

# Application of an Ecofriendly Heterogeneous Catalyst (CaO) for Synthesis of Biodiesel and its Characterization on VCR Engine

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**Abstract** – Waste crab shells after calcination have been used as a nonconventional heterogeneous catalyst for biodiesel synthesis from pongamia oil. Crab shell was calcined in muffle furnace at 1100 °C for 2hrs. The calcined catalyst was characterized on X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Scanning electron microscopy (SEM). A high biodiesel yield and conversion was obtained at 10:1 (alcohol/oil) molar ratio, 3.00wt% crab shell calcined catalyst, and 2.00hr reaction time at 65°C with 600rpm stirring speed. Conversion of pongamia oil feedstock to its respective fatty acid methyl esters was identified on a thin layer chromatography (TLC). The quality parameters, such as density, viscosity, calorific value, oxidation number, flash point, fire point cetane number, elements like C,H,O etc were analyzed as per ASTM -6751 standard. Further the same biodiesel was preceded for emission analysis on single cylinder variable compression diesel engine with various blending ratios as well load. Blends of KB00% (diesel), KB10%, KB20%, KB30%, and KB100% were prepared at 40°C. The parameters like Oxides of nitrogen (NO<sub>x</sub>), Carbon monoxide (CO), Hydro carbon (HC) etc were studied and compared with fissile fuel. Result showed that heterogeneous calcined methyl ester of pongamia B20% blend shows lower emissions as compared with running diesel fuel. **Copyright © 2015 Praise Worthy Prize S.r.l. - All rights reserved.**

**Keywords:** Biodiesel, Pongamia, Calcinations. Emissions, Non-Edible Oil, VCR Engine

## I. Introduction

The concept using vegetable oil as a fuel dates back to 1895 when Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil (pea nut). Rudolf Diesel stated: “the use of vegetable oil for engine fuels may seem insignificant today. But such oil may become in source of time as important as petroleum & the coal tar products of the present time. Biodiesel is a non petroleum based fuel defined as fatty acid methyl ethyl esters derived from vegetable oil or animal fats & it is used in diesel engines & heating systems.

Thus this fuel could be regarded as mineral diesel substitute with the advantage of reducing greenhouse emissions because it is renewable resource [1].

Mostly biodiesel is prepared from oils like soybean, sunflower, rapeseed etc. throughout the world.

Depending on the climate and soil conditions, different nations looking into different vegetable oils for diesel fuel substitute; soybean oil in USA, sunflower and rapeseed oil in Europe, palm oil in Malaysia and coconut oil Philippines are being considered as a substitute for diesel fuel seed oil. The extracted oil could not be used directly in diesel because of its higher viscosity.

High viscosity of pure vegetable oil would reduce the fuel atomization and increase the fuel spray penetration, which would be responsible for high engine deposits and thickening of lubricating oil.

The use of chemically altered vegetable oil called biodiesel does not require modification in engine or injection system or fuel lines and is directly possible in any diesel engine. Biodiesel can be synthesized from vegetable oils or animal fats via transesterification.

The transesterification is the reaction between oil and fat, with a short chain alcohol (methanol, ethanol, and propanol) in the presence of suitable catalysts in the transesterification reaction, as they give high production yield [2]. Few researchers have worked feedstock having higher FFA levels using alternative processes. But there are certain exceptional cases wherein direct transesterification cannot be performed.

Such cases appear in raw vegetable oils (non edible oils) like pongamia pinnata linn (Karanja) [3], Jatropha curcus linn [4], calophyllum inophyllum linn [5] and Citrulluscolocynthis schard [6].

We are able to synthesize biodiesel with heterogeneous solid acid, base catalyst and with homogeneous solid acid, base catalyst.

As Transesterification reaction with homogeneous solid base catalyst like sodium hydroxide and potassium hydroxide is most acceptable method. However, there are major problems associated with both the homogeneous catalysts. As both catalyst takes more time for conversion of triglyceride to ester, corrosive in nature and it increases P<sup>H</sup> of final product. That's why ester should be washed rinsed with warm distilled water.

It removes leftover catalyst, methanol. So there is loss of methyl ester with waste stream of water at the same time. To overcome these problems heterogeneous catalyst is been focused that can be easily separate outs after reaction, gives high yield & can be reused [7].

Heterogeneous solid acid and base catalyst includes zeolites, metal catalysts [8]-[10]. Biodiesel has recently gained popularity because it is a renewable and ecofriendly fuel [11], [29]-[30]. A common raw material used in biodiesel synthesis is vegetable oil from trees.

Because the feedstock is basically ME's of long chain fatty acid, they do not emit the toxic pollutants that are present in diesel fuel. Even when they are used in blended form, a significant decrease in carbon monoxide (CO), hydrocarbon (HC) and particulate matter is observed [12].

Crabs are consumed worldwide and waste crab shells creates disposal problem. It is typically about 6-8 gm weight. Contains calcium carbonates approximately 80-85%, 12% magnesium carbonates, 0.70% phosphates, 4% organic matter and traces of zinc, sodium, iron, manganese, copper etc [13],[14]. Basuri et. al. [15] and Engine et.al. [23] has been used egg shells as solid metal catalyst for tranesterification reaction. Ziku wei et.al [16] suggested that utilization of egg shell as a solid heterogeneous catalyst for biodiesel production not only provides a cost effective and environment friendly way of recycling this solid waste, significantly reducing its environmental effects, but also reduces the price of biodiesel to make biodiesel competitive with diesel fuel. Most of the works have been carried out with edible oils such as palm oil, soybean oil. However with heterogeneous catalyst not much data is available to study/ judge whether crab shell catalyst will be effective as a catalyst with high free fatty acid value of feedstock's. Sharma Y.C.et.al.[17] have been worked using karanja oil as a feedstock with calcined egg shell powder as a catalyst.

Fossil fuels such as diesel, gasoline, LPG etc. are diminishing sources of energy. Economies like India are highly reliant on such diminishing sources of energy for producing power and hence face tremendous challenges with respect to finding alternatives to oil. Diesel engines produce large amount of polluting gases such as carbon monoxide, un-burnt hydrocarbons and oxides of nitrogen (NOx) which pose threat to the environment and hence the living beings. Emission of these harmful gases and particles also result in greenhouse effect.

These gases and particles if inhaled by the humans and animals can cause various detrimental diseases. Liaquat et.al. [18] carried out experimental study to analyze performance and emissions characteristics for diesel engine operating on four fuel samples of jatropha and waste cooking oil biodiesel. It was observed that NOx emission for all biodiesel blends increased as compared to DF (diesel fuel). Regarding noise emission, it was observed that the sound level for all blend fuels was reduced compared to DF blend fuels with J5W5 producing the least level of sound.

Finally from the results they concluded that blends JB5, JB10 and J5W5 could be used in diesel engines without any engine modifications.

Singh et. al. [19] had used three different types of blends namely B10%, B20% and B30% were prepared using waste cooking oil as feedstock. The optimization of production of biodiesel for tranesterification process was evaluated on varying the various parameters such as reaction time, KOH concentration and molar ratio.

An experimental investigation was carried out to evaluate the performance and emission characteristics of a cooking oil biodiesel blends at various compression ratios like 12, 14 and 16 on a compression ignition engine and important fuel properties like oxides of nitrogen, HC and CO were determined.

The experimental results also showed that the smoke emissions were reduced for all biodiesel mixtures and hydrocarbon (HC) and NOx emissions of B10% blend is lowest among all. From all the results it was concluded that B10% blend of waste cooking oil biodiesel act as best alternative fuel among all tested fuel at full load condition. Baste S.V. et.al [20] has been reported that B20% OF Pongamia pinnata oil methyl ester can be used safely in a conventional CI engine without modifications in engine. Nagarhali M.V. et.al.[21] also concluded emission like HC and CO are lower at 200 bar while NOx emission were higher at 200 bar for mixtures of jatropha and karanja biodiesel.

This paper reviews the use of recycled crab shells as catalyst source for biodiesel production from pongamia (Karanja)oil. As yet no literature available for the same feedstock transesterified using CaO catalyst as well as engine trials with single cylinder VCR engine using pongamia biodiesel (synthesized with calcined crab shell as a solid heterogeneous catalyst). Transesterification is known for conversion of triglyceride to ester when free fatty acid is low. To study efficiency of catalyst process parameters like molar ratio, catalyst percentage, time of reaction, temperature of reaction, stirring speed have been studied[6], [22]. Then synthesized methyl ester was observed on gas chromatogram mass spectra to analyze yield and purification.

Important parameters like density, viscosity, flash point, fire point, cetane number, calorific value, cloud point, moisture have been analyzed as per ASTM- 6751 standard. The synthesized biodiesel then preceded for emission analysis such as Nitrous oxide (NOx), Carbon Monoxide (CO), and Hydrocarbon (HC) etc. and were compared with DF on variable compression ratios (VCR) diesel engine.

## II. Experimental Set Up

### II.1. Materials

Waste crab shells were collected then it was washed with lots of hot water to remove the organic matter on shells. Then it was dried in hot air oven at 105°C for 24 hrs. Then it was ground in an agate mortar in powder

form. Thereafter, powder were calcined in open furnace at 900°C for 2hr.

Pongamia oil was purchased from Indian Biodiesel Corporation Baramati, Maharashtra, India, Chemicals such as sulphuric acid, methyl alcohol, ortho-phosphoric acid, sodium sulphate were purchased from Merck Ltd. Mumbai, Maharashtra, India., variable compression ratios (VCR) diesel engine, Neptune-OPAX200 exhaust gas analyzer.

### II.2. Catalyst Preparation

Crab shells were washed thoroughly in hot water to remove any unwanted material adhered on its surface.

The washed crab shells were then dried in hot air oven at 105°C for 24hr. The dried crab shells were reduced in power form by mortar and calcined in a muffle furnace under different temperature ranges starting from 25°C to 1100°C. for 2.5hr to convert calcium species to CaO particle. Then catalyst was characterized by Scanning Electron Microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, X ray diffraction (XRD) etc.

### II.3. Experimental Procedure

The Transesterification reactions were performed in batch reactor having three necked round bottom flask of two liter capacity. The middle neck was used to insert a mechanical stirrer, left side neck was used to insert condenser and other neck was used to insert thermometer for temperature measurement. A total of 1000ml oil was dehydrated in oven at 105°C for 2 hr. & it was used for each experiment.

Acid esterification was performed with 1.7% (v/v) sulphuric acid as an acid catalyst with 8:1 molar ratio (methyl alcohol to oil) to reduce acid value of feedstock oil for 1.3hr. The speed of mechanical stirrer was kept constant at 600rpm to overcome mass transfer limitation.

When acid esterification completed, reaction mixture was settled for 4hr. in the same reaction, water was formed which was dehydrated for 2hr. then the esterified pongamia oil was proceeded for Transesterification reaction. Here calcined crab shell powder i.e. CaO was used as a solid base heterogeneous catalyst. The reaction conditions taken were as 10:1 (alcohol: oil) molar ratio with 3.00wt % of CaO catalyst at 65±0.5°C for 2.00 hr of reaction time. Then after Transesterification completion, byproduct glycerol was separated manually.

The important factors those affect on yield and conversion were studied separately.

### II.4. Preparation of Blends

The synthesized methyl ester was proceeded for emission analysis by NEPTUNE-OPAX200 exhaust gas analyzer. At present the amount of biodiesel available was less than that of diesel.

For comparative study with diesel fuel, the biodiesel blended with diesel by volume as B10 (i.e.10%

pongamia biodiesel & 90% diesel fuel), B20 (20% pongamia biodiesel & 80% diesel fuel), B30 (30% pongamia biodiesel & 70% diesel fuel), and B100 (100% pongamia biodiesel & 00% diesel fuel).

Finally B00% (i.e. pure diesel fuel). Then the samples were analyzed for their property testing's. (Table V).

## III. Experimental Set Up for Engine Trial

The technical engine specification was given in Table I. Initially the required blend of biodiesel is filled in the fuel tank and ensured the cooling water circulation for eddy current dynamometer and engine.

TABLE I  
TECHNICAL SPECIFICATION OF THE ENGINE

Make	Kirloskar (India)
Type	Four stroke, IC Diesel engine, water cooled
Number of strokes	Four
Number of cylinders	1
Compression ratio	12 to 18
Rated power	3.5 kw
Dynamometer arm length	234mm
Rated speed	1500rpm
Cylinder diameter	87.5mm
Stroke length	110mm
Crank angle	Resolution 1°

The required compression ratio was adjusted and engine started at no load for 10 min. then note down the observation for no load condition. Gradually increased the load on the engine by rotating dynamometer loading unit and emissions observations were noted every after 3 min of run at respected loads.

Then load was decreased to zero. The readings were noted down for performance and for emissions like NO<sub>x</sub>, CO and HC.

The same process was repeated at CR 14 to 18 for blends B00%, B10%, B20%, B30% and B100% with load from 0 to 9. Finally after completion of all trials, the engine again ran on diesel fuel (i.e. B00%) for clarification of result.

## IV. Result and Discussion

The extracted pongamia oil was then filtered and it was proceeded to perform important physico- chemical properties as well as to analyze available fatty acids by Gas chromatography mass spectra of respected oil.

The peaks were identified using standards of fatty acids and the identified fatty acids were listed in Table II. While the physico-chemical parameters were illustrated in Table III.

The Pongamia oil contains both saturated and unsaturated fatty acids.

Amongst these, Oleic acid (49.780%) found highest, Linoleic acid (17.750%) were in next quantity then Palmitic acid (12.370%), and Stearic acid (5.900%) were found. This stearic acid is responsible for cloud point of biodiesel.

TABLE II  
FATTY ACID COMPOSITION OF PONGAMIA OIL

Sr.	Fatty acid name	Formula	Composition(%)
1	Undecanoic Acid	C11:0	0.055
2	Lauric Acid	C12:0	0.037
3	Myristic acid	C14:0	0.160
4	Palmitic acid	C16:0	12.370
5	Heptadecanoic acid	C17:0	0.095
6	Stearic acid	C18:0	5.900
7	Cis-10 Heptodeconic Acid	C17:1	0.038
8	Oleic acid	C18:1	49.780
9	Linoleic Acid	C18:2n6c	17.750
10	Alpha-Linolenic acid	C18:3n3	0.990
11	Gamma- Linolenic acid	C18:3n6	2.940
12	Cis-Ecosatrienoic Acid	C20:3n3	3.002
13	Arachidonic Acid	C20:4n6	0.086
14	Cis- Ecosapentaenoic acid	C20:5n3	0.770
15	Cis- Docosadienoic acid	C22:2	0.038

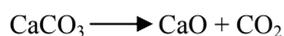
TABLE III  
PHYSICO CHEMICAL PROPERTIES OF PONGAMIA OIL

Sr.no	Parameter	Pongamia Oil
1	Density (gm/cc <sup>3</sup> ),30 <sup>0</sup> c	0.920
2	Viscosity (cst)	44.6
3	Moisture (%)	0.20
4	Acidvalue (mg of KOH)	27.87
5	Flash Point ( <sup>0</sup> c)	280
6	Fire Point ( <sup>0</sup> c)	285
7	Cetane value	49
8	Calorific value Kcal/Kg	8963

#### IV.1. Crab Shell Catalyst- CaO Characterizations

The sample weight used was 23.7mg for calcined catalyst. The temperature ranged from 27 to 1100°C. The weight loss observed from 1050 to 1100°C.

This indicated that, although decomposition of calcium carbonate started at 1050°C, complete decomposition occurred at 1100°C. At 1100°C, the calcium carbonate of crabshell decomposed to calcium oxide and carbon dioxide. This is given by the reaction (23):



Release of CO<sub>2</sub> confirms the formation of calcium oxide, which acts as catalyst in biodiesel synthesis.

The decomposition was observed from 1050°C, and complete decomposition occurred at 1100°C was observed. Afterwards the catalyst purity was analyzed by X- ray diffraction (XRD), SEM & by FTIR.

#### IV.2. Esterification Reaction

The Transesterification reaction was carried out with pongamia oil without lowering its acid value. However no conversion of triglycerides to their respective esters was observed. Therefore the Transesterification reaction was carried out after lowering the acid value of pongamia oil (i.e. after acid esterification), which resulted in high conversion and high yield of biodiesel.

The parameters optimized during acid esterification were molar ratio of 8:1 (methanol to oil) with 1.9% (v/v) H<sub>2</sub>SO<sub>4</sub> at 60± 0.5 °C for 1.3hr. The acid value of pongamia oil after acid esterification was reduced to 1.92

from 27.87mg of KOH/g. The conversion of FFA to ester has been calculated by the equation:

$$\text{Conversion} = \frac{[\text{Acid value (initial)} + \text{acid value (final)}]}{\text{acid value (initial)}} \times 100$$

The conversion was calculated to be 93.11% Niju et.al. [24] obtained biodiesel conversion up to 94.52% while it was for commercial catalyst was 67.57% with waste frying oil as feedstock. That is yield was increased up to 26.95%.

#### IV.3. Transesterification Reaction

The Transesterification reaction has been carried out with calcined crab shell as a catalyst with pongamia oil feedstock. The parameters that affected the Transesterification reaction were molar ratio of alcohol to oil, catalyst concentration, temperature of reaction, time of reaction, stirring speed. All these parameters were studied separately for yield optimization.

#### IV.4. Optimization of Reaction Variables

Granados et.al [25] report poisoning of the catalyst when kept in contact with air because of moisture and carbon oxide. Although the poisoning of the catalyst was less relevant with water, carbon dioxide poisoning was found to be significant. The catalyst was thus stored in a plastic bottle container and kept indessiccators to prevent the poisoning of the catalyst.

The reaction was carried out by taking 100ml of pongamia oil and 2.5wt % of catalyst with 8:1 (methanol/oil) molar ratio. No conversion of oil to ME's observed. This can be attributed to the effect of FFA playing a vital role in inhibiting the Transesterification reaction. The acid value of pongamia oil was reduced by acid esterification and then proceeded for its conversion to ME's by transesterification reaction. The sole objective during acid esterification was to reduce the acid value of the feedstock oil. It was observed that 8:1 molar ratio (alcohol/oil) with 1.9% (v/v) sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) for 1.3 hr of reaction time at 60 ± 0.5°C resulted in a reduction of the FFA value from 27.87mg to 1.92 mg of KOH/g by acid esterification, whereby the FFA present in the oil was converted to fatty acid methyl ester and moisture was formed. The transesterification reaction was then performed with calcined crab shell as the catalyst with reduced acid value.

Experiments were performed by taking 3.0wt% catalyst with 10:1(alcohol/oil) molar ratio at 60 ± 0.5°C.

The yield was optimum with a molar ratio of 10:1 (alcohol/oil) molar ratio. Further addition of methanol did not increase the yield (Fig. 1).

The effect of catalyst on yield was studied with catalyst concentration varying from 0.5% to 3.5% considering the weight oil in gram. Heterogeneous calcined crab shell were used as a catalyst. All the

reactions were carried out at  $60 \pm 0.5$  °C and the catalyst amount 3.0wt% was found to be optimum. With 1.00 wt %of calcined crab shell catalyst, yields only 71% yield was obtained, which increased to 87% with a 3.0wt% catalyst. Further addition of catalyst did not show any increase in the yield of methyl ester (Fig. 2).

For homogeneous catalyst like NaOH, KOH, only 0.5 up to 1.00% catalyst with feedstock's like calophyllum [5], citrillus colocynthis oil [6] was sufficient to carry out the reaction. However Sharma et.al. [17] have reported the optimum yield with 2.5wt% of catalyst with the Pongamia oil and wei.et.al [26] have reported the optimum yield with 3.0wt% of catalyst with the soybean oil as the feedstock.

An optimum yield of 90% was achieved when the reaction temperature  $65 \pm 0.5$ °C, which is just above the reflux temperature of methanol. The yield was less than 80% when the temperature was lowered to  $50 \pm 0.5$ °C, which increased with an increase in the temperature.

A higher temperature (i.e.  $70 \pm 0.5$ °C) resulted decreased yield, which can be attributed to the loss of some methanol at high temperature (Fig. 3).

In 30 min. of reaction time, 45% conversion of biodiesel was obtained, which increased gradually with an increase in time. A reaction time of 2hr (i.e. 120min) was found to give optimum yield 86% of biodiesel (Fig. 4). A further increase in time could not increase the yield of biodiesel. It was because of maximum triglyceride get converted into its particular ester. Hence 2.00 hr was the optimum reaction time for the reaction. The rate of stirring was varied from 150rpm to 1000 rpm. The yield was optimum with 600rpm of agitation. With the agitation lower than 600rpm, a lesser yield was obtained.

With an agitation rate higher than 600 rpm, no more increase in either yield was observed (Fig. 5).

#### IV.5. Study of Properties of Pongamia Methyl Ester and its Blends

The pongamia methyl ester and its blends were characterized for its fuel properties by ASTM- 6751 [27] which were given in Table IV and Table V. The acid value of pongamia raw oil was 27.87mg KOH/g while that of its biodiesel was reduced upto 1.92mg KOH/g, which was within the ASTM specifications. The density of raw oil was 0.920gm/cc while that of its methyl ester was 0.883gm/cc which was slightly dense. As viscosity is directly proportional to density, so viscosity was reduced by Transesterification reaction, automatically density was reduced & comes in ASTM limits. The cloud point and pour points were depends on presence of stearic acid in biodiesel. The flash point and fire point of pongamia biodiesel were 172°C and 186°C which was just above the ASTM limit. But both these parameters were considered as a safe for storage and transport. Cetane number indicates ignition delay time of the fuel upon injection into the combustion chamber & was 51. The calorific or heating value was found to be 35.86 which match diesel fuel up to 80%.

TABLE IV  
PROPERTIES OF PONGAMIA METHYL ESTER

Sr no	Parameters	ASTM- 6751 test method [27]	Pongamia methyl ester
1	Acid value (mg KOH/g)	D664-07	1.92
2	Density (gm/cc)	D1448-1972	0.883
3	Specific gravity	-	0.8359
4	Cloud point(°C)	D2500	4
5	Pour point(°C)	D2500	3
6	Flash point (°C)	D93	172
7	Fire point (°C)	D93	180
8	Cetane number	D613	51
9	Calorific value (MJ/kg)	D6751	35.86
10	Moisture(%)	D2709	0.02
11	Sulphur(ppm)		75.68
12	Refractive index		1.4643
13	Total glycerine (%)		0.28
14	Distillation temperature (°C)		85
15	Ash (%)		1.1
16	Copper corrosion		1a
17	Aniline point (°C)		1
18	Alcohol (%)		1.40
19	Iodine value		66.69
19	Saponification value (%)		173.24
20	Unaponifiable value (%)		0.73
21	Elemental Analysis		
21.1	Carbon (%)		74.90
21.2	Hydrogen		12.86
21.3	Oxygen		11.26

TABLE V  
PROPERTIES OF DIESEL AND BIODIESEL BLENDS

Properties	ASTM 6751 STD [27]	Diesel – KBD <sub>00%</sub>	KBD <sub>10%</sub>	KBD <sub>20%</sub>	KBD <sub>30%</sub>
Density in gm/cc	D 1448-1972	0.830	0.834	0.836	0.841
Flash point in °c	D93	64	68	76	82
Fire point in °c	D93	69	74	84	88
Calorific value in MJ/Kg	D6751	42.50	41.7	41.00	39.5

The moisture was found 0.02%which was in the ASTM limits. The elemental composition of pongamia biodiesel shows composition of carbon (74.90%), hydrogen (12.86) and oxygen (11.26%). The presence of oxygen in biodiesel helps in complete combustion as compared to diesel fuel (Table IV).

The pongamia methyl ester was blended with diesel fuel at 40°C and its major chemical properties were studied. The density of diesel fuel was 0.830gm/cc while that of KBD10%, KB20%, KB30% were 0.834, 0.836, 0.841gm/cc. As biodiesel was denser that diesel fuel so that density got increased with increase in blend. The reverse found in case of flash point and fire point.

The flash point and fire point of diesel fuel was 64°C and 69°C while that of KBD10%, KB20%, KB30% were 68°C, 76°C, 82°C and 74°C, 84°C, 88°C. The calorific value of diesel fuel were 42.50MJ/Kg while that of KBD10%, KB20%, KB30% were 41.7, 41.0, 39.5MJ/Kg (Table V).

The observed results were collected and graphs were plotted for respected CR against load. The CO emissions for diesel fuel, KB10%, KB20%, KB30% and KB100% with load were compared at CR 14 to CR 18.

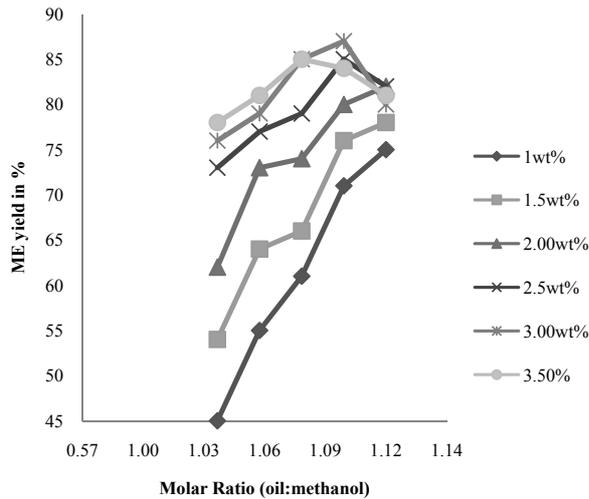


Fig. 1. Effect of molar ratio on ME yield

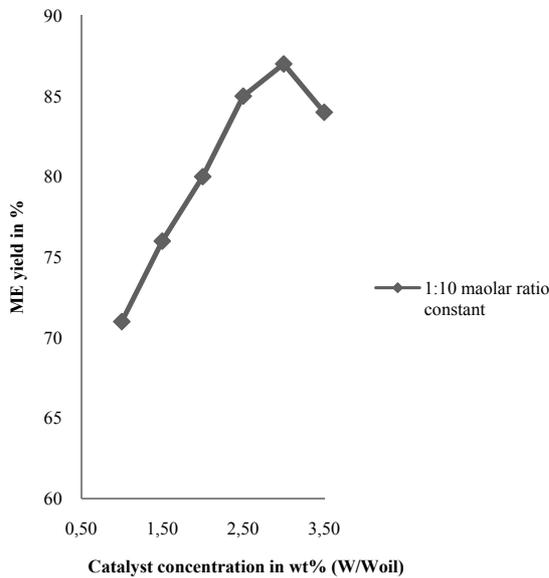


Fig. 2. Effect of catalyst on ME yield

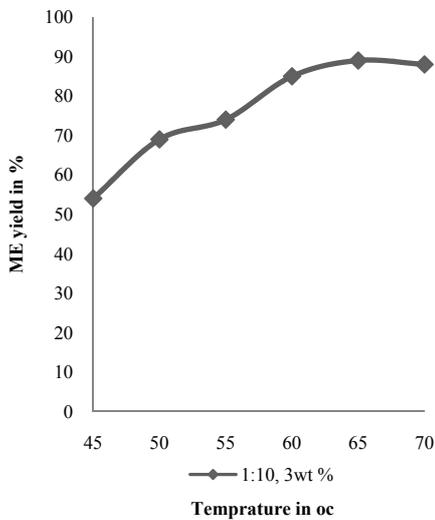


Fig. 3. Effect of temperature on ME yield

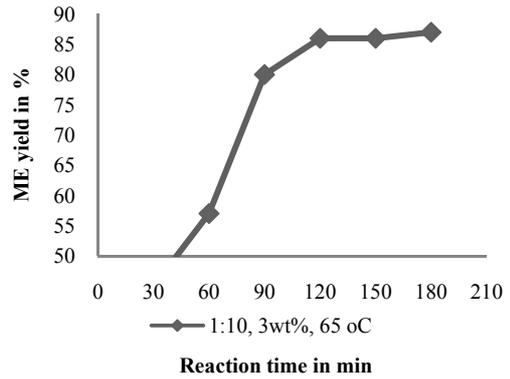


Fig. 4. Effect of time on ME yield

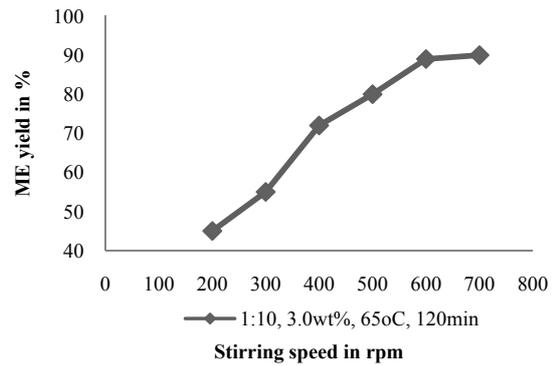


Fig. 5. Effect of stirring speed on ME yield

Figs. 6 (a), (b), (c), (d) and (e) show the variation of carbon monoxide (CO in %) with load. It was observed that with increase in load, CO emissions decreased.

The blend KB20% shows approximately nearby results with diesel fuel CO emissions at all CR and loads.

This was due to presence of oxygen in biodiesel which leads to complete combustion.

Baste S.V. [20] too concluded that, CO emission decreases by 80% when diesel engine fuel is replaced with karanja oil biodiesel at full load. Swapna G. K. et. al. [28] had successfully run CI engine on mixtures of jatropha and pongamia biodiesel with diesel fuel. She concluded that with increase in percentage of ester in blend, CO emissions decreases up to 58% compared with diesel fuel. It was observed that with increase in blend content, the HC emission decreases. This may be due to high cetane number of biodiesel blends.

Higher cetane number lowers combustion delay which improves the combustion. Another reason for low HC with increase in blend content was due to more oxygen content (11.68%) than diesel fuel. It was observed that HC emission for diesel fuel i.e. KB00% was 59ppm at no load with CR 14 and it was 1ppm at 12kg load with CR18 while for blend KB20% it was 50ppm at no load with CR 14 and it was 1ppm at 12kg load with CR18.

Compared with other blends, KB20% shows lowest HC emissions with all loads as well as with all CR. The HC emissions for different blends and for diesel fuel with various load at CR 14, 15,16,17,18 were illustrated in Figs. 7(a), (b), (c), (d) and (e). Swapna G.K. et. al. [28]

concluded that with increase in percentage of ester in blend, HC emissions decreases up to 75% compared with diesel fuel. The NO<sub>x</sub> emissions for diesel fuel, KB10%, KB20%, KB30% and KB100% with load are compared at CR 14 to 18. NO<sub>x</sub> emissions are temperature dependent.

It was observed that the NO<sub>x</sub> emissions increased with increase in load at all CR.

This was because increase in temperature inside the combustion chamber at high load. NO<sub>x</sub> emissions were observed to be increased with increase in blend content.

This was due to high oxygen content in biodiesel fuel. Nitrogen from air easily mixes with oxygen and produces NO<sub>x</sub>. These emissions were observed to be increased with compression ratio due to the lower ignition delay which increases the peak pressure and temperature.

There were some more reasons for this type of behavior that was regarding the reduction in soot formation with biodiesel.

Radiation from the soot produced in the flame zone was a major source of heat transfer away from the flame, and can lower the bulk flame temperatures, depending on the amount of soot produced at the engine operation conditions. Other reason was that, biodiesel usually contains more double bonded molecules than diesel fuel.

These double bonded molecules have slightly higher adiabatic flame temperatures, which deals with increase in NO<sub>x</sub> emissions.

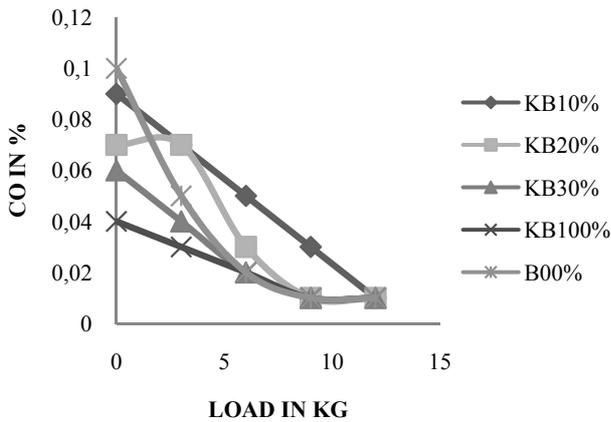


Fig. 6(a). Variation of CO with load at Compression ratio 14

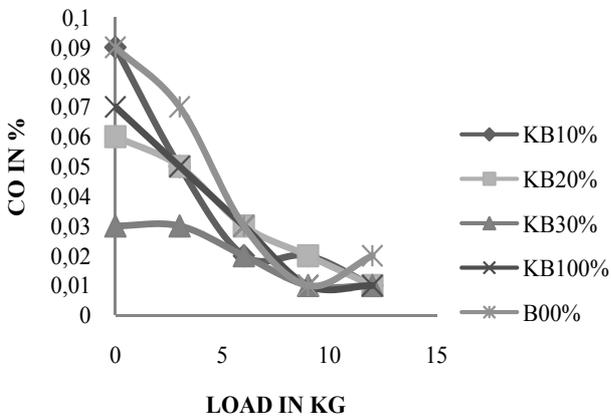


Fig. 6(b). Variation of CO with load at Compression ratio 15

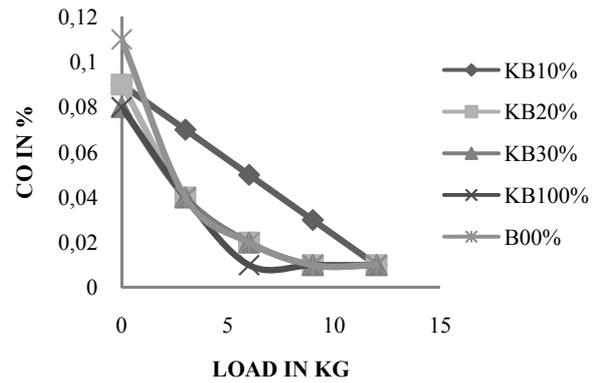


Fig. 6(c). Variation of CO with load at Compression ratio 16

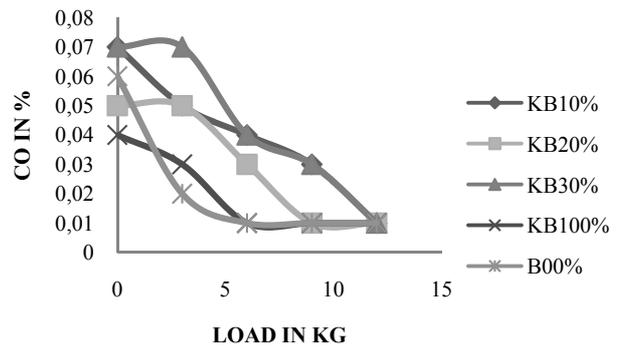


Fig. 6(d). Variation of CO with load at Compression ratio 17

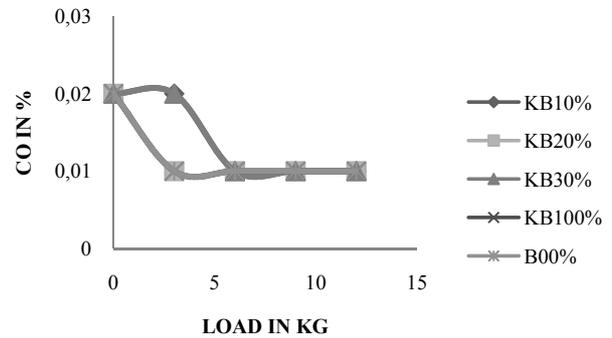


Fig. 6(e). Variation of CO with load at Compression ratio 18

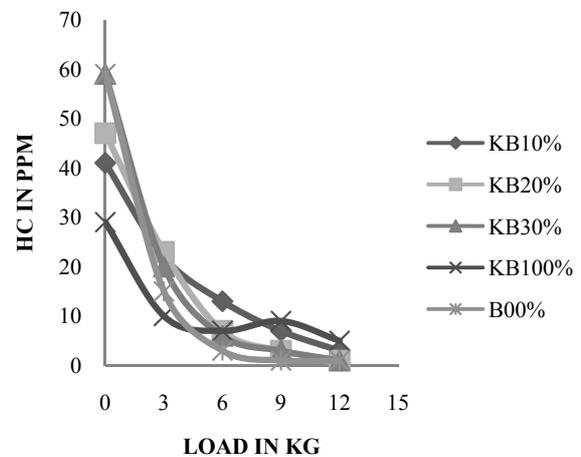


Fig. 7(a). Variation of HC with load at Compression ratio 14

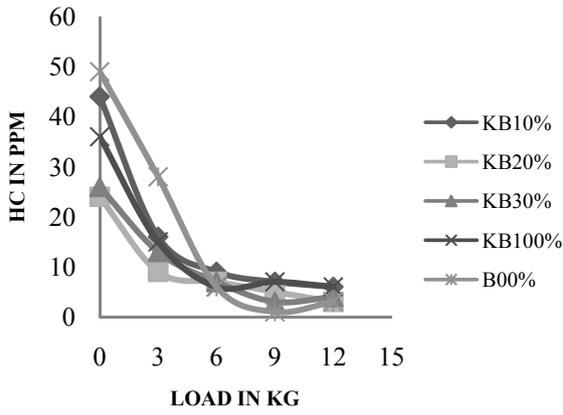


Fig. 7(b). Variation of HC with load at Compression ratio 15

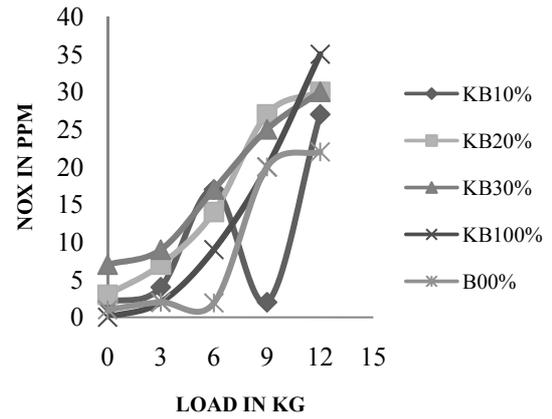


Fig. 8(a). Variation of NO<sub>x</sub> with load at Compression ratio 14

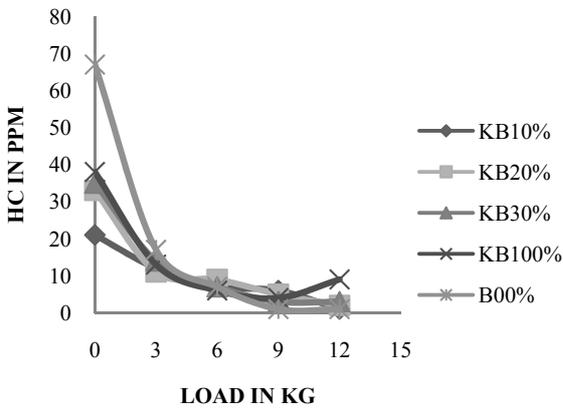


Fig. 7(c). Variation of HC with load at Compression ratio 16

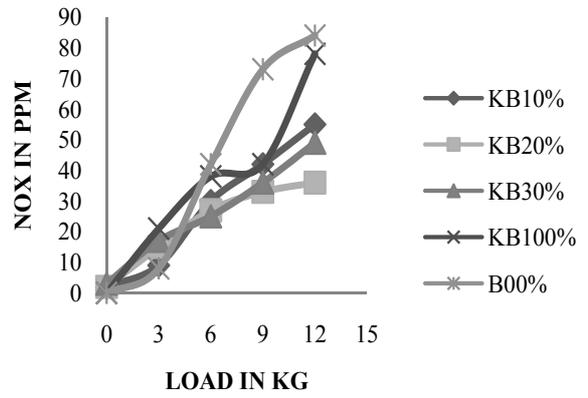


Fig. 8(b). Variation of NO<sub>x</sub> with load at Compression ratio 15

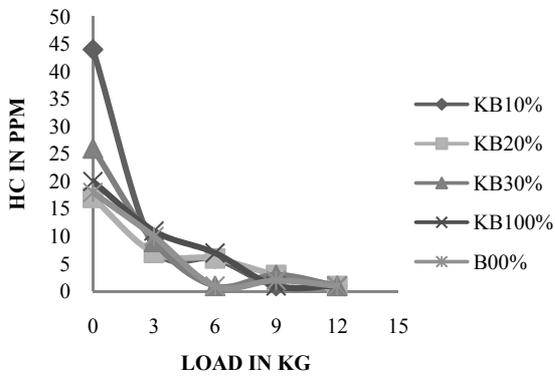


Fig. 7(d). Variation of HC with load at Compression ratio 17

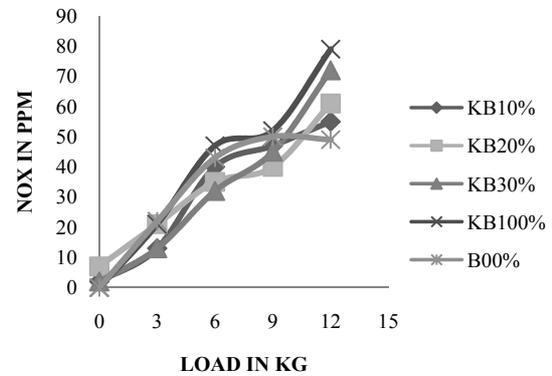


Fig. 8(c). Variation of NO<sub>x</sub> with load at Compression ratio 16

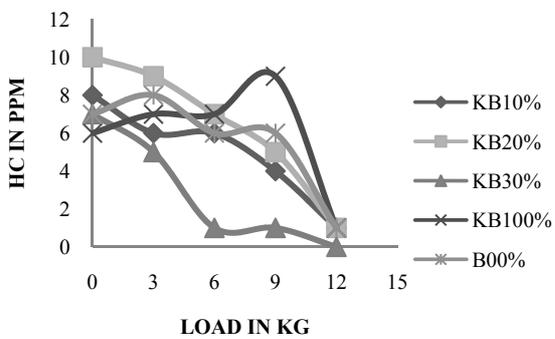


Fig. 7(e). Variation of HC with load at Compression ratio 18

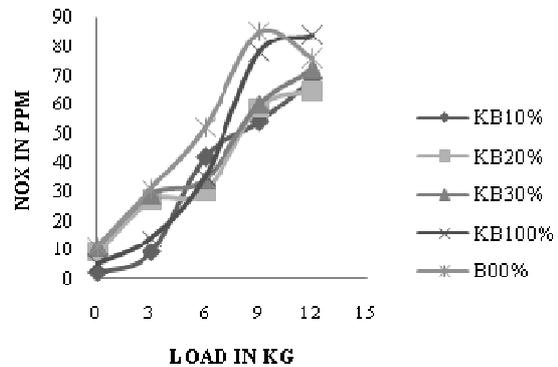


Fig. 8(d). Variation of NO<sub>x</sub> with load at Compression ratio 17

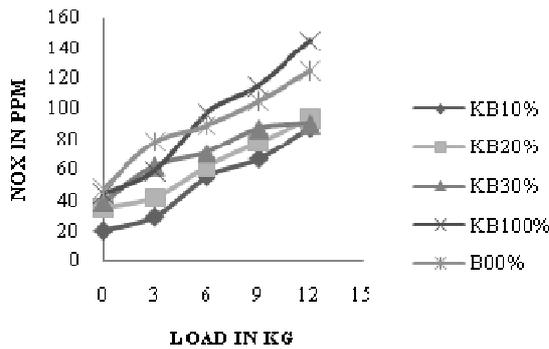


Fig. 8(e). Variation of NO<sub>x</sub> with load at Compression ratio 18

The NO<sub>x</sub> emissions for B00, KB10%, KB20%, KB30% and for KB100% were illustrated in Figs. 8(a), (b), (c), (d) and (e) respectively.

It can be seen from the figures that NO<sub>x</sub> emission for the diesel fuel were 1ppm at no load with CR 14 and it was 223ppm at 12kg load with CR 18 while the NO<sub>x</sub> emissions for the blend like KB20% were 3ppm at no load with CR 14 and it was 157ppm at 12kg load with CR 18. Blend KB20% shows lowest NO<sub>x</sub> at the entire compression ratio.

## V. Conclusion

The high yield and conversion of pongamia oil to biodiesel were achieved by optimizing the parameters such as molar ratio (alcohol to oil), catalyst concentration, time of reaction, stirring speed and temperature.

Pongamia oil possessing high FFA of 27.87 mg of KOH/g underwent acid esterification with sulphuric acid.

The acid value then lowered to 1.92mg of KOH/g and was followed by Tranesterification with calcined crab shell as a catalyst. The parameters optimized during acid esterification were molar ratio of 10:1 (methanol to oil) with 1.7% (v/v) H<sub>2</sub>SO<sub>4</sub> at 60± 0.5 °C for 1.3hr.

The same parameters were optimized for Tranesterification with calcined crab shell as a catalyst.

The optimized values obtained were molar ratio of 10:1 (methanol to oil) with 3.00wt% of catalyst (calcined crab shell) at 60± 0.5 °C for 2.00hr given yield 93.11% of pongamia biodiesel. The biodiesel synthesized from pongamia, fulfilled minimum ASTM-6751 specifications. The calorific value of optimized pongamia biodiesel was 35.86 MJ/Kg and that of diesel fuel is 42.5 MJ kg. The flash point and fire point of were determined as 167 °C and 176 °C which were higher than diesel fuel. That's why biodiesel is considered as a safe fuel for storage and transportation. The emission parameters like HC, NO<sub>x</sub> and CO were studied separately at different compression ratio (CR14to 18) with load (0 to 10).

It was observed that with increase in blend content, the HC emission decreases. It was observed that HC emissions for diesel fuel were highest and for KB20 blend it was lowest with all CR and all loads. The NO<sub>x</sub> emissions increased with increase in load at all CR. The

NO<sub>x</sub> emissions for blend B20% were observed to be lowest at all loads and all compression ratios. It was observed that with increase in load, CO emissions decreased. As compared with diesel fuel, the CO emissions for Blend B20% showed constantly reduction in emission at all CR.

The maximization & emission characteristics of pongamia biodiesel derived from (ecofriendly catalyst, CaO) and its blends were compared with conventional diesel fuel. The results were summarized as:

- Pongamia pinnata can be a potential feedstock for biodiesel production
- An ecofriendly catalyst (synthesized from crab shell) can be a low cost solution for biodiesel synthesis.
- It was observed that emission parameters like HC, CO shows significant reduction in biodiesel and all its blends while NO<sub>x</sub> emissions increased in some extent for biodiesel as compared with diesel fuel

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## References

- [1] J.P. Zaltica, *Fuel*, 87, 3522,2008.
- [2] P. Felizardo, M.J. Neiva Correia, I. Raposo, J.F. Mendes, R. Berkemeier and J.M. Bordado, *Waste Manage*, 87, 26, 2004.
- [3] S.N. Bobade, V.B. Khyade, Preparation of Methyl Ester (Biodiesel) from Karanja (Pongamia Pinnata)Oil, *Res. J. Chem. Sci.*,2(8), 43-50, 2012.
- [4] S.N. Bobade, R.R. Kumbhar and V.B. Khyade, Preparation of Methyl Ester (Biodiesel) from JatrophaCurcus Linn Oil, *Res. J. A.F.Sci.*,1(2), 12-19, 2013.
- [5] S.B. Chavan, R.R. Kumbhar, R.B. Deshmukh, Callophyllum Inophyllum Linn ("honne")Oil, A Source For Biodiesel Production, *Res. J.Chem.Sci.*, 3(11), 242-31, 2013.
- [6] S.B. Chavan, R.R. Kumbhar, Y.C. Sharma, Transesterification of Citrullus Colocynthis (Thumba) oil: Optimization for Biodiesel Production., *Adv. In Applied sci. Res.*, 5(3), 10--20, 2014.
- [7] A. Brito, M.E. Borges, Otero N.Zeolite. as a heterogeneous catalysis in biodiesel fuel production from used vegetable oil. *Energy Fuel*, 21, 328-3283, 2007.
- [8] Suppes, G.J.Dasari, M.A.Dosakocil, E.J.Mankidy, P.J Goff, Transesterification of soyabean oil with zeolite and metal catalyst, *Appl. Catal.*,257,213-223,2004.
- [9] M.J. Ramos, Cases,A.; Rodriguze,L.; Romero,R.; Perez,A., Transesterification of sunflower oil over zeolites using different metal loading: A case of leaching and agglomeration studies. *Appl. Catal.*, 346, 79-85, 2008.
- [10] Xuejun Liu, Huayang He, Yujun Wang, Shenlin Zhu, Xianglan piao, Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst, *Fuel* 87, 216-221, 2008.
- [11] Daming Huang, Haining Zhou, Lin Lin, Biodiesel:an Alternative to Conventional Fuel, *Energy Pro.*, 16, 1874-1885, 2012.
- [12] KalligerosZannikos,F.;Stournas,S.;Lois,E.;Anastopoulos,G.;Teas, C.;Sakellaropoulos,F.Aninvestigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine *Biomass Bioenergy*,24,141-149, 2003.
- [13] Chojnacka,K.Biosorption of Cr(III)ions by eggshells.*J.Hazard Mater*,121,167-173,2005.
- [14] Schaafsma, Pakan.I.Hofstede, F.A. Muskiet., Veer, E.V.D, Vries, P.J.D.Mineral, Amino acid, and hormonal composition of chicken

eggshell powder and the evaluation of its use in human nutrition, *Poult. Sci.*, 79, 1833-1838, 2000.

- [15] A. Buasri, N. Chaiyut, V. Lorryuenyong, C. W., S. Khamsrisuk, Application of eggshell wastes as a heterogeneous catalyst for biodiesel production, *Sus. Energy*, 1.1, (2), 7-13, 2013.
- [16] Ziku Wei, Chuli Xu, Baoxin Li, Application of waste eggshell as low-cost solid catalyst for biodiesel production, *Bioresource Tech.*, 100, 2883-2885, 2009.
- [17] Y.C. Sharma, S. Bhaskar, J. Korstad, Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from pongamia pinnata oil, *Energy and fuels*, 24, 3223-3231, 2010.
- [18] A.M. Liaquat, *Application of blend fuels in a diesel engine*, 2nd International Conference on Advances in Energy Engineering (ICAEE 2011), *Energy Procedia* 14, 2011.
- [19] J. Singh, Extraction and Optimization of Biodiesel Produced from Waste Cooking Oil and Comparing the Performance and Emission Characteristics with Diesel at Different Compression Ratios, *IJERT*, 3(8), 2014.
- [20] S.V. Baste, A.V. Bhosale and S.B. Chavan, Emission Characteristics of Pongamia Pinnata (Karanja) Biodiesel and Its Blending up to 100% in a C.I. Engine, *RJAFS*, 1.1(7), 1-5, 2013.
- [21] M.V. Nagarhalli, V.M. Nandekar, Performance of Diesel Engine using Blends of Esters of Jatropha and Karanja –A Novel Approach, *Inter. J. of Adv. Engg. Tech.*, 0976-3945.
- [22] Wan Norita Wan, Ab Rashid, Yoshimitsu Uemura, Katsuki Kuaskabe, Noridah B Osman, Bawadi Abdullah, Synthesis of Biodiesel from Palm Oil in Capillary Millichannel Reactor: Effect of Temperature, Methanol to Oil Molar Ratio, and KOH Concentration on FAME Yield, *Procedia Chemistry*, 9, 65 – 71, 2014.
- [23] Engin, B.; Demirtas, H.; Exten, M. Temperature effects on egg shell investigated by XRD, IR and ESR techniques. *Radiat. Phys. Chem.*, 75, 268-277, 2006.
- [24] S. Niju, K.M. Meera S. Begum, N. Anantharaman, Modification Of Egg Shell and its application in Bio-diesel Production, *J. of Saudi Chemical Society*, 18, 702-706, 2014.
- [25] Granados, M.D.Z.; Alonso, D.M.; Mariscal, R.; Galisteo, F.C. Tost, R.M. Santamaria, J.; Fierro, J.L.G. Biodiesel from sunflower oil by using activated calcium oxide. *Appl. Catal.*, B, 73, 317-2806, 2007.
- [26] Wei, Z.; Xu, C.; Li, B. Application of the waste eggshell as low-cost solid catalyst for biodiesel production, *Bioresource. Technol.*, 100, 2883-2885, 2009.
- [27] American Society for Testing and Materials (ASTM) International. An American National Standard. <http://www.astm.org> (accessed on May 14, 2008).
- [28] G.K. Swapna, M.C. Math, Experimental Studies on Performance and Exhaust Emission of a Injection (DI) Diesel Engine by using Mixtures of Jatropha and Pongamia Pinnata Methyl Ester and Its Diesel Blends, *IJETR*, 2, 6, 2321-0869, 2014.
- [29] Alvarez-Barrera, D., Segovia-Hernández, G., Castro-Montoya, A., Maya-Yescas, R., Chávez-Parga, M., Vegetable Oils for Biodiesel Production as Friendly Energetic Alternative: the Case of Mexico, (2014) *International Review of Chemical Engineering (IRECHE)*, 6 (1), pp. 59-67.
- [30] Cisneiros Vieira, P., dos Santos, V., Comparative Analysis of Investments for Biodiesel Production with Help of Excel Spreadsheet, (2014) *International Review of Chemical Engineering (IRECHE)*, 6 (1), pp. 31-37.

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