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Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine

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Abstract

Non-edible filtered high viscous (72 cSt at 40 °C) and high acid value (44 mg KOH/gm) polanga (*Calophyllum inophyllum* L.) oil based mono esters (biodiesel) produced by triple stage transesterification process and blended with high speed diesel (HSD) were tested for their use as a substitute fuel of diesel in a single cylinder diesel engine. HSD and polanga oil methyl ester (POME) fuel blends (20%, 40%, 60%, 80%, and 100%) were used for conducting the short-term engine performance tests at varying loads (0%, 20%, 40%, 60%, 80%, and 100%). Tests were carried out over entire range of engine operation at varying conditions of speed and load. The brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) were calculated from the recorded data. The engine performance parameters such as fuel consumption, thermal efficiency, exhaust gas temperature and exhaust emissions (CO, CO_2, HC, NO_x, and O_2) were recorded. The optimum engine operating condition based on lower brake specific fuel consumption and higher brake thermal efficiency was observed at 100% load for neat biodiesel. From emission point of view the neat POME was found to be the best fuel as it showed lesser exhaust emission as compared to HSD.

Keywords: Polanga seed oil; Biodiesel; Triple stage transesterification

1. Introduction

Energy is essential input for economics growth, social development, human welfare and improving the quality of life. Since their exploration, the fossil fuels continued as the major conventional energy source. With increasing trend of modernization and industrialization, the world energy demand is also growing at faster rate. Apart from their indigenous production, majority of developing countries import crude oil to cope up their increasing energy demand. Thus, a major chunk of their hard earned export earnings is spent for purchase of petroleum products. Besides the energy (fuel) crisis, the other problem of concern is the degradation of environment due to fossil fuel combustion. Thus life at the present moment is caught between two major crises due to fossil fuel depletion and environmental degradation. Internal combustion engines (both petrol and diesel engines) have fallen victim to the crises. Thus it is essential that low emission alternate fuels must be developed for use in diesel engines. Vegetable oil is one of the main sources from which alternate fuel can be generated for use in the CI engines.

Use of vegetable oil in diesel engines is not a radically new concept as the inventor of diesel engine "*Rudolf Diesel*" demonstrated his first diesel engine at the World Exhibition at Paris in 1900 by using peanut oil as fuel. However due to abundant supply of petro-diesel, R&D activities on vegetable oil were not seriously pursued. It received attention only recently when it was conclusively realized that petroleum fuels are dwindling fast and environment-friendly renewable substitutes must be identified [1]. In the recent years, serious efforts have been made by several researchers [1–6] to use different vegetable oils as fuel in existing diesel engines. Peterson [16] reviewed the current status of vegetable oils as possible substitute for

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diesel fuel. The most predominantly oil bearing crops considered as fuel substituted are sunflower, safflower, soybean, cotton, winter rape, canola and peanut. Further, the investigator discussed the transesterification, oil processing and storage, filtration and engine test aspects.

The research and development activities in several countries on this subject have been mostly on sunflowers, saffola, soybean, rapeseed, pea nut and a host of others. Most of these oils are edible in Indian context. Thus the emphasis of the present work is to experimentally evaluate the possibilities of using biodiesel developed from one of the number of non-edible oil seeds available in India. Biodiesel can be produced from non-edible oil seeds like jatropha, karanja and can be grown in the waste lands of the country. Other non-edible oilseeds tree such as neem, cotton, rubber and polanga (undi), etc. have an estimated annual production potential of more than 20 megatonnes, of which polanga contributes 70 thousand metric tonnes. These oils have a great potential to produce biodiesel for diesel engine application [2].

2. Limitations of straight vegetable oils

The use of straight vegetable oils is restricted by some unfavorable physical properties, particularly their viscosity. Due to higher viscosity, the straight vegetable oil cause poor fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats resulting serious engine fouling. It has been reported in some of the literature, when direct injection engines are run with neat vegetable oil as fuel, injectors gets choked up after few hours. Choking of the injectors leading to poor fuel atomization, less efficient combustion and dilution of lubricating oil by partially burnt vegetable oil, which runs down the cylinder walls [6–12]. This necessitates the reduction in viscosity of the neat vegetable oils for use as substitute in diesel engines [4].

It has been reported in literature that out of different methods available for reducing the viscosity, transesterification is one of the most reliable and commonly used techniques to produce biodiesel from oil seeds. Transesterification is the reaction of vegetable oils fats with an alcohol in presence of a catalyst to form fatty acid alkyl esters and glycerol. A catalyst is used to make possible the reaction rate and yield because the reaction is reversible, excess alcohol is used to complete the reaction [3]. The main factors affecting transesterification are the amount and type of alcohol and catalyst; reaction temperature, pressure and time; the contents of free fatty acids (FFAs) and water in oils. Conversion is complicated if oil contains large amounts of FFAs (>1% w/w) that will form soap with alkaline catalyst. The soap can prevent separation of the biodiesel from the glycerin fraction. Some researchers have worked with feedstock having higher acid value using alternative double stage transesterification process [4,5].

Canakci and Gerpen [17] studied the effects of process variables on acid-catalyst transesterification of soybean oil. They reported that ester conversion reached 98.4% at the molar ratio of 30:1 with sulphuric acid catalyst at 60 °C. It was reported that the ester conversions were 8.3%, 57.2% and 87.8% at 25, 45, and 60 °C temperatures, respectively. The specific gravity of ester decreased with increasing reaction temperature. They studied the effect of catalyst amount by conducting reaction for 48 h at 60 °C with a 6:1 molar ratio of methanol to oil. They reported that ester formation increased from 72.7% to 95.0% as the catalyst was increased from 1% to 5%. Ester conversion increased from 87.8% to 95.5% when the reaction time was increased from 48 to 96 h. The conversion to ethyl ester was 95.8% compared with 92.9%, 92.1% and 87.8% for 2-propyl ester, 1-bytyle ester and methyl ester, respectively. They added different amount of distilled water to the vegetable oil to study the effect of water on transesterification. It was reported that the addition of 5% water reduced the ester conversion by only 5.6%.

Schumacher et al. [18] note few differences when tractors were fueled with diesel fuel as compared with soy-diesel, a blend of soybean oil methyl ester and diesel fuel. They observed an average power difference of less than 0.4% when the tractors were fueled with a 20% soybean oil ester and 80% diesel as compared to diesel fuel only. The greatest reduction in power occurred when the tractor engines were fueled with 100% soy-ester. They observed a negative linear relationship between the concentrations of methyl soyate in diesel fuel and the amount of CO in the exhaust emissions. The CO exhaust emissions reductions ranged from 7% to 42% when the concentration of methyl soyate increased from 10% to 100%. The NO_x increased with an increase in the methyl soyate in the blend and ranged from 3% to 19% for 10–100%, respectively. The HC exhaust emissions reductions ranged from 22% to 38% as methyl soyate was increased by 5% and 4% when the diesel fuel was blended with 10% and 20% methyl soyate, respectively, but the smoke was reduced by 12–63% with 30–100% methyl soyate, respectively.

Research & development activities related to use of vegetable oil/biodiesel are being pursued in Engine and Unconventional Fuel Laboratory of Indian Institute of Technology, Delhi. This paper highlights a part of the experimental activities carried out in Indian Institute of Technology Delhi on production of biodiesel from polanga oil having high acid value in a pilot plant and its subsequent utilization in a single cylinder diesel engine widely used in rural/agricultural sector of the country. Crude polanga oil generally has high acid value 44 mg KOH/gm (22% FFAs) and thus a dependable technique for converting this polanga oil to biodiesel is very much required. In the present investigation, biodiesel was produced from polanga oil by way of triple stage transesterification in which the neat vegetable oil is under gone pretreatment process with acid catalyst to reduce the acid value below 2 for maximum biodiesel production. Based on the availability and production potential in the country, oil derived from polanga seeds was chosen for the present

investigations to evaluate the performance and the exhaust emission characteristics of a single cylinder diesel engine.

3. Potential and characterization of polanga seed oil

The species have been planted widely throughout the tropics and it is uncertain from where it originates. It is believed to be indigenous to India, Malaysia, Indonesia and the Philippines. It grows in areas with 1000–5000 mm rain per year at altitudes from 0–200 m. It essentially falls to a group of coastal species that grows on sandy beaches and, to a lesser extent, along river margins further inland. It is highly tolerant to strong winds, salt spray and brackish water tables. The trees are sensitive to frost and fire. The wind and salt tolerance makes it suitable for sand dune stabilization. The fruits are used for human consumption although they are reported to be slightly toxic. It is a medium-sized tree, normally up to 25 m tall, occasionally reaching up to 35 m and with diameter up to 150 cm. The bole is without buttresses; it is usually twisted or leaning especially on wind exposed sites. It has sticky latex that is either clear or white to yellowish. The fruit is a round drupe, 2–4 cm in diameter. The single, large seed is surrounded by a shell (endocarp) and a thin, 3–5 mm layer of pulp. The fruit is at first pinkish-green later turning bright green and when ripe, it turns dark grey-brown and wrinkled. There are 100–200 seeds/kg. The tree can flower and bear fruit all year round in Indian conditions, In Tamil Nadu and Mysore (India) flowers usually appear in the cold season and fruits ripen in March. In Kerala, flowers appear in March–April and fruits ripen in May–June, although both flowers and fruits can be found at other times of the year. In Orissa, there are two seasons, with flowering during May–June and October–November. In the Andaman Islands, the tree will flower profusely during the rainy season and, to a lesser extent, at other times of the year, with fruiting from June to August. The flowers are pollinated by bees and other insects, and fruits are dispersed by sea currents and fruit bats [13–15].

The unrefined but filtered polanga oil is dark green in colour and is used as feedstock for the biodiesel production in this study. The fatty acid composition and the important properties of polanga seed oil in comparison with other non-edible oils is given in Table 1 [4,14]. The type and percentage of fatty acids contained in vegetable oils depends on the plant species and on the growth conditions of the tree. Polanga oil contains 24.96% saturated acids (palmitic and stearic) and 72.65% unsaturated acids (oleic, linoleic and linolenic). Saturation fatty acid alkyl esters increase the cloud point, cetane number and stability. The free fatty acid content of unrefined filtered polanga oil was found to be 22%, i.e. acid value of 44 mg KOH/g. Its free fatty acid content was determined by a standard titrimetry method [5]. The yield of esterification process and quality of biodiesel decreases considerably if acid value is greater than 4 mg KOH/g, i.e. free fatty acid content is 2%. Therefore, development of any method to produce biodiesel from high acid value oils is significant. Hence, the efforts are made to esterify a typical high free fatty acid type of oil, i.e. polanga seed oil in this study.

4. Experimental system development for biodiesel formulation

4.1. Methodology

Experiments were conducted in a laboratory set up which consists of heating mantle, reaction flask (made of glass) and mechanical stirrer. The working capacity of reaction flask is 1 l. It consists of three necks: one for stirrer, and the others for condenser and inlet of reactant as well as for placing the thermocouple to observe the reaction temperature. The flask has a stopcock at the bottom for collection of the final product. The progress of the reaction was observed by measuring the acid value. In course of the test, it was observed that the appropriate quality of biodiesel could be produced from polanga oil in following three stages so that the physico-chemical properties were close to those of petro-diesel.

(i) Zero catalyzed transesterification: The first stage removes the organic matters and other impurities

Table 1
Properties of polanga seed oil in comparison with other oils

Property of the oils	Polanga (*Calophyllum inophyllum*)	Rubber (*Ficus elastica*)	Cotton (*Gossypium herbaceum*)	Karanja (*Pongamia pinnata*)	Jatropha (*Jatropha curcas*)
Fatty acid composition (%)					
(i) Palmitic acid $C_{16:0}$	12.01	10.2	11.67	11.65	16.0
(ii) Stearic acid $C_{18:0}$	12.95	8.7	0.89	7.50	6.5
(iii) Oleic acid $C_{18:1}$	34.09	24.6	13.27	51.59	43.5
(vi) Linoleic acid $C_{18:2}$	38.26	39.6	57.51	16.46	34.4
(v) Linolenic acid $C_{18:3}$	0.3	16.3	0	2.65	0.80
Specific gravity	0.896	0.91	0.912	0.913	0.920
Viscosity (cSt) at 40 °C	71.98	66.2	50	27.84	18.2
Flash point (°C)	221	198	210	205	174
Calorific value (MJ/kg)	39.25	37.5	39.6	34.0	38.5
Acid value (mg KOH/gm)	44	34	0.11	5.06	3.8

present in the unrefined filtered polanga oil using reagent.

(ii) Acid catalyzed transesterification: The intermediate stage reduces the acid value of the oil about 4 mg KOH/gm corresponding to a FFA level of 2%.

(iii) Alkaline catalyzed transesterification: The product of the intermediate stage (pure triglycerides) is transesterified to mono-esters of fatty acids (biodiesel) using alkali catalyst.

4.2. Biodiesel production procedure

The raw polanga oil was extracted by mechanical expeller in which small traces of organic matter, water and other impurities were present. These materials were creating problems in yield and in the phase separation between the glycerin and esters. This necessitates the pretreatment of polanga oil in the first stage. One litre of polanga oil was mixed with 350 ml of methyl alcohol and 5 ml of toluene as a reagent. Toluene helps in dissolving the organic matter with methanol and separating it from the neat oil along with other impurities. Different methanol to oil ratio (0.15, 0.20, 0.25, 0.30, 0.35, and 0.40) and reaction times (0.5, 1.0, 1.5, 2.0 h) were used to investigate for the optimization and their influence on the acid value of crude polanga oil. The mixture was stirred in the air closed reaction flask for 2 h at 65 °C. The heating set up should be just above the boiling point of the alcohol i.e. 65 °C to accomplish the reaction. The speed of the stirrer was kept same for all test runs. The reactions were carried out with continuous stirring with mechanical stirrer with stirring speed 450 rpm. The product from the first stage was allowed to settle for 1 h and complete phase separation was visualized. The upper layer which consisted of methanol–water fraction, organic matter toluene and other impurities was separated from the lower layer. The acid value of the required lower layer is determined and found to be 18 mg KOH/g corresponding to FFA of 9%.

Anhydrous sulphuric acid (98.4%) was used as catalyst in the acid catalyzed transesterification. Experimentally it was optimized that 0.65% by volume of the H_2SO_4 acid and a molar ratio of 6:1 gave the maximum conversion efficiency of free fatty acids to triglycerides and thereby reducing the acid value of the product of second stage below 4 mg KOH/g. The duration of the reaction was 4 h.

The product of second step having FFA less than 2% was used as the raw material for the final stage. A molar ratio of 9:1 and the 1.5% by weight of potassium hydroxide was found to give the maximum ester yield for reaction duration of 4 h. After the reaction was completed the products were allowed to separate in two layers. The lower layers contained impurities and glycerol. The top ester layer is separated and purified by using warm water. After washing, the final product was heated up to 70 °C for 15 min under vacuum condition and stored for further use. This resulted in a clear amber-light yellow liquid with a viscosity similar to petro-diesel.

Table 2
Properties of polanga oil methyl ester (biodiesel) in comparison with diesel and blends

Fuel blends	Viscosity (cSt)	Calorific value (MJ/kg)	Flash point (°C)	Cloud point (°C)	Pour point (°C)
HSD	2.87	44.22	76	6.5	−3
B20	2.98	43.85	86	7.8	2.8
B40	3.30	42.65	91	8.5	2.8
B60	3.61	40.98	96	10.6	3.2
B80	3.72	39.23	111	10.8	3.6
B100	4.92	38.66	140	13.2	4.3

4.3. Biodiesel characterization

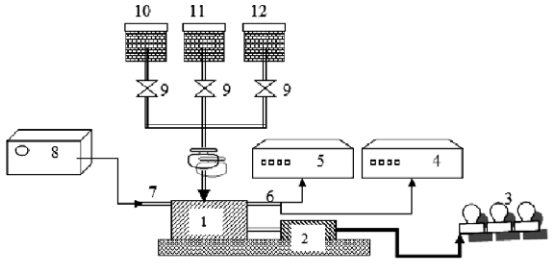
The formation of methyl ester by three stage transesterification stochiometrically requires six moles of alcohol for every mole of triglyceride. However, transesterification is an equilibrium reaction in which an excess of the alcohol is required to drive the reaction close to completion. The optimum ratio was found to be 6:1 molar ratio of methanol to oil (triglyceride) which is sufficient to give 85% yield of ester. It might be anticipated that, in such an equilibrium system, the observed phase separation of the by-product, glycerol, would play a major role in achieving a conversion close to 100. The completeness of transesterification was monitored with HPLC method. The reaction was completed up to 85% in 90 min and the reaction was carried out for 4 h to achieve complete reaction.

The physico-chemical properties of the polanga oil, neat petro-diesel, neat biodiesel (B100) and its blend of 20% at each step were evaluated as per the ASTM standard methods and the results are in accordance with ASTM. The fuel properties of polanga oil methyl ester and its different blends with diesel are shown in Table 2. It is observed that the chemical characteristics of the polanga oil methyl ester were found to be in the close range of engine requirement.

5. Engine performance study

Short-term engine performance tests were carried out on a small-size water-cooled direct injection diesel engine with neat diesel oil, neat biodiesel (B100) and its blend of 20% at each step. The objective of such a study was to ascertain the suitability of these fuels for engine application.

Engine systems was equipped with several experimental subsystems and was instrumented at the appropriate location (Fig. 1) to evaluate the performance parameters such as brake specific fuel consumption (BSFC), brake specific energy consumption (BSEC), brake mean effective pressure (BMEP), brake thermal efficiency, and volumetric efficiency. The dynamometer used to load the engine comprised a shunt wound AC generator and load bank. Pressure in the inlet manifold was measured by a normal U-tube manometer. Airflow was measured by means of a viscous flow meter. Thermocouples were installed to monitor gas temperatures at inlet and outlet ducts as well as cylinder wall temperatures. The fuel system was modified by



1. Single cylinder 4-stroke diesel engine
2. Altrenator
3. Lamp load
4. Gas Analyzer
5. Smokemeter
6. Exhaust manifold
7. Intake manifold
8. Air drum
9. Control valve
10. Fuel Tank for neat diesel
11. Fuel Tank for blends of diesel and biodiesel
12. Fuel Tank for neat biodiesel (B100)

Fig. 1. Schematic diagram of experimental set up for engine test rig.

adding an additional filter and three-way, hand operated, two position directional control valve which allowed rapid switching between the diesel fuel used as a standard and the test fuels. Fuel was fed to the injector pump under gravity and the volumetric flow rate was measured by the use of a 50 cm^3-graduated burette and stopwatch. The speed was also checked with an infrared type digital tachometer. The experiments were carried out by using diesel, B20 POME (20% POME + 80% diesel), B40, B60, B80 and B100 POME (100% neat biodiesel) at different load condition on the engine from 0% to 100% in approximate steps of 20%.

To evaluate the performance parameters, important operating parameters such as engine shaft speed in rpm, generator output, fuel consumption rate, airflow rate, temperature of engine cooling water and engine exhaust gases were measured and the performance characteristics were determined from their fundamental relations while varying the load on the engine from 0% to 100% in steps of 20%. Significant engine performance parameters such as brake specific fuel consumption (BSFC), brake specific energy consumption (BSEC), brake mean effective pressure (BMEP), brake thermal efficiency for petroleum based diesel and its blend with polanga biodiesel were calculated. These results are analyzed and represented graphically as shown in Figs. 2 and 3.

However, BSFC not a very reliable parameter to compare the fuel blends as the calorific value and the density of the blends follow a slightly different trend. Hence brake specific energy consumption (BSEC) is a more reliable parameter for comparison. A close look at the graphs indicates the variation of BSEC with respect to BMEP shows an improvement for neat biodiesel (B100) operation. This is due to the low calorific value of biodiesel. Brake specific fuel consumption is not a very reliable parameter to compare the two fuels as the calorific value and the density of the blend follow a slightly different trend. Hence brake specific energy consumption (BSEC) is a more reliable parameter for comparison of volumetric consumption of the two fuels. It is observed from Fig. 2 that BSEC is

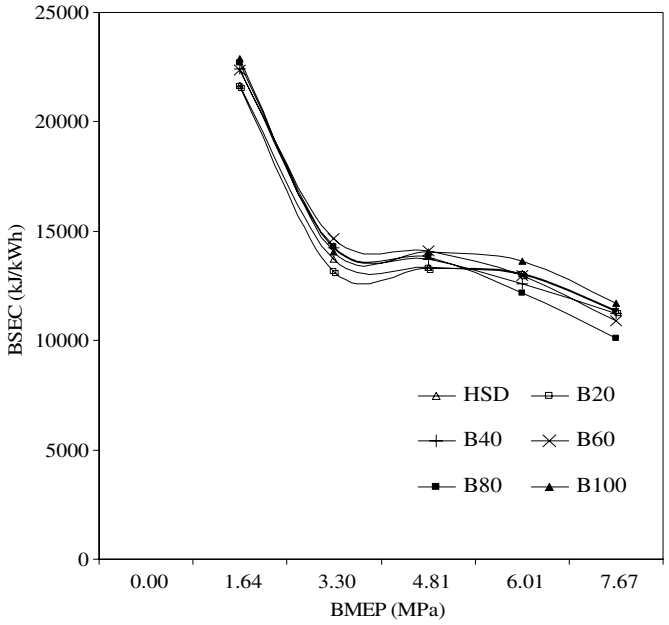


Fig. 2. Comparative plot of brake specific energy consumption vs. brake mean effective pressure.

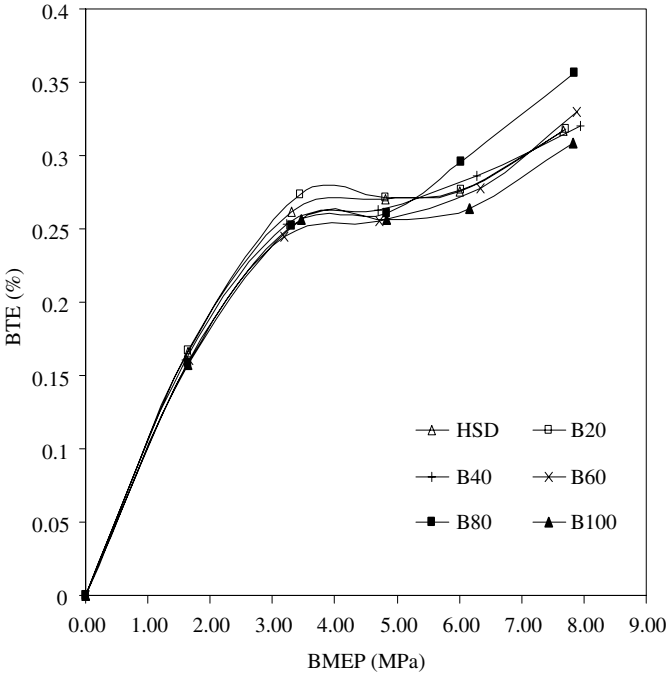


Fig. 3. Comparative plot of brake thermal efficiency vs. brake mean effective pressure.

slightly higher for B100 at lower loads and remains same at higher loads. The trends of the brake thermal efficiency of biodiesel for B100 have improved slightly specially at lower loads and remain same at higher loads as compared to neat petroleum based diesel fuel as shown in Fig. 3. This may be possibly due to better combustion and additional lubricity of biodiesel.

6. Exhaust emission characteristics

The engine exhaust emissions such as carbon monoxide, carbon dioxide, nitrogen oxides, and unburned hydrocarbon were measured with a five gas analyzer (AVL DiGas – 4000 model) and a smoke-meter (AVL 437 model). The sensor of the analyzer was exposed to the exhaust gas and the observations were recorded. The measured emissions were analyzed and interpreted graphically as shown in Figs. 4–7. The smoke is significantly reduced for biodiesel of higher blends (B60 and B100) as compared to neat petroleum based diesel fuel as shown in Fig. 4. This is due to the complete and stable combustion of the biodiesel, which contains more number of oxygen atoms.

Pollutants such as smoke and NO_x are of specific relevance to diesel combustion. Hence the optimum biodiesel concentration was analyzed in respect of NO_x emissions. From the NO_x curves given in Fig. 5, two important conclusions can be made. First, NO_x emissions are a direct function of engine loading. This is expected because with increasing load, the temperature of the combustion chamber increases and NO_x formation is a strongly temperature dependent phenomenon. Second important observation is that the NO_x emissions in the case of biodiesel fuel are lower by approximately 4%. These lower NO_x emissions may be due to lower temperatures of the combustion chamber using biodiesel. This is also evident from lower exhaust temperatures from the biodiesel-fueled engine. However these observations contradict the NO_x emissions from B20 (soybean oil methyl ester) fueled diesel engines were found to be 2% higher than conventional diesel oil according to a report on biodiesel from National Biodiesel Board of USA. In our study, 100% biodiesel blend gave 4% lower NO_x emissions with respect to percentage of load. This difference may be because of difference in engine geometry, compression ratio, less reaction time and temperature in case of biodiesel.

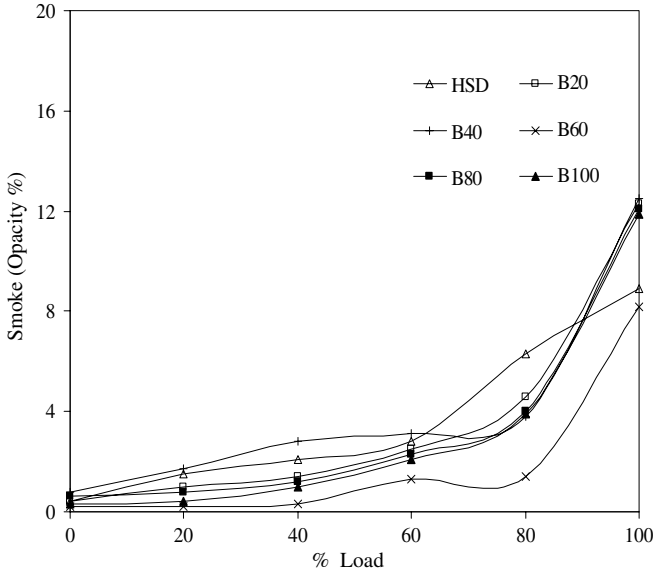


Fig. 4. Comparative plot of smoke (opacity %) vs. % load.

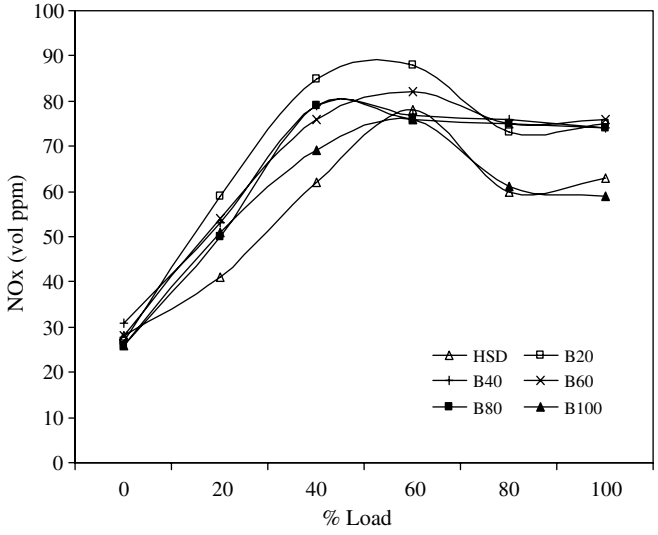


Fig. 5. Comparative plot of NO_x vs. % load.

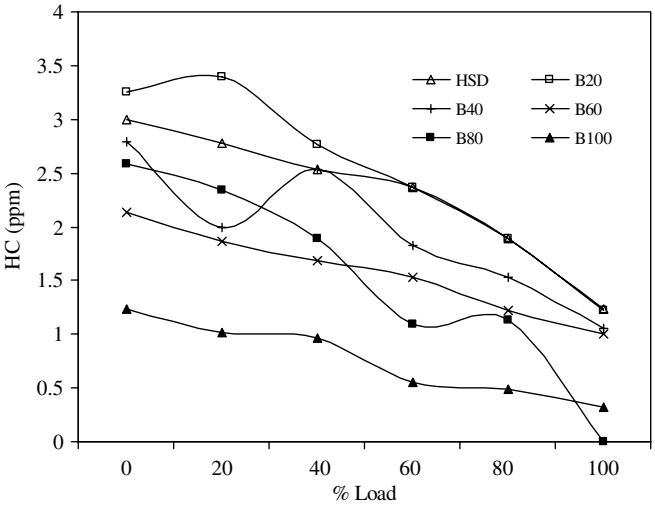


Fig. 6. Comparative plot of unburned hydrocarbons vs. % load.

Unburned hydrocarbon (HC) is also an important parameter for determining the emission behavior of the engines. It is observed from the graph (Fig. 6) that neat biodiesel (B100) gives relatively lower HC as compared to the neat diesel. This is because of better combustion of biodiesel inside the combustion chamber due to the availability of oxygen atom in biodiesel.

Carbon monoxide and carbon dioxide emission for B20 and B100 remain same over the entire range of load. But these are slightly reduced as compared to petroleum based diesel fuel. Green house emission like carbon dioxide emission has shown 40% of reduction for B20 and B100 as compared to neat diesel fuel operation as shown in Fig. 7. Functionally, emission of greenhouse gas such as carbon dioxide can be taken by the plant during the process of photosynthesis, while preparing seed for biodiesel.

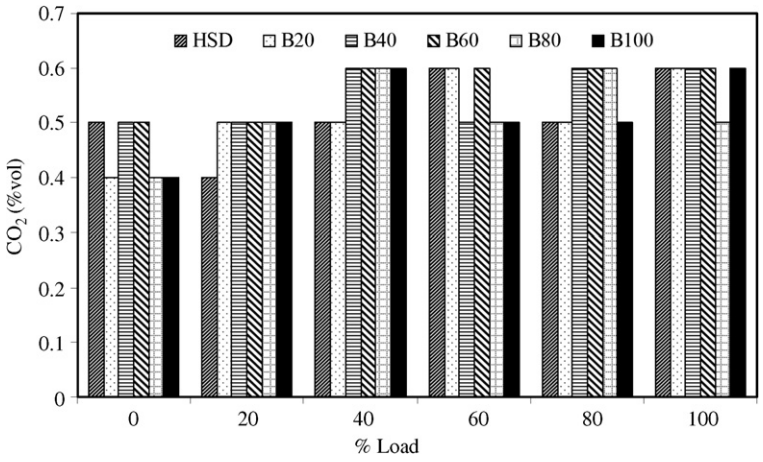


Fig. 7. Comparative plot of CO_2 vs. % load.

7. Conclusions

Based on the exhaustive engine tests, it can be concluded that polanga based biodiesel can be adopted as an alternative fuel for the existing conventional diesel engines without any major hardware modifications in the system. The viscosity of vegetable oil reduces substantially after transesterification. The density and viscosity of the polanga oil methyl ester formed after triple stage transesterification were found to be close to those of petroleum diesel oil. The flash point of all the blends of POME was higher than that of diesel oil. Particularly, the 100% biodiesel also demonstrated comparatively higher flash point than petroleum diesel oil and was in safe range for storage. All these tests for characterization of biodiesel demonstrated that almost all the important properties of biodiesel are in very close agreement with the diesel oil making it a potential fuel for the application in compression ignition engines for complete replacement of diesel fuel.

This diesel engine can perform satisfactorily on biodiesel fuel without any engine hardware modifications. The 100% biodiesel was found to be the best, which improved the thermal efficiency of the engine by 0.1%. Similar trend was shown by the brake specific energy consumption and the exhaust emissions were reduced. Smoke emissions also reduced by 35% for B60 as compared to neat petro-diesel. Decrease in the exhaust temperature of a biodiesel-fueled engine led to approximately 4% decrease in NO_x emissions for B100 biodiesel at full load.

The performance of biodiesel-fueled engine was marginally better than the diesel-fueled engine in terms of thermal efficiency, brake specific energy consumption, smoke opacity, and exhaust emissions including NO_x emission for entire range of operations. It was conclusively proved that excess oxygen content of biodiesel played a key role in engine performance. Neat biodiesel is proved to be a potential fuel for complete replacement of petroleum diesel oil. However long term endurance test and other tribological studies need to be carried out before suggesting long term application of polanga oil based biodiesel.

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