

FT-IR Determination of Free Fatty Acids in *Sardinella longiceps* Fish Oil and its Performance and Emission characteristics in DI Diesel Engine

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Abstract: In this investigation the extraction of oil from *Sardinella longiceps* fish were performed by using Bligh and Dyer method. To know the functional groups of the extracted fish oil FT-IR analysis was performed using IR spectrophotometer (Shimadzu 8400S) system. The physio-chemical properties of extracted fish oil *Sardinella longiceps* was characterized and the results were tabulated. The results revealed the presence of alcohols and phenols, carboxylic acids, alkanes, boron compounds, esters, saturated aliphatic, aromatics, halogen compounds and phosphorus compounds in the fish oil. The performance and emission characteristics of the test engine were investigated at different loads with Sardine Fish oil – Diesel blends of R20, R40, R60 and diesel. The effects of the Sardine Fish Oil-Diesel Blended fuels on the engine brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), exhaust gas temperature (EGT) and exhaust emissions were investigated. Experimental results reveal that there is an increase in BSFC and decrease in BTE when the fish oil content in the test fuel is increased. Emission analysis reveals that there is an increase in NO_x emission for all SFO Diesel blends when compared to diesel, whereas there is a significant reduction in CO₂, and Smoke emissions for SFO blends than diesel. From the engine test results it can be concluded that 20% of Sardine Fish Oil can be substituted for diesel without any engine modification as a fuel.

Keywords: Sardine Fish oil, FT-IR, Performance, Emissions.

Introduction

The global energy consumption rate of fossil fuel is increasing with increase in the rate of industrialization and motorization. Oil the product of the burial and transformation of biomass over the last 200 million years has historically had no equal as an energy source for its intrinsic qualities of extractability, transportability, versatility, and cost. But the total amount of oil underground is finite, and, therefore, production will one day reach a peak and then begin to decline. Such a peak may be involuntary if supply is unable to keep up with growing demand. Global energy demand will grow by more than one-third over the period to 2035 with China, India and the Middle East accounting for 60% of the increase^{1,2}. The amount of oil remaining in the ground is highly uncertain and some of the oil remaining in the ground can be accessed only by using complex and costly technologies that present greater environmental challenges than the technologies used for most of the oil produced to date.^{3,4} Other important sources of uncertainty about future oil production are potentially unfavorable political and investment conditions in countries where oil is located.

India has a coastline of 8118 kms having an Exclusive Economic Zone (EEZ) of 2.02 million sq.kms. The estimated sustainable resource potential in the marine sector is 3.94 million tonnes of fish per annum. The

estimated catch of sardine fish in India is about 1.15 million tonnes per annum⁵. The low cost, low value sardine fish are commonly used to produce fish meal which is used as food for livestock and as fertilizer. The byproduct crude oil which is extracted during the process may be used as a cheap, reliable alternate source of energy. The objective of the present investigation is to use the low cost, low value sardine fish as the feedstock. Bligh and Dyer method was used to extract sardine oil from sardine fish. The fatty acids present in the sardine fish oil was evaluated using FT-IR method. The fuel properties such as viscosity, density, calorific value were determined and are compared with standard diesel fuel. The sardine fish oil and its blends with diesel were used as the fuel to evaluate the performance and emission characteristics.

Materials and Methods

Collection of Sardine Fish

Sardinella longiceps were randomly collected from the landing centers of Kanyakumari District, Southwest coast of India. The collected sardine fish were cleaned, weighed and chilled in ice and packed in air-tight containers prior to arrival in the laboratory. They were visually inspected for its existence in good condition and for trace of spoilage. In the laboratory, the ice cubes were discarded and all the unwanted materials such as blood vessels and visceral materials were removed, cleaned well and stored at -60 °C in a deep freezer until further use.

Extraction of oil from Sardine Fish by Bligh and Dyer Method

100gm of sardine fish was weighed in 2 litre round bottom flask. To this 10ml of distilled water was added and the mixture was homogenized for two minutes whilst being cooled in ice. Then 200ml of chloroform was added and homogenized for one minute followed by the addition of 200ml of distilled water and finally homogenized for 30 seconds. The mixture was then centrifuged at 2000 rpm for 20 minutes. The chloroform fraction was dried with anhydrous sodium sulphate, filtered and the chloroform was evaporated using rotary evaporator. The remaining oil fraction was shaken to remove the chloroform completely. After the extraction was over, the oil was recovered by using a rotary evaporator. The extracted oil was dried, weighed, transferred into a sealed container, and was kept in a refrigerator at (-20°C) for further study and assessment. The percentage of oil yield was calculated as follows and is shown in Equation 1

$$\text{Yield of Oil (\%)} = \frac{\text{Weight of the extracted oil (g)}}{\text{Weight of fish (g)}} \times 100 \quad (1)$$

The Mean molecular weight of extracted sardine fish oil was calculated by using the following expression as shown in Equation 2

$$\text{Mean Molecular weight} = \frac{56.1 \times 1000 \times 3}{(SV - AV)} \quad (2)$$

Where SV is the saponification value and AV is the acid value. Some important chemical and physical properties of the extracted fish oil were also analyzed including density, viscosity, flash point, acid value, saponification value, iodine number, higher heating value and cetane number.

FT-IR Analysis

To know the functional groups present in the extracted sardine fish oil, the FT-IR analysis analysis was performed. For FTIR spectrophotometer analysis, the extract was centrifuged at 3000 rpm for 10 min and then filtered through Whatmann No. 1 filter paper by using high pressure vacuum pump. The sample is diluted to 1:10 with the same solvent. FT-IR analysis was performed using IR spectrophotometer (Shimadzu 8400S) system which was used to detect the characteristic peaks and their functional groups. The peak values of the FTIR were recorded. Each and every analysis was repeated twice to confirm the spectrum.

Engine Test

The performance of test fuels were investigated in a single cylinder four stroke, water cooled diesel engine. The test engine is coupled with an eddy current dynamometer. The tests were performed with varying

loads while engine speed was kept constant. An AVL flue gas analyzer is used to measure concentration of gaseous emissions NO_x, unburnt hydrocarbon (UBHC) and CO₂ in the engine exhaust. A smoke meter is used to measure the smoke opacity in the engine exhaust. A series of experiments were conducted using Sardine Fish Oil-Diesel blends as fuel under varying load conditions at the rated speed and loads. In each experiments engine parameters related to thermal performance and emission characteristics were measured.

Results and Discussion

Characterization of Sardine Fish Oil

The physiochemical properties of extracted fish oil from sardine fish are characterized and the same is given in Table 1. The results indicate that the viscosity of sardine fish oil is 22.9 Cst, and density is 930kg/m³.

Table 1 Physico Chemical Properties of Sardine Fish oil

Property	Sardine fish
Density (kg/m ³)	930
Kinematic Viscosity@40°C i n Cst	22.9
Flash Point (°C)	207
Fire Point (°C)	219
Cloud Point (°C)	+8
Pour Point (°C)	+2
Gross Calorific Value (MJ/kg)	41.823
Acid Value (mgKOH/goil)	1.6
Saponification Value	191.3
Iodine Value (mgKOH/goil)	69.7
Molecular Weight	888

Results of FT-IR and GC-MS Analysis

The FTIR spectrum was used to identify the functional group of the active components based on the peak value in the region of infrared radiation. The results of FTIR peak values and functional groups were represented in Table 2. The FTIR spectrum profile was illustrated in the Figure 1. The aqueous extract of *sardinellalongiceps* was passed into the FTIR and the functional groups of the components were separated based on its peak ratio. The results of FTIR analysis confirmed the presence of alcohols, phenols, carboxylic acids, alkanes, boron compounds, esters, saturated aliphatic, aromatics, halogen compounds and phosphorus compounds in the fish oil.

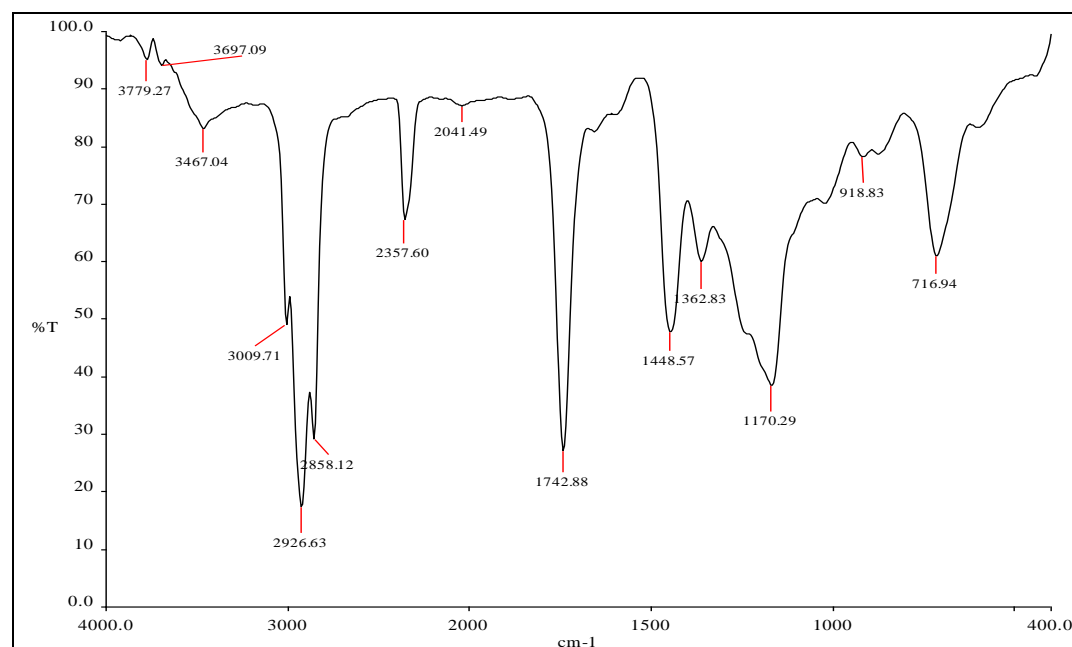


Figure 1: FT-IR Spectrum of Sardine Fish Oil

Table 2 FT-IR Spectroscopic Profile of Sardine Fish Oil

SI. NO	Peak values	Bond Stretching	Functional Groups
1.	3779.27	-	-
2.	3697.09	-	-
3.	3467.04	O-H str.	Alcohols and Phenols
4.	3009.71	O-H str.	Carboxylic acids
5.	2926.63	C-H str.	Alkanes
6.	2858.12	C-H str.	Alkanes
7.	2857.60	C-H str.	Alkanes
8.	2041.49	B-H str.	Boron compounds
9.	1742.88	C=O str.	Esters, saturated aliphatic
10.	1448.57	C-C str.	Aromatics
11.	1362.83	C-F str.	Halogen compounds
12.	1170.29	P=O str.	Phosphorus compounds
13.	918.83	O-H	Carboxylic acids
14.	716.94	C-H'oop'	Aromatics

Performance and Emission Characteristics of DI Engine Fuelled with SFO and its blends with

In order to evaluate the feasibility of *sardinellalongiceps* fish oil, the performance and emission characteristics of a CI engine operating on SFO and its blends with diesel are investigated and the results are compared with those of diesel. The blends selected for the experimental study are R20, R40 and R60. Table 3 gives the properties of different test fuels. The calorific value decreases and density increases with the increase in the content of SFO in the test fuels.

Table 3. Properties of Sardine Fish Oil and its blends with diesel

Tested fuel	Calorific value (kJ/kg)	Density
Diesel	44300	830
R20	44059	852
R30	43687	863.7
R40	43343	870.6
R50	42975	882.1

Brake Thermal Efficiency (BTE)

The variations in brake thermal efficiency with brake power for different sardine fish oil–diesel blends and diesel is shown in Figure 2. The brake thermal efficiency increases with increase in load for all the test fuels. The brake thermal efficiency is slightly lower for all diesel-sardine fish oil blends compared to diesel at all brake power. At low and high loads the efficiencies of SFO-diesel blends observed to be significantly low to that of diesel. The brake thermal efficiency of the engine is decreased by 4.01%, 8.87% and 11.30% for R20, R40 and R60 blends respectively in comparison to diesel fuel. It is observed that the blend which is containing 80% of diesel has the highest brake thermal efficiency of 30.186% whereas for diesel it is 31.42% at full load conditions.

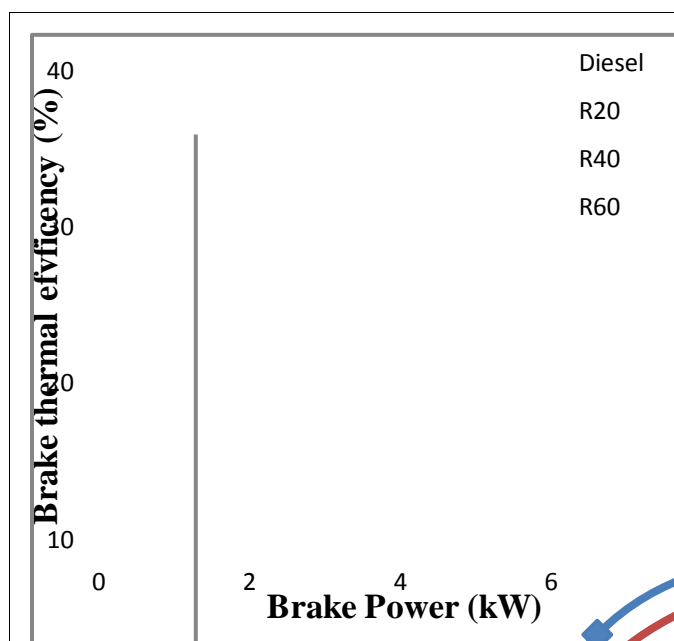


Figure 2. Variation in BTE with Brake Power for different SFO-Diesel blends

Brake Specific Fuel Consumption (BSFC)

Figure 3 shows the variation in brake specific fuel consumption with brake power for diesel and different Sardine Fish Oil-Diesel blends. The specific fuel consumption is higher for SFO diesel blends at all loading conditions compared to diesel and increases with increase in the content of sardine fish oil in the test fuel. BSFC of the engine is increased about 4.96%, 11.24%, and 14.34% for R20, R40, and R60 respectively than that of diesel. The higher densities of SFO and its blends result in increased mass injection for the same volume at the same injection pressure which results in higher BSFC than diesel⁶.

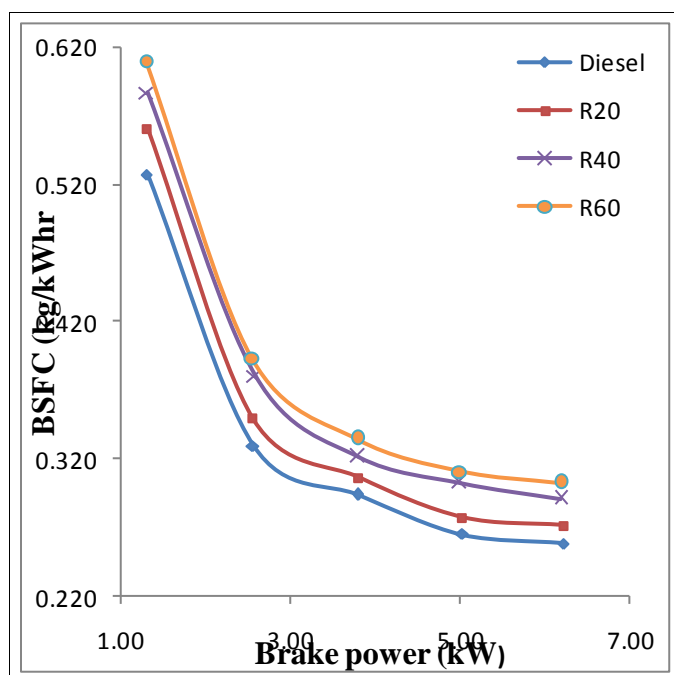


Figure 3 Variation in BSFC with Brake Power for different SFO-diesel blends.

Exhaust Gas Temperature (EGT)

Figure 4 shows the variation in exhaust gas temperature with brake power for different SFO-blends and diesel. It has been observed that with increase in load, exhaust gas temperature increases and at full load conditions the exhaust gas temperature is higher for diesel-sardine fish oil blends than that of diesel. There is no significant variation in exhaust temperature for sardine fish oil-diesel blends at lower loads, but at maximum load the EGT is increased by 11.43% for R60 sardine fish oil blend when compared with diesel.

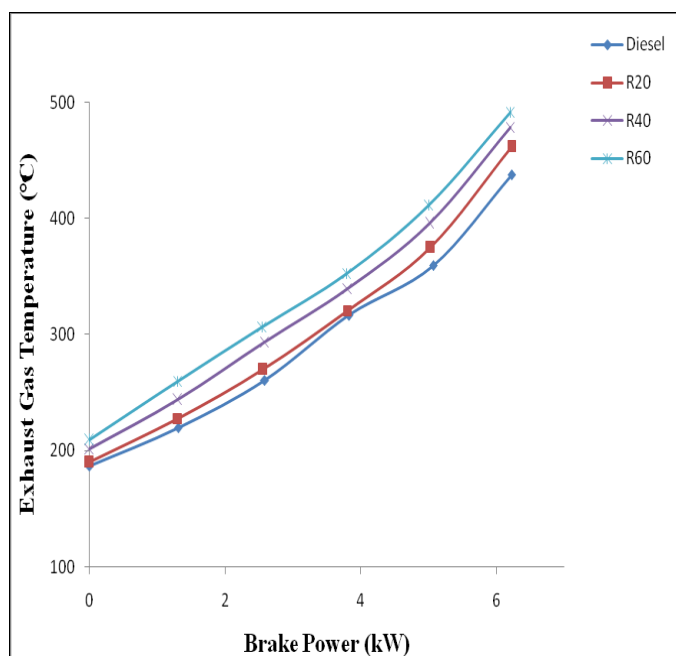


Figure 4 Variation in Exhaust Gas Temperature with Brake Power for different SFO-diesel blends.

Oxides of Nitrogen

The variations in NO_x emissions with brake power for sardine fish oil-Diesel blends are compared with those of diesel in Figure (4.5). It is observed that the NO_x emission for sardine fish oil and its blends is higher than that of diesel fuel. The NO_x emission increases with increase of sardine fish oil inclusion in the diesel fuel. NO_x formation depends on the combustion temperature, equivalence ratio, oxygen concentration and physical and chemical properties such as density, viscosity and cetane number. The NO_x emission is increased by 12.26%, 27.51% and 34.19 % for R20, R40 and R60 sardine fish oil-Diesel blends, respectively when compared with diesel fuel. The increase of NO_x emission is reported by several researchers and the results are in well agreement with most of the literature⁷.

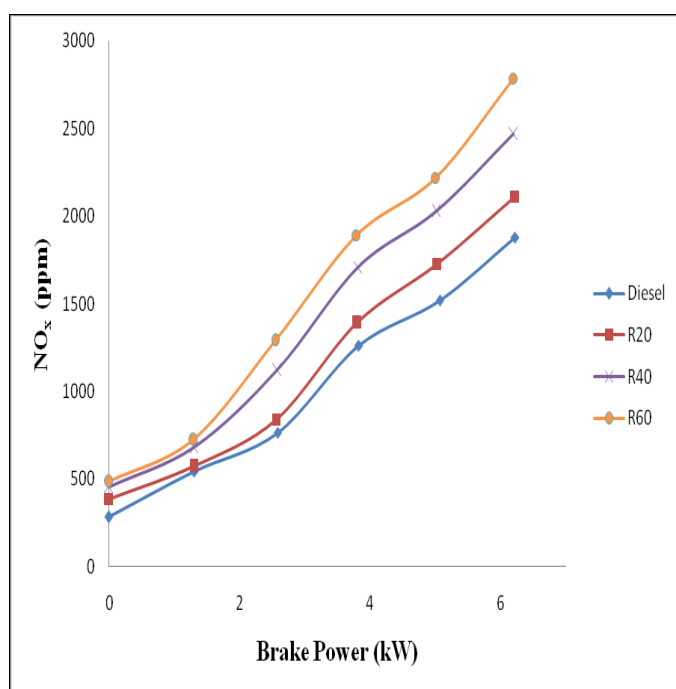


Figure 6.5 Variation in oxides of Nitrogen Emissions with Brake Power for different SFO-diesel blends.

Carbon Dioxide Emission

The variation in carbon dioxide emissions with brake power for diesel, sardine fish oil diesel blends are shown in Figure 6. The differences between the CO₂ emissions of sardine fish oil-Diesel blends with diesel fuel are relatively small. The CO₂ emissions of SFO and its blends are evidently lower than those of diesel fuel at high engine loads. It is observed that CO₂ emission is decreased by 9.35 %, 18.77%, and 20.72% for R20, R40 and R60 sardine fish oil-Diesel blends when compared with diesel. Experimental analysis reveals that all the sardine fish oil-Diesel blends exhibits less CO₂ emissions when compared with diesel fuel.

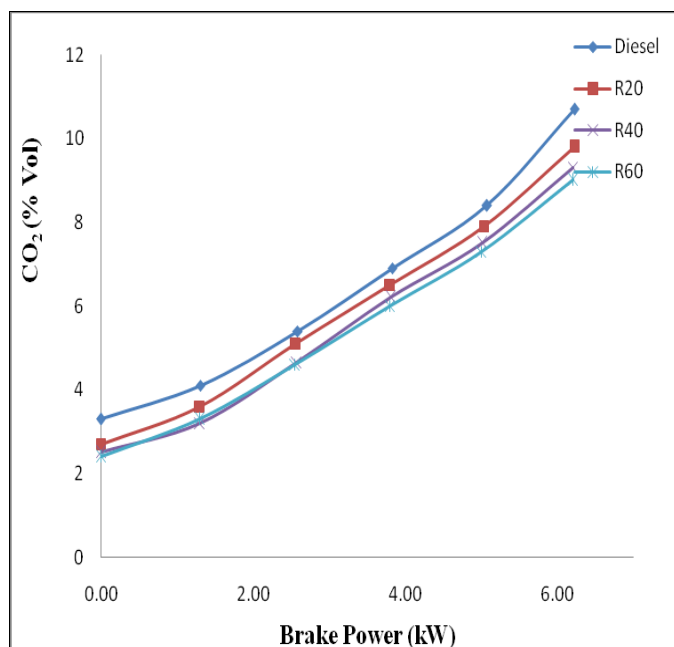


Figure 6. Variation in CO₂ with brake power for different SFO-diesel blends and diesel

Smoke Opacity

Smoke originates early in the combustion process in a localized volume of rich fuel-air mixture. Most of the smoke results from incomplete combustion of hydrocarbons in fuel and some is contributed by the lubricating oil. The amount of soot formed depends on fuel-air ratio and type of fuel used. If soot is not burned in combustion cycle, it will pass through exhaust, and if in sufficient quantity it will become visible. The difference of smoke levels between SFO blends is higher at higher loads as compared to that at lower load conditions. The variation of Smoke (%) at various brake power is shown in Figure 7 for sardine fish oil-Diesel blends. It is clear that smoke emissions are low for sardine fish oil diesel blends when compared with diesel at low loads and the smoke emission decreases with the increase in SFO content in the test fuels. It is observed that smoke emission is decreased by 11.54 %, 21.49% and 23.20% for R20, R40 and R60 SFO-Diesel blends when compared with diesel. The smoke emission reduction may be attributed to their lower aromatic and short chain paraffin hydrocarbons and higher oxygen content.

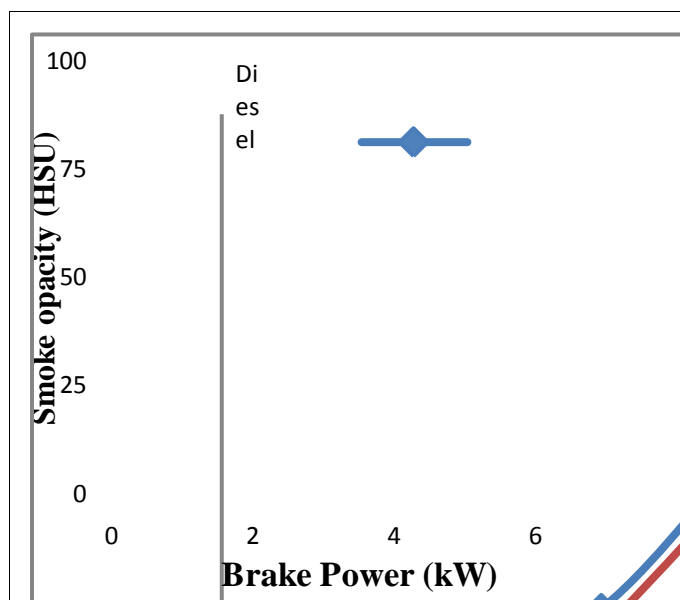


Figure 7 Variation in Smoke Opacity with brake power for different SFO-diesel blends

Conclusion

Sardine Fish Oil was extracted from Sardine Fish using Bligh and dyer method. Characterization of sardine fish oil was made and the results reveal that the viscosity of sardine fish oil is 22.9 Cst and the density is 930 kg/m³. The results of FTIR analysis confirmed the presence of alcohols, phenols, carboxylic acids, alkanes, boron compounds, esters, saturated aliphatic, aromatics, halogen compounds and phosphorus compounds in the fish oil. Experimental investigation on performance and emission characteristics reveals that BFSC increases whereas BTE decreases for all SFO and its blends when compared with diesel. Emission analysis reveals that there is an increase in NO_x whereas the other emissions such as CO₂ and HC are relatively low when compared with diesel.

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