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# Effect of Oxygenate on Emission and Performance Parameters of a CI Engine Fuelled with Blends of Diesel-Algal Biodiesel

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**Abstract-** In this present study, the bio-oil is derived from *Stoechospermum marginatum*, brown seaweed through soxhlet oil extraction method. *n*-hexane is used as a solvent for rupturing the cell wall membrane and extracting the bio-oil. Single-stage base catalysed transesterification method is adopted considering the presence of low free-fatty acid contents.-Mineral diesel and diesel-algal biodiesel blend are the primary test fuels. Di-ethyl ether is used as oxygenate to the diesel- algal biodiesel blend to enhance the performance and emission characteristics. The physio-chemical properties of oxygenated fuel blends showed a significant decrease in density and kinematic viscosity along with a notable increase in the Cetane number. The experimental investigation revealed that the addition of di-ethyl ether to diesel-algal biodiesel blend enhanced the brake thermal efficiency significantly along with reduction in brake specific fuel consumption. The emission parameters of oxygenated fuel blends like carbon monoxide and unburned hydrocarbon notably decreased along with a marginal increase in oxides of nitrogen emission.

**Keywords** Algal biodiesel, DEE, transesterification, performance emission.

## 1. Introduction

The petroleum reserves decreasing trends are seen drastically due to increased demand of fuel by industrial sectors and domestic consumption. The biofuel acts as an effective substitute to the petroleum fuel, reducing the environmental pollution by lesser emissions [1-2]. Biodiesel has experienced wide attention as a substitution for diesel because it is biodegradable, harmless and crucially reduce the exhaust emissions also the general life cycle emission of carbon dioxide ($CO_2$) from the engine. Many surveys showed that using biodiesel in the diesel engine can reduce the hydrocarbon (HC), carbon monoxide (CO) and particulate matter (PM) emissions, but increases the nitrogen oxide ($NO_x$) emission [3]. Many vegetable plants like soybeans, neem, cotton seed, Jatropha, karanja, rapeseed etc, were found suitable for the production of biodiesel. The utilization of biodiesel significantly minimizes the emission and improved the performance of engine. The organic biodiesel stockpile such as oil crops and waste cooking oil are not adequate to fulfil the global transportation fuel demand. Therefore, need to consider different prospective source for alternative fuel is necessary. Macro algae are interpreted as a promising alternative fuel for IC engines. Many researchers have investigated on the feasibility towards production of biodiesel from macro algae. The alga proliferates by photosynthesis using sunlight and nutrients. Algae have the potential to fix the atmospheric carbon dioxide and can grow the culture elaborately in an infertile land [4-9, 18].

Many researchers have investigated the performance and emission characteristics of diesel, biodiesel and its oxygenate blends among which a few of them are reported here. Seaweed , a macro algae is mostly found in marine environment. Its lipid content present inside is less but carbohydrates are more in which both can be used for biodiesel production. The algae are an excellent source for high quality bio-energy production with reduced environmental pollution hazards [10]. Two step fermentation processes gave an optimal yield in the industrial production of algal bio-fuel. [11].

Hariram *et al*. studied the feasibility of extracting biodiesel from *Spirulina maxima*, a green algae and analyzed the effect of its combustion, performance and emission parameters in a DI CI engine. It was noted that an appreciable change occurred with the algal biodiesel blend on brake thermal efficiency with the significant reduction in $NO_x$ emission [4]. Marine macro algae *Padina Tetrastromatica* was considered as a bio-fuel. The biomass was dried and this dried biomass was processed to extract the lipid content present by first-order kinetics method. Biodiesel was produced through esterification and trans-esterification process from this lipid content. The algae bio-fuel was tested for its fuel properties and it had 883 kg/m$^3$ of density, 4.92 mm$^2$/s of viscosity, Cetane number 57.50 and Calorific value of 38.5 MJ/kg. This showed that *Padina Tetrastromatica*, a macro alga, was a potential source for biodiesel production [12]. Another research work was carried out on marine macro algae *Enteromorpha compressa* for the production of biodiesel through two step process namely acid esterification and base trans-esterification. Highest biodiesel yield resulted through base transesterification method where the parameters were kept as 9:1 methanol to oil ratio, 600 rpm agitation speed and 60$^o$C temperature for 70 minute reaction time. The biodiesel yield was 90.60% and its fuel properties were within the ASTM limits [13].

Biodiesel extraction from macro algae, *Ulva Lactuca* was made through solvent extraction method based on the kinetic study for optimal biodiesel production. In order to enhance the oil yield, the following parameters were followed for extraction: moisture content (2 to 6%), particle size (0.359 to 0.104 mm), stirrer speed (200 to 600 rpm), extraction temperature (35 to 65$^0$C), extraction time (20 to160 min) and solvent-to-solid ratio (3:1 to 7:1). The GCMS test revealed the presence of fatty acid composition which includes Lauric acid, Tridecanoic acid , Myristic acid, Pentadecanoic acid, Palmitic acid, Heptadecanoic acid, Streacic acid, Nonadecanoic acid, Arachidic acid, Heneicosanoic acid, Behinic acid, Oleic acid, Linoleic acid and Linolenic acid. These results confirmed that *Ulva Lactuca* was one of the good sources for algal-biodiesel production [14]. The possibilities of off-shore macro algae cultivation and its conversion into liquid biofuels and bio-ethanol fuel production were found to be feasible study [15]. Rocio Maceiras *et al.* reported that under controlled conditions the yield of lipid content varied from 1.60 to 11.5% [16]. Three marine macro algae namely, *Jania rubens, Ulva linza and Padina pavonica* were evaluated for its lipid and fatty acid profiles. Lipid content was found to be varying between 1.56 to 4.14%. It was reported that *Padina pavonica* had the highest total fatty acid content and was found suitable for oil extraction [17]. Acceptable fuel properties like cold filter plugging point, kinematic viscosity and oxidation stability were found to be within limits and the GCMS test showed the presence of prime compounds namely, methyl oleate (65.2 wt%) and methyl linoleate (18.5 t%). The blending ratio recommended was up to 20% with mineral diesel [19]. Few other researchers have experimentally studied the effect of biodiesel in CI engine and obtained similar results [20-26].

*Stoechospermum marginatum* macro algae are found abundantly in the southern peninsular India and its biodiesel yield was around 72.19% which is found to be economically viable to partially replace the use of mineral diesel for commercial activities. This study is focused on using this *Stoechospermum marginatum* macro algae based biodiesel as a fuel and its effect on the performance and emission characteristics of direct injection CI engine. DEE an oxygenate, is used an additive to the diesel-algal biodiesel fuel blend to enhance the performance and emission characteristics and it is compared with mineral diesel and diesel-algal biodiesel fuel blend. The experimental study is carried out on a single cylinder, four stroke diesel engine coupled with an eddy current dynamometer. The blended compositions used in this study are D100, D80AB20, D70AB20DEE10, and D60AB20DEE20.

## 2. Materials and Methods

### *2.1. Bio-oil extraction and Transesterification*

The macro algae, *Stoechospermum Marginatum* used in this study is harvested from the Gulf of Mannar, Tamil Nadu, India. The chemicals (i.e., *n*-hexane and methanol) used for processing the extraction of oil content is purchased from Organic chemicals, SANMAR Pvt, Ltd., Tamil Nadu, India. Bio-oil is extracted by soxhlet extraction method which is a multiple step process. In the primary step, 12 grams of processed seaweed are placed in the thimble. 540 ml of n-hexane is placed in the round bottomed flask of the extractor. Upon elevating the temperature upto 72$^o$C, the vaporized *n*-hexane reacts with the dry processed algae in the thimble through the condensation arm causing cell wall membrane to rupture resulting in diluting the lipid and settling down at the bottom layer of the flask. This cycle is repeated several times for enhanced lipid extraction which resulted in 3.20 ml of bio-oil. By this process, a total of 273 ml algal oil is obtained with an efficiency of 32%.

Base catalysed transesterification is adopted as the free fatty acid content is found to be lower than 2.10% through titration method. Using an Erlenmeyer flask, the sodium methoxide solution is prepared by mixing NaOH and methanol at the proportion of 0.50 grams and 450 ml respectively. After complete mixing, the extracted algal oil is mixed at the molar ratio of 8:1. The reaction environment is maintained at 400 rpm agitation speed, 65$^o$C reaction temperature and 120 min reaction duration. This process yielded 197 ml of algal biodiesel at an esterification efficiency of 72.16%.

### *2.2. Fatty acid Composition*

GC/MS test is conducted using JEOL AccuTOF GCV system on the methyl esters of algal biodiesel. The identified fatty acid methyl esters are namely, Hexacosanoic acid methyl ester, Docosenoic acid methyl ester, Hexadecanoic acid methyl ester, Tetradecanoic acid methyl ester, Heptadecanoic acid methyl ester, Eicosenoic acid methyl ester, Octadecenoic acid methyl ester, Tricosanoic acid methyl ester and Heneicosanoic acid methyl ester. The presence of these fatty acid methyl esters are again confirmed by FTIR analysis using 3000 Hyperion Microscope with Vertex 80 FTIR System.

### *2.3. Test Fuel Formulation*

The primary test fuels are mineral diesel (D100) and diesel-algal biodiesel blend (D80AB20). As 20% of *Stoechospermum Marginatum* algal methyl ester and 80% of mineral diesel is the most proven blending ratio [19], the similar blending ratio is used to prepare the test fuel in this present study. Further, di-ethyl ether oxygenate of 10% (D70ABD20DEE10) and 20% (D60ABD20DEE20) is added to the diesel-algal biodiesel blends by means of ultra-sonication with agitation speed of 3000 rpm and same concentration level of diesel is reduced by maintaining the mass balance. Processed *Stoechospermum Marginatum*, its crude and algal biodiesel along with oxygenate blends are shown in Figure 1.

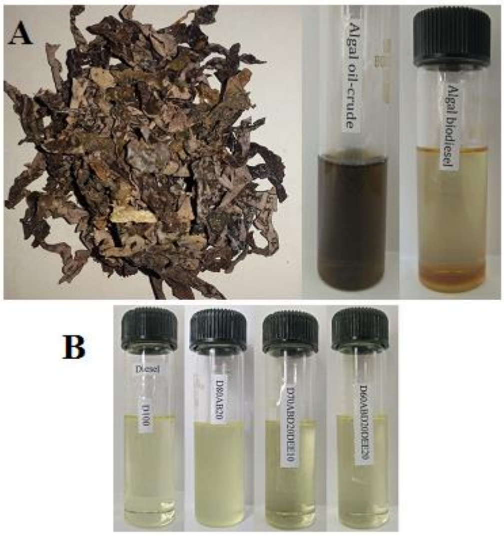


**Fig 1**. Crude and Algal biodiesel along with oxygenate blends

### *2.4. Physio-Chemical Properties*

The physio-chemical properties of diesel, algal biodiesel blends and oxygenated blends are given in Table 1. The properties are analyzed using ASTM D975 and ASTM 6751 standards and are found to be within the limits. The density of algal biodiesel is found to be 869 kg/m$^3$ which are 2.70% higher than diesel. D80AB20 showed a slight increase in density upto 853.8 kg/m$^3$. Addition of oxygenate significantly reduced the density by up to 3.10%. The kinematic viscosity of algal biodiesel is determined as 4.19 mm$^2$/s at 40ºC. D70AB20DEE10 and D60AB20DEE20 represented lower kinematic viscosity of 2.681 mm$^2$/s and 2.444 mm$^2$/s respectively. The gross calorific value exhibited a gradual decreasing trend with the addition of oxygenate. The calorific value of algal biodiesel is noticed as 39152 kJ/kg whereas, oxygenated blends showcased value of 42579.6 kJ/kg and 41488 kJ/kg for D70AB20DEE10 and D60AB20DEE20 fuel blends respectively. The Cetane number of biodiesel and oxygenated blends showed an increasing trend. Flash point being an important aspect for fuel combustion showed a decreasing trend as given in Table 1.

### *2.5. Experimental Setup*

The performance and emission study are carried out in a direct injection variable compression ratio engine. The test analysis consists of a single cylinder, four stroke, constant speed water cooled diesel engine. The representational arrangement of the experimental setup is shown in Figure 2. The engine is incorporated with a water cooled eddy current dynamometer controller. The power control panel contains fuel tank, manometer, fuel measuring element and transmitter. The engine runs at a constant speed of 1500 rpm and test is done under stable state of the engine. The engine technical features are represented in Table 2. The engine manufactured by Kirloskar with 110mm stroke length and 87.5mm bore diameter. Engine rated power is 3.5 KW at rated speed of 1500 rpm and the compression ratio of 17.5:1. The temperature of exhaust is measured by a thermocouple. The exhaust emissions like CO, HC, $CO_2$, $NO_x$ and $O_2$ are evaluated using AVL 444 N exhaust gas analyser. The volume of smoke is measured by using Bosch smoke meter.

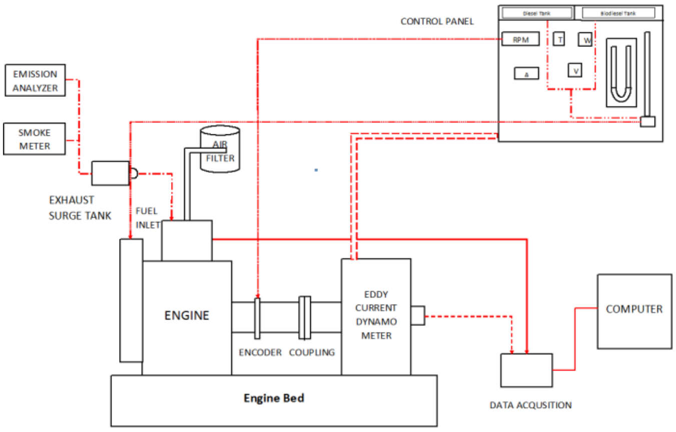


**Fig 2**. Schematic of Experimental Setup

## 3. Result and Discussions

The engine performance features such as brake power, specific fuel consumption, brake thermal efficiency and exhaust emissions like carbon monoxide, hydrocarbon and nitrogen oxides are evaluated from the experimental data.

Brake Thermal Efficiency (BTE) is the ratio of brake power of engine to fuel power. The fluctuation of BTE with brake power for D100, D80AB20, D70AB20DEE10 and D60AB20DEE20 are shown in Figure 3.

**Table 1.** Comparison of physio-chemical properties-Algal biodiesel and their oxygenated blends

| S.No | Properties | D100 | ABD | D80 AB20 | D70 AB20 DEE10 | D60 AB20 DEE20 |
|---|---|---|---|---|---|---|
| 1 | Density @15ºC (kg/m$^3$) | 850 | 869 | 853.8 | 840.1 | 826.4 |
| 2 | Kinematic Viscosity @ 40ºC (mm$^2$/s) | 2.6 | 4.19 | 2.918 | 2.681 | 2.444 |
| 3 | Calorific Value (kJ/kg) | 44800 | 39152 | 43670.4 | 42579.6 | 41488.8 |
| 4 | Cetane Number | 46 | 41 | 45 | 52.9 | 57 |
| 5 | Flash point (ºC) | 64 | 72 | 65.6 | 54.7 | 50.3 |

**Table 2.** Details of Kirloskar test engine

| | |
|---|---|
| Engine | Kirloskar, Model TV1, single cylinder, water cooled, four stroke diesel engine |
| Bore and Stroke length | 110 mm and 87.5 mm |
| Cubic capacity | 661 cc |
| Compression ratio | 17.5 : 1 |
| Rated power | 5.2 kW |
| Rated speed | 1500 rpm |
| Dynamometer | Eddy current, water cooled |
| Air Box | M S fabricated with orifice meter and manometer |
| Fuel tank | Capacity 15lit with glass fuel metering column |
| Temperature sensor | Type RTD, PT100 and, Type K thermocouple |
| Load indicator | Digital, range 0-50 Kg, supply 230 V AC |
| Load sensor | Load cell, type strain gauge, range 0-50 kg |
| Rotameter | Engine cooling 40-400 LPH; Calorimeter 25-250 LPH |

The thermal efficiency achieved is 39.45%, 36.48% for Diesel and D80AB20, while 37.19% and 38.71% is achieved for D70AB20DEE10 and D60AB20DEE20 at full load condition respectively. The decrease of BTE for D70AB20DEE10 and D60AB20DEE20 is due to superior vaporization of DEE along with homogeneous mixing with air. The lower BTE of D80AB20 is due to poor surface tension among algae oil and mineral diesel which leads to inferior atomization of fuel thereby diminishing the performance of D80AB20. Oxygenated blends of 10% and 20% had an increased BTE trend compared to diesel-biodiesel blend which may be due to the availability of surplus oxygen content present leading to a better combustion.

Brake Specific Fuel Consumption (BSFC) is the efficiency of the fuel of an engine regards to power. Figure 4 represents the deviation of BSFC, with brake power for D100, D80AB20, D70AB20DEE10 and D60AB20DEE20. The data acquired for diesel and D80AB20 are 1.28 kg/KWhr and 1.45 kg/KWhr, whereas for D70AB20DEE10 and D60AB20DEE20 these are 1.39 kg/KWhr and 1.34 kg/KWhr respectively at full load. Due to high viscosity and density of diesel-algal biodiesel blend the mixture formation genesis is affected deliberately which leads to significant increase in BSFC of D80AB20. The assimilation of DEE boosts the combustion of biodiesel which lowers the BSFC of D70AB20DEE10 and D60AB20DEE20 on comparison with D100 and D80AB20. The reduction in BSFC on addition of di-ethyl ether oxygenate may be due to higher miscibility thereby providing better atomization leading to enhanced engine performance. This phenomenon brings the BSFC value closer to mineral diesel.

Carbon Monoxide (CO) is generated by improper combustion of hydrocarbons present in the fuel. The variation of CO emissions with brake power for D100, D80AB20, D70AB20DEE10 and D60AB20DEE20 is shown in Figure 5. The values of CO observed for D100 is 0.062%, whereas these are 0.069%, 0.067% and 0.059% for D80AB20, D70AB20DEE10 and D60AB20DEE20 at full load condition respectively. Higher density and viscosity leads to improper oxidation of fuel ensuring incomplete combustion which raises the CO concentration of D80AB20. Increase in CO emissions of D70AB20DEE10 is due to poor oxidation and atomization of fuel which leads to abnormal combustion. Higher CO formation may be also due to excess air factor less than 1 and poor air-fuel mixture concentration. With D60AB20DEE20 blend, better combustion occurs due to existence of elevated oxygen content present in DEE which gives improved latent heat of evaporation. This leads to better fuel mixing with air thereby forming a consistent mixture resulting in lower CO formations. Incomplete combustion is observed for diesel-algal biodiesel blend due to the viscous nature of biodiesel, which led to releasing of more CO. But, CO formation got reduced as oxygenate is added leading to better miscibility and increased atomization providing complete combustion.

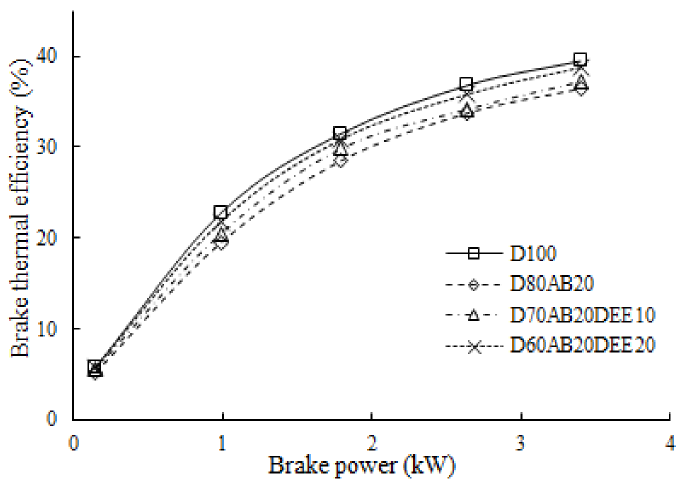


**Fig 3.** Variation of BTE

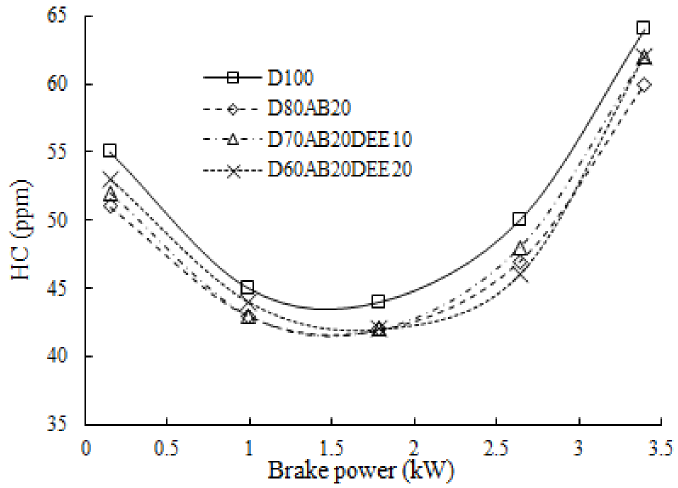


**Fig 6.** Variation of HC

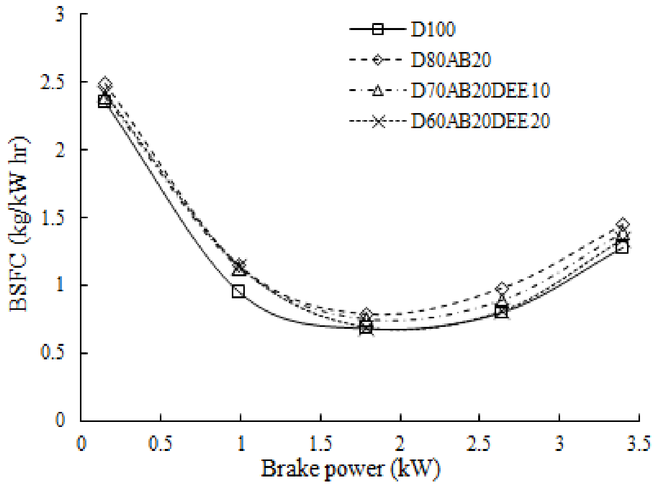


**Fig 4**. Variation of BSFC

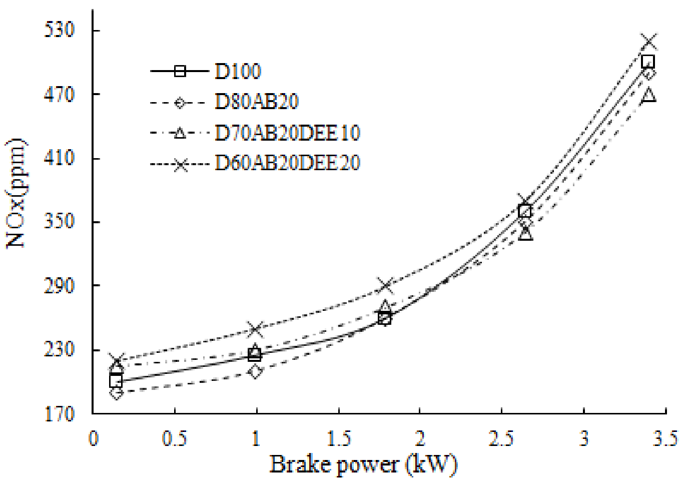


**Fig 7.** Variation of $NO_x$

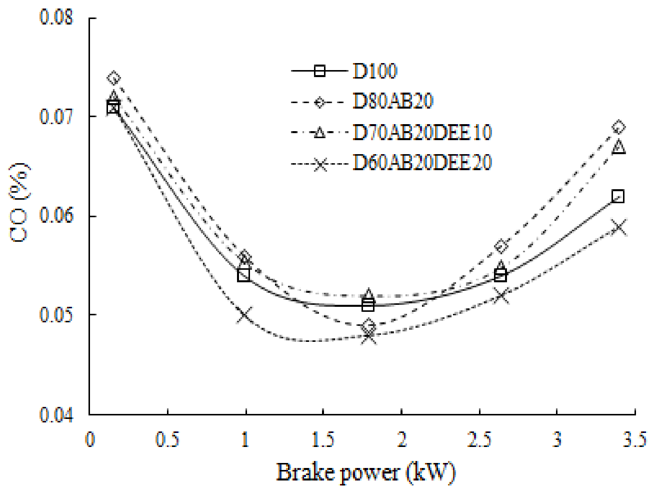


**Fig 5.** Variation of CO

Hydrocarbon (HC) emission is mainly due to low temperature reactions and deposition of carbon particles in the crevice volume of the cylinder walls. The variations of HC emissions with brake power for D100, D80AB20, D70AB20DEE10 and D60AB20DEE20 is shown in Figure 6. HC emissions is found to be 64 ppm and 60 ppm for D100 and D80AB20 respectively whereas, oxygenated algal biodiesel blends exhibited 62 ppm at full load condition. The addition of DEE in the fuel makes a uniform fuel composition with air thereby making an enhanced evaporation of DEE at increased cylinder temperature. The frequency of ignition booms formed by the ignition booster (DEE) leads to a better combustion and lessened HC emission compared with diesel. It is clear from the plot that oxygenated algal biodiesel blends reduced the HC emissions due to the better combustion.

Nitrogen Oxides ($NO_x$) is produced by reaction between nitrogen and oxygen at elevated temperature during the combustion process. The variation of nitrogen oxides emissions with brake power for D100, D80AB20, D70AB20DEE10 and D60AB20DEE20 are illustrated in

Figure 7. At full load condition, 500 ppm and 490 ppm of $NO_x$ are reported for D100 and D80AB20, whereas, D70AB20DEE10 and D60AB20DEE20 showed 470 ppm and 520 ppm respectively. Due to difference in surface tension between mineral diesel and D80AB20, the combustion temperature is considerably reduced resulting in lower $NO_x$ value in comparison with mineral diesel. As additional oxygen content is supplemented through DEE by 20%, the combustion phenomenon is enhanced thereby leading better combustion. This results in elevated combustion temperature causing disassociation of oxygen and nitrogen atoms. These mono atomic atoms combines with each other following the Zeldovich mechanism and results in the formation of (NO, $NO_2$ and $N_2O$) $NO_x$.

## 4. Conclusion

The extraction of biofuel from *Stoechospermum Marginatum* and its effect on the engine performance and emission parameters is focused in this present study. Lipid extraction through Soxhlet extraction process in the presence of *n*-hexane at 72ºC yielded 32% of bio oil. Single stage base catalyzed transesterification at the molar ratio of 8:1 and 65ºC reaction temperature yielded 197 ml of algal biodiesel at an efficiency of 72.16%. Performance and emission characteristic are evaluated for the blends of Diesel-algal biodiesel. BTE showed a decrease of 7.50% with respect to mineral diesel while BSFC is higher by up to 1.45 kg/kWhr. CO emissions are increased up to 0.069% whereas, decrease in HC and $NO_x$ emissions upto 60 ppm and 490 ppm respectively is noticed.

The addition of DEE by 10% and 20% to diesel-algal biodiesel blends marginally decreased the BTE to 37.19% and 38.71% on comparison with diesel. On the other hand, BSFC value is increased to 1.39 kg/kWhr and 1.34 kg/kWhr at full load condition compared with D100. CO emissions are found to be 0.067% for D70AB20DEE10 which is higher than diesel fuel, whereas, the value is 0.059% for D60AB20DEE20 which is lower than diesel-algal biodiesel blend. Both D70AB20DEE10 and D60AB20DEE20 showed a decreasing trend of HC emission upto 62 ppm. The addition of DEE at 10% fuel blend decreased $NO_x$ emission up to 470 ppm but D60AB20DEE20 showed a higher emission of $NO_x$ by up to 520 ppm.

Based on this study, it can be concluded that the CI engine can be able to operate without any further modification using diesel-algal biodiesel blends. Addition of DEE to diesel-algal biodiesel blends with a variation in diesel concentration further enhanced the performance and emission characteristics.

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