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Optimization and Performance Characteristics of Methyl Esters Produced from Chicken Fat

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ABSTRACT

Biodiesel (Methyl Esters) derived from renewable feed stock like vegetable oils and animal fats can be a very successful fuel due to the fact that it reduces engine wear, it is biodegradable, non toxic, and better lubricity resulting in longer life for diesel engines. . In the present investigation an attempt has been made to use chicken fat as low cost sustainable potential feed stock for biodiesel production. Effect of various process parameters such as amount of catalyst, methanol, temperature and reaction time on biodiesel production were optimized and the yield of chicken fat methyl esters (CFME) was 93.2% . The fuels properties were found within the limit of Indian standard for Biodiesel. The engine was tested at various load conditions with CFME and its various diesel blends and results were compared with Diesel. The results of the experiments revealed that performance and combustion characteristics of CFME are almost similar to diesel fuel. It was demonstrated that 20% CFME blends have lower NOx emissions than other blends of methyl esters produced. Additionally, the CO, UBHC are also low for 20% CFME blends of the same level of diesel compared to other blends. Since the animal fat-derived esters can be NOx neutral, they should be considered as alternatives to Diesel in fuel blends or as fuel additives.

Keywords: Biodiesel, Vegetable Oil, Chicken Fat, Engine Performance, Exhaust Emissions

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INTRODUCTION

One of the most important elements to effect world economy and politics is sustainability of petroleum resources which is the major source of world energy supply. As energy demand increase and fossil fuels are limited, research is directed towards alternative renewable fuels, which should be technically feasible, economically competitive, environmentally acceptable and readily available [1]. Fatty Acid Methyl Esters (FAME), from vegetable and animal fat have shown promise as biodiesel due to improved viscosity, volatility and combustion behavior relative to triglycerides and can be used in conventional diesel engines without significant modification. Biodiesel is free from sulphur and aromatics while conventional diesel can contain up to 500 ppm SO_2 and 20-40 wt% aromatic compounds. This could also be an important solution to reduce the problem of urban pollution since the transport sector is an important contributor to the total gas emissions.

Biodiesel is prepared from oils like sunflower, safflower, rapeseed etc throughout the world [2]. These oils are essentially edible in nature. The use of edible vegetable oil for biodiesel production would not be an appropriate alternative as the demand for vegetable oil as food has increased tremendously in the recent years. The use of low- cost feed stock such as waste animal tallow would lower the cost of feed stock as the cost of the raw material contributes to 70% of the overall production cost of the biodiesel [3]. More over the use of waste animal tallow for biodiesel production has various advantages like (i) they do not compete with the food market (ii) recycles the waste and (iii) reduces production costs therefore increasing biodiesel economic competitiveness [4]. One such animal fat is poultry fat, a feed stock that is relatively inexpensive when compared to other oil and fat sources such as soybean oil, sunflower oil etc. [5].   However, the free-fatty acid content of poultry fat can vary greatly depending on the fat profile of the bird which in turn can be affected by seasonal feed ratio changes as well as exposure of trimmings to ambient temperatures during transport from slaughter to rendering facilities [6]. This is important, since the FFA content affects the biodiesel yield potential [7]. And thereby has a major impact on the economic feasibility of the feedstock [5]. High FFA content, in combination with conventional base catalyzed transesterification, lowers the yield of biodiesel and produces by-products like soap stock and glycerin.

Transesterification of oil/fat can be catalyzed by alkali, acid or enzyme. Among, alkali and acid – catalyzed transesterification, reaction is much slower with acid catalysts. Moreover, the corrosive acid-catalyzed transesterification needs extreme temperature and pressure conditions. The promise of cheaper process still exists because there is a constant need of developing an improved cost-effective and eco-friendly process for manufacturing biodiesel that could potentially lead to easier refining of the produced biodiesel and glycerol, recycling of the catalysts and hence, lower production costs.

Many researchers have investigated the availability of animal fats and waste oils for biodiesel production [8], [9]. However, few researchers have worked on the chicken fat especially with high FFA. Mattingly [5] produced biodiesel from chicken fat with 2.3% FFA. He concluded that a pretreatment on the chicken fat was needed to get high biodiesel yields. Bhatti et al. [10] obtained high ester yields up-to 99% from chicken fat after 24 h in the presence of sulfuric acid. [11] chose chicken fat for biodiesel production; potassium hydroxide was used to remove FFA in the form of soap. After separating the soap, the optimizations of transesterification parameters were researched. They obtained good results and produced biodiesel whose fuel properties were suitable for American society of testing and materials (ASTM) biodiesel standards. Schulte [12] investigated optimum reaction parameters for biodiesel production from chicken fat. He obtained high biodiesel yields up-to 91% using supercritical methanol. Investigations have shown that chicken fat is a promising feedstock for biodiesel production.

[13] carried out the pretreatment with 20% sulfuric acid and a methanol molar ratio of 40:1 for 80 min at 60 º C which was sufficient for reducing the FFA level to less than 1% to get high ester yield after transesterification. Alptekin et al [14] again produced biodiesel from chicken fat with high FFA. Therefore, the optimization of biodiesel production from the chicken fat was investigated with different alkaline catalysts, reaction temperatures and reaction times. However, there are not many studies on the biodiesel production from chicken fat having high FFA, as the fresh fat have only a very low FFA.

This study was initiated to examine the possibility of transesterifying chicken fat for the production of biodiesel. Chicken fat is an appealing raw material since it serves as a cheap source and its utilization serves

the environmental cause. In particular the aspects of catalyst concentration, excess alcohol, reaction temperature, time of reaction and agitation were investigated as to their effect on yield. The intention was to optimize the yield in terms of these fundamental process variables and the engine testing was performed for the various blends of CFME's.

MATERIALS AND METHODS

Pretreatment of Chicken Fat:

The chicken fat obtained locally was washed, cleaned with deionised water and was free of flesh and skin. The solid fat was melted at around 80°C to give a clear pale yellow liquid. This was then filtered, centrifuged and decanted to remove other suspended particles. The processed chicken fat which was homogeneous in nature was stored in air tight opaque plastic jars to prevent oxidation. The free fatty acid (FFA) of this fat was determined and found to be 0.3 mg of NaOH/gm of fat. All reagents used were of analytical grade.

Transesterification:

The setup consists of a three-necked round bottom flask kept in an oil bath heated by an electrical heater. The motor driven stirrer was inserted into the flask through the central neck. The stirrer passes through an airtight gland, which prevents the methanol from escaping out of the flask. A thermocouple was inserted through the other neck for measuring the temperature of the oil inside the flask. The thermocouple in turn was connected to a temperature controller relay, which turns the heater on/ off to maintain the constant temperature of the oil. A variable voltage regulator was also used to regulate the voltage applied to the heating coil. The third neck was used for pouring the oil and the base catalyst into the flask. The oil was heated to the desired temperature. The stirrer enables uniform mixing of the oil to ensure uniform temperature and also improves the contact between the oil and methanol molecules. The homogeneous catalyst already prepared was added into the flask. The reaction was allowed to continue for a selected time interval. The reaction mixture was then taken out and allowed to separate in a separating funnel. The cloudy looking part of the product is glycerol, which sinks to the bottom, and methyl ester, which is a translucent liquid, floats on top. The reaction was arrested by adding 10 – 15 drops of water. The reaction mixture was poured into a separating funnel. The mixture was allowed to settle for atleast 8 hours.

Table 1 Fatty acid ester composition of Chicken Fat.

Fatty acid	C:N[a]	Structure	Chicken fat (Weight %)
Myristic acid	14: 0	$C_{14} H_{28} O_2$	0.7
Myristoleic acid	14:1	$C_{14} H_{26} O_2$	0.3
Palmitic acid	16:0	$C_{16} H_{32} O_2$	25.2
Palmitoleic acid	16:1	$C_{16} H_{30}O_2$	7.8
Stearic acid	18:0	$C_{18} H_{36} O_2$	5.9
Oleic acid	18:1	$C_{18} H_{34}O_2$	40.5
Linoleic acid	18:2	$C_{18}H_{32}O_2$	18.4
Linolenic acid	18:3	$C_{18}H_{30}O_2$	0.7

[a]*C*, no. of carbon; *N*, no. of carbon–carbon double bond.

The separation of methyl esters and glycerol occurs due to the density difference between methyl esters and glycerol. The methyl esters obtained was separated and water was added to the methyl esters gently along the sides so that traces of glycerol present along with the methyl esters mixes with water to form soap and settles down. This process was repeated until all the impurities were removed completely. The methyl esters were then mixed with water and it was gently agitated through a bubbling process in which air was pumped into the methyl ester-water mixture. The bubbling process was done for about 30 min. Thus, the methyl ester obtained after the bubbling process was completely devoid of glycerol. The variables affecting transesterification such as catalyst concentration (1-5% wt of oil), methanol/oil ratio (3:1-7:1), Reaction temperature (40-65° C) and reaction time (0-90 min.) were studied to get higher conversion.

Engine test apparatus and method

A single cylinder four stroke direct injection air-cooled diesel engine coupled with an electrical dynamometer. The detailed technical specifications of the engine are given in Table 2. The engine was coupled to an electrical dynamometer to provide brake load. The fuel consumption was measured with the aid of a glass burette and stopwatch on a volume basis. A Chrommel alumel thermocouple was used along with a digital temperature indicator for measuring the exhaust gas temperature. 5-gas MRU 1600 Delta exhaust gas analyzer measures Hydrocarbon (HC), CO and NO*x* emissions. An infrared measurement technique with an accuracy of 95% is used to measure the CO and HC emissions, while NO*x* is measured by means of electrochemical sensors with an accuracy of *95%*. Smoke levels are measured with the help of an AVL 415 Variable Sampling Smoke Meter with an accuracy of 95%. The engine tests are carried out at various load conditions using diesel, CFME and blended fuels. XX% CFME denotes the XX% volume of CFME in CFME-diesel fuel blends. For example, 20%CFME is a blend of 20% volume of CFME and 80% volume of diesel oil.

Table 2: General specifications of the test engine

Engine Type	Direct injection, air cooled
Make	Kirloskar
Model	TAF1
Maximum Power	4.4 kW @ 1500 RPM
Maximum Torque	28 N-m @ 1500 RPM
Bore x Stroke (mm)	87.5 x 110
Cubic capacity	661 cc
Compression Ratio	17.5:1
Injection Timing	23.4^0 bTDC
Loading Type	Electrical Dynamometer
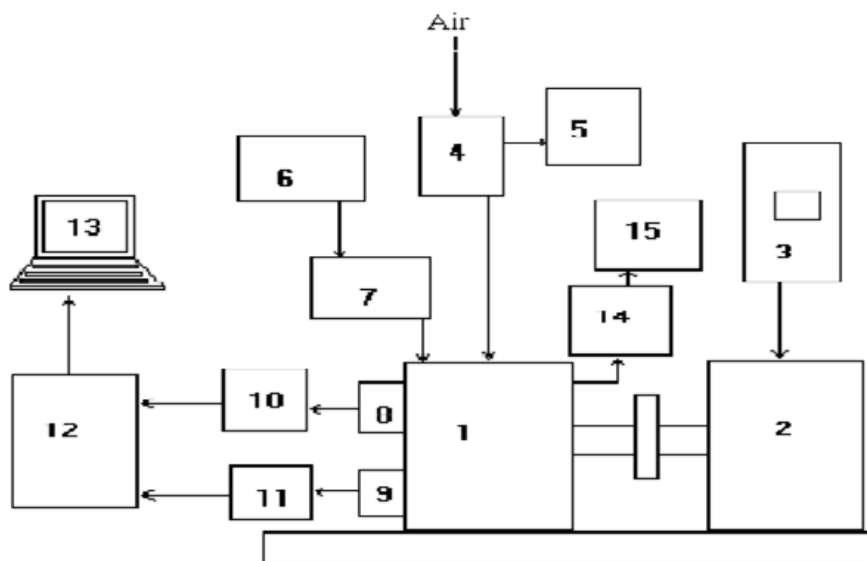
1-Diesel engine, 2-Electrical Dynamometer, 3-Rheostat, 4-Air box 5-Manometer, 6-Fuel tank, 7-Fuel measurement, 8-Pressure pick up, 9-TDC position sensor, 10-Charge amplifier, 11-TDC amplifier circuit, 12-A/D card, 13- Computer, 14-Exhaust gas analyzer, 15- AVL variable sample smoke meter

Fig 1: Layout of experimental set-up

RESULTS AND DISCUSSION

Raw material and Methyl ester properties:

The properties of raw materials, biodiesel and commercial diesel such as density, viscosity, acid value, Flash point, Cloud point, Pour point, Calorific value, iodine value, saponification number and sulfated

ash were determined and are reported in Table 3. The physical and fuel properties of biodiesel from chicken fats in general were comparable to those of recommended properties of diesel.

Optimization of Reaction Parameters:

The percentage of yield of methyl esters are presented as graphs for the different conditions of molar ratios of methanol to Chicken fat, reaction temperature and catalyst amounts. The percentage yield of methyl esters is calculated by using the following equation

% of yield= [methyl ester (in gms)/ oil (in gms) in the reaction] * 100   - - (1)

Table 3: Properties of Diesel, Chicken Fat and Chicken Fat Methyl Esters

Properties	Unit	Chicken Fat	Chicken Fat Methyl Ester	Diesel	Test methods	ASTM Standards for Biodiesel
Density (at 15 ^{o}C)	g cm^{-3}	0.932	0.875	0.830	ASTM D4052	0.860-0.900
Viscosity	mm^2 s^{-1}	59.20	4.62	3.522	ASTM D445	1.9 – 6.0
Acid Value	mg NaOH/g	0.3	0.15	--	ASTM D664	0.80 $_{max}$
Flash Point	^{o}C	260	150	49	ASTM D93	130 $_{min}$
Cloud point	^{o}C	11.5	4.8	-15 to 5	ASTM D2500	12-15
Pour point	^{o}C	3.6	6.7	-35 to -15	ASTM D97	10 $_{max}$
Calorific value	kJ/kg	16,873	39580	44310	ASTM D240	--
Iodine Value	G I$_2$/ 100 gm	66.8	105	--	ASTM D5554	120 $_{max}$
Saponification value	mg NaOH/g	189.4	251.33	--	ASTM D94	255 $_{max}$
Sulfated ash	Mass %	0.025	0.006	0.80	ASTM D874	0.020 $_{max}$

Effect of catalyst concentration in biodiesel yield:

Methanolysis of chicken fat was carried out with NaOH as a catalyst at a concentration of 0.2 – 1.0 % of NaOH with MeOH/Fat molar ratio of 6:1 at stirring speed of 600 rpm. Figure 2 shows the yield of chicken fat Methyl Esters vs. catalytst concentration for different reaction time. Lower catalytst concentration of 0.2% NaOH was insufficient to catalyze the reaction to completion. However, 0.6% of NaOH was found to be optimal for chicken fat methyl esters in the reaction with a yield of 93.2% for chicken fat at 60°C. Increasing the catalyst amount above the optimal value decreased the yield due to the fact that, soap formation occurs at higher amounts of catalyst and also backward reaction was favored at high catalyst concentrations.
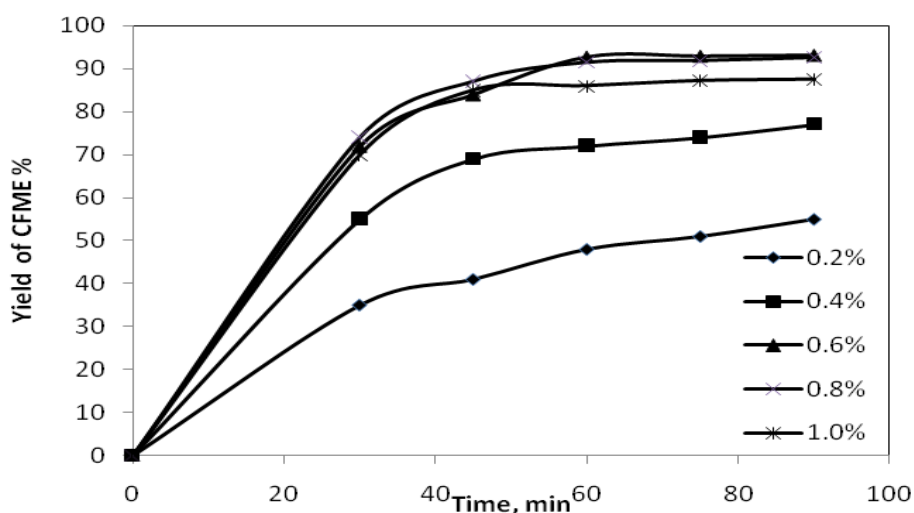
Fig 2: Effect of NaOH concentration on methanolysis of Chicken fat (MeOH/fat molar ratio 6:1, temperatures 60°C, rate of stirring 600 rpm)

Effect of temperature in biodiesel yield:

Temperature for chicken fat methyl ester reaction is important due to the high melting point of chicken fat. While the reaction temperatures were varied between 40°C and 65°C, all other parameters like methanol to fat molar ratio, catalyst concentration and rate of stirring speed were held constant throughout the experiments. At 40°C, the reaction did not start and the glycerin phase did not form hence this data is not shown in Fig 3. At 50°C, the reaction was slow and very small amounts of glycerin phase were observed at the bottom. Temperature and time are actually interacting parameters in the reaction. This low yield probably is the result of very slow reaction at these temperatures. Hence the reaction could not be completed in 90 minutes. The yield versus time for various temperatures (50°C, 55°C, 60°C, 65°C) is shown in Fig. 3. Increase in temperature from 60°C to 65°C caused a slight decrease in yield, the probable reason for this decrease could be due to the loss of methanol from the liquid phase at higher temperatures due to its vaporization and formation of a large number of bubbles which inhibits the reaction rate. Decomposition of chicken fat methyl esters at higher temperatures and saponification being favorable at higher temperatures are probably the other reasons contributing to the falling yield. [15] and [16] conducted the methanolysis of vegetable oil and observed that the optimal reaction temperature for biodiesel production varied from 60 °C and 65°C. Therefore the optimum reaction temperature was fixed at 60°C, which is the lower of the two temperatures.
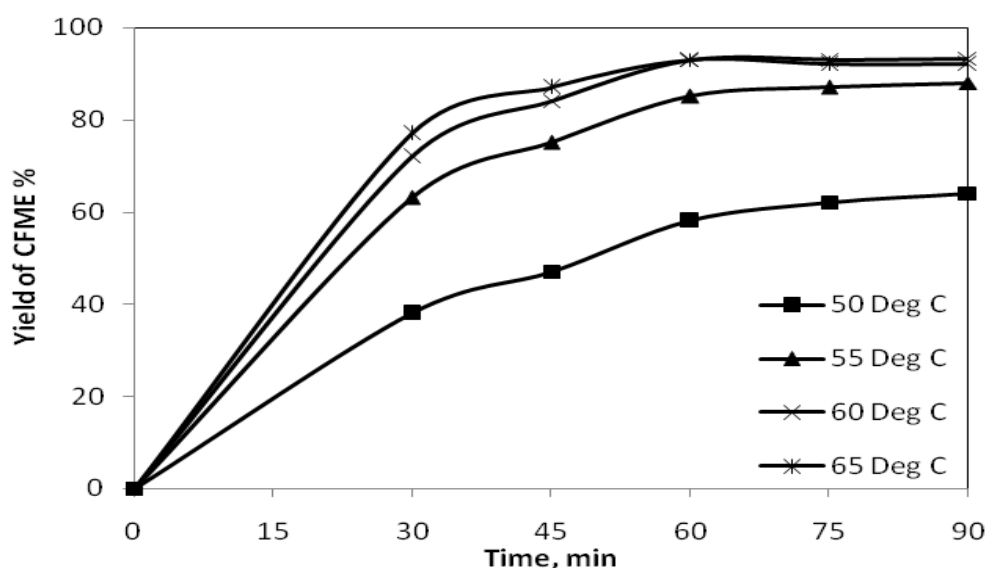

Fig 3 : Effect of temperature on methanolysis of CFME (NaOH 0.6% w/w, MeOH/oil molar ratio 6:1, rate of mixing 600 rpm).

Effect of Methanol in biodiesel yield

The biodiesel yield could be improved by introducing excess amounts of methanol to shift the equilibrium to the right hand side. The experimental results, illustrated in Fig 4 indicate that the molar ratio of methanol to oil has a significant impact on the biodiesel yield. The biodiesel yield increased as the molar ratio of methanol to oil increased. As can be seen from Fig 4, the increase in the molar ratio of alcohol/oil from 3:1 to 6:1 led to a significant rise in yield, while for ratios beyond 6:1 the improvement was slight. The commonly employed molar ratio for single step transesterification is 10:1, although an optimum molar ratio varying from 6:1 to 13:1 has been employed by other researchers. Sharma et al [17] has reported that a molar ratio higher than the optimum value reduces the yield and makes the separation process of esters and glycerol difficult. As a result, the optimum molar ratio of 6:1 was fixed for all other experiments.
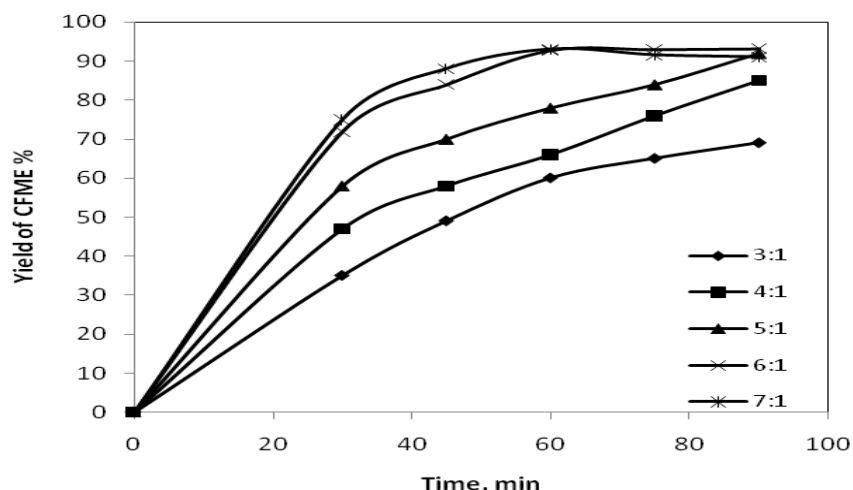
Fig 4 : Effect of molar ratio on methanolysis of CFME (NaOH 0.6%, temperature 60 °C, rate of mixing 600 rpm).

Evaluation of performance, combustion characteristics and exhaust emissions

Brake thermal efficiency

Brake thermal efficiency is the ratio of brake power to the product of heating value and mass of fuel input. Figure 5 shows that brake thermal efficiency of CFME and its blends are lower compared to that of diesel fuel. Since the engine is operated under constant injection advance and CFME has a smaller ignition delay, combustion is initiated much before Top Dead Center (TDC) is reached. This increases compression work and more heat loss and thus reduces the brake thermal efficiency of the engine. This can also be explained by the fact that maximum efficiency is obtained when most of the heat is released close to TDC [20]. The start of heat release much before TDC for CFME and its blends results in larger deviation from the ideal cycle and hence lower thermal efficiency is recorded. It was observed that diesel exhibits slightly higher.

Brake thermal efficiency at most of the brake power than CFME and its blends. Lower heating value and higher viscosity of the esters than diesel may affect the mixture formation process, which results in a slow combustion process and hence reduces the brake thermal efficiency for the esters. This is due to the better lubrication property of CFME, which decreases frictional power of the engine [18] & [19].

$$\text{Brake thermal Efficiency } (\eta_{BT}) = \frac{\text{Brake Power (BP)} \times 3600}{\text{Mass } (m_f) \times \text{Calorific value (CV)}}$$
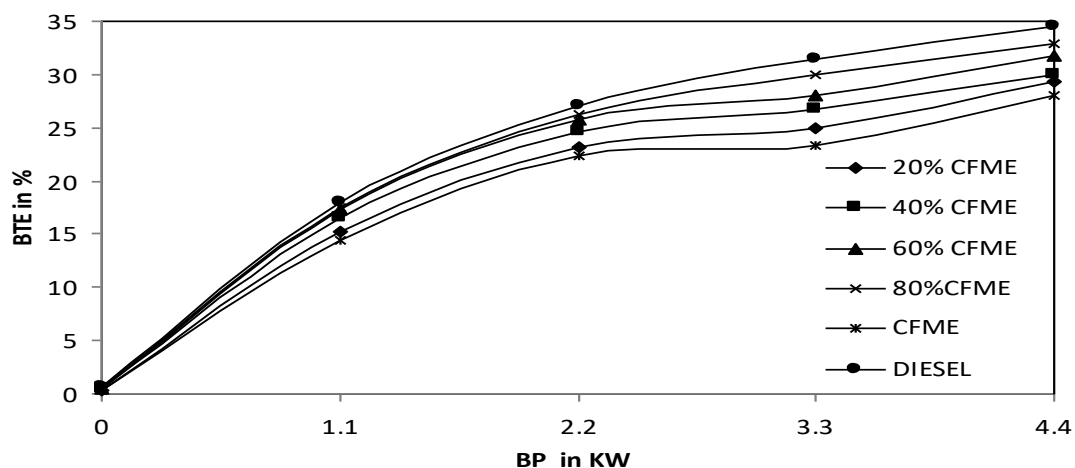

Figure 5 Comparison of brake thermal efficiency

Unburned Hydrocarbon (UBHC) emissions:

Emissions of UBHCs are substantially less in Compression Ignition(CI) engines in general compared to Spark Ignition(SI) engines due to lean mixtures. This is still reduced when CFME is used as fuel due to the oxygen content of CFME, which results in improved combustion. Blending CFME with diesel fuel causes a substantial reduction in UBHC emissions especially at higher engine loads. The UBHC emissions with CFME and its blends are compared with diesel fuel in Figure 6. UBHC emissions are reduced over the entire range of loads for CFME-diesel fuel blends. It also decreases with increase in percentage of CFME in the blend. Since the CFME is an oxygenated fuel, it oxidises the UBHC and hence results in reduction in UBHC emissions, compared to diesel fuel.
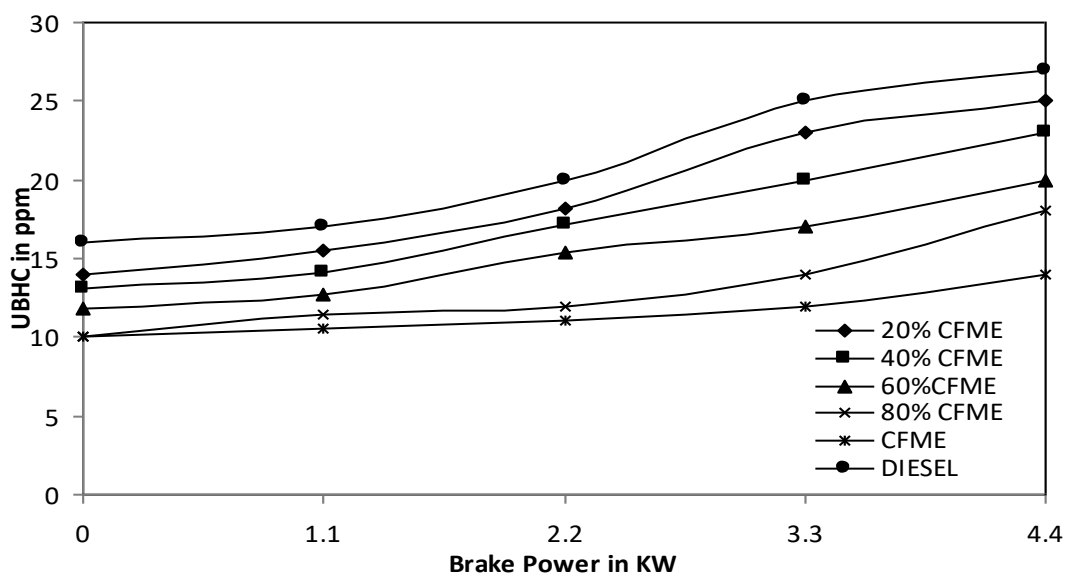

Figure 6: Comparison of UBHC emissions

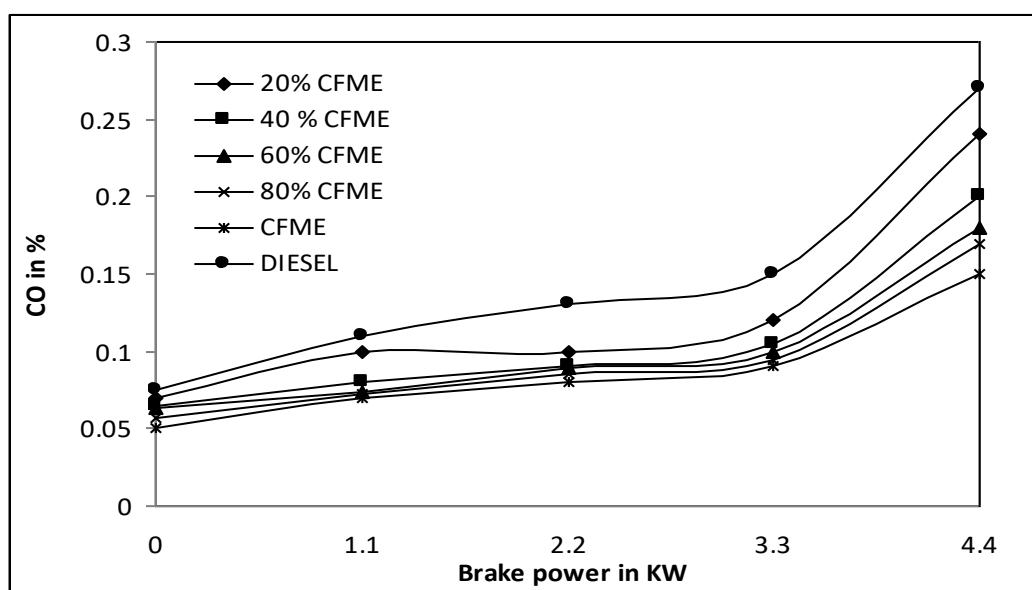**Carbon monoxide (CO) emissions:**

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Figure 7 Comparison of CO emissions

The CO emissions measured during the experiment for the various CFME-diesel fuel blends across different engine loads are shown in Figure 7. Naturally CFME has lesser CO emissions than diesel fuel due to intrinsic oxygen content in the fuel. CO emissions of CFME-diesel fuel blends decrease with an increase in proportion of CFME in blend and due to complete combustion
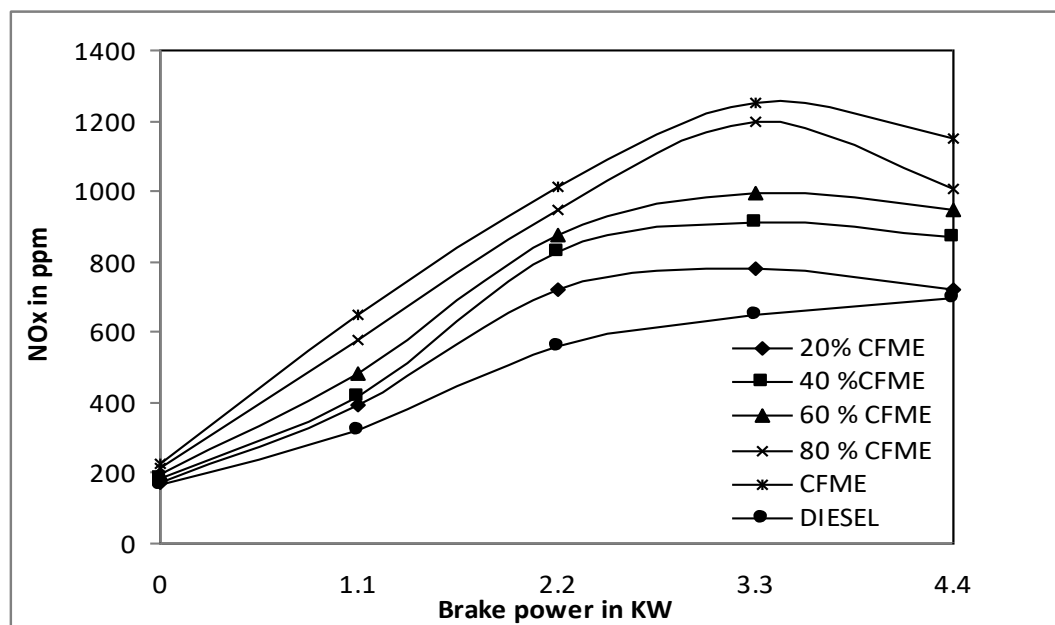
Nitrogen oxides (NOx) emissions

Figure 8 Comparison of NO*x* emissions.

Like other bioesters, CFME has higher NO*x* emissions than that of diesel fuel. NO*x* emissions refer to stable oxides of nitrogen formed at high temperatures in the combustion chamber. NO*x* emissions are predominant in CI engines as they traditionally operate under lean mixtures, even more so in case of bioesters as they have substantial oxygen content. High NO*x* emissions are the main disadvantage of biodiesels and CFME are no exception. Figure 8 shows the variation of NO*x* emissions with respect to load and blend. It can be seen as stated earlier that diesel has least NO*x* emissions while CFME records very high NO*x* nearly twice as that of diesel fuel and for the blends it is being distributed between these limits increasing with percentage of CFME in blend. 20%CFME fuel shows only very slight increase in NO*x* emission when compared with diesel fuel. At 100% load, the availability of oxygen in the combustion chamber is high for CFMEs when compared to other blends, which favors NO*x* formation.

CONCLUSION

The NaOH catalyst is an active and promising base catalyst for the production of biodiesel from oil of waste chicken fat. When the reaction was carried out with a molar ratio of methanol to oil of 6:1, a reaction time of 60 minute, catalyst concentration of 0.6% wt., and reaction temperature of 60°C, the conversion of chicken fat oil was 93.2% over the catalyst. The high reactivity and less corrosivity of the NaOH catalyst underline the advantage of base catalyst compared with the acid catalyst. The as-synthesized biodiesel contain oleic acid as a dominant component.

The fuels properties, namely, kinematic viscosity, density, acid value, Flash point, Cloud point, Pour point, Calorific value, iodine value, saponification number and sulfated ash were found within the limit of Indian standard for Biodiesel.

Under the test conditions reported herein, it was demonstrated that 20% CFME blends of methyl esters of Chicken fats in petrodiesel have lower NOx emissions than other blends of methyl esters produced. Additionally, the CO, UBHC are also low for 20% CFME blends of the same level of diesel compared to other

blends. Since the animal fat-derived esters can be NOx neutral, they should be considered as alternatives to Diesel in fuel blends or as fuel additives.

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