A Comparative Study of Neem and Palm Oil Methyl Ester and its Test on the Diesel Engine

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Abstract - Diesel fuels have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods, operation of diesel tractor and pump sets in agricultural sector. Unlike rest of world, India's demand for diesel fuels is roughly six times that of gasoline hence seeking alternative to mineral diesel is a natural choice. Esters from vegetable and non vegetable oils are the best substitutes from diesel because they do not demand any modification in the diesel engine and have a high energetic yield. Present work reports an optimized protocol for the production of biodiesel through alkaline catalyzed transesterification of both edible and non edible oils, Two edible and non-edible sources of the oils were identified i.e neem and palm oil. The quality of the methyl ester produced is analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR). FTIR and GC-MS analysis were studied to identify and confirm the presence of functional groups and fatty acid methyl esters. The performance of the Diesel Engine was studied when it was fueled with the blends (B10 & B20) of Diesel fuel and Neem and palm oil methyl ester. The blends of NOME brake thermal efficiency are almost nearer to the BTE of the diesel fuel. Production of biodiesel from non-edible oils (Neem) for diesel substitute is particularly important because of the decreasing trend of economical extracted oil reserves and the environmental problems caused due to the use of fossil fuel.

Keywords: Transesterification, Neem Oil, Palm Oil, GC-MS, FTIR, Diesel Engine Performance.

I. INTRODUCTION

Petroleum resources are finite and therefore search for alternative is continuing all over the world. The major energy demand is fulfilled from the conventional energy resources like coal, petroleum and natural gas. Petroleum-based fuels are limited reserves concentrated in certain regions of the world [1]. These sources are in the verge of getting extinct. The scarcity of known petroleum reserves will make renewable energy resources like biodiesel more attractive. Bio- fuels like ethanol and bio-diesel being environment friendly, will help us to conform to the stricter emission norms. International experience has demonstrated the advantages of using ethanol and methanol as automotive fuel and blends below 20% of biodiesel do not present any problem and reduce harmful emission. The gases emitted by petrol and diesel driven vehicles have an adverse effect on the environment and human health. There is universal acceptance of the need for reducing such emissions by adopting ways to reduce emission without affecting the process of growth and development. One of the ways in which this can be achieved is through the use of biodiesel and blending them with diesel.

Biofuels are generally considered as offering many opportunities including sustainability, reduction of greenhouse gas emissions, regional development. In developed countries there is a growing trend towards employing modern technologies and efficient bio energy conversion using a range of biofuels, which are becoming cost-wise competitive with fossil fuels [2]. The scarcity of conventional fossil fuels, growing emissions of combustion generated pollutants and their increasing costs will make biomass sources more attractive.

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With increasing petroleum prices biofuel production has been of great interests these days. Therefore feedstock with low cost are needed as it is not so economical to produce biofuels from food grade oils. Hence for the production of biofuels non-edible oils are found to give the good crude oils for production and also in addition they are economical nature. Also the feedstock depends mainly on availability and price and non-edible oils are available in large amounts in world like jatropha oil, mahua oil, linseed oil, cotton seed oil, olive oil, neem oil, and rice bran oil and at very economical prices as compared to edible oils[3]. The major difficulty in commercialization of biodiesel is its cost feedstock which can be reduced by using non edibles instead of edibles and also it sort the issues of food verses fuel which arise due to use if edible oil for biodiesel production. The objectives of this work are to evaluate the physical and chemical characteristics of Methyl ester (Biodiesel) produced, to analyse GC-MS, Elemental Anlayser (CHNOS) and FTIR and to test the performance of the Diesel engine with the blends of diesel engine and Neem oil methyl ester and Palm oil methyl ester.

II. MATERIALS AND METHODS

In this chapter, the various experimental works carried out in the course of this research project are discussed in detail. These include the materials, pre-treatment operations, experimental procedures and characterization of oils.

2.1 Feedstock: The following materials used to produce Methyl Ester from neem and palm oil.

2.2 Chemicals: Methanol (99.5% purity) of E.Merck India Ltd., Potassium hydroxide (97% purity) of Indian drugs and pharmaceutical limited, Sulphuric Acid, phosphric acid were used in the experimental work.

2.3 Experimental Setup: Three necked flat bottomed glass flask of 2000ml capacity was used for transesterification reaction. A double coiled reflux condenser(joint size 24/29) was fitted to a neck of the glass flask for condensing methanol vapours during the reaction. Cool water was circulated through coils of the condenser. A glass thermometer of the range 0–360^{o}C was fitted to the second neck of the flask to measure the temperature of the reaction mixture. A plate heater with a magnetic stirrer(220/230 V 50 ~ 1 AC Amperes 1.8) was used for uniform heating of the contents of the flask and separating funnel 500 ml (made of borosil glass). Oil, methanol and other chemicals were transferred through the third neck of the flask at the start of each experimental run using glass funnel and was stoppered during the reaction. A constant water bath was provided to maintain the temperature of the contents in the flask in the range 60 – 63^{o}C.

2.4 First stage (Acid catalyzed stage):

The free fatty acids can be reduced to esters by two processes viz. hydrolysis, methanol with acid catalyst. The treated oil is taken in litres and heated to 35 ^{o} C to melt the solid fats presented in the oil[5]. Methanol of 99% pure is added (0.1 litres/litre of oil) to the heated oil. It is stirred for five to ten minutes (methanol is a polar compound; oil is strongly non –polar; hence a suspension will form). One millilitre of 95% pure sulfuric acid (H_2SO_4) is added for each litre of oil using a graduated eye dropper. The compound is stirred for one hour maintaining the temperature at 35^{o}C. Heating is stopped and the mixture is stirred for another hour. The mixture is allowed to settle for eight hours in a decanter to remove glycerin and chemical water.

2.5 Second stage (Base catalyzed stage):

For each litre of oil/fat 0.12 litre of methanol (12% by volume) is measured to which it is added 6.5 grams/litre of Potassium hydroxide,(KOH). The mixture is stirred thoroughly until it forms potassium methoxide. Half of the prepared potassium methoxide is poured into the unheated mixture and the mixture is stirred for five minutes. This will neutralize the sulfuric acid. The mixture is heated to 55^{o}C and the whole reaction is maintained. Remaining potassium methoxide is added to the heated mixture and stirred at low speed of not more than 500 to 700rpm for one hour. After the confirmation of completion of methyl ester formation, the heating was stopped and the products were cooled and transferred to separating funnel. It is allowed for settling for 8-10 hr in separating funnel.

2.6 Purification of products:

Bubble wash method is used, but there is no need to monitor pH value of the oil any more one millilitre of phosphoric acid (H_3PO_4) is added to the washing water first. One third water by volume to the oil is being used and the oil is bubble washed for two hours. The mixture is allowed to settle in a decanter for one hour and the water is drained off later. The biodiesel is heated to 100^{o}C to dispense with the traces of water and preserved.

2.7 FFA analysis of Methyl Ester using GC- MS:

Oils are natural products consisting of ester mixtures derived from glycerol (triglyceride), whose chains of fatty acid contain about 14 to 20 carbon atoms with different degrees of unsaturation [4]. The transesterification reaction consists in the conversion of the triglyceride molecules, by means of the action of short chain alcohol, i.e., methanol, ethanol into the corresponding fatty acid esters. According to the source of oil seed, variations in the chemical composition of the oils are expressed by variations in the molar ratio among different fatty acids in the structure.

The prepared methyl ester i.e., used neem oil methyl ester and palm oil methyl ester was analyzed by Agilent 6890 series GC-MS system to determine the composition of fatty acids. The methyl ester is mainly formed by transesterification of saturated and monounsaturated fatty acids while the remaining polyunsaturated and some bulk saturated fatty acid are responsible for high viscosity. The higher level of unsaturated fatty acid reduces fuel quality, because of its easy oxidation.

2.8. Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR Spectroscopy is a powerful scientific tool which have an incorporated computer system and which can be used for analyzing the biodiesel and biodiesel blends.

2.9. Elementary Analyzer:

The CHNOS Analyzer find utility in determining the percentages of Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen of organic compounds, based on the principle of "Dumas method" which involves the complete and instantaneous oxidation of the sample by "flash combustion". The combustion products are separated by a chromatographic column and detected by the thermal conductivity detector (T.C.D.), which gives an output signal proportional to the concentration of the individual components of the mixture.

2.10. Diesel Engine Performance Test

First, load test was conducted on the engine by using diesel at no load, 2 kg, 4 kg, 6 kg, 8 kg, 10 kg and 12 kg. After that different blends of Neem oil methyl ester& Palm oil methyl ester and diesel are prepared at different proportions 10% of NOME +90% of diesel (B10), 20% NOME +80%of diesel (120) and same for POME respectively. Using these blends the load test is conducted at no load, 2 kg, 4 kg, 6 kg, 8kg, 10 kg and 12 kg. The time taken (sec) for the consumption of 10cc of fuel is noted at each load. Brake Power, Mass of fuel consumption, Brake thermal efficiency are calculated and tabulated. Corresponding graph between brake power and brake thermal efficiency is plotted and results are compared for diesel, B10 & B20 of NOME & POME

2.10.1. Measurement of performance:

Brake power is one of the most important parameter in the engine experiment. The rope brake dynamometer is used to measure the power of the engine. The mass of fuel was calculated by multiplying volumetric fuel consumption to its density. An air box with orifice meter and manometer was used for accurate volumetric measurement of air consumption and finally mass flow rate was determined. Digital type temperature sensor (thermocouples) was used for temperature measurement.

2.10.2. Brake power:

The part of power developed in the engine cylinder is used to overcome the local friction The net power output is available at the shaft is known as brake power and it is denoted by RP depends on speed of engine (R.P.M) and the load All the readings were taken at constant RPM by varying the load on the engine. Thus, all of the following graphs in this chapter will be placed engine Brake power.

2.10.3. Brake thermal efficiency

It is the ratio of the thermal power available in the fuel to the power the engine delivers to the crank shaft. It is the ratio of brake power developed by engine to the heat supplied to the engine. This generally depends on the manner in which the energy is converted since the efficiency normalized with fuel heating value.

III. RESULTS AND DISCUSSION

3.1. FFA Analysis of biodiesel using GC-MS

The fatty acid composition of the oils seems to have an important role in the performance of the biodiesel in diesel engines. Based on the fatty acid composition and many other parameters, the EU biodiesel specifications will be mandatory to limit the oxidative stability, as it may be a crucial parameter for injection pump performances Moreover, the stability of the fuel is a quality parameter established by the ANP- National Petroleum Agency in Brazil, being its evaluation and control necessary.

Vegetable oils are natural products consisting of ester mixtures derived from glycerol (triglyceride), whose chains of fatty acid contain about 14 to 20 carbon atoms with different degrees of unsaturation. The transesterification reaction consists in the conversion of the triglyceride molecules, by means of the action of short chain alcohol, i.e., methanol, ethanol into the corresponding fatty acid esters. According to the source of oil seed, variations in the chemical composition of the vegetable oil are expressed by variations in the molar ratio among different fatty acids in the structure. The prepared Methyl Esters i.e., Neem methyl ester was analyzed by Agilent 6890 series GC-MS and Palm methyl ester was analysed by Agilent GC- 5973 N GC-MS system to determine the composition of fatty acids. The methyl ester is mainly formed by transesterification of saturated and monounsaturated fatty acids while the remaining polyunsaturated and some bulk saturated fatty acid are responsible

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for high viscosity. The higher level of unsaturated fatty acid reduces fuel quality, because of its easy oxidation. The GC-MS report of both the methyl esters is shown in Figure 1&2.

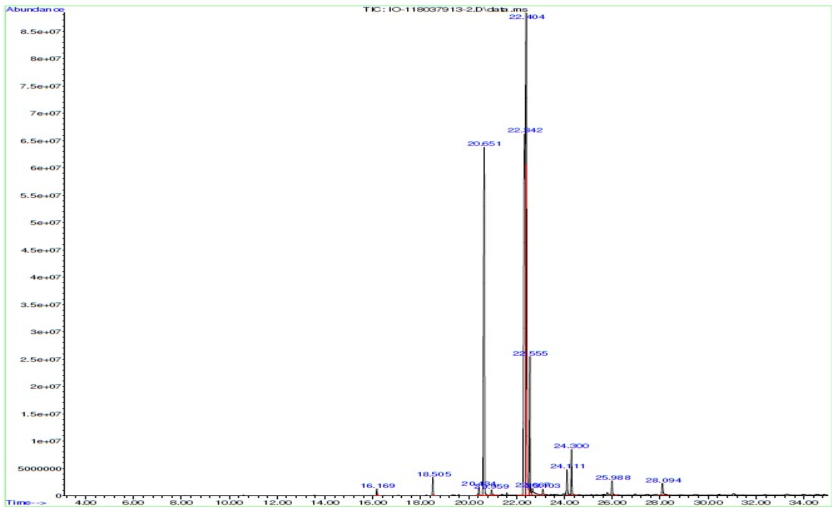

Figure 1 : GC- 5973 N MSD Analysis for Methyl Ester of Neem Oil

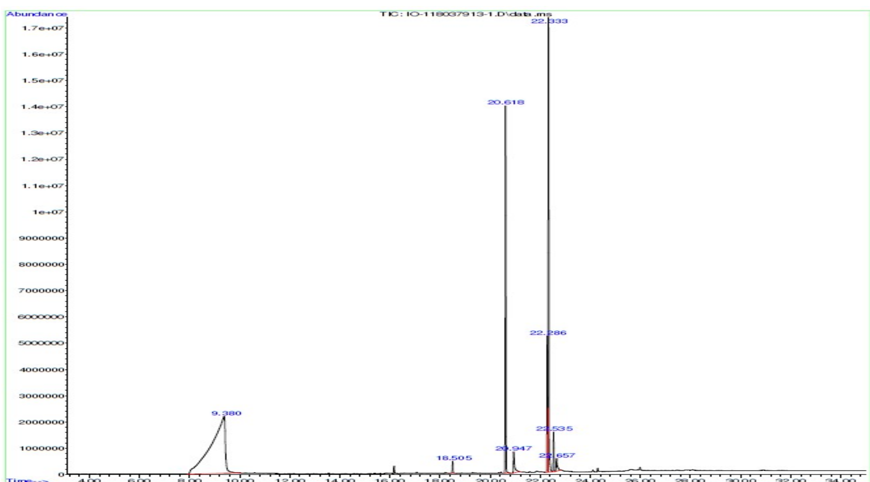

Figure-2 : GC- 5973 N MSD Analysis for Methyl Ester of PalmOil

3.2. Fourier Transform Infrared Spectroscopy (FTIR) analysis

FT-IR is used to determine the different functional group such as alcohol, alkane, alkynes, alkenes and other such groups present in the substance which here is neem methyl ester and Palm methyl ester. Interpreting infrared (IR) spectra is of immense help to structure determination. Not only will it tell you what functional groups and structural elements are there, it will also clarify which ones are not there, and also concentration of bands by using values of transmittance. FTIR studies of NOME & POME were shown in Figure 3 & 4.

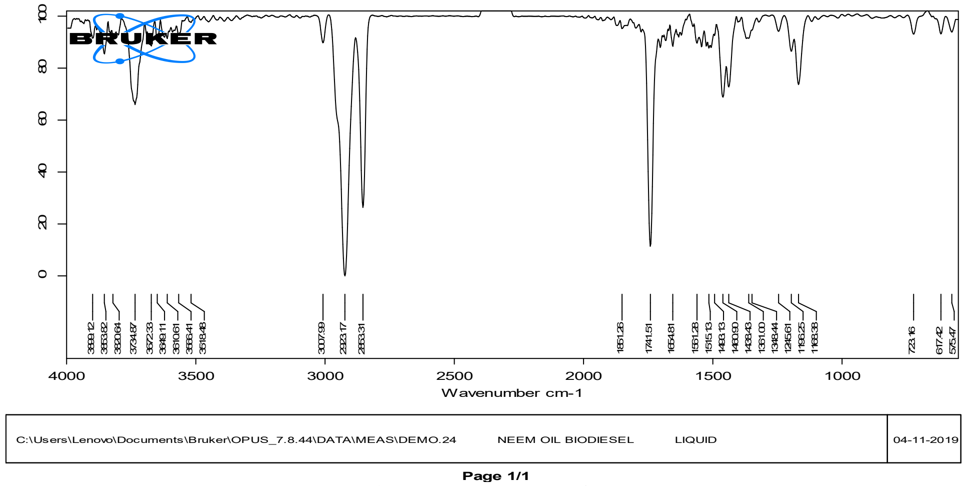

Figure 3: FTIR Spectra of NOME

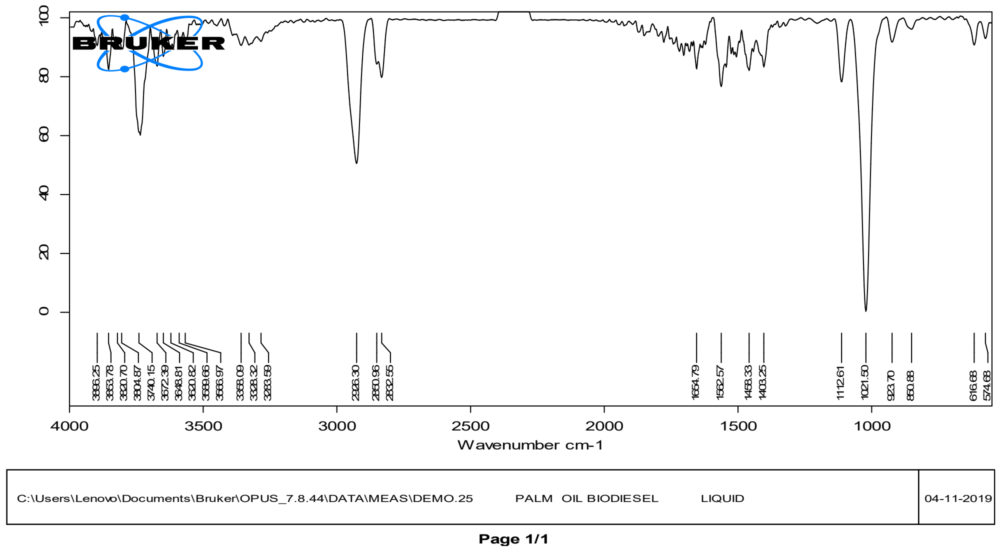

Figure 4 FTIR Spectra of POME

3.3. Elemental analysis

The methyl ester consists of three basic elements namely: carbon, hydrogen, significant amount of oxygen [5]. The increase of O_2 in methyl ester is related to the reduction of C and H, causes the lower calorific value of NOME& POME as compared to that of diesel. The NOME contains 75.87% Carbon, 12.55% Hydrogen and 10.77% of oxygen. All the elements reached ASTM standards which is suitable for environment. and POME contains 56.97% Carbon, 9.18% Hydrogen and 33.11% of oxygen. All the elements reached ASTM standards (Table-1).

Table 1 Elemental composition and C/H ratio

Element (wt %)	Petro Diesel	NOME	POME	ASTM
Carbon(C)	86.25	75.87	56.97	77
Hydrogen(H)	12.5	12.55	9.18	12
Nitrogen(N)	0	0.24	0.48	----
Sulphur(S)	0.25	----	0.08	0.05
Oxygen(O)	1.0	10.77	33.11	11
C/H Ratio	6.9	6.04	6.22	----

3.4. Comparison of NOME & POME with ASTM biodiesel standards

The NOME & POME properties are reached to ASTM D 6751-02 standards as in Table 2.

Table 2 Physical and chemical properties of NOME & POME compared to ASTM standards

Property	**Units**	**Petro Diesel**	**NOME**	**POME**	**ASTM D6751-02 (Biodiesel)**
Carbon chain	C_n	HC C_8-C_{32}	C_8-C_{25}	C_8-C_{26}	FAME C12-C22
Density @30^{0}C	Kg/m^3	825	884	867	870-900
Kinematic viscosity@40^{0}C	cSt	2.25	5.77	2.12	1.9-6.0
Cetane number	-----	49	50	---	47 minimum
Iodine value	g iodine/100g	38	90	52	120 maximum
Flash point	^{0}C	70	158	153	130 minimum
Fire point	^{0}C	98	162	160	----

3.5 Brake Thermal Efficiency for NOME

For NOME brake thermal efficiency was calculated with two different blends NOME10 and NOME20 as shown in Table 3 & 4.

Table 3 Brake Thermal Efficiency of NOME 10

Load Kg	Brake power(kW)	Q(m^3/sec)	Mass of fuel Consumption(Kg/sec)	Heat Input(kW)	Brake Thermal Efficiency
0	0	1.17E-07	0.00010439	4.66	0
2	0.66	1.46E-07	0.00013081	5.84	11.23
4	1.31	1.78E-07	0.00015925	7.11	18.44
6	1.97	2.07E-07	0.00018557	8.28	23.74
8	2.62	2.48E-07	0.00022236	9.92	26.42
10	3.28	2.83E-07	0.00025368	11.32	28.95

Table 4 Brake Thermal Efficiency of NOME 20

Load Kg	Brake power(kW)	Q(m^3/sec)	Mass of fuel Consumption(Kg/sec)	Heat Input(kW)	Brake Thermal Efficiency
0	0	1.19E-07	0.00010607	4.73	0
2	0.66	1.48E-07	0.00013275	5.92	11.06
4	1.31	1.80E-07	0.00016086	7.18	18.26
6	1.97	2.10E-07	0.00018826	8.40	23.40
8	2.62	2.50E-07	0.00022386	9.99	26.24
10	3.28	2.93E-07	0.00026200	11.69	28.03

Fig 5 shows that the variations of brake thermal efficiency of Neem oil methyl ester blends with respect to diesel fuel. It was found that the BTE of NOME10 and NOME20 are lower than that of diesel fuel. The maximum BTE of diesel fuel is 31.55% and those of NOME10 is 28.95% and NOME20 is 28.03%.

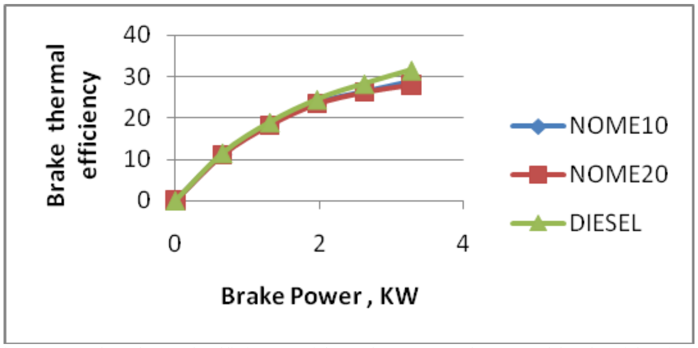

Figure 5 Brake Thermal Efficiency with Brake Power of NOME blends with Diesel

3.6 Performance Characteristics of Diesel Engine

Time taken for 10CC of fuel consumption for varying loads starting from no load to 10kg is observed from the diesel engine test with different blends (B10, B20) of Palm oil methyl ester and compared to that of diesel as shown in Table 5.

Table 5 Time taken for fuel Consumption (sec)

Load(kg)	**Diesel**	**POME 10**	**POME 20**
0	88	86.82	85.24
2	72.13	68.48	68.2
4	59.36	56.74	55.12
6	51.18	49.2	48.24
8	44.3	39.82	38.86
10	39.6	36.12	35.42

3.7. Brake Thermal Efficiency for POME

For POME brake thermal efficiency was calculated with two different blends POME10 and POME20 as shown in Table 6 & 7.

Table 6 Brake Thermal Efficiency of POME 10

Load Kg	Brake power(kW)	Q(m^3/sec)	Mass of fuel Consumption(Kg/sec)	Heat Input(kW)	Brake Thermal Efficiency
0	0	1.15E-07	0.00010309	4.66	0
2	0.66	1.46E-07	0.00013070	5.91	11.08
4	1.31	1.76E-07	0.00015774	7.14	18.37
6	1.97	2.03E-07	0.00018191	8.23	23.89
8	2.62	2.51E-07	0.00022476	10.17	25.78
10	3.28	2.77E-07	0.00024779	11.21	29.23

Table 7 Brake Thermal Efficiency of POME 20

Load Kg	Brake power(kW)	Q(m^3/sec)	Mass of fuel Consumption(Kg/sec)	Heat Input(kW)	Brake Thermal Efficiency
0	0	1.17E-07	0.00010500	4.75	0
2	0.66	1.47E-07	0.00013123	5.94	11.04
4	1.31	1.81E-07	0.00016237	7.35	17.84
6	1.97	2.07E-07	0.00018553	8.40	23.42

8	2.62	2.57E-07	0.00023031	10.42	25.16
10	3.28	2.82E-07	0.00025268	11.43	28.66

Fig 6 shows that the variations of brake thermal efficiency of Palm oil methyl ester blends with respect to diesel fuel. It was found that the BTE of POME10 and POME20 are lower than that of diesel fuel. The maximum BTE of diesel fuel is 31.55% and those of POME10 is 29.23% and POME20 is 28.66%.

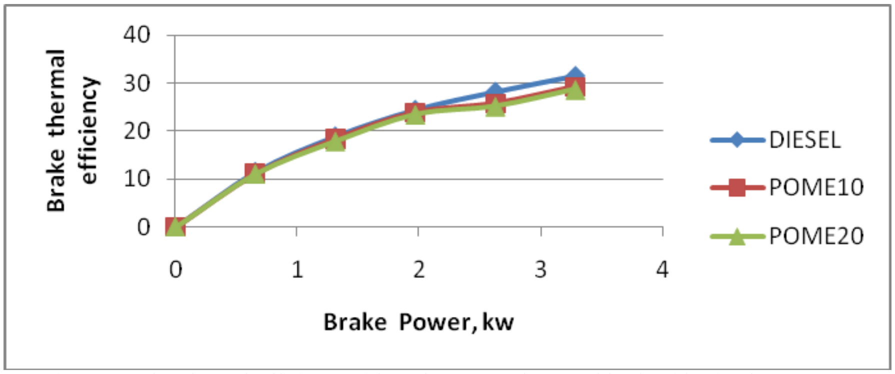

Figure 6 Brake Thermal Efficiency with Brake Power of POME blends with Diesel

IV. CONCLUSION

This study revealed that methyl ester could be produced successfully from the neem and palm oil by alkali-catalyzed transesterification. We can conclude that using water as a washing agent does not affect the reaction productivity at the same time it increases purity of the product [6].

NOME and POME was analyzed by GC-MS system to determine the composition of fatty acids. From FTIR analysis it was observed that the bonds such as C-H, C-O, O-H and C-N are abundant in Neem oil methyl ester and Palm oil methyl ester. The modes of the bonds are stretch, bending and rocking.

From the result of the Diesel engine when fueled with NOME10, NOME20, POME10, POME 20 and diesel at various loads, diesel fuel gave 31.55%, NOME10 gave 28.95% and NOME20 gave 28.03% and POME gave 29.23%, POME gave 28.66% BTE. The blends of NOME brake thermal efficiency are almost nearer to the BTE of the diesel fuel.

Production of biodiesel from non-edible oils for diesel substitute is particularly important because of the decreasing trend of economical extracted oil reserves and the environmental problems caused due to the use of fossil fuel. Non-edible oils can be an important source for methyl ester production in India as there is large quantity of non-edible oils available. Use of nonedible oil helps improve the biodiesel economics.

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