Biodiesel production and characterisation from Pongamia oil using low cost Pisthia shell catalyst: engine performance and emission studies

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Abstract: Production of fatty acid methyl esters from pongamia oil through trans-esterification was reported in this paper. The GC – MS analysis of oil was studied and the major fatty acids content was found to be 12.25% by weight. The molecular weight of the oil was 887.039 g/mol. A maximum yield of 85% biodiesel was reported when the reaction temperature, time, methanol/oil ratio and catalyst loading rate were 60°C, 45 min, 12:1 and 0.5% by (wt. %) respectively. The low cost pisthia shell catalyst was prepared and characterised in the laboratory setup. Partial purification of the fatty acid methyl esters was proposed for increasing the purity of the biodiesel and better engine performance and that was obtained from the oil firm itself. The flash point and the fire point of the biodiesel were found to be 172°C and 225°C, respectively. The brake thermal efficiency of B10 blend of biodiesel was 34% for maximum load, specific fuel consumption for diesel was 0.55 kg/kWhr at maximum load and for the blend of B50. The use of biodiesel blends showed a reduction of carbon monoxide and hydrocarbon emissions and a marginal increase in nitrogen oxides (NO_x) emissions.

Keywords: Pongamia Pinnata oil; characterisation; transesterification; hetrogenuous catalyst; biodiesel; engine performance; emission studies.

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1 Introduction

Biodiesel are mono alkyl esters of fatty acids obtained through processes like trans-esterification, emulsification and pyrolysis. Trans-esterification can be done using acid or base as catalyst. Base being widely used (Meher et al., 2006; Sureshkumar et al., 2008). Along with this, oils having higher free fatty acid content has to go through acid and base catalyst as well. Thus two step process is used. First acid esterification followed by base transesterification. Homogenous catalysts are widely used like KOH and NaOH. However due to increase in cost of high quality feedstock and less performance of low quality feedstock with bases for biodiesel production, heterogeneous catalysts are introduced. Heterogeneous catalysts have better catalytic activity, simple catalyst recovery, reusability and less energy and water consumption. They give better performance for esterification and transesterification processes. There are a variety of edible and non-edible oils that are used for biodiesel production. Pongamia is one of the non edible species which can be used as the biodiesel production and which is abundantly available in the coastal areas and the forest areas of most of the states of India. It can grow in all type of land with annual rainfall of 5–25 mm and temperature range of 0–50°C. The output obtained from single Pongamia tree is approximately 27–50% of oil per 25–100 kg of seeds. Recently use of edible oils is reduced. Catalysts play an important role in any process.

Basically homogenous catalysts are used, only drawback of these catalysts being high water production and soap formation. Thus heterogeneous catalyst is used in the form of low cost pisthia shell powder. It gives calcium oxide as main product. Use of low cost pisthia shell as a catalyst instead of conventional homogenous KOH or NaOH provides superior catalytic activity. Homogeneous alkaline catalysts which are conventionally used possess drawback, as it is an energy intensive, produces excess amount of water, and difficult to separate. Heterogeneous catalysts consume very less energy, produce less water and can be reused. CaO which presents in large quantity in nature is one of the mostly used as a catalyst due to its low cost, and high activity during production biodiesel. Low cost pisthia shells were calcined to derived CaO which shows superior catalytic activity, alkaline property, special porous structure and used as a heterogeneous

catalyst. After proper catalyst preparation it is used with methanol for trans-esterification process. Performance and emission studies are also done and are important (Marchetti et al., 2007; Agarwal and Bajaj, 2009; Sharma and Singh, 2010).

2   Materials and methods

2.1   Materials

In this study, readily available pongamia oil was obtained from Bannari Sugars pvt. Ltd. Pisthia shells were obtained from nearby locality. Anhydrous methanol chemical of analytical grade was purchased from local market.

2.2   Oil characterisation and catalyst preparation

The oil was characterised using GCMS. The low cost pisthia shells were cleaned thoroughly in tap water and dried in an oven at 100°C for 12 h. The dried Pisthia shells were crushed into small pieces and calcined in a muffle furnace at 800°C for 3 h to convert the calcium species present in the shells into CaO particle. Then the CaO originated from the shells was refluxed in water at 70°C for 4 h and the calcined shells particles were taken out and dried in hot air oven at 100°C for 10 h. The calcined shell catalyst product was dehydrated by drying at a temperature 500°C for 5 h. The catalyst prepared through calcination was subjected to scanning electron microscopy (SEM) to study the microstructure and catalyst property (Sinha and Murugavelh, 2006; Babu and Devaradjane, 2003).

Table 1   Physical and chemical properties of oil feedstock

Sr. no	Properties	Characteristics
1	Colour	Dark brown
2	Acid value (mg KOH/g)	12.27
3	Saponification value (mg KOH/g)	185–195
4	Kinematic viscosity at 40°C (mm^2/s)	27.84
5	FFA content % by weight	12.25%
6	Calorific value (mJ/Kg)	34
7	Flash point (°C)	263
8	Specific gravity	0.912

2.3   Trans-esterification process

Pongamia oil, methanol, and catalyst were used for the production of biodiesel. Batch reactor for the trans-esterification was performed in a 3-necked round bottomed flask of 500 ml capacity which was equipped with a reflux condenser and magnetic stirrer. A measured volume of 500 ml pongamia oil, methanol to oil molar ratios (6:1, 9:1, 12:1 or 15:1) and amount of catalyst 0.5% (wt.%) were added into the round bottom flask and was preheated at the various temperature of about 60°C which was then fixed with the

mechanical stirrer, condenser and the temperature measuring device. After the reaction is complete, a mixture was allowed to cool and then the solid catalyst was removed by filtration to get the product. Methyl ester and glycerol phases were allowed to stabilise and then separated by using a separating funnel (Sinha and Murugavelh, 2016; Venkatraman and Devaradjane, 2011). Table 2 well describes above condition.

Table 2   Molar ratios and catalyst concentration

Molar ratio	Catalyst % by weight	Temp in °C	Time in min	% yield
6:1	1% of Pisthia shell	60	45	20
9:1	5% of sulphuric acid	65	45	42
6:1	0.5% Pisthia shell	60		
12:1 9:1	5% 1%	65 60	45	55
12:1 6:1	5% 0.5%	65 60	45	85
15:1 6:1	5% 0.5%	65 60	45	75

2.4   Engine tests and emission studies

Biodiesel obtained from Pongamia oil was used as fuel in a single cylinder diesel engine. Earlier the flash point and fire point was measured by using Cleveland open cup apparatus. The engine was allowed to run with the blend made with B10, B20, B30, B40 and B50. The experimental setup consisted of a four stroke, single cylinder, air cooled and direct injection diesel engine connected to an electrical dynamometer. The exhaust gas analyser and diesel smoke metre were placed in the exhaust manifold to measure the exhaust emission, such as CO, CO_2, NO_x and unburnt hydrocarbons (HC). At the beginning engine was operated with neat diesel fuel for addressing the reference data. The fuel blends were obtained by mixing different percentages of biodiesel with pure diesel fuel (Karmee and Chadha, 2005; Altin et al., 2001).

2.5   Engine specifications

Name of the manufacturer: Kirloskar brothers pvt. Ltd

Rated speed: 1,500 rpm

Brake power: 3.7 KW efficiency of the generator: 92%

Fuel used: diesel rated voltage on generator: 220 V

Arm length to load cell = 0.145 m

Maximum load on engine = 16.58 Kg

Orifice metre (orifice diameter) = 17 mm

Stroke length: 110 mm

Piston diameter/Bore diameter = 80 mm

Density of diesel = 804 Kg/m^3

Calorific value of diesel 43,500 KJ/Kg

Gas analyser ECO gas 100 and diesel smoke metre ECO smoke 100.

## 3   Results and discussions

3.1   Oil characterisation

Acid value of the oil was found to be 12.27 mg KOH/g. Free fatty acid content was found to be 12.25%. Calorific value was 34 MJ/kg. Molecular weight of the oil was found to be 887.039 g/mol. All the characteristics are mentioned in the Table 1 at the end of this manuscript.

3.2   Catalyst characterisation

3.2.1   SEM analysis

SEM image Figure1 of the catalyst before reaction resembles to honey comb. It is porous in structure and possesses active sites. This indicated the catalyst has more surface area for reaction. SEM image Figure 2 of the catalyst after reaction has fewer voids because of the shear change during trans esterification. The number of pores in the catalyst after reaction was found to be reduced. It can be attributed to the fact that the active sites were utilised for trans-esterification reaction (Meher et al., 2006; Sinha and Murugavelh, 2016).

Figure 1   SEM image of the catalyst before reaction
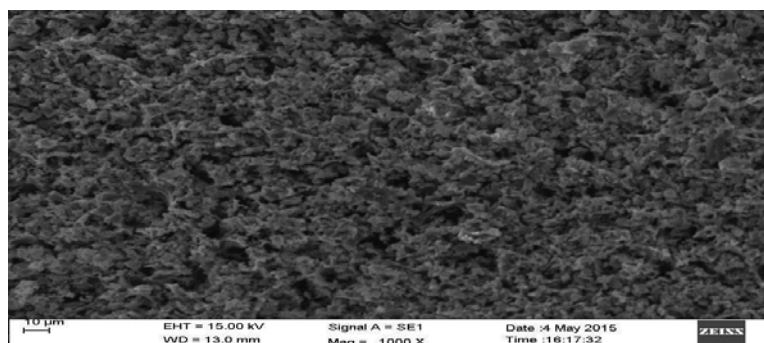
Figure 2   SEM image of the catalyst after reaction
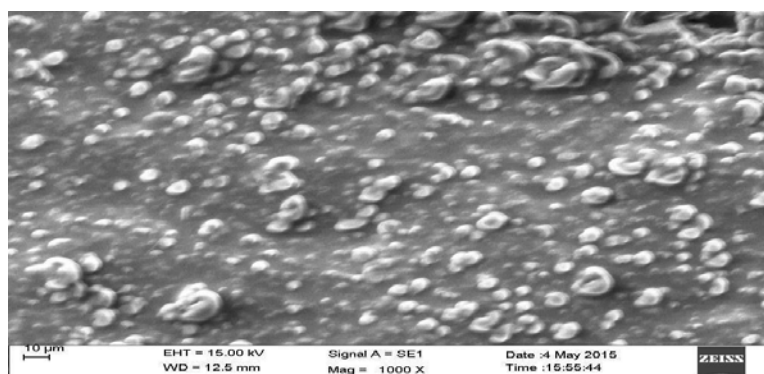
3.2.2 Biodiesel characterisation

Table 3 elaborates about biodiesel properties compared with standard ones. Density is 880 kg/m^3. Calorific value is found to be 35.36 MJ/kg. All other values are found to be much in accordance with the standard ones. ASTM standards were used as benchmark for validation purpose.

Table 3   Properties of biodiesel

Property	Std. range	Obtained value	ASTM standards
Density at 40°c (kg/m^3)	876–890	880	D 1298
Kinematic viscosity (mm^2/s)	4.37–9.60	8.64	D 445
Calorific value (MJ/Kg)	36–38	35.56	D 613
Flash point (°C)	163–187	172	D 93
Cloud point (°C)	13–15	14.3	D 2500
Fire point (°C)	200–250	225	D 2500
Cetane number	32–38	35	D 613
Acid value	2–4	2.63	D 1298
Specific gravity	0.70–0.95	0.878	D 633

3.2.3 Characterisation of blends

Table 4 elaborately states all the characteristics of varying blends of biodiesel along with neat diesel. They all are found in accordance with the nature of blend addition. As the blend percentage is increased, *diesel properties of the oil go on diluting*. Viscosity increases and thus flammable properties of oil decreases.

Table 4   Characteristics of biodiesel blends

| Properties	B10	B20	B30	B40	B50	Diesel
Kinematic viscosity (mm^2/s)	3.1	4	4.5	5	5.6	3.07
Calorific value (MJ/Kg)	40	38	37.5	37	36.8	43.5
Flash point (°C)	58	66	70	75	78	67
Fire point (°C)	60	65	70	75	80	82
Specific gravity	0.834	0.838	0.845	0.852	0.856	0.804

3.3 Effect of reaction parameters

3.3.1 Effect of molar ratio

The reaction was maintained at 60°C for 45 min and 0.5% by wt of pisthia shell catalyst is used. Various molar ratio ranging from 6:1 to 18:1 was studied. Figure 3 shows the biodiesel yield with respect to different methanol to oil molar ratio. A maximum yield of 85% percentage was reported for 12:1 molar ratio.

Subsequently it was observed that the biodiesel yield increased from 20% to 85% when methanol to oil molar ratio was stepwise increased from 6:1 to 12:1. Consequently when methanol to oil molar ratio was achieved up to 15:1, the biodiesel yield decreased to 75%. This could be because of excess amount of methanol deceased the concentration

of catalyst, and also shifted the equilibrium in the backward direction, finally lower the yield of biodiesel fuel (Karmee and Chadha, 2005; Altin et al., 2001).

Figure 3   Comparison between molar ratio and % yield obtained (see online version for colours)
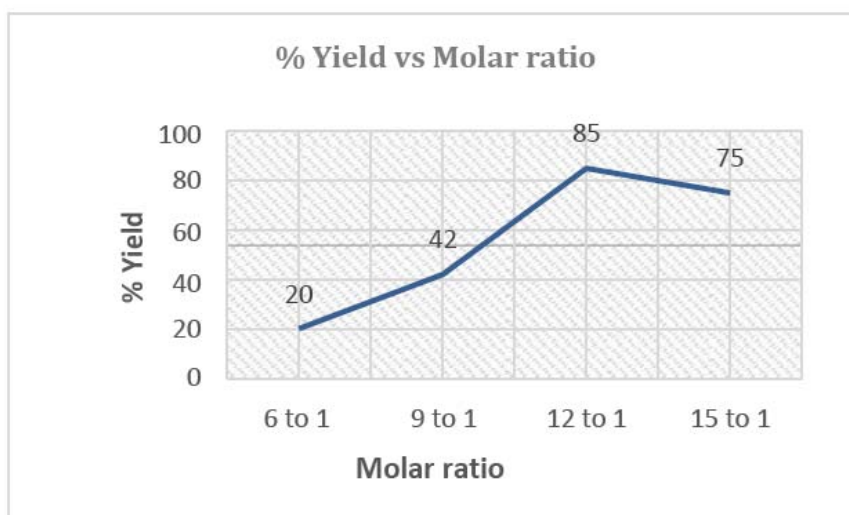
3.3.2   Effect of catalyst loading

The reaction was performed at 60°C for 45 min by using 12:1 methanol to oil molar ratio. In Figure 4 the effect of catalyst loading concentration on biodiesel fuel yield was examined. The catalyst loading was increased gradually from 0.25% to 0.3%. Subsequently the amount of wt% catalyst loading concentration increased with biodiesel yield increased from 20% to 85% and also recorded that highest yield of 85% was found at 0.5 wt.% amount of catalyst during trans-esterification process. *Consequently, for 0.2% and 0.25% amount of catalyst loading a minimum of % and 85%, respectively yield was recorded*. At higher concentration of catalyst loading, the triglycerides produced more soap during the trans-esterification reaction than ester formation. Experiments were conducted at lower wt.% of catalyst loading concentration ranging from 0.2% to 0.5% but the results were insignificant (Sinha and Murugavelh, 2016; Ma and Hanna, 1999; He et al., 2007).

The engine performance and emission characteristics were performed by using air cooled four stroke diesel Kirloskar engine. The flash point and fire point of the biodiesel was found to be 175°C and 225°C, respectively. The engine was operated for the experimental results of the engine tests by using neat diesel, B10, B20, B30, B40 and B50 fuels.

Figure 5 depicts the brake thermal efficiency at varying load for both pure diesel and biodiesel blends. It was examined that efficiency decreases with increase in load. It was studied that brake thermal efficiency with various blends of biodiesel mixtures were slightly less than that of neat diesel fuel. This was due to poor air fuel mixing, higher viscosity, poor spray property, higher volatility and lower calorific value. Blend B10 has maximum efficiency of 34% and minimum of 30% at B40.
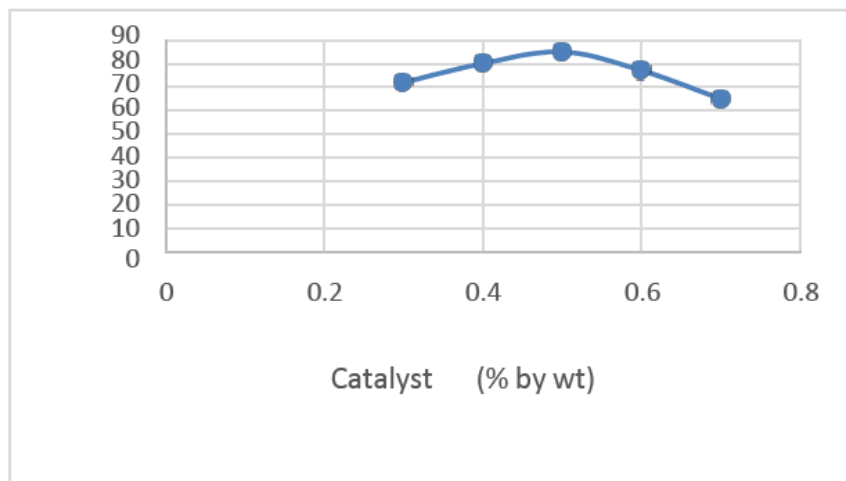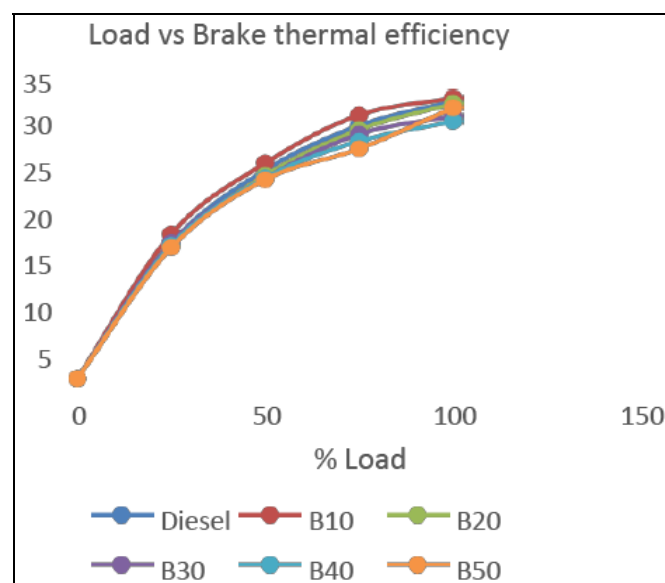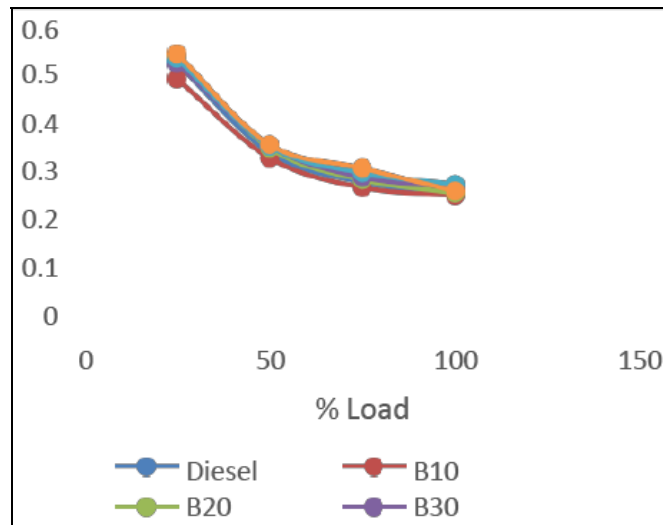
Figure 4 Comparison between catalyst and % yield (see online version for colours)

Figure 5 Comparison between % load and brake thermal efficiency (see online version for colours)

Figure 6 depicts the variation of specific fuel consumption with respect to varying loads. It was examined that the fuel consumption for the blends of biodiesel fuels were higher as compared to neat diesel fuel. This was due to the higher density of Pongamia oil. Oil based biodiesel fuels need more quantity of fuels for the same movement of the plunger in the fuel injection pump. The specific fuel consumption is reciprocal to the brake thermal efficiency. Beyond certain load the engine become overheated and a results in a slightly increase in specific fuel consumption for the biodiesel blends. Brake specific fuel consumption for diesel was 0.55 kg/kWhr at maximum load and for the blend of B50.

Figure 9 depicts the hydrocarbon emissions with respect to different engine loads decreases with increase in the biodiesel blend fuels. It was due to the proper combustion of biodiesel blends which resulted in decreased hydro carbon emissions. The decrease in HC emission with biodiesel blends fuel can be attributed to longer length of carbon chain, advance injection timing, lower saturation level of biodiesels and combustion of biodiesel blends. Minimum hydrocarbon emissions were found for B50 blend around 31ppm and maximum for diesel 45ppm.

Figure 6   Comparison between % load and BSFC (see online version for colours)

Figure 7   Comparison between % load and % CO (see online version for colours)
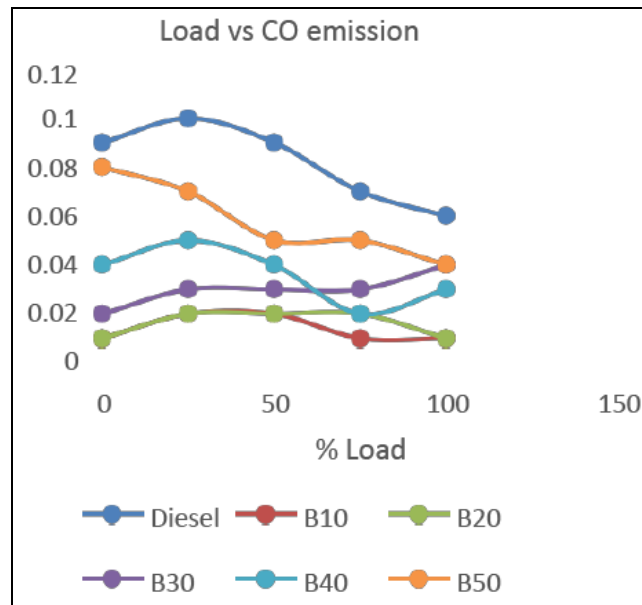
Figure 7 depicts the carbon monoxide emissions with respect to different engine loads decrease with increase in the amount of biodiesel blends whereas for pure diesel fuels slightly increase with increased in quantity of the pure diesel fuel. The carbon monoxide emissions are produced mainly due to improper combustion of fuel. This was due to low carbon content present. CO emission from conventional diesel is more than that of the various blends of the pongamia for all loads. However, for B10 the CO emission is very less due to dissolved oxygen present in the methyl ester of pongamia which causes complete combustion of fuel and hence reduces the CO emissions. But for higher concentration of blends the adverse effect of high viscosity and little increase in specific gravity suppress the complete combustion of fuel hence produce more CO emissions. Maximum was for diesel 0.06% and minimum for B10 as 0.01%.

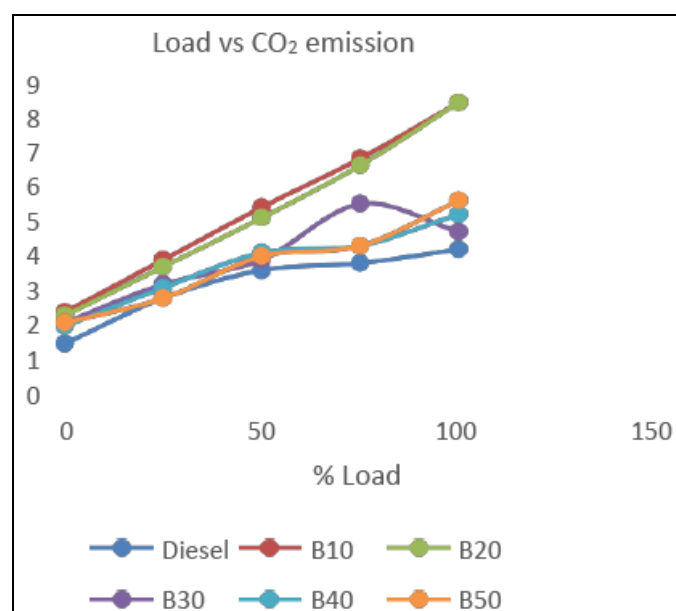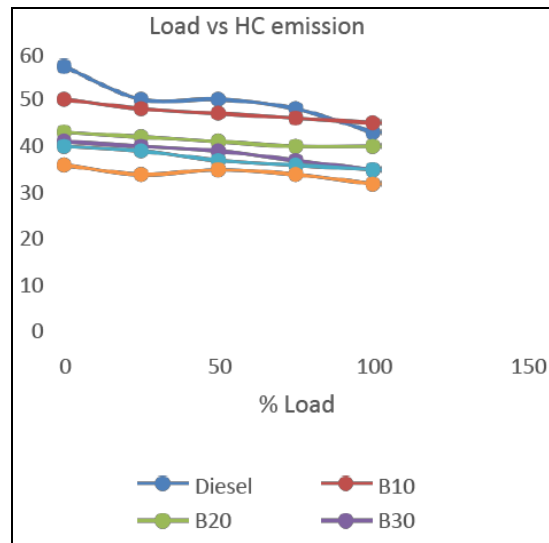**Figure 8** Comparison between % load and % CO_2 (see online version for colours)

Figure 8 depicts carbon dioxide emissions CO_2 emission of various blends of pongamia oil and diesel fuel. It is increasing along with the load. Lower values of blends, emits more amount of CO_2 as compare to the higher concentration of blend because of oxygen present in the pongamia ester, presence of oxygen causes complete combustion of fuel and hence CO_2 emission increases. Higher concentration of blend of biodiesel contain lower carbon content, hence reduces the CO_2 emission. Maximum for B10 is 8.5% and minimum is 4% (Sinha and Murugavelh, 2016; Karmee and Chadha, 2005).

Figure 10 Nitrogen oxide emission is observed mainly due to high combustion temperature and presence of oxygen. Exhaust gas temperature increases with the % increase in load because of increased amount of injected quantity of fuel. This is to maintain the required power output. At all loads, diesel was found with highest exhaust temperature and the temperatures of the different blends showed a down decrease with increasing concentration of Pongamia Pinnata methyl ester in the blends. This is due to the improved combustion provided by the PPME due to its 11% dissolved oxygen

content concentration of Pongamia methyl ester in the blends. NO_x emission is further reduced due to higher cetane number which helps to reduce the cylinder temperature and hence emissions. With increase in concentration of biodiesel, viscosity increases and atomisation of fuel results in drop of cylinder temperature. Hence NO_x emission of blends decreases with higher blends. Maximum is for diesel of 1180 ppm and minimum for B50 of 600 ppm (Sinha and Murugavelh, 2016; Karmee and Chadha, 2005; Agarwal and Bajaj, 2009).

Figure 9   Comparison between % load and HC ppm (see online version for colours)

Figure 10   Comparison between % load and NO_x ppm (see online version for colours)
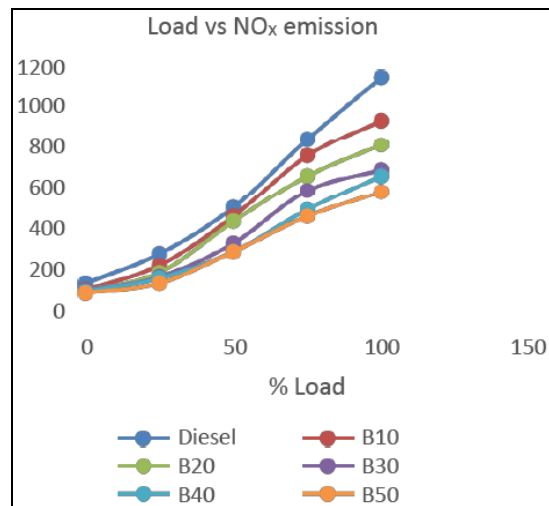
4   Conclusions

A low cost calcium oxide catalyst developed from waste Pisthia shells was prepared by calcination, hydration and followed by dehydration process. The optimum conditions were found to be oil/methanol molar ratio of 1:12, catalyst loading of 0.5% by wt%. Used cotton Pongamia oil yielded 85% of biodiesel. The Brake thermal efficiency of the diesel was 34% at full load (100%) for the blend of B10. The specific fuel consumption of biodiesel fuel blends (B50) was 0.550 kg/kW. Carbon monoxide emissions are maximum for neat diesel of 0.06% and minimum for B10 and B20 of 0.01%. Carbon dioxide emissions are maximum for B10 and B20 of 8.5% and minimum for diesel of 4%. Hydro carbon emissions are maximum for diesel of 45 ppm and minimum of 31 ppm for B50. NOx are maximum for diesel that is 1,180 ppm and minimum for B50 of 600 ppm (Sharma and Singh, 2008; Ramadhas et al., 2004).

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