Effect of addition of bio-additive clove oil to ternary fuel blends (Diesel-Biodiesel- Ethanol) on compression ignition engine

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Abstract. The use of biodiesel reduces emissions like hydrocarbon (HC), carbon monoxide (CO), carbon dioxide (CO2), particulate matter (PM); but increases nitrogen oxide emissions. Additives inculcated in diesel and biodiesel has served as one of the means to decrease NOx emissions. An attempt is made to investigate the effect of the addition of ethanol and clove oil, to Pongamia biodiesel, on performance and emission characteristics. Pongamia biodiesel was extracted by transesterification using potassium hydroxide (KOH) as a catalyst. 5% Ethanol and 0.5 and 1 ml clove oil were added to the esters produced. B20 (20% biodiesel + 80% diesel), B20E5 (20% biodiesel + 75% diesel +5% ethanol), B20E5CL0.5 (20% biodiesel +75% diesel+5% ethanol +0.5 ml Clove oil) and B20E5CL1 (20% biodiesel + 75% diesel+5% ethanol +1 ml Clove oil) were analysed. The test was performed on a single-cylinder, four-stroke engine connected to an eddy current type dynamometer for loading. The addition of 1 ml of antioxidant (clove oil) resulted in an increase in brake thermal efficiency by 8.9% and brake specific fuel consumption marginally by 1.53%. At higher loads, the B20E5CL1 blend showed a 13% reduction in NOx emission. B20E5CL1 blend also resulted in a reduction in CO emission at higher loads. Ethanol addition to the biodiesel (B20E5 blend) resulted in the highest brake thermal efficiency but at the cost of NOx emissions. Blends with ethanol and clove oil reported good results at higher loads.

Keywords: Additives; Ethanol; Pongamia Biodiesel; Performance; NOx Emissions

1. Introduction
Fossil fuel depletion and environmental degradation are the two major global problems. Inadequacy in petroleum fuel reserves, because of irresponsible extraction and usage of fossil fuels has led to explore the potential of an alternative fuel, which ought to be sustainable and also renewable [1, 2, 3]. India is a developing nation where more than 95% of transportation depend on petroleum products [4]. Among the alternative fuels available, biodiesel seems reassuring as a favorable renewable alternative to diesel fuel [5, 6].
The 2014 report from the Renewable Energy Policy Network for the 21st century states that, biodiesel and ethanol have been responsible for most of the renewable fuels used in the global transport fleet [7, 8]. Biodiesels are extracted from vegetable oils and animal fats, and also from alcohols of lower sub-atomic weights in the presence of catalysts [9]. As biodiesel reflects almost similar properties as conventional diesel, both can be amalgamated in any proportion to prepare blends [10]. Though biodiesel shows such excellent potential, there are certain shortcomings to its total acknowledgement [11]. The unsaturated fatty methyl esters (FAME) in biodiesel leads to oxidation compared to petroleum [12, 13]. The oxidation process increases viscosity, acidity and peroxide content of biodiesel [14]. Such fuels can corrode the whole fuel injection system and can be responsible for jamming of the moving parts. The rubber parts in the engine are also subjected to hardening due to usage of such fuels [15].

The potential of biodiesel fuel can be enhanced using additives at the same time deceasing difficulties [16]. Research has proven that the impact of additives has led to lower emissions and improved performance of the engine [17]. The additives can be sorted as fuel handling and distribution additives, fuel stability additives, engine protection additives, and combustion additives [18]. Wide range of alcohols find their application in diesel engines as additives. Ethanol is one of the alcohol having a high octane rating and is a promising alternative additive to biodiesel [19].

Corn, starch, sugarcane etc. are some of the sources of ethanol production. Latent heat of vaporisation for ethanol is high, accounting to which it can lower the intake in charge temperature inside the cylinder and significantly improve the volumetric efficiency [20]. Direct injection of ethanol in the cylinder is possible or can also be mixed with other fuels [21]. In one study at lower loads, higher proportion of ethanol with diesel showed a reduction in brake thermal efficiency (BTE) compared to diesel whereas lower proportion of ethanol with diesel had increased the BTE [22]. This can attributed to proper diffusion during combustion. Lower proportions of ethanol with Rice Bran Biodiesel (RBD) were tested over the entire load range [23]. Lean combustion and long ignition delay assists in burning more amount of fuel in premixed combustion zone with ethanol blends, resulting in higher BTE for all blends. In another study, combination of biodiesel with ethanol and methanol were studied [24]. Methanol addition to biodiesel showed a higher brake specific fuel consumption (BSFC) than ethanol addition to biodiesel. As the concentration of both the alcohols increased, BSFC increased as well. In a similar study coconut biodiesel was investigated with addition of lower proportion of ethanol [25]. Higher consumption of fuel was noted for B20E5 by 2.0-2.7%. Additives like n-butanol and diethyl ether have depicted lower BSFC and higher BTE compared to diesel [26, 27].

Blends with antioxidant additives like butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) resulted in an increase in BTE and decrease in BSFC [28]. BHA antioxidant additive exhibits a better stability than BHT for the blended biodiesel [29]. It has been reported that addition of antioxidant to biodiesel reduces CO and HC emissions at the cost of NOx emissions [30, 31]. Reduction of 57% in CO2 emissions was observed with blends of waste cooking oil and bio ethanol from liquefied sago starch (LSS) [32]. At lower as well as higher speeds of engine NOx emission increased with ethanol emulsions in different proportions [33]. Whereas the CO emissions of ethanol and biodiesel emulsions dropped drastically while operating at higher speeds [34]. Studies have revealed that addition of ethanol to the blends of waste frying oil biodiesel and diesel significantly impacts the emissions compared to diesel emissions. The study is also supported by the findings of similar research work by other researchers.

Therefore, the present study is formulated based on the understandings from the literatures on the correlations of the fuel blends to the characteristics of internal combustion engine. A novel ternary approach of fuel blend is adopted in which clove oil and ethanol are used as additives to the blend of diesel and Pongamia methyl esters and was tested to understand the performance and emission characteristics of the engine.
2. Materials and methods

2.1. Engine test
The test was conducted on a computerised 4 stroke-single cylinder engine. The schematic layout of the engine is depicted in figure 1. The engine was coupled to a water cooled eddy current dynamometer with a loading unit. A DAQ system (Data acquisition system) allows interfacing of sensors from the sensors to the computer. Air flow, fuel flow, temperatures and load measurement are interfaced. Fuel flow measurement is facilitated by DP transmitter whereas pressure transducer is used to measure the air flow inducted into the engine. k-type thermocouples are used for measuring the temperature.

Figure 1. Schematic layout of experimental set up

A standard engine running test is conducted before the present study to ensure that the engine is running smoothly and to avoid fluctuations in the data. Previous engine running data with the present data is compared to prepare the engine for the proposed study. The graphical user interface of the software allows easy collection of data from all sensor points. The test started by loading of the blended fuel to the corresponding fuel tank. The fuel consumption is measured for 60 seconds and the data is recorded. The crank angle sensor captures the corresponding angle (degree) during loading and unloading conditions. The flow of cooling water to the engine and calorimeter is measured and controlled by the rotameters. Specifications of the engine is depicted in table 1.

Table 1. Engine specifications

| Manufacturer       | Apex Innovations                  |
|-------------------|-----------------------------------|
| Engine            | Four stroke, 1-Cylinder, Constant Speed |
| Rated Power       | 3.50KW at 1500 rpm                |
| Stroke length     | 110.0 mm                          |
| Bore diameter     | 87.5 mm                           |
| Capacity          | 661.0 cc                          |
| Compression Ratio | 12:1 to 18:1                      |
| Injection Variation | 0-25° BTDC                     |
| Calorimeter       | Type Pipe in Pipe                 |

2.2. Biodiesel production and blending
The production of biodiesel starts with the collection of Pongamia oil and alcohol (methanol) to conduct transesterification reaction. KOH as homogeneous base catalyst is used for the study. The Pongamia oil is heated to about 80°C in the presence of methanol at 1:6 molar ratio and 1% w/w of KOH [35] using a hot plate magnetic stirrer maintained at 500 rpm. The temperature and rpm are constantly...
monitored. An alcohol recovery system is incorporated to allow condensation and reusability of the evaporated alcohol during the transesterification process. The mixture is then cooled down in a separator funnel for about 24 hours to allow proper separation of glycerol from the esters. After separating glycerol, the methyl esters are washed with distilled water to remove any unwanted substances (alcohol, catalyst). The catalyst is separated, washed and dried for reusage. The methyl esters are then oven dried for removing any excess moisture and are then stored properly to avoid contamination.

The preparation of blends starts with unloading the methyl esters in a clean beaker. The esters are continuously stirred, and fuel additives such as ethanol and clove oil, along with diesel are added correspondingly. The corresponding fuel blend prepared are B20 (20% biodiesel with 80% diesel), B20E5 (5% ethanol blend with 20% biodiesel and 75% diesel), B20E5CL0.5 (5% ethanol blend with 20% biodiesel, 75% diesel and 0.5 ml clove oil), B20E5CL1 (5% ethanol blend with 20% biodiesel, 75% diesel and 1 ml clove oil). The physio-chemical properties are shown in Table 2.

Table 1. Physiochemical properties of blends

| Property                           | Diesel | B100 | B20  | B20E5 | B20E5CL 0.5 | B20E5CL 1ml |
|-----------------------------------|--------|------|------|-------|-----------|------------|
| Density at 15 °C (gm/cc)          | 0.867  | 0.883| 0.876| 0.879  | 0.872     | 0.870      |
| Kinematic Viscosity at 40 °C (mm²/s)| 2.813  | 4.731| 3.174| 2.937  | 2.851     | 2.830      |
| Lower heating value (kJ/kg)       | 42882  | 35700| 36624| 37380  | 38640     | 37884      |
| Flash point °C                     | 72     | 174  | 76   | 79     | 80        | 80         |

Emissions were measured using AVL Di 444 gas analyser and AVL 437C smoke meter approved by the Automotive Research Association of India, government of India. The measurement of smoke is fully compatible with Hatridge smoke units and is in compliance with Central Motor Vehicle Rule regulations. The engine was first operated with diesel followed by different blends. Performances were measured by fuel consumption measurement at different loads of the engine. Emission measurement was done after performance measurement to prevent back pressure of the exhaust gas in the pipe which can hinder the performance readings. Each readings were taken thrice and the average of it was taken in the calculations. All the readings were taken on the same day to avoid any deviations in readings due to change in atmospheric condition like temperature and humidity. For better accuracy the gas analyzers were calibrated. Percentage uncertainties of the measured parameters are calculated and tabulated in Table 3.

Table 3. Uncertainties of measured parameters

| Measured Parameters | Range | Accuracy | % Uncertainty |
|---------------------|-------|----------|---------------|
| CO (% vol)          | 0-10% | ±0.03%   | 1.1           |
| HC (ppm)            | 0-20000 | ±10 ppm vol | 1             |
| NO (ppm)            | 0-5000 | ±90 ppm vol | 0.9           |
| HSU                 | 0-100% | ±1%      | 0.9           |
| Brake Power         | ***** | *****   | 0.5           |
| BSFC                | ***** | *****   | 0.3           |
| BTE                 | ***** | *****   | 1.87          |
3. Result and Discussions

3.1. Brake thermal efficiency

The BTE is the measure of effectiveness of fuel conversion to power. From figure 2, it can be observed that BTE ascends with the rising load. B20E5 blend and B20 blend depicted the highest BTE on peak loads. Average increase of BTE compared to diesel fuel was 13.69%, 16.6%, 5.08%, and 8.9% for B20, B20E5, B20E5CL0.5, and B20E5CL1. At higher load minimum BTE was observed for diesel. B20E5 depicts increase in BTE which is in line with Taghizadeh et al., 2016 reports of 3.8% increase in power with addition of 6% of ethanol to biodiesel [36]. In combination with ethanol, blend with clove oil depicted maximum of 8.9% increase in BTE compared to diesel. Clove oil bio-additive accelerates the process of fuel combustion reactivity, as it is largely composed of eugenol as the main component and eugenol has a bulky structure with two oxygen atoms [37, 38].

3.2. Brake specific fuel consumption

In general, properties of fuel such as the viscosity, density, cetane number and heating value influences fuel consumption [39]. Figure 3 depicts variation in BSFC with respect to load. The BSFC diminishes with the increase in the engine load. Blends depicted higher BSFC than the diesel. The overall percentage increase of BSFC for B20, B20E5, B20E5CL0.5, B20E5CL1 compared to diesel fuel was 3.55%, 1.58%, 5.21%, and 1.53%. At higher loads the values of Diesel, B20, B20E5, B20E5CL0.5, and B20E5CL1 are 0.29, 0.29, 0.3, 0.29 and 0.29 kg/KW hr respectively. High specific gravity of blends resulted in higher BSFC of the blends [40]. The high specific gravity affects the flow pattern of the fuel from the fuel injector which hinders fuel flow.

3.3. NO\textsubscript{x} emissions

NO\textsubscript{x} emissions of blends increased with the ascending load. Figure 4 discerns that, at part loads NO\textsubscript{x} emissions increased for B20 and B20E5 blends, compared to diesel. Increase in NO\textsubscript{x} emissions can be ascribed to the inertness of nitrogen towards oxygen at lower temperatures, but as the temperatures in cylinder increases, nitrogen reacts with oxygen and produces NO\textsubscript{x} emissions [41]. B20 blend depicted decrease of 0.9 % of NO\textsubscript{x} emission than diesel. B20E5 showed 2.6% increase in NO\textsubscript{x} emission than diesel which is higher than all the blends. Addition of ethanol reduced the cetane number of fuel and promoted ignition delay. The result is contradicting to Lei Zhu et al., 2011 [42] claim of decrease in NO\textsubscript{x} emissions with 5% ethanol in biodiesel. At full load blend B20E5CL1 depicted significant reduction of 13% in NO\textsubscript{x} emissions. Clove oil’s catalytic activity resulted in improved reactivity of combustion process. Lower combustion temperature due to increased reactivity resulted in less NO\textsubscript{x} emissions [43]. Prompt emissions of NO\textsubscript{x} during biodiesel combustion depends upon reaction between
molecular nitrogen and hydrocarbon-free radicals (CH, C₂, C and CH₂). Radical reactions are intercepted by antioxidants reducing the formation of NOₓ [44].

Figure 4. NOₓ vs BP

Figure 5. HC vs BP

3.4. HC emissions

Figure 5 illustrates the HC emissions of different blends with respect to the variation in brake power. HC emissions decreased till mid loads but then increased at higher loads. The values of HC emissions at full load, for diesel, B20, B20E5, B20E5CL0.5, B20E5CL1 are 22 ppm, 12 ppm, 21 ppm, 23 ppm and 19 ppm. B20 blend showed 45.5% reduction in HC emission in comparison to diesel. The flame speed increases during mixing of the air and fuel inside the combustion chamber due to the O₂ content present in the B20. Increased O₂ content improved oxidation of unburnt HC thus reducing the HC emissions [45]. B20E5 depicted 4.5% decrease in HC emissions. The addition of antioxidants exhibited a slight increase in HC emissions, which may be attributed to the reduction in oxidative free radical formation [46]. B20E5CL0.5 increased HC emissions by 4.3% compared with diesel. However, B20E5CL1 blend, showed only 5.5% decrease in HC emissions compared to diesel.

3.5. CO emissions

Figure 6. CO vs BP

Figure 7. Smoke opacity vs BP

From figure 6, it is observed that CO emissions descends with the increase in torque power. CO is result of incomplete combustion. Operation of engine at maximum brake power facilitates fuel air mixture to attain a maximum temperature and that leads to complete combustion. B20 showed a reduction of 5.2% in CO emissions compared to diesel. Addition of clove oil to biodiesel and ethanol blend proved to very
significant in reducing the CO emissions. B20E5CL1 blend showed 50% significant reduction in the CO emission at peak load. This decrease in CO emissions of B20E5CL1 blend can be attributed to the presence of OH radicals in antioxidant (clove oil) which lead to a reduction of oxidation of carbon monoxide molecules [47, 48]. But at part loads B20E5CL1 and B20E5CL0.5 showed increased CO emissions than diesel and B20 blends.

3.6. Smoke opacity
Figure 7 depicts increase in smoke emission as the load increases. Air fuel ratio has significant effect on smoke emissions. Increment in load reduces air fuel ratio and that at higher loads the amount of fuel injected increases, which results in increase in the smoke emissions. However, B20 and B20E5 showed 5% and 2.4% less smoke emission than diesel. B20E5CL0.5 and B20E5CL1 blend showed 27.19% and 28.39% increase in smoke emissions than diesel. Oxygenated fuel resulted in increased smoke.

4. Conclusion
Performance and emissions of blends with two additives ethanol and clove oil were studied. Test results discerned that addition of bio additives like clove oil improves performances and emissions of the engine.

Following are the main conclusions.
- Addition of only ethanol to biodiesel (B20E5 blend) resulted in highest BTE and lowest smoke emission. However, the NOx emissions were at peak level.
- No significant variation in BSFC was observed at full loads for all the blends.
- B20E5CL1 reported 8.9% increase in the BTE than diesel and a marginal increase of 1.53% of brake specific fuel consumption than diesel. The blend also showed significant reductions in exhaust emissions at full load. Overall only 5.5% of decrease in HC emissions were reported for B20E5CL1 blend. It showed significant reduction of NOx emission by 13% at full load.
- Addition of higher concentration of clove oil to biodiesel and ethanol blend gave optimum results. Clove oil has the potential as bio-additive to biodiesels as alternative fuel.

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