with diesel. Lesser ignition delay period with higher combustion duration, slight reduction in in-cylinder pressure and heat release rate (HRR) were observed while adding WCOB. There was a drop in BTE, HC, smoke, CO and increment in brake specific fuel consumption (BSFC) were found. NOx and CO2 were slightly higher. Hwang Joonsik et al. [3] did a research using WCOB by modifying the engine parameters. The BSFC and NOx were observed higher. HC, CO, smoke at high injection pressure were noted lower. Cheung et al. [4] examined the particulate and tail pipe emissions using WCOB blends with diesel. There was a drop in particulate mass concentration, HC, CO with slight increment in NOx observed. Kathirvel et al. [5] did an extensive review on articles related to WCME and its applications in CI engines. The following findings were noted by the authors. They are: WCME proved as viable alternative source of fuel; this biofuel is non-toxic, renewable, biodegradable; physiochemical properties were closer to diesel; exhaust gas emissions were lesser except NOx. Abed et al. [6] used WCOB and its blends as fuels and observed that BTE, CO, smoke and HC emissions were lower; NOx, CO2, exhaust gas temperature and SFC were higher. Khan et al. [7] conducted a detailed study on WCOB production from WCO and its effective utilization of energy. It was recommended that WCOB could be a future alternative source of energy. From the above literatures, the following findings were noted. The physiochemical properties of WCOB were closer to diesel and mainly depends upon the quality of transesterification process. The engine output such as BTE and SFC was inferior than diesel. In emission side, HC, CO and smoke were better; this was due to enhanced combustion and oxidation of WCOB. NOx and CO2 were found higher; this was due to the oxygen availability in WCOB.

Next, research was conducted to improve BTE, BSFC and to diminish NOx and CO2 emissions. Many researchers used different techniques such as circulating few volumes of exhaust gas into the intake, emulsification, dual fuel mode, adding chemical additives and nano particles/ nanofluids in the base fuel. It was found from many articles that adding nanoparticles improved the engine performance and reduced the harmful tail pipe emissions. In this context, some of the research articles and their findings are listed below.

Balamurugan et al. [8] used Soya bean biodiesel (SBB) and its blends with copper nanoparticles. In this study, electrolysis method was used to synthesis nanoparticles. Nanoparticles were tested using XRD, SEM and found that the size of nanoparticles were around 50nm. 42nm and 50nm sizes of Copper nanoparticles were doped with SBB B10 blend and evaluated their performance. It was observed that 42nm size copper nanoparticles doped B10 blend released better performance with lesser NOx emission. Karthikeyan et al. involved methyl esters of pomolion stearin wax (PSWME), grape seed oil (GSOME) and canola oil (COME) in their research. In these studies, 50ppm and 100ppm of nanoparticles of zinc oxide were added with diesel-PSWME (B20) blend, diesel-GSOME (B20) blend and diesel- COME (B20) blends separately. It was noted from the studies that the calorific value was improved while adding nanoparticles. BTE and SFC were improved; CO, HC and smoke were drastically reduced [9-11]. Shaafi et al. [12] reviewed many research articles related to nano additives and their influences on biofuel and its blends. It was reported that adding nanoparticles in diesel/biodiesel improved the physical properties, thereby enhanced the performance and reduced the tail pipe emissions. Gumus Soner et al. [13] investigated by adding aluminium oxide and copper oxide nanoparticles in diesel. The output said that
nano blended diesel stability, flash point and cetane index were improved; BSFC and NOx were reduced. Nantha Gopal et al. [14] used methyl esters of Calophyllum Inophyllum (CIME) as fuel. 50ppm and 100ppm of nano emulsions of titanium dioxide and zinc oxide were prepared and blended with CIME. The output showed that BTE, HC, smoke and CO were improved; NOx was reduced; combustion characteristics were improved because of positive action of nanofluids. The same authors did a research using the same CIME by adding metal zinc oxide nano particles and an antioxidant ethanox. The results showed that 100ppm of zinc oxide blend produced higher BTE with lesser NOx at full load. Also, further addition of 500ppm of ethanox reduced NOx considerably [15]. Soudagar et al. [16] did a detailed review on effectiveness of dosing nanoparticles in biodiesel. Many literatures were collected and studied the following: various methods of preparing nanofluids; stability improvement and characterization of nanofluids; blending proportions; engine efficiency and emission reduction; health aspects and industry applications. It was discovered that nanofluids have good positive action and behaviour in diesel engine depends upon the quantity of addition. Hawi Meshack et al. [17] investigated using nano iron added cerium oxide nanoparticles in WCME and its blends with diesel. The experimental output revealed that NOx and CO were considerably reduced; BTE and SFC were also improved. Venu Harish and Prabu [18] conducted a research using Polanga biodiesel (PBD) added with aluminium oxide nanoparticles. The results showed that 50ppm of Al₂O₃ nano blended PBD had improvement in BTE and SFC; reduction in emissions; lesser ignition delay with higher mass fraction burnt.

So, after reviewing many literatures, it was clearly found that adding nanoparticles or nanofluids in the biodiesel improved the engine output and behaviour due to many advantages such as higher surface spreading area to volume ratio (SA/V ratio), rapid evaporation, thermal conductivity, enhanced oxidation process, micro explosion, catalytic combustion and faster heat transfer. The research gap found from the literature was the preparation method of nano fluid based on stability; So, in this work, nanofluid was prepared by chemical synthesis method.

2. Objectives

The first objective of this experimental research was to test the WCOB and measuring the output. The second objective was to prepare a chemically synthesized zinc oxide nanofluids in two mass proportions, blended with WCOB and evaluated the engine characteristics. The third objective was to prepare a chemically synthesized zinc oxide with copper oxide mixed nanofluids in two mass proportions, blended with WCOB and evaluated the engine output. Finally, the objective was to compare the output received from zinc oxide nano blended WCOB with zinc oxide + copper oxide nano blended WCOB.

3. Materials and Methods

3.1 Waste cooking oil biodiesel
The base fuel used in this research was WCO. This WCO was collected from a hotel near the Institute after frying vegetable food items. The food residues in WCO was removed. This WCO was given to a chemical laboratory for converting into WCOB by the usual transesterification process. The prepared WCOB was given for testing in a standard fuel characterization laboratory to measure the physio chemical properties of the WCOB.

3.2 Zinc oxide nanofluid preparation
The zinc oxide nanofluid was prepared by a novel wet chemical synthesis method. In this method, for preparing 50ppm of zinc oxide nanofluid, 0.27g of zinc nitrate and hexahydrate powder were taken and mixed with 10ml of sodium hydroxide and this nanofluid was sonicated in an ultrasonicator for 15
minutes. Then this nanofluid was blended with 1 litre of WCOB and this blend was again sonicated for 15 minutes. The prepared nano blended biodiesel was kept in a closed container and periodically checked the stability of this fuel. The fuel was found stable for 4 weeks. No fuel separation and sedimentation were observed during the observation period. The same procedure was followed for preparing 100ppm of ZnO nanofluid with WCOB using different mass proportions of the above said chemicals. These two fuels were named as WCOBZ50 and WCOBZ100. These fuels were tested in the engine set up. The readings were measured and analysed. The figure 1 presents the clear view of WCOB. The figure 2 represents the pictorial view of WCOB with zinc oxide.

3.3 Zinc oxide with copper oxide mixed nanofluid preparation
Zinc oxide with copper oxide mixed nanofluids were synthesized using the same chemical synthesis method. But, the procedure for this fuel preparation was slightly different from the previous one. For preparing 50ppm of mixed nanofluids, first 0.314g of copper acetate was taken, dissolved in 5ml of ethanol followed by dropwise addition of liquor ammonia and hydrazine hydrate. Next 0.0913g of zinc nitrate was dissolved in ethanol in the presence of ammonia and added to the already prepared copper oxide suspension by sonication using ultrasonicator for 15 minutes. Then this mixed nanofluids were blended initially with 200ml of WCOB and sonicated for 10 minutes. Then this prepared blend was added with remaining 800ml of WCOB and sonicated for 10 minutes. The procedure was carefully followed to preserve the stability of mixed nano blended WCOB. The prepared fuel was allowed to stand in a container for two weeks. It was observed that the fuel was not having any separation and sedimentation and was found stable for two weeks. These fuels were named as WCOBZC50 and WCOBZC100. These fuels were tested in the engine set up. The readings were measured and analysed. The figure 3 presents the view of ZnO and CuO mixed nano blended WCOB. Figure 4 represents the pictorial view of ultrasonication set up.
3.4 Property testing and study

The physical properties of fuels were tested and the readings were tabulated as shown in table 1. The readings revealed that density and viscosity of nano blended fuels were increasing, it might be due to the addition of nanofluids. It was also observed that cetane number and calorific value of nano blended fuels were increasing, it might be due to energy content in nanofluids.

| Properties     | Diesel | WCOB | WCOBZ50 | WCOBZ100 | WCOBZC50 | WCOBZC100 |
|----------------|--------|------|---------|----------|----------|-----------|
| Density (kg/m³) | 830    | 880  | 881     | 883      | 880.5    | 881       |
| Viscosity@40°C (Cst) | 2.95 | 4.48 | 4.51    | 4.56     | 5.93     | 6.45      |
| Calorific Value (kJ/kg) | 44,500 | 37,195 | 37,512 | 38,213   | 38,187   | 38,358    |
| Cetane Number (or Cetane Index) | 50 | 44 | 45.1    | 45.83    | 45       | 46.5      |

4. Experimental Setup

In this experimental study, diesel engine with full experimental set up was used. The line sketch of engine set up is shown in figure 5. The pictorial view of engine set up is shown in figure 6.

Figure 5. Line sketch of experimental set up
Figure 6. Pictorial view of experimental set up

The varying load was given to the engine using eddy current dynamometer. An exhaust gas measuring device AVL DiGAS 444N Gas analyser was involved to quantify the engine tail pipe harmful gases. A smoke measuring device AVL 437C smoke meter was used. The engine specification is shown in table 2. The standard fuel injection timing of $23^\circ$ before TDC and 200 bar fuel injection pressure was used. Compression ratio was 17.5:1. This engine is a constant speed engine which maintains the speed constant by a governor. Engine was loaded at 4 levels; three sets of emission and performance readings were taken for each test fuel.

Table 2. Specification of Engine

| Description          | Specification                  |
|----------------------|--------------------------------|
| Make & Model         | Kirloskar/240PE                |
| Bore/Stroke          | 87.5mm/110mm                   |
| Rated Power          | 3.5KW @ 1500rpm                |
| Compression Ratio    | 17.5:1                         |
| Swept Volume         | 661CC                          |
| Injection timing     | $23^\circ$bTDC                 |
| General Details      | Four stroke, Single cylinder, CI Engine |
| Loading              | Eddy current Dynamometer       |

5. Results and Discussion

5.1 Brake Thermal Efficiency (BTE)

Engine performance is regularly calculated by a parameter called BTE. The variation of BTE with respect to brake power (BP) for various test fuels is shown in the figure 7. The following observations were recorded. BTE increased proportional to engine load. BTE (in %) at full load for the fuels WCOB,
WCOBZ50, WCOBZ100, WCOBZC50 and WCOBZC100 were observed as 22, 22.83, 24.397, 23.46 and 25.375 respectively. The fuel WCOBZ100 released 23.46% of BTE which is 6.6% higher than neat WCOB. The fuel WCOBZC100 was producing 25.375% of BTE which is 15.34% higher than neat WCOB and 4% higher than WCOBZ100. This improvement in BTE is due to higher SA/V ratio, catalytic effect, rapid evaporation and combustion characteristics of nanofluids. Also, it was observed that WCOBZC100 released higher BTE than WCOBZ100 because ZnO with CuO was having better catalytic effect than ZnO. Similar results were found by Nantha gopal et al. [14].

Figure 7. Variation of BTE with respect to BP

Figure 8. Variation of BSFC with respect to BP

5.2 Brake Specific Fuel Consumption (BSFC)
BSFC is another data to determine the fuel economy of engine. It depends upon density of fuel, atomization, evaporation and fuel air mixing. The variation of BSFC with respect to BP is presented in the figure 8. The following observations were made. BSFC was higher during starting and getting reduced when load increasing. The BSFC (in Kg/kW-hr) at full load for WCOB, WCOBZ50, WCOBZ100, WCOBZC50 and WCOBZC100 are 0.439, 0.42, 0.386, 0.4 and 0.36 respectively. It was noted that WCOBZC100 consumed 0.36 kg/Kw-hr which is 17.99% lesser than neat WCOB and 6% lesser than WCOBZ100. The drop in fuel consumption is due to the positive action of nanofluids such as faster evaporation, oxidation, catalytic reaction and combustion. Similar results were observed by Balamurugan et al. [8]

5.3 Hydrocarbon emission (HC)
HC emission depends on oxidation property of fuel. The variation of HC with respect to BP is presented in the figure 9. The following observations were presented. HC emission increases when engine load increases. HC emission (in ppm) for WCOB, WCOBZ50, WCOBZ100, WCOBZC50 and WCOBZC100 are 63, 60, 56, 58 and 53. WCOBZC100 released 53ppm of HC which is 15.87% lower than WCOB, 5.3% lesser than WCOBZ100. This reduction in HC was due to enhanced combustion and oxidation of WCOBZC100. The nano particles in the fuel droplet enhanced the hydro carbon oxidation process. [11, 13]

5.4 Carbon monoxide emission (CO)
CO emission will be released mainly due to insufficient O₂ and time during oxidation process. The CO variation with respect to BP is presented in the figure 10. From the experimental output, the following
observations were made. CO (in % by volume) at full load for WCOB, WCOBZ50, WCOBZ100, WCOBZC50 and WCOBZC100 are 0.21, 0.2, 0.18, 0.19 and 0.175 respectively. The maximum reduction in CO was found for WCOBZC100 compared to neat WCOB. WCOBZC100 released 0.175% of CO which is 16.6% lesser than WCOB and 2.7% lesser than WCOBZ100. This drop was due to better oxidation of nano blended fuel. [12]

5.5 NOx Emission
NOx formation in diesel engine is due to peak combustion temperature inside the cylinder, oxygen availability and time of reaction. The NOx variation with respect to BP is presented in the figure 11.

The following observations were made here. The values of NOx (in ppm) at peak load for WCOB, WCOBZ50, WCOBZ100, WCONZC50 and WCOBZC100 are 664, 590, 530, 580 and 510 respectively. It was clearly understood that adding nanofluids in WCOB reduced the NOx emission because nanoparticles
enhances the combustion, faster heat transfer and reduced the peak combustion temperature. The NOx value for WCOBZC100 is 510ppm which is 23.19% lesser than neat WCOB and 3.7% lesser than WCOBZ100. By adding ZnO with CuO, heat transfer was improved and in-cylinder combustion temperature was reduced, thereby NOx was reduced. [15]

5.6 Smoke
Smoke emission is mainly due to density, viscosity, atomization and droplet size of fuel. The smoke emission variation with respect to BP is presented in the figure 12. The following observations are made here from the data. Smoke opacity (in %) at peak load for WCOB, WCOBZ50, WCOBZ100, WCOBZC50, WCOBZC100 are 73, 68, 55, 53 and 51 respectively. WCOBZC100 released 51% which is 30% lesser smoke opacity than neat WCOB and also 7.2% lesser than WCOBZ100. This smoke reduction is due to micro explosion of fuel droplet which contains nanoparticles. Nano blended fuel droplet enhanced the catalytic combustion, exploding the carbon particles into smaller size, thereby lessening the smoke opacity. [18]

6. Conclusion
This research was carried out to enhance the engine effectiveness using the biofuel (WCOB). Overall attention was given while preparing the ZnO, ZnO and CuO mixed nanofluids and blending with WCOB. Experiments were conducted using the test fuels carefully. The outcome of the experimental research is listed here.

- The nanofluids prepared by chemical synthesis method was noted as a novel method.
- The stability of the nanofluids blended with WCOB was found good.
- The engine was running smoothly. The engine design parameters have not been changed.
- The BTE and BSFC were greatly improved while using WCOBZC100 compared to WCOBZ100 and neat WCOB because of enhanced catalytic combustion of nano particles in the nanofluid.
- HC and CO emissions were extremely reduced while using WCOBZC100 compared to WCOBZ100 and neat WCOB because of better oxidation property of nanofluids.
- NOx and smoke emissions were also reduced while using WCOBZC100 compared to WCOBZ100 and neat WCOB because of faster heat transfer and micro explosion phenomena of nanofluids.
- These improvements achieved was mainly due to the positive characteristics of nanofluids.
- Finally, it is concluded that WCOB blended with ZnO and further with ZnO and CuO nanofluids could be a future source of fuel for diesel engines.

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