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Performance and Emission Characteristics of Biodiesel with CaO Nanocatalyst

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Abstract: ***With the depletion of fossil fuels worldwide, country has been sort for different fuel opportunities which can enrich the vehicle and give the best operating performances as like normal fuel sources. Hence the best way is the alternative fuels like Biodiesel, Castor, Jatropha, Pongamia Pinnata oil and other edible and non-edible oils respectively. As like chemical reactions increasing in this world, reactions like homogenous and heterogeneous reactions are also increasing in the world which is also best suitably can be used in alternative fuels as catalysts. Nanoparticles are also being used in some kinds of alternative fuels as safer environment process. In this proposed project we are using edible or non-edible castor oil with synthesised calcium oxide (CaO) as nanoparticles respectively. Calcium oxide nanoparticles are synthesised by using solution combustion method and urea as an additional fuel for the process and conducted several tests such as SEM, XRD and FTIR spectrum rays are also been examined.***
Keywords: Diesel, Bio-castor Oil, Production, Nanoparticles, SEM, FTIR Spectrum, Experimental Analysis.

I. INTRODUCTION

Castor bean or Ricinus Communis is the castor oil plant which is an species of flowering plant in the surge family called as Euphorbiaceae. It generally reproduces with mixed pollination system which favour selfing by geitonogamy but at the same time can be an out-crosser by anemophily. It contains normally about 40% to 60% oil which has a rich mixture of triglycerides, mainly ricinolein. The seed contain a water soluble toxin called ricin, which is also present in lower concentrations in the plant. Vegetable oils and animal fats are synthesised to form alkyl monoesters of fatty acids which are used as an alternative fuel which is called as "Biodiesel". These reduce the pollution from the vehicle and have been a major area of focus research applied in this kind of research. Rapeseed oil based esters are mostly used in European countries as an alternative fuel. A number of researchers have investigated vegetable oil based fuels. Most have concluded that vegetable oils can be safely burned for a short period of time in a diesel engine[1]. However, using raw vegetable oil in a diesel engine for extended periods of time may result in severe engine deposits, injector coking and thickening of lubricating oil. The high viscosity of raw vegetable oil reduces fuel atomization and increases fuel spray penetration. A higher spray penetration is thought to be partly responsible for the difficulties experienced with engine deposits and thickening of lubricating oil[1]. But, these effects are reduced or eliminated through transesterification process which removes glycerol from the triglycerides and it has been replaced with radicals from it respectively. Rudolf Diesel, who invented the diesel engine, presented the concept of bio-fuels at the world exhibition held at Paris exposition in the year 1900. Engine is the basic concept need for economic development of any country. The single largest source of energy in India after coal is petroleum, about 2/3rd of which is imported from OPEC (Oil and Petroleum Exporting Countries).

It is pale yellow or a colourless transparent viscious liquid with a faint mild odor and nauseating taste. It is normally a mixture of glycerides and chiefly ricinolein. A considerable amount of flammable hydrogen is generated by interaction with caustic solutions. Castor oil is an effective motor lubricant and has been used in internal combustion engines, racing cars and some modern airplanes also. It became popular as a lubricant due to high resistance to heat compared to petroleum based oils. It has largely been replaced by synthetic oils that are more stable and less toxic. Due to its low pour and cloud points it is a best alternative as biofuel in winter conditions. It is the only source of 18-carbon hydroxylated fatty acids with one double bond in each of the fatty acid chain and ricinoleic acid which makes up about 89% of the fatty acids composition.

But to increase the efficiency of these bio-fuels, Nanoparticles is another technology where the area focus shifts to. Nano-dimension materials have extended a considerable attention because of their usefulness as coating materials, for the use of sensor devices and for device miniaturization. Nano-crystalline alkaline earth metal oxides have gained a significant attention as effective chemisorbents for toxic gases, HCl, chlorinated and phosphorous containing compounds[2-5]. In a research work of chemical reaction of hydrogen combustion during aqueous MgO nano-catalyst combustion in diesel fuel, the result shows that hydrogen burns in a diesel engine in the presence of an active MgO nano-catalyst. During combustion the alumina had served as a catalyst and the coated MgO nano-catalyst were demanded and had decomposed the water to yield the hydrogen. The combustion of the diesel fuel mixed with aqueous MgO nano-catalyst shows that the total combustion heat increases when the concentration of smoke and nitrous oxide in the exhaust emission from diesel engine decreases[6]. Homogeneous base catalysts such as potassium hydroxide, sodium hydroxide, sodium methoxide, potassium methoxide and homogeneous acid catalysts such as strong mineral acids, p-toluene sulphonic acids are most frequently used in the industrial process to produce biodiesel[7-8]. But, the heterogeneous catalysts such as zeolites and ion-exchange resins possess many advantages, since they are non-corrosive, easy separation and require no washing of the ester. The disadvantage of biodiesel produced by heterogeneous catalyst gives low yield of product and disposal problems[9-10].

II. PRODUCTION OF BIODIESEL IN INDIA

The major producers unit of biodiesel in India but most exporters are from some parts of Andhra Pradesh and Tamilnadu respectively are,

A. TMN Biofuel Pvt Ltd
B. Natural Bioenergy Limited.
C. Coastal energy Limited.
D. Gomti Biotechnology Limited.
E. Reliance Life Sciences Limited.
F. Royal Energy Limited.
G. Chemical Biotech Limited.
H. Southern Online Biotechnologies Limited.

III. TRANSESTERIFICATION PROCESS OF CASTOR OIL

Transesterification is the only process which can convert the raw non-edible oil into a pure biodiesel for use in the vehicles. Without conversion Free Fatty Acid (FFA) are produced and the density will be higher than the normal diesel fuel which creates deposits in the engine cylinder. 30% of free fatty acids are produced in the normal crude oil which is far beyond 1% level. Pre-treatment process was setup upped to reduce the amount of FFA present in the oil and this can be reduced by first esterification process and then followed by the transesterification process. Such cases appear in the raw vegetable oil like olive oil, jatropha oil, cotton seed oil and pongamia oil because these raw vegetable oil possess high FFA[1]. The reaction of transestrification is as follows:

$$Triglyceride + ROH \leftrightarrows Diglyceride + R'COOR$$
$$Diglyceride + ROH \rightleftharpoons Monoglyceride + R''COOR$$
$$Monoglyceride + ROH \rightarrow Glycerol + R'''COOR$$
$$Triglyceride + Methanol \rightarrow \text{Glycerol} + \text{Biodiesel}$$

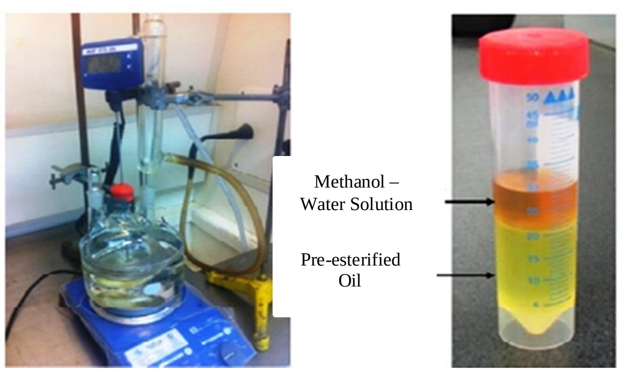

Figure 1: Preparation of Bio castor oil.

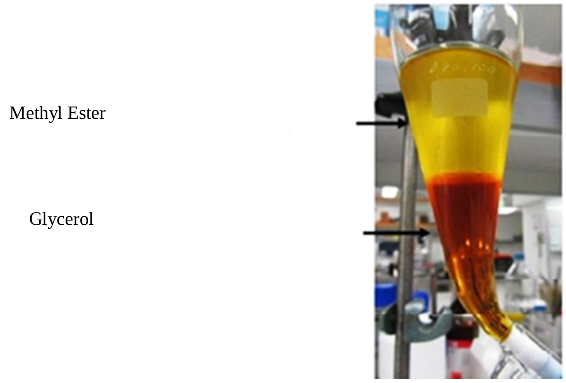

Figure 2: Removal of Glycerol.

The methodology adopted for the preparation of bio-diesel is given below and the whole process is described for a one litre castor oil. The timing and heating, separation of oils, settling and washing of oils has been configured according to the oil properties. One litre quantity of castor oil is taken and about 350-450 ml of methanol and 20 ml of concentrated sodium hydroxide (NaOH) is added in the oil. The temperature of the oil for this combination process is kept at 70^0C and it is to be maintained still for about 5-6 hours and also to be continuously stirred. After this mixture the reactant is to be kept settled for about 6-7 hours which would consists of two layers, one is the traces of bio-diesel and glycerine and other by product on the upper layer and gums are formed on the bottom layer. A tap is provided on the bottom of the layer to remove the by product and the gums. But by removing the traces will occur simultaneously on the prepared bio-diesel. To remove the traces, the biodiesel is taken to a separate reactor and mixed with hot water of about 200-300 ml at 40^0C and settled for nearly 6-7 hours and this is done frequent for two to three times such that the soaps, gums and glycerine will be entirely removed from the bio-diesel.

IV. PREPARATION AND SYNTHESIS OF CAO NANOPARTICLES

Nanoparticles that occur obviously such as volcanic ash, soot from forest fries and the incidental by products of combustion process are physically and chemically heterogeneous and often termed as ultrafine particles. Calcium oxide (CaO) being cheap, has a high basicity and non-corrosive, economically easy to handle compared to other homogenous acid and base catalysts[4]. Transesterification of sunflower oil[13], Artificial Photosynthesis[14], Transesterification of Palm Oil[15] are the recently used nanoparticles in the production of biodiesel process. Calcium is basically a Block S, Group 2, Period 4 element and Oxide is basically a Block P, Period 2 element. These nanoparticles are spherical or faceted high surface area oxide magnetic nanostructure particles that serve as absorbent for decolorizing various dye solutions. Their size can be determined by using Powder X-Ray Diffraction methods. The CaO nanoparticles were prepared by solution combustion method with urea as a fuel. The normal crystal size was found to be about 36nm. The raw materials which were used in the process are Calcium Nitrate $(Ca(NO)_2)_2.4H_2O$ and fuel urea (NH_2CONH_2) with a purity level of about 99% and 99.5% respectively. Distilled water is also used as a substrate in this process. At the start calcium nitrite of 14.16g and fuel urea 6g was dissolved in a silica crucible with a help of distilled water respectively. The crucible was heated in a muffle furnace at 500-600°C and it was further grinded to make it has amorphous reaction. The reaction can be stated as follows (Madhusudhana et.al., 2012),

$$6Ca(NO_2)_2 + 10NH_2CONH_2 \rightarrow 6CaO + 10CO_2 + 20H_2O + 16N_2$$

The prepared nanoparticles are characterized by Scanning Electron Microscope, XRD process and FTIR Spectrum respectively. The SEM images show the particles shape and crystal structures. The average particle size was characterized using XRD method and found to be 36nm to 40nm with peak at $2\theta=0^0$ to 100^o using Debye-Scherrer formulae[16,17]. The FTIR spectrum says about the heights at 1632.82 and 1350.22 cm^{-1} which assigned to absorb CO_2 surface nanoparticles. At 3429.24 cm^{-1} has a spectrum evidence of O-H vibration absorbed on it and different temperatures were tested on the basis of the structures and values produced from the nanoparticles.

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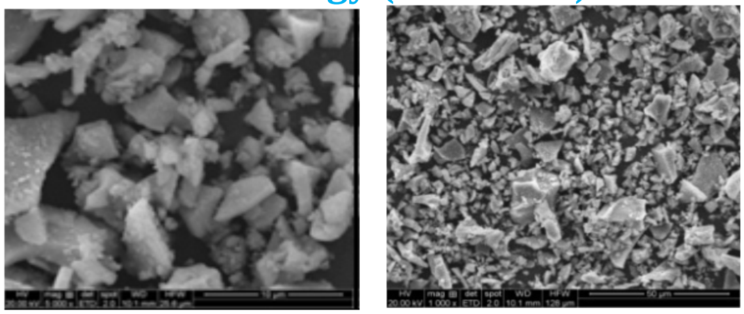

Figure 3: (a) (b) shows the synthesized CaO nanoparticles structure

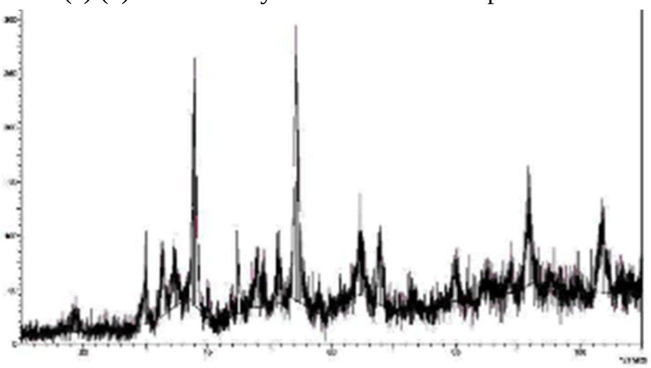

Figure 4: XRD pattern of synthesized CaO nanoparticle

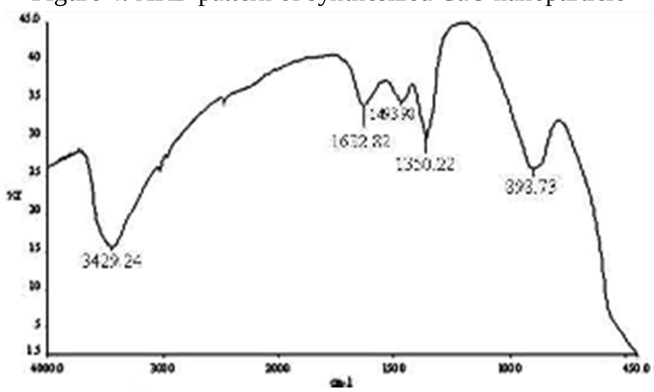

Figure 5: FTIR Spectrum of CaO nanoparticle

V. EXPERIMENTAL CHARACTERISTICS AND RESULTS

A. Fuel Properties Of Castor Oil

The fuel properties of castor oil were tested using Saybolt or Redwood Viscometer for measuring the density and specific gravity of the fuel. The cloud point and pour point were tested using ASTM Distillation of fuels respectively. The various properties are described below.

Table 1: Various Fuel Properties of Castor oil

Properties	Castor Oil
FFA (%)	0.35
Density (Kg/m^3)	960
Fire Point (^{0}C)	330
Flash Point (^{0}C)	290
Cloud Point (^{0}C)	15
Specific Gravity	0.8965
Calorific Value (kJ/kg)	38756.5
Kinematic Viscosity (mm^2/s)	107.55

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B. Prepared Biocastor Properties

The biodiesel were prepared by using transesterification process as discussed above and mixed with CaO nanoparticles of various proportions. The various properties were tested using the same apparatus as like used for testing the properties of fuel respectively and they are described below.

Table 2: Biodiesel CaO Nanoparticles Properties

Properties	BCaO 15	BCaO 30	BCaO 40	BCaO 50	Diesel
Density (Kg/m^3)	860.4	865.45	871.2	885.12	845
Flash Point (^{0}C)	95	85.2	120	154	68
Cloud Point (^{0}C)	-3.5	-5.4	-6.2	-9.5	-
Pour Point (^{0}C)	-12	-19	-29	-33	-6
Specific Gravity	0.85214	0.8632	0.8678	0.8946	0.845

C. Performance Characteristics

The performance characteristics of the produced biodiesel are tested at various proportions and various load conditions and various readings have been observed from the test engine respectively. These are briefly described as follows.

1) Brake Thermal Efficiency

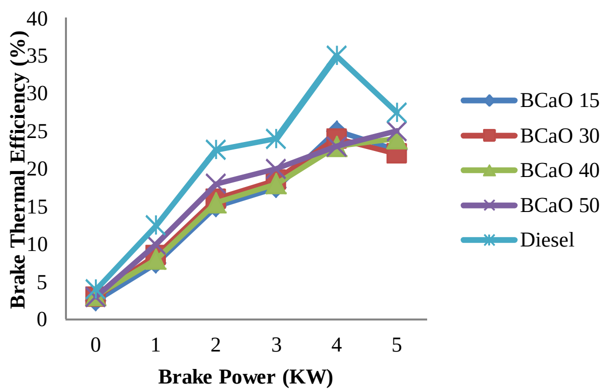

Figure 6: Brake Power vs Brake thermal Efficiency

The Figure 6 shows the variation between brake thermal efficiency and brake power at different load conditions. It has a very low comparatively lower brake thermal efficiency of 21.45% than the diesel fuel of 35%. Because of higher density oils the efficiency is reduced to 22% than compared to diesel fuels.

2) Brake Specific Fuel Consumption

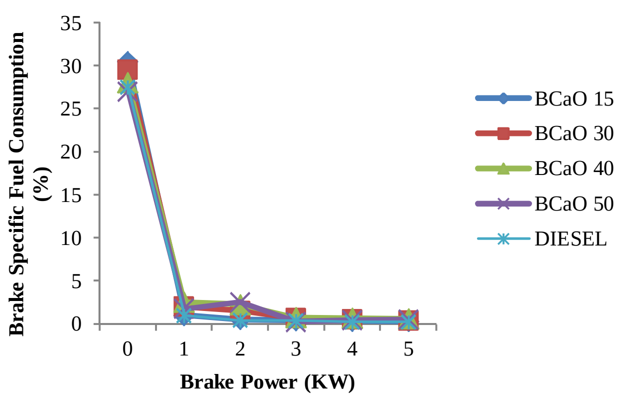

Figure 7: Brake Power vs Brake Specific Fuel Consumption

The Figure 7 shows the variation between brake specific fuel consumption and brake power at different load conditions. It has higher values of BSFC of about 0.4 Kg/kW-hr when compared to diesel of 0.245 Kg/kW-hr. A delay in the ignition system can lower the efficiency of a brake specific fuel consumption of about 20% at normal load conditions.

3) Exhaust Gas Temperature

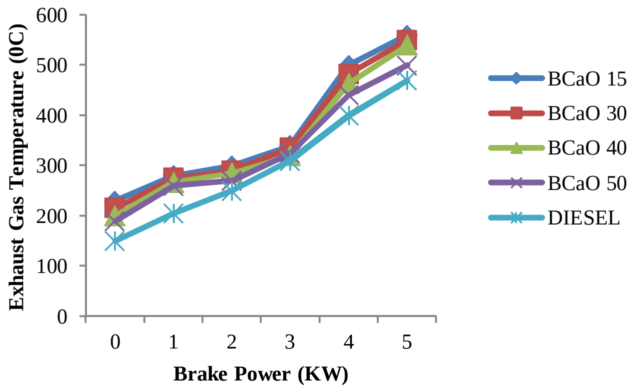

Figure 8: Brake Power vs Exhaust Gas Temperature

The Figure 8 shows the variation between exhaust gas temperature and brake power at different load conditions. At normal load conditions, it is experienced about 480^0C than compared with diesel of 440^0C, because of higher deposits formation in the cylinder and exhaust gas respectively.

4) Volumetric Efficiency

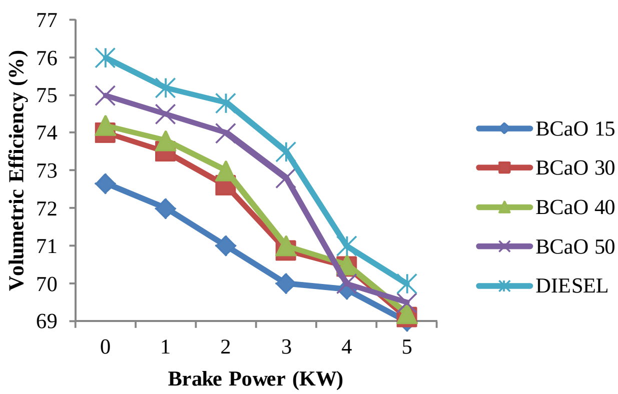

Figure 9: Brake Power vs Volumetric Efficiency

The Figure 9 shows the variation between volumetric efficiency and brake power at different load conditions. A lower volumetric efficiency is obtained at any load conditions. Diesel has a volumetric efficiency of 74% and the produced biodiesel has 69% and it has been lowering at different load conditions by 0.45% when compared with diesel. The incoming fresh air is heated with the high exhaust gas temperature which suitably lowers the volumetric efficiency of the fuel in the engine.

5) *Emission Characteristics:* The emission characteristics of the produced biodiesel are tested at various load conditions such as CO, CO_2, Smoke etc. and various readings have been observed from the test engine respectively. These are briefly described as follows.

a) *Carbon Monoxide*

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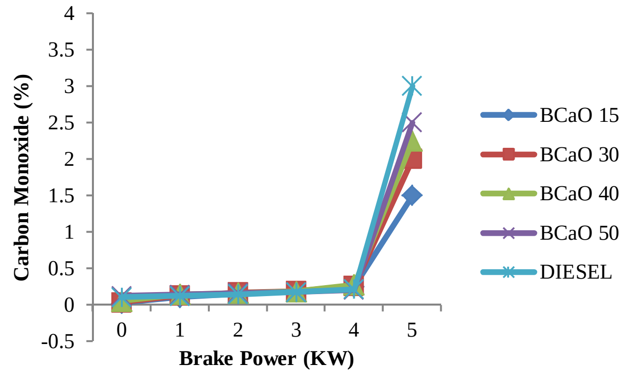

Figure 10: Brake Power vs Carbon Monoxide

The Figure 10 shows the variation between Carbon Monoxide and Brake power at different load conditions and resulted in a complete combustion of fuel. At initial load and rated load conditions it has a CO of about 0.07% and 2.5% when compared with diesel of 0.25% and 3.25%. The amount of CO has been reduced is of 60% than the original produced diesel fuel respectively.

b) Carbon Dioxide

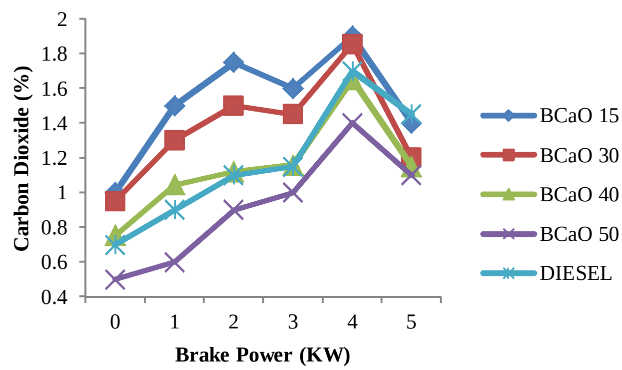

Figure 11: Brake power vs Carbon Dioxide

The Figure 11 shows the variation between Carbon Dioxide and Brake power at different load conditions and lowered the CO due to excess oxygen content present in biodiesel. At normal and rated load conditions it consists of about 1% when compared with diesel fuel of 2% which shows that about 18% of CO has been lowered from this castor oil nanoparticles biodiesel respectively.

c) Unburned Hydrocarbons

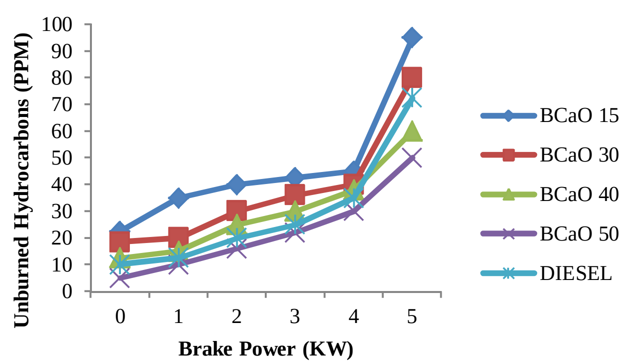

Figure 12: Brake Power vs Unburned Hydrocarbons

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The Figure 12 shows the variation between unburned Hydrocarbons and Brake power at different load conditions. At normal load and rated load conditions, the produced fuel nano consists of 15 and 22 PPM when compared to diesel of 35 and 78 PPM. The lowered UHC compares of about 49% and 65% respectively and this also due to excess oxygen content present in the fuel nanoparticles.

d) Nitrogen Oxides

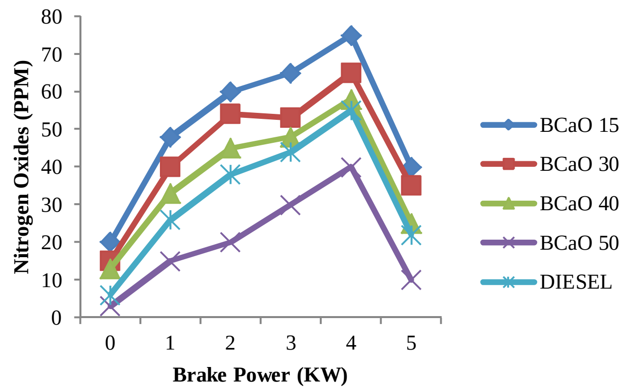

Figure 13: Brake power vs Nitrogen Oxides

The Figure 13 shows the variation between Nitrogen Oxides and Brake power at different load conditions. At any load conditions, the NO_x has not been lowered because of excess oxygen content present in the fuel nanoparticles. It was revaluated that about fuel nanoparticles are still 15% higher than the diesel and considerable efforts are being solved to reduce the NO_x content in the vehicles respectively.

e) SMOKE

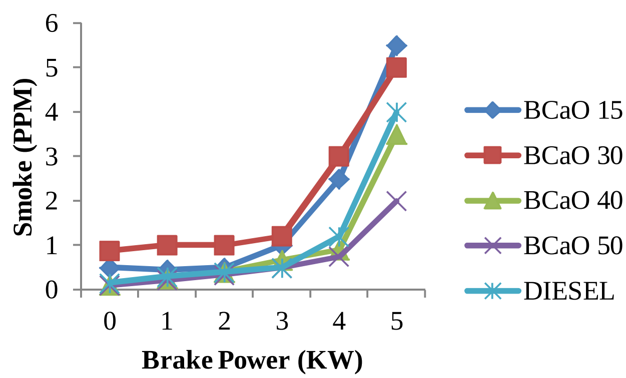

Figure 14: Brake Power vs Smoke

The Figure 14 shows the variation between Smoke and Brake power at different load conditions and was tested by using Bosch Smokemeter. At any load conditions, the fuel nanoparticles consists of about 2.5 and diesel of about 4.5 smoke units. it has been evaluated that about 40% of Smoke particles from the fuel are reduced with an equal to combustion of fuel. Less viscosity, flash point and other characteristics of fuel are the main reasons to improve an combustion quality when compared to diesel and other straight castor oil properties.

VI. CONCLUSION

Experiments were done in a single cylinder, direct injection diesel engine and the results and discussions were obtained, it can be said that the performance parameters of biodiesel nanoparticles were higher with the normal diesel fuel and the emission parameters were lower except NO_x because of large amount of oxygen content produced in the biodiesel respectively. But when used as a pure castor oil (without transesterification process) the amount of NO_x has been reduced and increase in other emission parameters respectively. While doing the esterification process, the viscosity and flash point are being reduced, whereas density and viscosity are higher when compared with other types of biodiesels. Brake Thermal Efficiency, BSFC and Exhaust Gas Temperature are compared with normal load conditions and verified that about 20% lower BTE, 38% higher BSFC, 5% higher in EGT when compared with diesel fuel. Likewise, UBHC, CO, CO_2 and smoke are lower by 65%, 82% and 35% respectively when compared with diesel fuels because of complete combustion of fuels in the engine due to rich air-fuel ratio. But NO_x emissions are higher by 32% when compared with that of diesel because of excess amount of oxygen content present in the fuel nanoparticles. Nanoparticles play an important role in the part of biodiesel processing which can increase and as well as decrease the emission parameters of an engine respectively. They were synthesized by using chemical combustion method. The product was tested under different characteristics such as Scanning Electron microscope, X-Ray Diffraction, Fourier Transform Infrared Ray Spectrum respectively. The average size of the nanoparticle or a nanocrystal was found to be in 36nm to 40nm and the energy band gap was found to be 4.9eV. It possesses excellent catalytic ability as an heterogeneous catalyst in the transesterification process of various oils respectively. Various products can also be used as additional fuel in the process of CaO nanoparticles such as 2-amino-3,5-dicyano-6-sulfanyl pyridine, Polyvinylpyrrolidone (PVP) can be synthesized by either combustion method or by co-precipitation method or by sol-gel technique respectively.

VII. ACKNOWLEDGEMENT

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