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Research paper

Production of Biodiesel from Waste Cooking Oil and Its Performance on Four Strokes IC Engine

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Abstract

Majority of biodiesel is produced from plant oil (Jatropha, Pongamia, Mahua, Neem, Cotton seed oil etc.), which requires large land area to grow. The major drawback of production of biodiesel in large scale is the cost of raw materials. One of the satisfactory methods to limit the Biodiesel (Methyl esters) production cost is to employ low price/quality raw material, for instance biodiesel production using waste cooking oil (WCO). Simultaneously solves the disposal problem of waste cooking oil. This is socioeconomic and environment friendly and it does not compete with fresh food oil resources. Waste cooking oil collected from different hotels in and around Manipal/Udupi of Karnataka, India. Transesterification reaction of WCO with methanol in presence of alkaline catalyst KOH has been accomplished in transesterification reactor. Experiments have been carried out at different operating conditions viz. catalyst loading (over the range of 0.4 to 3 wt %), oil to methanol ratio (1:3, 1:5, 1:6, 1:8, 1:9, 1:10 and 1:12), reaction temperature (50, 60 and 70 ºC) and reaction time (40, 50, 60, 70, 80 and 90 minutes) to identify optimized conditions for preparation of biodiesel. At these conditions gave that maximum yield (~91.60 %) of biodiesel at catalyst loading of 0.85 wt %, oil to methanol ratio of 1:8, reaction temperature of 60 ºC and reaction time of 60 minutes. Biodiesel properties at different blends (B100, B30, B20, and B5) as prescribed by **ASTM D6751-12** methods have been carried out. Its performance and emission test on diesel engine were also carried out.

Keywords: *Waste cooking oil (WCO), free fatty acid (FFA), Transesterification, Biodiesel, alkaline catalyst.*

1. Introduction

Raising uncertainty of international energy output and provides, global warming effects because of the utilization of conventional energy sources and the high cost of petroleum primarily based goods are the main cause for invention of replacement for petroleum based products [1]. The global supply of petroleum based products from the traditional sources is improbable to satisfy the increase in power call for over the next quarter century [2]. One of the main driving force for biodiesel widespread is the emission of greenhouse gases (CO_2 being the major one). On this perspective, significant interest has been given in the direction of the production of biodiesel as a petrodiesel replacement [1]. Biodiesel represents in large part closed CO_2 cycle (about 78 %), as it's far derived from renewable biomass sources [1].

Moreover, biodiesel and its blends have emerged as extra appealing due to its environmental advantages because of the fact that vegetable oils and animal fats are renewable biomass resources. Use of biodiesel blends instead of diesel in engines will substantially improves emission of unburnt hydrocarbons, carbon monoxide, and particulate matter. It will also effectively reduce sulfur oxides and sulfates which are major contributors to acid rain. NOx emissions may somewhat increase, but can be reduced with adopting modern technology's diesel engines. Usage of biodiesel will enhance agriculture, economic growth and the environmental pollution problems [3]. The major drawback to commercialization of biodiesel production in world is cost of fresh vegetable oil (raw material) which is much more than diesel. Hence, it is essential to discover the routes to reduce total cost of biodiesel production. The focus has been shifted to reduce the cost of feed stock which is the major contribution of production of biodiesel. The use of waste cooking oil (WCO) in production of biodiesel is best alternative to reduce the feedstock price [4]. Moreover, the use of WCOs as raw material in biodiesel production, further their positive effect in reducing the critical environmental pollutants inducing from waste oils can be reduced. However, the physical and chemical characters of the raw material drastically have an effect on biodiesel manufacturing reaction in addition to fuel properties. Due to this, with the intention to attain high quality biodiesel, the raw materials properties to be processed have to be controlled in detail prior to biodiesel production

The developed and developing countries are generating huge amount of WCO and animal fats. Disposal of such oils and fats leads to feasible contamination of the water and land resources and not simplest contribute to pollutants problems however is also dangerous to humans. In US, 40% of the sewage structure blockages are due to the WCO poured into kitchen sink. WCO have eco-toxic properties, if they are spilled onto ground, they will contaminate the soil and so harm plant life. WCO, which is otherwise wasted, is one of the maximum competitively priced choices to produce biodiesel. As shown in Table 1, India is producing around 9.2 million tonnes of WCO per year. In future India may emerge as top WCO producing county in the world because of its population growth and in next few years India may cross the United States WCO production. China has highest population in world,

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even though its WCO is around 4.5 million tons per year. It's mainly because of unawareness of usage of waste cooking oil in people. United States is producing more WCO in world. In US, WCO is major raw material for biodiesel production. United States has separate collection units to collect waste cooking oil in major cities to produce biodiesel.

Table 1: Generation of WCO in different nations (Gui et al., 2008)[5].

Country	Quantity (million tonnes/year)
India	9.2
China	4.5
European	0.7-1.0
Canada	0.12
United States	10.0
Malaysia	0.5
Japan	0.45-0.57

Most of the regular biodiesel production follows the base catalyzed transesterification. This is most economical method because of its low operating conditions compare to other methods. The catalysts used in the process are inclusive of homogeneous and heterogeneous acidic catalysts, basic catalysts and enzyme catalysts. The homogeneous alkaline catalyst used in the process inclusive such as sodium hydroxide (NaOH), potassium hydroxide (KOH). These catalysts are very typically used inside the industries due to following motives: (I) operates at low response temperature and pressure; (II) High yield may be attained in a minimum time, (III) Extensively available and more budget friendly. In fact, it was mentioned that the reaction rate of alkaline-catalyzed process might be 4000 times quicker as likened to acidic catalyst (Fukuda et al., 2001 [6], Kulkarni and Dalai et al., 2006 [7]Error! Reference source not found.). The advantage of using KOH rather NaOH is decrease in the quantity of FAME dissolved within glycerol after transesterification process, though the NaOH is relatively cheap. This phenomenon limits the formation of soap as a result lowering methyl esters losses. Another raw material in the process is Alcohols. Usually alcohols utilized in biodiesel production process are methanol, ethanol, butanol and higher alcohols.

Blazˇ Likozar and Janez Levec, (2014) [8] notices higher yield of biodiesel with methanol compare to ethanol, iso-propanol and tert-butanol. Higher alcohols are less prone to react with tri glycerides due to the apparently-prevailing steric hindrance of hydroxyl. Ethanol causes difficulties during the downstream processing of product due to the formation of the azeotrope with water, which is used for the washing of the soaps from biodiesel. Most of the research suggests that methanol will give better conversions and studied the various parameters such as methanol to oil ratio with various catalyst ratio for the production of biodiesel [9], [10], [11]. Main problems associated with these homogeneous base catalysts are, sensitive to FFA content of oil and hard to be removed and reused Hence base catalyzed transesrtification method requires feedstock having less free fatty acid and must be less than 1 wt%. A pretreatment step has to be used for WCO if FFA is more than 1 wt% to reduce the FFA level to less than 1 wt% and if more than 6 wt% alkaline catalyst is not appropriate for biodiesel production.

The pretreatment methods include acid catalyzed reaction, two step acid-base catalyzed reaction, acid esterification, esterification with methanol, esterification with glycerol and utilization of acid heterogeneous catalysts, utilization of adsorbents. But the most of these methods require high cost and energy requirement and may lead to increase in production cost.

The information on use of WCO as raw material for biodiesel is meager. Present study mainly focuses on optimization of biodiesel production by varying the key parameters of reaction such as oil to alcohol ratio, catalyst loading, time, temperature to get high yield and to produce fuel grade biodiesel and finally performance test of produced biodiesel on IC engine and its emission characterization.

2. Experimental

2.1 Materials

WCOs were obtained from the different hotels in and around Manipal, Udupi district of Karnataka state, India. About, 10 kg waste cooking oil was collected for the optimization of the biodiesel production experimentation and engine performance test. The materials used for experimentation were Oxalic acid, Potassium hydroxide, Ethanol, Methanol, Hydrochloric acid, Chloroform, Hanus solution, Potassium Iodide, Sodium thiosulfate, Petroleum Ether, Acetone, Acetic acid, Phenolphthalein indicator, Starch indicator.

2.2 Cleaning of Waste Cooking Oil

The collected waste cooking oil was filtered through normal sieve to remove food debris, unwanted solids and heated to evaporate the viable water content found in oil. The WCO kept in a storage bottle for further use.

3. Transesterification Reaction

A laboratory scale reactor with a capacity of 500 ml RBC was used for experimentation. The reactor consists of 3 neck round bottom flask fitted with a reflux condenser which was used as transesterification reactor. Out of these three necks, spiral condenser was fixed in one neck, a thermometer was fixed in the second neck, and other neck was used for loading the waste cooking oil. The reactor was placed in a heating mantle equipped with a stirrer and temperature controller. The stirrer speed was set at 600 rpm. A quantity of 50 gms was taken in the reactor and pre-heated. Calculated amount of KOH and known quantity of methanol taken in conical flask to prepare methanolic KOH and mixed with waste cooking oil present in reactor. The stirrer rpm was set at constant speed and allowed the reactants for specified time and temperature. As soon as reaction finished the reaction mixture was allowed to cool. The product was taken in a separating funnel and allowed to settle; the product mixture separated into three layers. The upper layer, which was biodiesel and bottom layer mostly, contains glycerol, salts, soap, other impurities and excess methanol. A very small layer of unused catalyst was present in between these layers. The bottom layer along with catalyst layer was drained from the separating funnel. The biodiesel layer was transferred and heated to evaporate methanol residue. This biodiesel was washed with hot distilled water to remove residual catalyst, soaps and other impurities until clear. Again heated the biodiesel to remove any water molecules present in biodiesel, to get pure moisture free biodiesel. This biodiesel stored in air tight bottle for further usage.

The distinct operating conditions employed in the present study, to optimize the yield of biodiesel from mixed WCO, include oil to methanol ratio(1:5, 1:6, 1:8, 1:9 and 1:12), catalyst concentration (over the range of 0.4 to 1.5 wt %), reaction temperature (40, 50, 60 and 70 ºC) and reaction time (40, 50, 60, 70, 80 and 90 minutes).

$$Biodiesel\ Yield = \frac{WFAME}{Wieght\ of\ oil}\ x100$$

Where WFAME is weight of fatty acid methyl esters

4. Results and discussion

4.1. Optimization of Transesterification Reaction

4.1.1 Influence of Oil to Alcohol Ratio

The alcohol to oil molar ratio is another important factor which influences the yield of biodiesel. The stoichiometry of the transesterification reaction requires methanol to oil ratio in the molar ratio of 3:1; commonly transesterification reaction performed with an excess amount of alcohol to shift the reaction towards the forward direction to get the proposed product, fatty acid methyl ester. Furthermore, the oil to methanol ratio is related with other key process conditions such as the type of catalyst used and the quality of oils. The effect of methanol to oil ratio on yield of biodiesel was studied with other three process parameters kept constant such as KOH loading (0.85 wt %), temperature (60 ºC) and time (60 minutes). Oil to methanol ratio was varied from 1:5 to 1:12 (Molar ratio). As shown in **Figure 1** the yield of biodiesel increased initially with the increase in oil to methanol ration from 1:5 to 1:8. At 1:5 oil to methanol ratio, yield was 34.20 % and at 1:8 yield was 91.56 %. When further increase in oil to methanol ratio 1:9, yield was decreased due to excess amount of methanol could pose difficulty in separation of biodiesel, by enhancing solubility of glycerol, a by-product and it ends with foam formation and therefore maximum loss in biodiesel yield. Similarly, higher methanol could minimize the contact of access triglyceride molecules on the catalyst's lively sites which could reduce the catalyst activity.

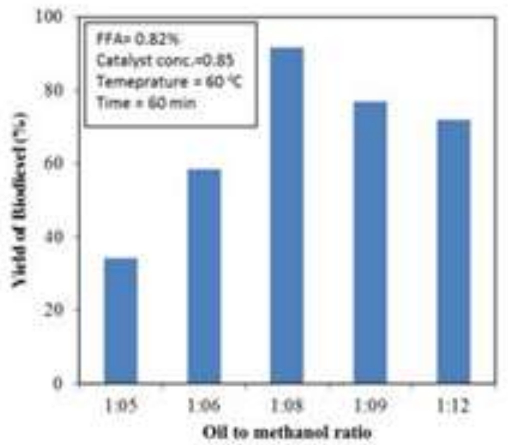

Fig 1: Influence of oil to methanol ratio on yield of biodiesel

4.1.2 Effect of Process Temperature

Transesterification reaction can be performed at room temperature; however the system is particularly laid low with the process temperature. Ideal reaction temperature of transesterification reaction is regularly near the boiling point of alcohols. However process temperature depends on the physio-chemical properties of the oil used. Usually base catalyzed transesterification reaction temperature in the range of 55-65 ºC.

Figure 2 show the effect of reaction temperature on biodiesel yield, at catalyst (KOH) loading of 0.85 wt %, oil to methanol ratio (1:8) and process time of 60 minutes. Temperature varied from 40-70 ºC. From the figure the yield of biodiesel is low at low and high temperatures while at intermediate temperature of 60^0 C, the yield is reached maximum. Higher temperature may be accelerates the side saponification reaction and at higher temperature methanol molecules vaporizes and form more numbers of bubbles that limits the process by minimizing the contact between triglycerides on active sites of catalyst. 60 ºC was the optimum time to attain up to ~92% biodiesel yield.

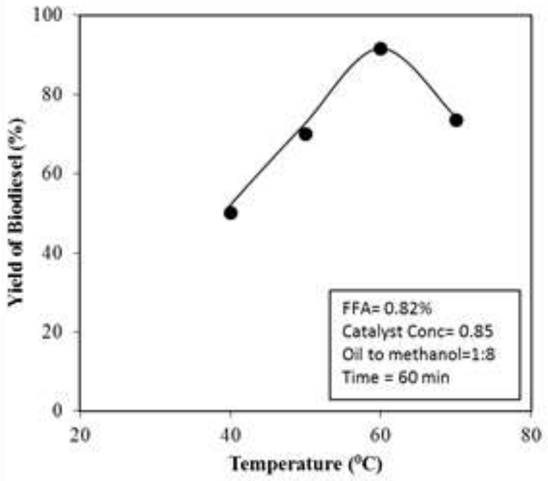

Fig 2: Effect of temperature on biodiesel production

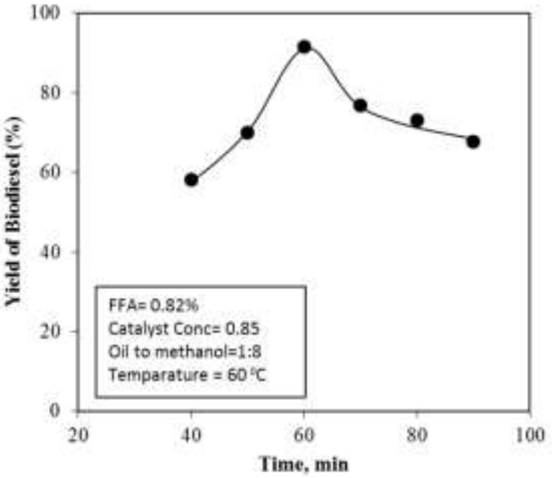

Fig 3: Effect of process time on biodiesel production

4.1.3 Effect of Process Time

In the study of influence of process time on Biodiesel, reaction time was chosen between 40 minutes to 90 minutes. The reactions were carried out by using 1:8 oil to methanol molar ratio, 0.85 wt % potassium hydroxide concentration and reaction temperature 60 ºC. **Figure 3** represented the yield of biodiesel at different reaction times. From the results, 60 minutes of reaction time gave better yield when compared to 40 minutes. Further increase in reaction time beyond 60 minutes, yield of biodiesel decreased. This is because of longer time enhancing the hydrolysis of ester resulting in low yield. It might produce FFAs at the end, and these FFAs would result in soap formation, thus reducing the biodiesel yield.

4.2. Properties of Pure Biodiesel and Its Blends Compared With Diesel

Table 2 summarizes that various important physio-chemical properties of pure biodiesel derived from the mixed WCO. From the above table it is cleared that properties of biodiesel and its blends are closely resemble to the properties of diesel and in accordance with ASTM D6751-12 limits.

Table 2: Properties of pure biodiesel and its blends

Properties	**Diesel**	**B5**	**B20**	**B30**	**B100**
Density (kg/m^3)	830	838	854	860	868

Specific gravity	0.833	0.839	0.854	0.860	0.869
Kinematic viscosity (cSt)	2.2	2.4	3.5	3.65	3.95
Acid value (mg KOH/gm)	0.35	0.37	0.40	0.42	0.48
Flash point (ºC)	60	64	72	80	160
Fire point (ºC)	68	70	82	92	170
Calorific value (kJ/kg)	44800	43926	42639	41091	38987

4.3 Performance of Biodiesel and Its Blends on IC Engine

Performance and emission test of biodiesel and its blends (B5, B20, B30 and B100) was conducted on single cylinder, 4 strokes diesel IC engine in Department of Mechanical Engineering, MIT Manipal. Engine run under different load conditions and constant engine running speed. In this experimentation, diesel fuel performance on engine was taken as bench mark to study the performance of biodiesel blends. The performance parameters consists of brake power (BP), specific fuel consumption (SFC), brake specific energy consumption (BSEC), brake thermal efficiency (BTE) and mechanical efficiency (ME). **Table 3** summarises the load details of IC engine. **Table 4** summarises the engine specification, on which performance of biodiesel conducted.

Table 3: Load details

0% load	Zero load on engine
25% load	4.5 kg load on engine
50% load	9.0 kg load on engine
75% load	13.5 kg load on engine
100% load	18.0 kg load on engine

Table 4: Engine specifications

Make	Kirloskar TV1 VCR
No. of cylinders	1
No of strokes	4
Fuel	H.S. diesel
Rated power	5.2 kW @ 1500 RPM
Cylinder diameter	87.5 mm
Stroke length	110mm
Compression ratio	17.5:1
Orifice diameter	20 mm
Dynamometer arm length	185

4.3.1. Break Thermal Efficiency Vs Break Power

Brake thermal efficiency is the ratio of brake power to the energy generated during the combustion process. **Figure 4** represented the increase in brake thermal efficiency (BTE) with the increase in brake power. In all cases, BTE increases with an increase in brake power. It is also observed that diesel shows slightly higher thermal efficiency at most of the loads than other fuels. BTE of B5 and B20 are comparable with BTE of diesel fuel. B30 and B100 showed less BTE compare to other blends. The elements like lower calorific values and higher viscosity of the biodiesel may additionally have an effect on the combination formation technique and subsequently bring about sluggish combustion consequently reducing the BTE. The molecules of biodiesel contain some quantity of oxygen, which participate in the combustion process.

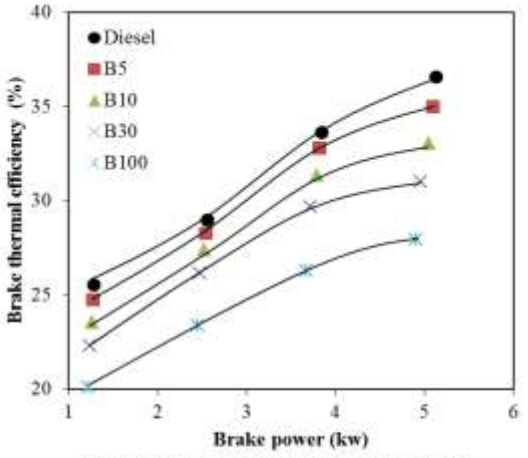

Fig 4: Variation of brake thermal efficiency with break power

Test consequences imply that when the mass percent of oxygen in biodiesel exceeds a certain limit, the oxygen losses its advantageous effect on the fuel energy conversion efficiency. So the BTE of diesel is higher than that of biodiesel blends.

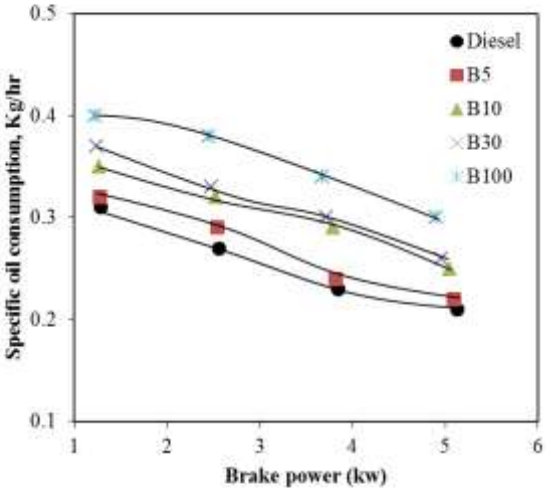

Fig 5: Variation of specific fuel consumption with break power

4.3.2 Specific Fuel Consumption Vs Break Power

Intake of fuel per unit energy at output shaft is referred to as specific fuel consumption. Specific fuel consumption (SFC) is reciprocally proportional to the brake thermal efficiency. As shown in **figure 5**, the variation in specific fuel consumption (SFC) with the change in brake power. For all blends and diesel examined, SFC reduced with increase in brake power (BP). B5 confirmed higher overall performance than other biodiesel blends and it was very near to that of diesel performance. B20 and B30 have almost same SFC. B100 has SFC higher than that of diesel, B5, B20 and B30. This is due to as biodiesel quantity increases in blends; its calorific value reduces thus results in higher SFC value.

4.3.3 Brake Specific Energy Consumption Vs Break Power

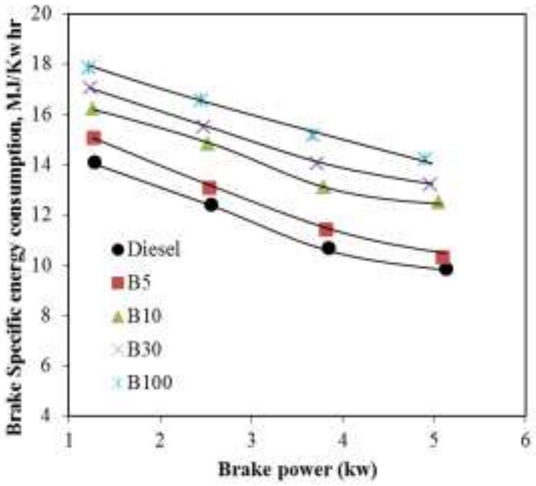

Fig 6: Variation of brake specific energy consumption with brake power

Brake Specific Energy Consumption (BSEC) is the energy utilised by engine to develop unit power. As represented in **figure 6** break specific energy consumption (BSEC) reduced with increase in brake power. BSEC reduced to minimum at full load condition by observing related results at full load engine condition, the value of BSEC for diesel, B5 and B20 blends were minimum compared to B30 and B100. BSEC of B5 was comparable with that of diesel fuel. But when compared to B5, B20 has higher BSEC. B30 and This isB100 have more BSEC value compared to all fuels. This is due to higher biodiesel blend like B30 and pure biodiesel have less calorific value compared to diesel, B5 and B20.

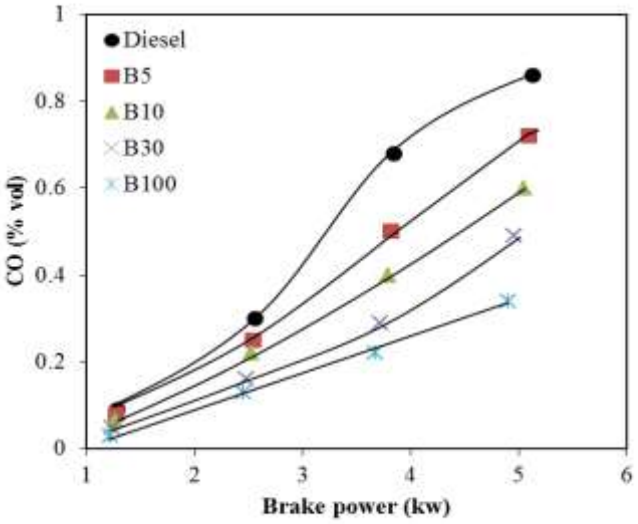

Fig 7: Variation of CO with brake power in emission test

4.4. Emission Test of Biodiesel and Its Blends

Emissions test of the engine was conducted by Non-Dispersive Infra-red (NDIR) Analyzers.

4.4.1 Emission of Carbonmooxide

Figure 7 represented the increase diesel fuel. Biodiesel and its blends showed lower CO emission compared to diesel due to oxygen content material inherently present in biodiesel which helps greater complete oxidation of fuel. It is can be seen from the graph of CO emission with increase in brake power. B100 has the lowest CO emission compares to other blends and diesel at full load of engine. Emission of CO from B5, B20 and B30 were lesser than that of emission of CO first of all decreased at 25% load however elevated at complete load because of better burning conditions at higher temperature.

4.4.2. Emission of Hydrocarbons

The variations of unburned hydrocarbons emission for diesel and biodiesel are shown in the **figure 8**. The emissions of unburnt hydrocarbons for biodiesel were relatively lower than that of diesel fuel. B20, B30 and B100 have lower HC emission compared to diesel and B5. Out of all biodiesel blends, B100 has lowest HC emission. This is due to the increased gas temperature and higher cetane number of biodiesel.

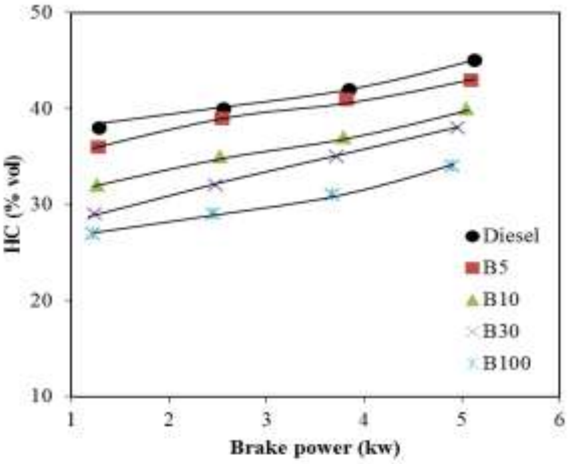

Fig 8" Variation of hydrocarbons with brake power in emission test

4.4.3. Emission of NO_x

As shown in Figure 9 emissions of NO_x increased with variation in brake power. Pure biodiesel and its blends showed increased emission than that of diesel fuel and B5. At full load B20, B30 and B100 have increased NO_x emission compared to diesel and B5. Increase in exhaust gas temperature due to lower heat transfer and the fact that biodiesel has some oxygen content in it which facilitates NO_x formation.

4.4.4 Emission of Carbon di-oxides (CO_2)

The emissions of CO_2 increased with increase in brake power. Pure biodiesel and its blends showed lower emission than that of diesel fuel. At full load B20, B30 and B100 have lower CO_2 emission compared to diesel and B5. Out of all biodiesel blends, B100 has lowest CO_2 emission. This is due to lower carbon to hydrogen ratio.

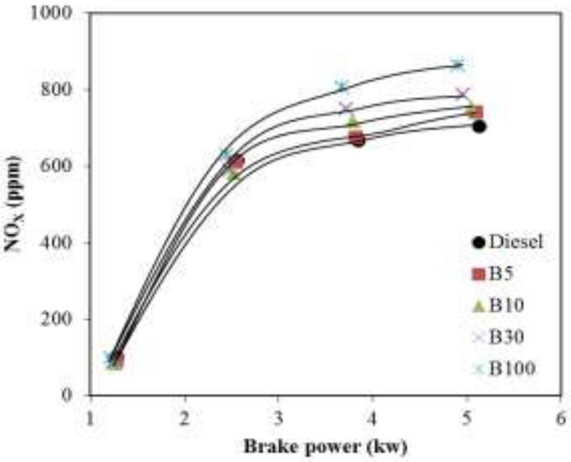

Fig 9: Variation of NOx with brake power in emission test

5. Conclusion

Waste cooking oil is a potential feedstock for biodiesel production because of its availability and low cost; it has been proven the best substitute for petroleum based products. Otherwise discard of waste cooking oil will pose serious environmental pollution. Production of biodiesel using the WCO as feedstock was done in the laboratory scale reactor. The highest yield of biodiesel was obtained at the ratio of oil to methanol of 1:8, reaction time 60 minutes, temperature 60 ºC, 0.85 wt% of KOH loading. The most of properties of the biodiesel were within standards of ASTM D6751-12.

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