ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY
School of Mechanical, Chemical and Materials Engineering

The Comparative Performance and Emmission Analyisis of Argemone Mexicana Biodiesel Blended With Petro Diesel Fuel With and Without Nanoparticle Additives

A thesis submitted to Adama Science and Technology University in partial fulfillment of the requirements for the award of the degree of Master of Science in Automotive Engineering

by

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the thesis entitled "**The Comparative Performance and Emission Analysis of Argemone Mexicana Biodiesel Blended with Petro Diesel Fuel With and Without Nanoparticle Additives**'' in partial fulfillment of the requirement for the award of the degree of Master of Science in Automotive Engineering is an authentic record of my own work carried out from November, 2017 to September, 2018 under the supervision of Mr. N.Ramesh Babu (Assistance Prof.) and Mr. Deresse Firew (Msc.), Department of Mechanical Systems and Vehicle Engineering, Adama Science and Technology University, Ethiopia.

The matter embodied in this project has not been submitted by me for the award of any other degree or diploma. All relevant resources of information used in this project have been duly acknowledged.

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Student name	Signature	Date

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief. This thesis has been submitted for examination with my approval.

Mr. N.Ramesh Babu (Assistance Professor)	-------------------------	--------------
Advisor name	Signature	Date

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LIST OF ACRONYMS AND ABBREVIATIONS

AB15	Argemone Biodiesel 15%
AB20	Argemone Biodiesel 20%
AB25	Argemone Biodiesel 25%
AB20+50ppm	Argemone Biodiesel 20% + 50ppm CeO_2
AB20+100ppm	Argemone Biodiesel 20% + 100ppm CeO_2
AlO_3	Aluminium oxide
AME	Argemone Mexicana Ester
ANP	Aluminum nanoparticle
ASTM D6751	American Society of Testing and Materials
BTE	Brake thermal efficiency
CeO_2	Cerium Oxide
CI	Compression Ignition
CN	Cetane Number
CO	Carbon monoxide
CO_2	Carbon dioxide
$CuCl_2$	Copper II Chloride
CuO	Copper Oxide
CRGE	Climate Resilient Green Economy
DI	Direct injection
EPSE	European Standard

EU	European Union
EN	European Standard
FAAE	fatty acid alkyl esters
FAME	Fatty Acid Methyl Ester
FFA	Free fatty acide
GHG	Green House Gas
HC	Hydrocarbon
IC	Internal Combution
ID	Ignition Delay
ITE	Indicated thermal efficiency
Kg	Kilogram
KOH	Potassium Hydroxide
NaOH	Sodium hydroxide
NOx	Nitrogen Oxide
O_2	Oxygen
ppm	parts per millions
rpm	revolution per minus
SFC	Specific Fuel Consumption
ZnO	Zink Oxide

ABSTRACT

Due to the fear on the availability of fossil fuel reserves and the environmental problems caused by fossil fuels, considerable attention must be given to biodiesel production as an alternative to conventional diesel fuels. Because biodiesel offer a very promising alternative to diesel fuel since they are renewable, biodegradable and have similar properties with the conventional fuel. However, as the biodiesel is produced from vegetable oils and animal fats, there was concerns that biodiesel feedstock may compete with food supply in the long-term. Hence, the recent focus is to find oil bearing plants that produce non-edible oils as the feedstock for biodiesel production. As the argemone seeds are rich in oil and none edible the present study is to convert the oil to Fatty Acid Methyl Ester (FAME) through trans-esterification processes to get argemone oil methyl-ester by using methanol alcohols in the presence of KOH as a catalyst.

In this context, this study have been investigated the performance and emission analysis of the argemone Mexicana biodiesel blended with diesel fuels with and without cerium oxide nanoparticle additives in diesel engine. The experiment was conducted on single cylinder, four strokes, air cooled, direct injection diesel engine (CT 100.22) with a power output of 5.5KW and the engine is placed in the CT 110 test stand for small combustion engines of maximum power output 7.5kw. The blend were prepared as (B0, AB15, AB20, and AB25) without cerium oxide (CeO_2) *nanoparticle additives and (AB20 +50ppm and AB20 +100ppm) with cerium oxide nanoparticle for comparison. The result investigated that, mixing of additives on biodiesel improves the properties of the fuels. From performance test result the mixture of AB20 +50ppm* CeO_2 *shows (5.3%, 1.67% and 0.37%) reduction in brake power, torque and brake specific fuel consumptions respectively. AB20 +100ppm* CeO_2 *shows (0.26%) an increment in brake torque and the reductions in brake power and brake specific fuel consumption by (1.38% and 0.65%) respectively. Moreover, the* CeO_2 *nanoparticle additive improves the exhaust emissions. Generally, it can be concluded from the experimental investigations that mixing of nanoparticle additives in biodiesel can improve the performance and emissions.*

Keywords: - *Argemone Mexicana oil, Bio-diesel, Cerium oxide nanoparticle, fuel properties, performance, trans-esterification.*

1. INTRODUCTION

The need for energy is increasing because, the increasing industrialization and motorization of the world has led to a steep rise for the demand of the petroleum based fuels. Therefore, the world is confronted with major problems like wide spread misuse of the petroleum reserves, which are being depleted at a rapid rate. Due to this the fossil fuel is near future will become rare due to its limited reserves, indiscriminate extraction and consumption, while at the same time, the request for improving the pollutant emissions behavior of the existing vehicle fleets powered by diesel engines has become mandatory. Hence, it is necessary to look for alternative fuels which can be produced from locally available such as alcohol, vegetable oils, animal fats etc. [1].

1.1.Background

The growth of biofuels around the world is encouraged largely by energy security and environmental concerns and a wide range of market mechanisms, incentives and supports have been put in place to facilitate their growth. Developing countries, apart from these considerations, also view biofuels as a potential means to speed-up rural development and create employment opportunities. Therefore, biodiesel also known as "mono-alkyl ester" considered as promising choice as they are clean renewable fuels and best substitute for diesel fuel in any CI engine [2]. That could be the product of the reaction of alcohol, such as methanol or ethanol with oil or fats (triglyceride) by trans-esterification reaction, which conform to ASTM D6751 and EU 14214 specification for use in diesel engine. However, neat biodiesel or its blends may be used in the existing diesel engines with little or no modification to the engine [3, 4].

As a future promising fuel, biodiesel has to compete economically with petroleum diesel fuels because, the economic feasibility of biodiesel depends on the price of the feedstock used for production. One way of reducing the biodiesel production costs is availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel price. Recently, food verses fuel controversy makes edible oil not an ideal feed stock for biodiesel production this is why the non- edible oil sources are picking up as the demand for biodiesel is expected to increase sharply in the near future [5].

The non-edible vegetable oils are preferred as potential low priced biodiesel sources [1]. They are well adapted to arid, semi-arid conditions and require low fertility and moisture demand to grow. Moreover they are commonly propagated through seed or cuttings. Since these plants do not compete with food, seed cake after oil expelling may be used as fertilizer for soil enrichment

In different countries various oils have been used as raw materials for biodiesel production owing to its availability. Soybeans are commonly used in the United States. Palm oil is used as a significant biodiesel source in Malaysia and Indonesia. In Europe rape seed is the most common base oil used in biodiesel production. In India and South Africa the Jatropha tree is used as significant fuel sources. These fuels are not only green in nature but also help to reduce dependence on imports oil [6, 8, 9].

The advantages of bio-diesels as diesel fuel, apart from their renewability, minimal sulfur and aromatic content, higher flash point, higher lubricity, higher cetane number and higher biodegradability and non-toxicity. On the other hand, they have drawbacks including their higher viscosity, higher pour point, lower calorific value and lower volatility. Furthermore, their oxidation stability is lower, hygroscopic and as solvents, they may cause corrosion of components, attacking some plastic materials used for seals, hoses, paints and coatings.

In order to overcome the drawbacks associated with the biodiesel fuels use of chemical substances like fuel additives derived from organic, inorganic and metals were used by mixed thoroughly with diesel and biodiesel blend fuel for improving both performance and emission. Therefore, the nanoparticle fuel additives are helps in the improvement of biodiesel blend fuels efficiency by improving the properties while comparing with diesel.

In this study, there was a production of argemone Mexicana biodiesel, characterization's and an experimental investigation was done to examine the performance and emission of produced biodiesel with their different blends with and without nanoparticle additives and compared with diesel fuel. Moreover, the experimental study intentions was at the investigation of the effect of cerium oxide (CeO_2) in the form of nanoparticles, as an additive in biodiesel blends, on the physicochemical properties of fuel samples as well as the engine performance and emissions. The experimental investigations were carried out by varying the dosing levels of CeO_2

nanoparticles in the fuel (i.e. 50ppm and 100 ppm). The various blends of diesel/AME (AB15, AB20, AB25, AB20 + 50ppm CeO_2 and AB20 + 100ppm CeO_2) were prepared and used as a fuel in CI engine. The objective is to investigate the performance (Tb, Pb and Bsfc) and emission of (CO, HC, CO_2 and O_2) characteristics and compare with neat diesel fuel to see the effects of nano particle. Single cylinder 4 stroke air-cooled direct injection diesel engine was used for conducting the performance and emission characteristics that were obtained and analyzed.

1.2.Statement of Problem

Mankind is using energy in many ways to improve its living standard. The world energy consumption increasing, this is related to growing population, technologies and consumption. Fossil fuel resources are continuously depleting and these fixed reserves are very much concentrated in certain regions of the world. Therefore, those countries not having these resources are facing a foreign exchange crisis, particularly due to the import of crude oil. The scarcity and rising price of fossil fuels together with dread about the environmental harm created by them have resulted in increasing efforts to search for alternative energy sources mainly emphasis on biofuels. Ethiopia is one of the world countries which totally import the petroleum fuel from other countries. The demand for modern energy sources such as petroleum fuels is increasing with increase in population and economic growth. Therefore, the government priority agenda for alternative fuels will be to some extent substitute imported petroleum fuels and prevent environmental degradation due to conventional fuels. So the aim of this thesis work is to reduce dependency on conventional fuel by introducing biodiesel derived from Argemone maxicana as alternative fuel by blending it with diesel fuel and also check its performance and emission on a single cylinder four stroke IC engine with and without cerium oxide nanoparticle additives. Furthermore, investigations were done on the effects of cerium oxide nanoparticle additive on the performance and emission characteristics of produced biodiesel blended fuel samples and comparing with net diesel fuel.

1.3.Objectives

1.3.1. General objective

The general objective of this thesis work is to analyze the effect of cerium oxide nanoparticle additive on the performance and emission characteristics of argemone Mexicana biodiesel blends.

1.3.2. Specific objectives

The specific objectives of the study are as follows:

- To produce biodiesel from argemone mexicana seed oil.
- To determine fuel samples by varying blend ratio and additive amount.
- To check standard characteristic of blended biodiesel fuels with and without cerium oxide (CeO_2) nanoparticle.
- To investigate the performance and emission of specific fuel samples and analyse on it.

1.4. Significance of the study

The significance of the study is as follows:

- Reduce our dependency on petroleum based fuels.
- Show how to use different natural resources to produce biodiesel in small scale which will reduce our dependency on fossil fuels.
- Provide cheap, locally available energy to catalyze the all-rounded socioeconomic development process.
- Optimize the performance and reducing emissions of the engine using nanoparticle based fuel additives with biodiesel blended fuels.
- Generally the result is very important for future that it will alleviate problems of energy supply while simultaneously helping to mitigate GHG and other atmospheric pollution emissions.

1.5. Scope of the study

The scope of this study are extracting the oil from argemone Mexicana seed, producing the biodiesel from the oil and to see the properties of the fuel, characterization is the activity included in this work with and without metallic nanoparticle additives to the blended biodiesel fuel samples. Moreover, analysis focused on investigation of the performance and emission of blended biodiesel for different samples (AB15, AB20 and AB25) in diesel engine. At last, investigate the performance and emission analysis of blended biodiesel with nanoparticle additives for (AB20) with 50ppm and 100ppm to see the possibility and advantage of using nanoparticle additives.

1.6. Limitation of the study

Tis research was limited to a certain factors. While conducting the research various problems have faced like lack of getting engine dynamometer which is used to measure the brake power and brake torque directly from the engine so, it was too difficult to conduct tests of biodiesel blended fuel samples. Due to the absence of the testing materials it was impossible to conduct calorific value testing of the samples. Moreover, the NOx emissions could not be studied due to absence of analyzer.

1.7. Organization of the study

This study is divided into five chapters. Following this chapter the second chapter, Literature Review, deals with the overview of the biodiesel and the related experimental investigations done in this area.

The third chapter, Material and Methods, involves description of the materials and their procedure used to attain the objectives. Moreover it deals with the extraction of oil, laboratory production procedure of biodiesel and the procedure followed during the performance testing. Also the method and equations used to analyzer the data observed were included in this chapter.

The fourth chapter, Results and Discussions, describe the result that were obtained and discuss with those results and compare and contrast the results obtained by different blends.

The fifth chapter, Conclusions and Recommendation, describes the conclusion made from the result obtained and point out some points recommended for future work that is possible in this area.

2. LITERATURE REVIEW

This chapter reviews the history, source, production, properties and the specification of the biodiesel. Moreover, there are also the previous studies which are assisting to introduce the current study were reviewed in this section in detail that are directly or indirectly related to the current study. These are international journals, thesis and dissertations works.

2.1. Vegetable oils as fuels

Use of vegetable oils in diesel engines is not a new development; rather it is as old as the diesel engine itself. Rudolph diesel (1858-1913), the inventor of compression ignition engine (1892 AD) used peanut oil as fuel to run one of the engines in Paris discussion in 1900 AD. In 1911 he stated “the diesel engine can be feed with vegetable oils and would help considerably in the development of agriculture of the countries which use it” [1].

In 1912 Diesel said, “The use of vegetable oils for engine fuels may seems insignificant today’’. But, such oil may become in course of time as important as petroleum and the coal tar product of the present time” Since diesel untimely death in 1913, his engine has been modified to run on the polluting petroleum fuel now known as diesel’’. Nevertheless, his idea on agriculture and his invention provided the foundation for a society fuelled with clean, renewable, locally grown fuel [6].

In the 1930s and 1940s, vegetable oils were used as diesel substitutes from time to time, but usually only in emergency situations. However, because of an increase in crude oil price, environmental concerns and limited resources of petro oil fuels, there has been a focus on renewable biofuels to make biodiesel fuel. Continued and increasing use of fossil fuel will change local air conditions and intensification the global warming problems caused of exhausted emissions. But the use of biodiesel as substitution fuels has the potential to reduce the level of the pollutants and the price of the fossil fuels [10, 12, 13, 14].

On August 31, 1937, G. Chavanne of the University of Brussels (Belgium) was granted a patent for a 'Procedure for the transformation of vegetable oils for their uses as fuels. This patent described the alcoholysis (often referred to as trans-esterification) of vegetable oils using ethanol and methanol in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols. This appears to be the first account of the production of what is known as 'biodiesel' today.

In 1973, there was a sharp oil crisis associated to the second Arab-Israeli war. During this period, the fuel price was doubled in just three months. The scarcity of this non-renewable resource jeopardized the supply. This fact encouraged the search a substitute for the oil.

Throughout the 1990s, Rudolph Diesel's prediction is becoming true today with more and more bio-diesel being used all over the world. In 2003 the EU promote the use of biofuels for transport. The target was that quantity of biofuels to be placed on the market should be 2% in 2005 and 5.75% in 2010 in relation to the fossil fuel. In 2007 the EU proposed with the objective to reduce the increase in global average temperature that, 20% of the energy will come from renewable sources. In 2020, 10% of the transport fuel should come from biofuels.

2.2. Definition for biodiesel

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which defined by ASTM D6751 as a fuel comprised of alkyl (methyl, ethyl or propyl) esters that specified for use in diesel engines. Biodiesel refers to the pure fuel (B100) before blending with diesel fuel. Biodiesel fuel is considered to be the environmentally friendly fuel because of its renewability, highly biodegradability, low pollutant emission, high flash point and excellent lubricity. Biodiesel fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats leading to severe engine problems, all this is due to the viscosity of vegetable oil that is greater than the viscosity of diesel. This problem is overcome by lowering the viscosity of vegetable oil [15, 16].

2.3. Biodiesel as a future prospective fuel

The best way to use vegetable oil as fuel is to convert it to biodiesel. Biodiesel, also known as "mono-alkyl ester" based oxygenated fuel that is the product of the reaction of alcohol, such as methanol or ethanol with oil or fats (triglyceride) by tran-esterification reaction [2]. Biodiesel has to compete economically with petroleum diesel fuels. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel price. Recently, food verses fuel argument makes edible oil not an ideal feed stock for biodiesel production. In this competition the non- edible oil sources are preferred as feed stock for the production of biodiesel fuels. The use of non-edible oils as alternative feedstock is picking up as the demand for biodiesel is expected to increase sharply in the near future [10, 12]. The properties of biodiesel generally has higher density, viscosity, cloud point, cetane number, lower volatility and heating value compered to diesel fuel that is affecting on the engine performance and emissions. However, neat biodiesel or its blends may be used in the existing diesel engines with little or no modification to the engine [3, 4].

Biodiesel contains no petroleum products, but it is compatible with conventional diesel fuels and can be blended in any proportion levels with petro diesel to create a stable biodiesel blend. The proportion of blending with petroleum diesel is referred as “Bxx”, where xx indicates the amount of biodiesel in the blend. Slight concentration, such as B5, B10, B15 and B20 are suitably referred to as biodiesel blends have been accepted worldwide as potential renewable alternate fuels to substitute petroleum diesel.This can be used in diesel engine with no major modifications in the engine mechanical parts.

2.4. Biodiesels Feedstock’s

There are different types of oilseeds and animal fats that could be used as biodiesel sources. These vegetable oil based ester fuels can be derived from a number of edible, non-edible grade oil sources as described below:

Selecting the appropriate feedstock is a vital issue to ensure low production cost of biodiesel. As much as possible the biodiesel feedstock should fulfill two requirements for production of biodiesel which are low production costs and large scale production. In general, biodiesel feedstock can be categorized into four groups:

- Edible vegetable oil: soybean, palm oil, sunflower, safflower, rapeseed, coconut and peanut; etc.
- Non-edible vegetable oil: jatropha, karanja, mahua, linseed, argemone Mexicana, neem, camelina and beauty leaf tree/polanga; etc.
- Waste or recycled oil: cooking oil, frying oil, vegetable oil soap stocks and pomace oil; etc.

- Animal fats: beef tallow, pork lard, yellow grease, chicken fat and by-products from fish oil.

Among those, non-edible vegetable oils, waste or recycled oil as well as animal fats are regarded as the second generation biodiesel feedstock. The algae have been considered as third generation biofuel and an emerging non-edible oil of growing interest because of their high oil content and rapid biomass production.

Non-edible biodiesel crops are expected to use lands that are largely unproductive and can also be planted on cultivators' field boundaries, fallow lands, and in public land such as along railways, roads and irrigation canals. Non-edible oil plants are well adapted to arid, semi-arid conditions and require low fertility and moisture demand to grow. Moreover, they are commonly propagated through seed or cuttings. Since these plants do not compete with food, seed cake after oil expelling may be used as fertilizer for soil enrichment.

2.5. Argemone Mexicana Plant (Common name: Mexican prickly poppy)

A. Mexicana is a species of poppy found in Mexico and now widely naturalized in the United States, India and Ethiopia and belongs to the Papaveraceae family. It has been used by the Natives of the western US and parts of Mexico. The plants prefer slight (sandy) soils, require well-drained soil and can grow in nutritionally poor soil [18]. The plant grows to a height of 0.5–1.5 m and matures in 110 to 120 days. It requires moderate rainfall and temperate and tropical areas. The plant prefers all types of soil. The seeds are black in appearance and are heavy in weight as shown on Fig. 2-1. The seeds contain about 25-40% oil with 25% oleic and 55% linoleic acid in fatty acid composition. The main fatty acid present in Argemone mexicana seed oil are myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid and arachidic acid [9]. The non-edible oil from this plant has been found most suitable for biodiesel purpose [10].

Figure 2-1 Argemone mexicana plant and seed

2.6. Source of Biodiesel in Ethiopia

Different plants have been used as raw materials for biodiesel production owing to its availability. In different countries various oils have been used as raw materials for biodiesel production. Soybeans are commonly used in the United States. Palm oil is used as a significant biodiesel source in Malaysia and Indonesia. In Europe rape seed is the most common base oil used in biodiesel production. In India and South Africa the Jatropha tree is used as significant fuel sources. These fuels are not only green in nature but also help to reduce dependence on imports oil [6].

In light of the various cost items considered, first, it appears that the viability (and competitiveness) of biodiesel production in Ethiopia will largely depend on the cost/price of feedstock. Therefore, measures that drive down the cost/price of feedstock could be envisaged to enhance viability. Plants like, Jatropha, castor bean and palm are used for biodiesel production. Plants like Argemone mexicana and Croton macrostachyus are also being promoted and tested in some parts of Ethiopia.

However, the viability (and competitiveness) of biodiesel production in Ethiopia will largely depend on cost/price of feedstock. Although the recently launched Climate Resilient Green Economy (CRGE) strategy of Ethiopia predicts 5% biodiesel blending in transport fuel by 2030 biodiesel blending in transport fuel has not yet started in Ethiopia [11].

2.7. Biodiesel Production and Process

Biodiesel is defined as the alkyl monoesters of fatty acids from renewable biological resources, such as vegetable oils, animal fats, and waste restaurant oils that are used as renewable fuel that has drawn more and more attentions recently. The main components of vegetable oils and animal fats are triglycerides, which are esters of FFA with glycerol. The triglyceride typically contains several FFA, and thus different FFA can be attached to one glycerol backbone. The FFA composition is the most important factor influencing the corresponding properties of vegetable oils and animal fats [20- 23]. Unfortunately, vegetable oils or animal fats have high viscosity, it is necessary to reduce the viscosity in order to use them in a common diesel engine. There are many methods and processes that have been used recently to decrease the viscosity of oils and to produce biodiesel from different feed stocks. These methods are including; pyrolysis, micro-emulsifications, dilutions and trans-esterification's [1]. From all types' production methods, trans-esterification method is the reaction of a triglyceride with an alcohol in the presence of catalysts [20]. The alkaline catalyzed production of biodiesel generally has the following process steps.

2.7.1. Trans-esterification

The main components of vegetable oils and animal fats are triglycerides, which are esters of FFA with glycerol. The triglyceride typically contains several FFA, and thus different FFA can be attached to one glycerol backbone. With different FFA, triglyceride has different physical and chemical properties. The FFA composition is the most important factor influencing the corresponding properties of vegetable oils and animal fats [21-23].

Biodiesel can be synthesized by the trans-esterification reaction of a triglyceride with a primary alcohol in the presence of catalysts. Trans-esterification is a chemical reaction in which the vegetable oil, a triglyceride react with alcohol (methanol or ethanol) in the presence of catalyst (homogenous or heterogeneous), that can be producing a mixture of fatty acid (methyl or ethyl ester) and glycerol. Commonly, the trans-esterification can be catalyzed by a base or acid-catalyst [24-27, 29-32].

2.7.2. Chemistry of Transesterificatio Process

The long and branched chain triglyceride molecules are transformed to monoesters and glycerides [21]. Trans-esterification process consists of three consecutive reactions. That is, conversion of triglycerides to di-glycerides followed by the conversion of di-glycerides to mono-glycerides. Further the overall reaction between triglycerides and alcohol to give biodiesel (fatty acid alkyl esters, FAAE) is a three sequential reaction [29, 31]:

Triglyceride + R^1OH = Di-glyceride + FAAE

Di-glyceride + R^1OH = Mono-glyceride + FAAE

Mono-glyceride + R^1OH = Glycerol + FAAE …....………………………………………Eq 2-1

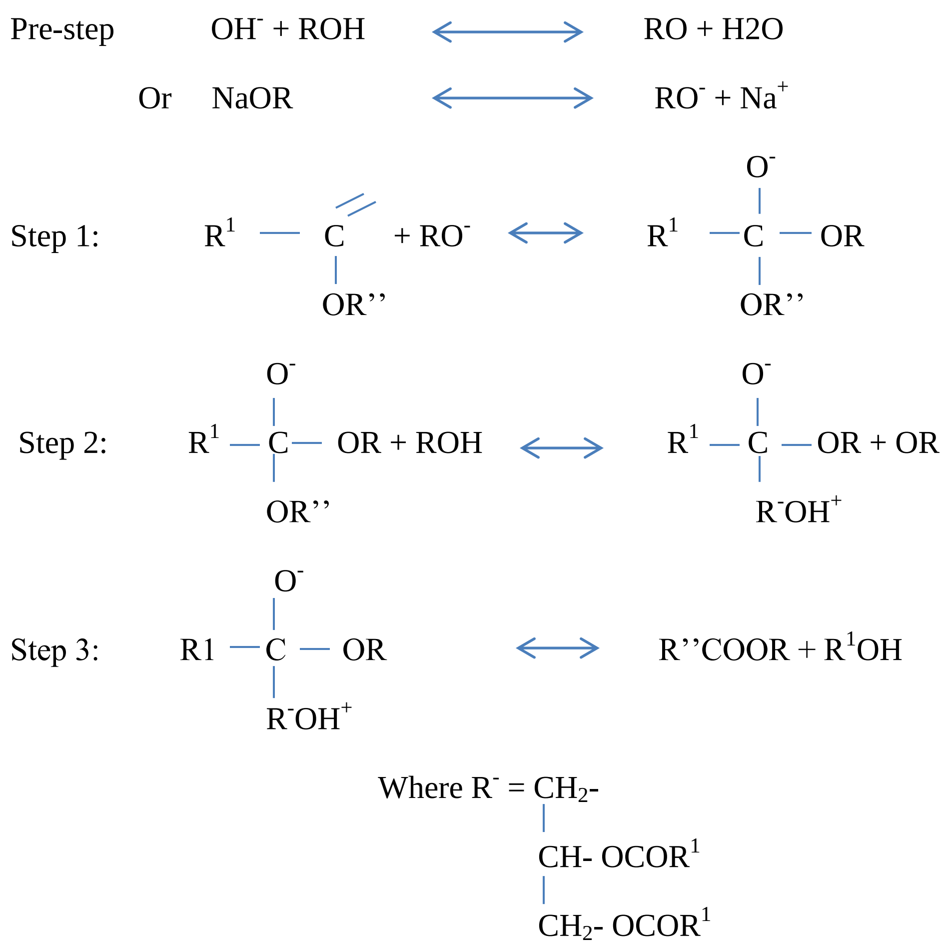
The choice of a catalyst for the trans-esterification mainly depends on the amount of FFA and of raw materials. Among primary alcohols, methanol is favored for the trans-esterification due to its high reactivity (the shortest alkyl chain and most polar alcohol) and the least expensive alcohol, except in some countries. Furthermore, methanol has a low boiling point, thus excess methanol from the glycerol phase is easily recovered after phase separation.

If methanol is used in the process is called methanolysis. The methanolysis of triglycerides represented in Eq.2.2 below.

$$\begin{array}{l} CH_2 - COOR_1 \\ | \\ CH - COOR_2 \\ | \\ CH_2 - COOR_3 \end{array} \quad + \quad 3CH_3OH \quad \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \quad \begin{array}{l} CH_2 - OH + R_1COOCH_3 \\ \\ CH - OH + R_2COOCH_3 \\ \\ CH_2 - OH + R_3COOCH_3 \end{array} \quad \text{……..Eq. 2-2}$$

Vegetable oil Alcohol Glycerol Methyl-ester

The alkali-trans-esterification of vegetable oils proceeds faster than the acid catalyzed reaction and the mechanism of this alkali-catalyzed trans-esterification have been shown in Fig.2.2 below.



R1 = Carbon chain of fatty acid, R = Alkyl group of alcohol

Figure 2-2 Mechanism for base catalyzed trans-esterification process.

2.7.2.1. Most important variables that influence the trans-esterification reaction

There are different factors that influence the trans-esterification process of biodiesel productions. The main factors affecting trans-esterification are alcohol/oil molar ratio, reaction time, reaction temperature and pressure, catalyst, water content, and FFA content [25, 26].

a) Reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. However, the reaction is conducted close to the boiling point of methanol (60–70°C) at atmospheric pressure for specified time. Though alkaline alcoholysis of vegetable oils is normally conducted near the boiling point of the alcohol and that the reaction can be carried out at room temperature [1, 36]. When the reaction temperature exceeds the boiling point of alcohol, the alcohol will vaporize and form large bubbles which may hinder the reaction and decrease of biodiesel yield because higher reaction temperature accelerate the saponification of triglycerides [40].

b) Ratio of alcohol to oil

Another important variable is the molar ratio of alcohol to vegetable oil that affecting the conversion efficiency, the yield of biodiesel, as well as biodiesel production cost [30]. Also, since the stoichiometric molar ratio of alcohol to oil for the trans-esterification is 3:1 and the reaction is reversible, higher molar ratios are required to increase the miscibility and to enhance the contact between the alcohol molecule and the triglyceride.

Trans-esterification is an equilibrium controlled reaction in which excess of alcohol can be used to get complete conversion and alcohol is easily recoverable. Moreover, increase in the amount of alcohol to oil increases biodiesel yield and biodiesel purity. Therefore, higher alcohol to oil molar ratios gives rise to greater alkyl ester conversion in a shorter time [29]. But the molar ratio is associated with the types of catalyst used such as; for the alkali catalyzed trans-esterification reaction the alcohol to oil molar ratio is ranging 5:1 to 12:1 that are the most acceptable for maximum conversion to ester. However, when using acid catalyst the desirable maximum conversion is obtained with sulfuric acid with alcohol to oil molar ratio of 30:1 [30, 31, 32]. This is in line with the result reported based on neat vegetable oils. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% (w/w). The molar ratio of alcohol to oil has no effect on acid value, saponification values and iodine values of esters [27].

c) Catalysts concentration

A catalyst is used to improve the transesterification reaction and amount yield produced. Alkali metal alkoxides are found to be more effective transesterification catalysts compared to acidic catalysts. The most common and efficient catalysts for biodiesel production KOH and NaOH can also be used. A concentration in the range of 0.5–1% (w/w) has been found to yield 94 to 99% conversion to vegetable oil esters [2], and further increase in catalyst concentration does not affect the conversion but adds to extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction [33]. In consequence, with vegetable oils or fats containing low FFA and water, the base-catalyst trans-esterification is much faster than the acid-catalyst trans-esterification and is most commonly used commercially on the industrial scale [34].

d) Mixing intensity

During the transesterification reaction, the reactants initially form a two-phase liquid system because oils and alcohols are not totally miscible, for this reason dynamic mixing is required to increase the area of contact between the two immiscible phases. Alcoholysis process can be enhanced by the agitation intensity of the reactor. Mass transfer of biodiesel from the oil phase towards the alcohol-oil interface might be a vigorous step that limits rate of alcoholysis reaction because the reaction is heterogeneous. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on the kinetics of the trans-esterification process forms the basis for process scale-up and design. Therefore, fast string accelerates trans-esterification reactions that variation in mixing strength is expected to change the kinetics of the trans-esterification reactions [29].

e) Effect of Moisture and Free Fatty Acid

Substantially, impurities in the oil affect the conversion level of crude oil to biodiesel. The free fatty acids and moisture content are the key parameters to determine the viability of vegetable oils to be used for trans-esterification process. The presence of moistures in the oil could increase the free fatty acids in the oil. To carry out the trans-esterification reaction, the free fatty acids in the oil must be less than 3% [37]. Higher the acidity of the oil, the smaller is the conversion efficiency. As little as 0.3% water in the reaction mixture reduced glycerol yields by consuming catalyst. Other investigators have also stressed the importance of a nearly dry oil substantially free (<0.5%) of fatty acids [37, 38]. High free fatty acid content oils are processed with an immiscible basic glycerol phase as to neutralize the free fatty acids and cause them to pass over the glycerol phase.

2.8. Selection of Catalyst

Sodium hydroxide (NaOH also called Caustic soda) and Potassium hydroxide (KOH also called Caustic potash), both are commonly used to make biodiesel. I selected KOH as catalyst for this project as it dissolves faster in methanol than NaOH and it also easy to handle than NaOH.

2.8.1. The base catalyzed production of biodiesel

The base catalyzed production of biodiesel generally has the following process steps [39].

a) Mixing of alcohol and catalyst

Initially, during the process alcoxy is formed by reaction of the catalyst with alcohol and then the alcoxy is reacted with any vegetable oil to form biodiesel and glyceron.This process is done before the alcohol and catalyst are mixed with the oil first mix the alkali hydroxide; commonly potassium and sodium hydroxide with common alcohols (methanol or ethanol) in the mixer with a standard agitator to more facilitate the mixing. Alkali hydroxide is dissolved in the alcohol to produce alkolysis solution.

b) Chemical reaction

The alcohol and catalyst mixture is then charged into the oil sample prepared for trans-esterification which is heated nearly with the boiling point of the alcohol nearly (60-65 ^{0}c) to prevent the loss of alcohol and speed up the reaction. Therefore, reaction process is totally closed to the atmosphere to prevent the loss of alcohol because it is easily vaporized. The excess alcohol is normally used to ensure total conversion of the oil to its esters as there is no problem of recovering of the alcohol for later use after recovering.

c) Separation

After the reaction is completed, there happens glycerol and biodiesel formation. Therefore, both have a significant amount of the excess alcohol that was used in the reaction which is in need of being recovered. The reacted mixture is sometimes neutralized at this step if the basic media that is caused by alkali hydroxide is occurred. The glycerol phase is much denser than biodiesel phase, that making biodiesel to be floated.

During this step, the two products can be separated by gravity using settling vessel. The glycerol drawn off at the bottom of the settling vessel and the biodiesel is drawn off at the top. Sometimes, in some cases a centrifuge is used to separate the two materials faster by screening both phase.

2.9. Biodiesel Washing and Drying

After the biodiesel is separated from the glycerol, it is should be purified by washing gently with warm water which is heated for about 50^{0}c to remove residual catalyst, alcohol and soap to make more unadulterated until clear water appear. The washed biodiesel should be drying for about 150 ^{0}c in order to remove traced moisture of water and impurities for about 40- 45 minutes.

2.10. Biodiesel Properties

2.10.1. Cold Weather Issues

1. Cloud Point: is a temperature at which a haze or cloud of wax crystals first appear in a fuel when it is cooled under test condition. The Cloud Point is the most conservative temperature at which components begin to precipitate from the fuel that may cause operability issues. Cloud Point results will vary significantly depending upon the feedstock from which the methyl ester was created and typically higher than the conventional diesel [15]. It can then be modified in the following ways to get the lower cloud point. These are: The use of additives that retard the formation of solid crystals in the B100 by various mechanisms. The blending feedstock that is relatively high in saturated fatty acids with feedstock that have lower saturated fatty acid content.
2. Pour point: is the lowest temperature at which the diesel fuel will flow when cooled under test conditions. That is related to lower temperature at which diesel engine will be able to operate.
3. Kinematic Viscosity: It is the resistance to flow of a fluid under gravity. It is a basic design specification for fuel injectors used in diesel engines. Maximum allowable viscosity, on the other hand, is limited by considerations involved in engine design and size, and the characteristics of the injection system. The upper limit for the viscosity of biodiesel (6.0 mm^2/s at 40°C) is higher than the maximum allowable viscosity in Specification D975 Grade 2-D and 2-D low sulfur (4.1 mm/s at 40°C). Blending biodiesel with diesel fuel close to its upper limit could result in a biodiesel blend with viscosity above the upper limits contained in Specification D975 [35].

2.10.2. Corrosion and Deposits

1. Acid Number: The acid number is a relative indicator of the acidic impurities, degradation and/or oxidation of the fuel. It is a direct measure of free fatty acids in the biodiesel (B100). It is a quantity of base that can be expressed as a milligram of potassium hydroxide per gram of sample, that required for titrate a sample to specified end point. Free fatty acids arise in part through the hydrolysis of the feedstock fats and

oils. Improper processing or oxidation may also lead to higher values. These oxidative products are associated with fuel system deposits and corrosion [15].

2. Free and Total Glycerin: The Free Glycerin value records the level of by-product glycerin that remains in B100. The Total Glycerin result measures the amounts of unconverted and partially converted fats and oils. Excessive levels of these components may lead to storage tank and fuel system filter plugging, along with engine fouling [15].
3. Sulfated Ash: It is the residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. This test monitors the mineral ash residual when fuel is burned. For biodiesel this test is an important indicator for the quantity of residual metals in the fuel that may be came from catalyst used in the trans-esterification process.
4. Oxidative Stability: The oxidative stability of the fuel is related in part to the acid number results. As the biodiesel degrades, or oxidizes, organic acids or polymers are created as a by-product which may lead to corrosion or filter plugging. The Oxidation Stability result is an accelerated test used to predict the fuel's stability for longer-term storage, possibly up to six months [15].
5. Water and Sediment: It is a test that determines the volume of free water and sediment in middle distillate fuels having viscosities at $40^{o}c$ in the range 1.0 to 4.1 mm^2/s and densities in the range of 700 to $900 kg/m^3$. For biodiesel, this test is determinant of presence of free water droplets and sediment particles.

2.10.3. Combustion

1. Cetane number: Cetane number (CN) is a measure of the ignition quality of diesel fuel during combustion ignition. It provides information about the ignition delay (ID) time of a diesel fuel upon injection into the combustion chamber. High CN implies short ignition delay. The value provides a measure of the ignition characteristics of the fuel in compression ignition engines. The lowest value for typical biodiesel is the same as a "premium petroleum diesel" at 47 [15]. The CN of biodiesel is generally higher than diesel fuels [25]. The CN of biodiesel specified by ASTM D613 is 47 min and EN ISO 5165 is 51 min [26].
2. Flash point: Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or a spark. Flash point varies inversely with the fuel's volatility. The flash

point is the lowest temperature at which fuel emits enough vapors to ignite. Biodiesel has a high flash point which is usually more than 150 ^{0}C, while generally conventional diesel fuel has a flash point of 55–66 ^{0}C. It is important to note that a typical result of 130°C for biodiesel is almost twice that of petroleum diesel (approximately 70°C) and therefore much safer to handle and transport. The Flash point is also used to ensure the residual methanol left in the fuel after biodiesel processing will not negatively affect combustion and other fuel system components [15].

3. Iodine value: Indicates the level of saturation of the molecules according to ASTM, the iodine number helps to indicate the oxidation stability of the biodiesel. The higher iodine number represents the lower oxidation stability.
4. Sulfur: This method covers the determination of total sulfur in liquid hydrocarbons, boiling in the range approximately 25 to 400^{o}C, with viscosities between approximately 0.2 and 20 mm^{2}/s at room temperature. Even though, biodiesel feedstock's typically having very little sulfur, this test is an indicator of contamination of protein material and carryover catalyst material from a production process.
5. Carbon Residue: In petroleum products, the part remaining after a sample has been subjected to thermal decomposition is the carbon residue. The carbon residue is a measure of how much residual carbon remains after combustion. The most common cause of excess carbon residues in biodiesel is an excessive level of total glycerin.

2.11. Biodiesel Specification Standards

According to the American Society of Testing & Materials (ASTM), the Standard Specification for biodiesel (B100) is ASTM D6751-02 [23]. Also the European standard (EN 14214) is adopted by all 31 member states of the European Committee for standardization of biodiesel (B100) [28]. The standard ASTM D6751 describes the quality requirements and the methods of analysis used for biodiesel blended with diesel oil, applying to methyl esters as well as for ethyl esters. The ASTM and EU biodiesel property specifications with the recommended test methods are given in the table below.

Table 2-1 Specification for biodiesels

Properties of biodiesel	Units	ASTM D6751		EN 14214	
		Limits	Test methods	Limits	Test methods
Kinematic viscosity 40 ^{o}c	mm^2/s	1.9-6.0	D445	3.5-5.0	EN ISO 3104
Density (15 ^{o}c)	kg/m^3	N/S	D4052	860-900	EN ISO 3675
Ester content	mass%	N/S	N/S	96.5min	EN 14103
Cetane number	-	47min	D613	51min	EN ISO 5165
Flash point	^{o}c	93min	D93	120min	ISO/CD 3679
Water content	volume %	0.050max	D2709	500max	EN ISO 12937
Sulphated ash	mass%	0.020max	D874	0.02max	ISO 3987
Copper corrosion	grade	No.3max	D130	No.1	EN ISO 2160
Acid number	mg KOH/g	0.80max	D664	0.5max	EN 14104
Iodine number	-	N/S	N/S	120max	EN 14111
Oxidative stability (110^{o}c)	h	N/S	N/S	6max	EN 14112
Oxygen content	%	N/S	N/S	N/S	N/S
High calorific value	MJ/kg	N/S	N/S	N/S	N/S
Free glycerol	mass%	0.020max	D6584	0.020max	EN 14105
Total glycerol	mass%	0.240max	D6584	0.25max	EN 14105
Phosphorous content	mass%	0.001max	D4951	10max	EN 14107

2.12. Fuel Additives

Biodiesel has become more attractive recently because of its environmental benefits and the fact that the biodiesel is made from renewable energy source. However, there are a major draw backs in the use of biodiesel blends because there was a change in physical and chemical properties compered to diesel fuel that is affecting on the engine performance and emissions. The neat biodiesel or its blends may be used in the existing diesel engines with little or without modification to the engine [3, 4]. There are different methods to improve the fuel properties of biodiesel for different conditions and suitable handling. Now, fuel additives become vital tools not only to decrease these drawbacks but also produce specified products that can meet international standards.

2.12.1. Types of fuel additives

At present for vehicular fuels, there are combustion of numerous chemical additives is used to improve the quality of biodiesel fuel and diesel fuel to accumulate up the most wanted performance level. There are different additives that used for diesel and biodiesel fuels in various forms to modify those fuels. Therefore, additives are being isolated in terms of their application and drawbacks are listed out.

a) Oxygenated additives

The most important additives for diesel and otto engine are oxygenated additives. The fuels that are containing oxygen and blending components contain at least one oxygen atom by the molecules at the side of the hydrogen and carbon atoms. The oxygenated additives are very useful to develop the combustion process and octane rating.

By blending oxygenated additives in biodiesel and diesel sufficient cetane number should be there in oxygenated additives and allowed the blend to increase the cetane number. The oxygen helps to support for burning the fuel without emitting any high amount of inert material such as nitrogen into the air and it causes the harmful material such as NOx emission at some operating load condition in CI diesel engine. The generally used oxygenated additives are alcohols, ether and ester. The few names of alcohols contain butanol, propanol, methanol and ethanol. By addition of oxygenated additives, the ignition temperature of biodiesel will be minimized and also reduction in smoke emission is observed in the diesel engine. According to the composition of diesel and biodiesel, the oxygenated additives will affect directly the properties such as cetane number, density, viscosity, volatility, flash point and calorific value [6]. To ignite the fuel more efficiently oxygenated additives will support and as well as diminish environment pollution. The engine fuels will burn more completely due to the presence of oxygenated additives.

b) Cetane number improver additives

Delay period is the one of the most important role plays in diesel engine, in which the delay period varies with chemical and physical properties of the diesel or biodiesel fuels. To differ the delay period cetane number improvers are the main important parameter. To minimize the ignition delay during the combustion cetane number improvers help to get better working in diesel engine ignition. During the combustion process, shorter ignition delay period leads to more complete combustion of the fuel there in the internal combustion engine, reduces the noise of the engine and also reduces the unwanted harmful pollutants in the environment. Alkyl nitrates have been proved the most important vital in commercially used cetane improvers. The 2-Ethylhexyl nitrate is the cetane improved which has been used very commercially for a number of years, but today it is major cetane number improving additives [6].

c) Antioxidant additives

The major purpose of using antioxidant to biodiesel fuels was to slow down the development of slush deposits and darkening of color. Petroleum products are very quick moving diesel fuels, but they are very rarely, are stored in for 1–3 years and are subjected to corrosion. Few names of antioxidant additives are butylated hydroxyl anisole (BHA), butylated hydroxyl toluene (BHT), pyrogallol (PL), diphenylamine (DPA), tert-butylhydroxyquinone (TBHQ) and propyl-gallate (PG). From the survey TBHQ, PL and PG are mainly successful among all the antioxidants. These additives are mainly used in biodiesel mixing to get a better stabilizing potential. As the amount of free radicals and peroxide species increases, the oxidative chain reaction raises at a produced exponential rate. By decomposing the peroxides, the antioxidant works by disturbing the chain propagating steps.

d) Metal based nano-particle additives

Addition of some metal and metal oxide in the form of nano-powder to the base fuel could enhance the properties of the fuels. These additives consist of copper(II) chloride ($CuCl_2$), iron (III) chloride ($FeCl_3$), copper(II) oxide (CuO-nano structured), cobalt (II) chloride ($CoCl_2$), cerium oxide (CeO_2), aluminium oxide (AlO_3) are added in fuel as a catalyst for diesel and biodiesel based on the necessity requirement. This is due to the stimulating properties of nano particles like higher specific surface area, thermal conductivity, catalytic activity and chemical properties as compared to their bulk form. Reduced size of the nano-particles increased specific surface, surface to volume ratio, and surface area improving catalytic reactivity and magnetic properties as compared to their bulk form. Hence metal and metal oxide nano-particles addition to biofuel will improve the performance as well as reduce the emissions from engine exhaust [44].

Addition of cerium oxide nano-particles to biodiesel may also be effective as they enhanced surface area to volume ratio. Flash point of biodiesel, which is an indication of the volatility, was found to increase with the inclusion of such additives making them safer fuels. The viscosity of biodiesel was found to increase with the addition of cerium oxide nano-particles to biodiesel. The viscosity and the volatility were found to hold direct relations with the dosing level of the nano-particles [51].

2.13. Summary of Related Works

2.13.1. Biodiesel Productions and Its Properties

As the objective of the study concerns the production and characterization of biodiesel from argemone Mexicana the related experimental studies observed by different researchers are discussed below. It includes the paper done locally and internationally by the by researchers previously:

Singh et al. [32] produced esters from A. Mexicana seed which contains 30% of oil. They extract oil from seeds through solvent extraction process and purification by expeller. Ester is produced by trans-esterification. The results were showed that, the calorific value, flash point and fire point of methyl ester was found out to be lower than diesel oil whereas viscosity and density of methyl ester oil was higher than diesel oil. They conclude that A. Mexicana is a viable source of production of ester.

Abrar Abdela et al. [19] have studied the performance of cotton seed biodiesel in diesel vehicle. From the experimental result optimum transesterification reaction for optimal biodiesel yield of 75.5% was 2.5gm per liter at reaction time of 1hr, reaction tempeture of 65^0c and volume ratio of oil to methanol as 5:1.

Rajeshwer Y. Rao et al. [33] they explore the viability of biodiesel production from a weed plant Argemone Mexicana seed oil using effective crystalline manganese carbonate catalyst. To gain the maximum yield, investigated by varying catalyst concentration (0.2 to 3.0%), methanol/oil molar ratio (3:1 to 8:1), reaction time (20 to 90 min) and temperatures (25–75^{o}C). It was observed that the ester conversion increases with the increase in molar ratio but decreases with increase the manganese carbonate concentration. From the result, the optimum process conditions for the conversion of Mexicana oil to its methyl ester by trans-esterification required 1% manganese carbonate as catalyst with alcohol to oil ratio 5:1 at $60^{o}C$ to yield biodiesel of 99.99% purity. The maximum biodiesel yield of 90% was obtained with 1wt% catalyst.

Raksh kumar et al. [34] studied the application of biodiesel produced from argemone mexicana oil in direct injection compression ignition engine. Experiments were conducted to determine the performance and emission characteristics of a single cylinder direct injection diesel engine operated on diesel/ biodiesel blends (B20, B40, B60, B80, and B100). Finally, no problem was happened at the time of starting the compression ignition engine and the engine run smoothly with Argemone Mexicane oil methyl ester and its various blends with diesel fuel. B20 can be used in C.I engine without any modification and without any adverse effect.

Manoj Sarma et al. [35] they have done on Trans-esterification of A. Mexicana oil. The extraction was done with Soxhlet extraction apparatus using light petrol as solvent. The dried rice straw was burnt and ash formed. Ash was calcined in oven at temperature $250\text{-}300^{0}C$ for 2-3 hours and then it was used as catalyst. For trans-esterification process of Mexicana oil was carried out in 250ml flask with addition of catalyst, rice husk and methanol. The reaction was carried out at $40^{0}C$ for 4 hours using 5% ethyl acetate in petroleum ether as solvent. The Fatty Acid Methyl Ester (FAME) test result shows that, relative density 0.859 g/cc, kinematic viscosity 4.38 mm^{2}/s, cetane number 44.8 and flash point less than $120^{0}c$. Hence, they concluded that, heterogeneous catalytic trans-esterification method was successful.

Gopukumar S T [36] he was carried out on Argemone Mexicana oil and its potential use as a biodiesel fuel. Moreover, evaluated for blended of A.mexicana biodiesel physical and chemical properties of (B10 and B20) and concluded that falls within the range of ASTM and EN standard values. A.mexicana biodiesel blend B20 was the most effective source of biodiesel fuel. The acid value of blends is slightly higher than that of the ASTM standard but the iodine values and the saponification values are less than that of the petro diesel however it is within the range of ASTM standard for the biodiesel.

Dereje Dagne et al. [37] studied on production of biodiesel from Argemone Mexicana seed oil and testing its performance in Diesel Engine. The oil was extracted by mechanical pressing machine. The transesterification reaction was carried using the quantity of potassium hydroxide catalyst for optimal biodiesel yield of 90% is 2.5gram for 150ml argemone oil and 10ml of methanol with reaction time of 20- 30min, reaction temperature of 65^0C to 80^0C and volume ratio of oil to methanol as 1:6 the experimental results.

Jachak Sayli B1, et al. [38] had an experimental investigation on biodiesel production from Argemone Mexicana seed oil. The optimum condition for argemone Mexicana oil production were a methanol to oil molar ratio of 5:1, a catalyst concentration of 0.7% w/w of oil, a reaction temperature of 60-65^0c and reaction time of 50 minutes with mixing (string) speed of 600rpm. With this optimum condition the biodiesel produced was higher and its properties was satisfied the ASTM standards of biodiesel and the blends that prepared for testing the performance and emission was found to be satisfied.

Parmjit Singh et al. [39] they have studied on the optimization of biodiesel from argemone oil with different reaction parameters and performance analysis in CI engine. Argemone oil was extracted using Solvent Extraction Method and the trans-esterification reaction was carried out in Biodiesel Redley Reactor equipped with reflux condenser, magnetic stirrer and thermometer. To establish the optimum conditions for biodiesel production by trans-esterification, effects of certain factors were investigated, these factors are oil-to-methanol molar ratio (1:3, 1:6, 1:9, 1:12), Base catalyst (NaOH, KOH, NA metal of 1%, 1.5%, 2%, 2.5% w/w of oil), reaction temperature (55°C, 65°C, 75°C, 85°C) at steady conditions and reaction time of 2hrs with string speed 650rpm. Result showed that the optimum conditions for argemone Mexicana biodiesel production were obtained with 1:6 oil to methanol ratio, catalyst sodium metal concentration 1.5% w/w of oil, reaction time 2 hour, reaction temperature 75ºC, and stirring speed 650 rpm. The methyl ester produced under these optimum conditions was maximum 90% and kinematic viscosity of minimum 5.07mm^2/s.

Generally, for the present study the extraction condition [37] was used to get more oil and the reaction condition used in [38] was selected for the production of biodiesel from argemone mexicana oil due to its higher production yield and shorter reaction time it takes.

2.13.2. Performance and Emission Analysis of Biodiesel Fuels

As the objective of this study concerns on the performance and emission analysis of biodiesel, the related experimental studies investigated by different researchers are discussed below. The performance parameters such as torque, power, specific fuel consumption and exhaust emissions like CO, HC, NOx and O_2 have been reviewed as follows:

Rakesh Kumar et al. [35] studied on the blend of biodiesel from A. Mexicana oil and made blend having as B20, B40 B60, B80 and B100 and carried out test on the C.I engine and compared with normal diesel. For brake power the B20 result was 3 BHP which was higher than the normal diesel which comes out to be 2.87. For Brake thermal efficiency the optimum result was found for B20 blend which was much closer to the normal diesel fuel. The emission like CO, HC and SOx was minimum for the B100 but the brake power and the Brake thermal efficiency was to low compared to the normal diesel so it could not be used instead of diesel. So, the optimum result was found out on the B20 blend which had more efficiency than the normal diesel and less emission.

Dereje Dagne et al. [37] investigated on the 4 cylinder, 4 strokes, water cooled diesel engine that results, the brake torque and brake power was maximum for B20 than B0 at different speed and different gear conditions. The higher torque is registered to B0, however the percentage B20 increases the torque that increase throughout all the speed increment. The specific fuel consumption was decreased for B20 than B0 at different speed and different gear condition. This is due to excess of oxygen content are present in biodiesel and lower viscosity and density of fuel. It can be concluded that the Argemone Mexicana biodiesel blend B20 (biodiesel 20%+80% diesel by volume) has improved fuel properties for diesel engine and improved performance.

Paramjit Singh et al. [39] investigated the performance parameters of single cylinder, four stroke engine connected to eddy current dynamometer fuelled with argemone biodiesel and blend with diesel fuel under different load condition (0%, 20%, 40%, 60%, 80%, 100%) and constant engine running speed. Five blends were prepared and the result showed that brake power was increased with increase in load that was maximum value (4.27 KW) for AB20 at full load condition. The brake thermal efficiency was maximum for AB20 (31.95%) at full load conditions that was increased with load. The specific fuel consumption value was slightly higher than that of diesel fuel for AB10; AB30 but AB20 value was lower than that of diesel fuel at full load condition. Therefore, they concluded that the argemone biodiesel blend AB20 (biodiesel 20% + 80% diesel by volume) has improved fuel properties for diesel engine and improved performance.

Ashish Sagar et al. [40] they have studied on argemone oil used as biodiesel in commercial IDI CI engine. Biodiesel produced from argemone oil was blended with diesel fuel at the volumetric ratios of 10% (B10), 20% (B20), 30% (B30) and 40% (B40). The engine performance and emissions was performed on a four cylinders, four strokes, and variable speed indirect injection (IDI) compression ignition (CI) engine with rated power of 52KW@4000 rpm and compression ratio of 18.5:1. The test fuels were runs at different engine speeds from (2500-4000rpm) with an interval of 500 rpm under the conditions of 25%, 50% and 75% load. From the result, the biodiesel blends shows improved in brake thermal efficiency and brake specific fuel consumption but, these improvement is seen up to 30% blending of AOME only and after that deterioration was seen as a result of higher oxygen, higher blends of biodiesel have less calorific value, high density and viscosity compared to diesel fuels. Generally, engine does not need any modifications in its configuration for its utilization of 30% biodiesel blend of argemone methyl ester.

C.D. Rakopoulos et al. [41] they have studied on the performance and emissions analysis of a direct injection diesel engine using blends of diesel fuel with vegetable oils or bio-diesels of various origins. An experimental study is conducted for bio-diesels of various origins as supplements to conventional Diesel fuel at blend ratios of 10/90 and 20/80 in a direct injection (DI) Diesel engine. The experiment was conducted at a speed of 2000 rpm and at a medium and high load. Brake specific fuel consumption (bsfc) and brake thermal efficiency were computed from the measured fuel volumetric flow rate and calorific values. The NOx and CO emissions were slightly reduced with the use of bio-diesel blends of various origins with respect to that of the neat diesel fuel. But the unburned hydrocarbons (HC) emissions showed no definite trend, with either the use of bio-diesel blends of various origins or their percentage increase in the blends. The engine performance with the bio-diesel blends of various origins were similar to that of the neat diesel fuel with nearly the same brake thermal efficiency, showing higher specific fuel consumption for the high load and a minimum at the 10/90 blends for the medium load.

Nikhil Sutar and M.H. Attal. [52] they have studied on effect of compression ratio (16, 17, 18), fuel injection pressure (200,210,220 bar) and at various loads (0, 3, 6, 9, 12, 15, 18kN) for B0 and argemone Mexicana biodiesel blend fuels of B10 and B20 with CI engine. On an average the BTE increased by 13.33 % as compression ratio increased from 16 to 18 whereas BSFC reduced by around 14.2%. Thus higher compression ratio gives better engine performance. And CO_2 emission increased by 25.73%, NOx emission increased by 42.72%, the HC emission decreased by 50.94% and CO emission decreased by 45% as compression ratio increased from 16 to18. The smoke opacity reduced by 24.58 % averagely. Therefore, higher injection pressure is beneficial for engine performance. The NOx emission is increased by 21.83% and smoke opacity decreased by 34.56% when the diesel is replaced by B20 (20% biodiesel and 80% diesel) blend of argemone Mexicana biodiesel.

Mandeep Singh et al. [43] they have investigated on performance and emission characteristics of variable speed multi-cylinder compression ignition engine using Diesel/Argemone biodiesel blends of different samples at varying loads (0, 25, 50 and 75%) and speeds (2500–4000 r/min). They were observed that diesel/AOME blends show better results at higher loads as compared to lower load condition. From the result, biodiesel blends show poor performance at lower loads and high speed conditions. All the tested blends AB10, AB20, AB30 and AB40 show better performance and emission characteristics than conventional diesel. AB30 shows maximum ITE and minimum SFC and HC, CO and smoke are also minimum. However, AB30 blend shows higher emissions of CO_2 and NOx as compared to diesel and other tested blends. Reduction in NOx and CO_2 emissions were observed for AB40 fuel when compared with AB30. AB 40 shows improvement in performance and emission characteristics as compared to diesel but deterioration in performance characteristics when compared with AB30.

2.13.3. Experimental Investigations on the Effect of Nanoparticle Additive on Fuel's Physio-chemical Properties

The current study concerns with the effects of nanoparticles fuel additives on the performance and emissions that result from the effects on physiochemical properties of the fuels. Therefore, the previous related work done by different researchers are reviewed here below:

Hariram Venkatesan et al. [44] they had an experimental investigation on the effect of nano metallic additives on fuel properties. From the result they were understood that nanoparticles like Al_2O_3, Al, and CeO_2 shows good results as additives with diesel and biodiesel blends in all aspects. ZnO also gives better results but, more amount of ZnO should be added than other nanoparticles to get an equivalent performance and the use of ZnO as fuel additive increases the cost of fuel.

Addition of CuO and Al_2O_3 nanoparticles with neat diesel increased the flash point and Cetane number whereas; addition of CeO_2, Al_2O_3, Al, Ag and graphene nanoparticles with neat biodiesel reduced the flash point values whereas the same increased the viscosity and density values. Addition of ZnO nanoparticles increased the flash point, viscosity, density and calorific value of the fuel. Mn, Mg, aluminum nanoparticles in diesel-biodiesel blends reduced the flash point values. Therefore, addition of nanoparticles with diesel / biodiesel blends increased the calorific value and Cetane number of the fuel.

Attia et al. [45] investigated the effect of B20-Jojoba methyl ester with addition of aluminium oxide nano particle on properties of fuel, performance and emission characteristics of the diesel engine. The result showed that there was a considerable change in fuel properties. It was also noticed that the addition of Al_2O_3 reduced the kinematic viscosity of the fuel along with an increase in density and Cetane number.

Dreizin [46] observed that the nanoparticles dispersed test fuels shows better thermo physical properties due to its higher surface to volume ratio and acts as an oxygen buffer with respect to NO emission. He was observed that nanoparticles enhance the heat transfer rates due to its higher specific surface area.

C. Syed Aalam et al. [47] showed the enhancement of fuel properties with the addition of alumina nanoparticles with the Mahua biodiesel blend. ANP-blended biodiesel (MME20+ANP50 and MME20+ ANP100) showed an improvement in the calorific value and a reduction in the flash point compared to MME20. The peak pressure increases with the addition of ANP. The addition of ANP reduces the ignition delay period and the heat release rate also increases with the addition of ANP.

Prabhu Arockiasamy et al. [48] mentioned that the addition of 30 ppm Al_2O_3 and CeO_2 with Jatropha methyl ester improved the kinematic viscosity, density and calorific value as 4.25 Cst, 875 kg/m^3 and 38.9 MJ/kg for JBD30A blend. JBD30C blend was found to have similar fuel property values as 4.30 Cst, 876 kg/m^3 and 38.7 MJ/kg respectively. The addition of alumina and cerium oxide with Jatropha biodiesel improved the fuel properties.

Mehta et al. [49] investigated the effects by sonicating nano particles of aluminum (Al) having 30-60 nm, iron (Fe) 5-150 nm and boron (Bo) 80-100 nm in size in base diesel with 0.5wt% and 0.1wt% Span80 as a surfactant for stable suspension. The nano fuels reduced ignition delay, longer flame sustainable and agglomerate ignition by droplet combustion mechanism test. Peak cylinder pressures decreased at higher load conditions and were registered as 55, 59, 60 and 62 bars for Al, Bo, Fe and diesel respectively**.**

V. Sajith et al. [50] experimental investigations on the effects of cerium oxide nanoparticle fuel additives on biodiesel. Results show, the flash point, viscosity of biodiesel was found to increase with the dosing level of the nanoparticles, within the range analyzed (20–80 ppm). The cold temperature properties of biodiesel do not show significant variation and an improvement in the efficiency of the engine.

Abbas Alli Taghipoor Bafghi et al. [51] investigated the effects of cerium oxide nanoparticle addition in diesel and diesel-biodiesel blends. The tests revealed that cerium oxide nanoparticles improved complete combustion of the fuel significantly. The major observation was an increasing tendency for the flash point with the dosing level. However, the viscosity of the fuels decreased with an increase for all dosing levels.

H. K. Imdadul et al. [52] investigated on the assessment of fuel additive effects on combustion behavior in CI engine fuelled with diesel biodiesel blends. Addition of additives in diesel, biodiesel and their blends has a great effect on fuel properties such as viscosity, flash point, fire point, pour point, calorific value etc. which in turns influences the combustion parameters. Metal-based additives such as $FeCl_3$, alumina nanoparticles showed an increased in HRR, CGP and PP with earlier start of combustion and decreased ignition delay.

Demirba et al. [53] Studied about the importance of adding nano metal additives in biodiesel and its effect in improving the physio-chemical properties. The experimental investigations were carried out by varying the dosing levels of CeO_2 nanoparticles in the fuel (from 5 to 35 ppm). It shows that the flash point and fire point increase with the dosing level of cerium oxide nanoparticles in diesel. Even though kinematic viscosity increases with the catalytic nanoparticle addition in fuel, it was found to be decreasing with the addition of surfactant DDSA.

Generally, biodiesels as a diesel fuel has different advantages like minimum sulfur and aromatic content, higher flash point, lubricity, cetane number biodegradability and no toxicity. But it has different drawbacks like, higher viscosity and pour point and lower calorific value and volatility. To overcome the drawback with diesel-biodiesel blended fuels the use of different additives were used as my understanding from the review literatures that addition of some metal and metal oxide in the form of nano powder to the base fuel may enhance the properties of the fuels. This is due to the interesting properties of nanoparticles like higher specific surface area, thermal conductivity, catalytic activity and chemical properties as compared to their bulk form.

2.13.4. Experimental Investigations on the Effect of Nanoparticle Additive on performance and emissions

As the objective of this study concerned with the effects of nanoparticle additives on the performance and emissions analysis of diesel and diesel-biodiesel blend fuels and the related experimental studies investigated by different researchers are discussed below. The performance parameters such as torque, power, specific fuel consumption and exhaust emissions like CO, HC, NOx and O_2 have been reviewed as follows:

C. Syed Aalam et al. [47] investigated on the effects of nano metal oxide blended Mahua biodiesel. In this investigation, aluminium oxide nanoparticles were added in different proportions (50 and 100 ppm) to a biodiesel blend (MME20) to investigate the performance, emission and combustion of the CRDI system assisted diesel engine. With the addition of Aluminium oxide nanoparticles, there was a considerable reduction in fuel consumption compared to biodiesel operation. A minor increment in BTE was observed and reduced HC and CO emissions up to 26.04% and 48% compared with a biodiesel blend (MME20).

Prabu Arockiasamy et al. [48] experimentally investigated about the combustion and emission characteristics of Jatropha biodiesel with addition of alumina and CeO_2 nanoparticles as additives. During investigation, for the better dispersions of nano particles in the biodiesel they were used ultrasonic shaker that helps for both blends to stable without any phase separation up to 48 hrs. Results showed that the BTE increased up to 5% for both samples. JBD30A showed 9% reduction in NOx, 33% reduction in UBHC, 20% reduction in CO and 17% reduction in smoke opacity than neat biodiesel. Similarly, for JBD30C showed 7% reduction in NOx, 28% reduction in UBHC, 20% reduction in CO and 20% reduction in smoke opacity than neat biodiesel. Additionally, due to its high surface area to volume ratio of nanoparticle promoting better combustion by enhancing atomization, better mixing of air-fuel mixture and rapid evaporation of the fuel.

Sajith et al. [50] experimented with cerium oxide nanoparticle at 20, 40 and 60 ppm addition in jatropha biodiesel in a four strokes, single cylinder, and water-cooled compression ignition. The results showed that an average reduction of 25% to 40% in the HC emission was obtained for the additive dosing level ranging from 40 to 80ppm of the additive. They observed that the significant reduction of NOx 30 % for cerium oxide nanoparticles dispersed test fuel, besides percentage improvement of brake thermal efficiency by 1.5% were mainly due to the catalytic activity of nanoparticle. Whereas, the reduction influence on the fuel additive on CO emission was not as prominent.

Abbas Alli Taghipoor Bafghi, et al. [51] an experimental investigation on effects of cerium Oxide nanoparticle of size 10 to 30 nanometers and density of 7.13 g/mL addition in diesel and diesel-biodiesel blends. The dosing level of CeO_2 by weight in the base fuel was varied from 5 to

25 ppm measured using a precision electronic balance and mixed with the fuel by means of an ultrasonic shaker, applying a constant agitation time of 30 minutes to produce a uniform suspension. The performance tests were conducted on a single cylinder CI engine using the modified and base fuels. Results showed that up to 2400 rpm speeds range, the power of mixtures increases gradually but from 2400 to 2600 rpm range, the power of mixtures decreases or in some compounds increases slightly. By increasing engine speed, torque decreases gradually in all fuels. In these speed ranges, B5D95-25 mixture has the highest value and B0D100 fuel has the lowest value. B20D80-5 compound has the highest fuel consumption reduction compared to other compounds. B5D95-15 compound has the highest fuel consumption. Generally, B5D95-25 compound has the highest amount of power and torque increase, while its specific fuel consumption increase is about 1.4% compared to pure diesel fuel. In higher percent of biodiesel and nanoparticles, B20D80-5 compound is a suitable compound due to having low fuel consumption and specific fuel consumption and relatively good power and torque.

Shiva Kumar, et al. [54] investigated on the influences of nanoparticles on the performance and emission characteristics of a biodiesel fuelled engine. In this research the tests were carried out on a Kirloskar TV1 four stroke single cylinder, water cooled compression ignition engine to study the effect of ferrous nanoparticle addition to biodiesel-diesel blend. Experimental results showed that the addition of Ferro-fluid improved the performance of B_{20} with, the blend having 1% volumetric additive giving the maximum BTE and lesser BSFC. The addition of 1% ferrofluid with B20 showed a reduction of 35.8% of CO emission and HC emission was reduced by 22.9% at full load condition. Moreover, with 1% volumetric additives there were maximum reductions in NOx and smoke emissions.

Rolvin D'Silvaa, et al. [55] investigated on TiO_2 nanoparticles as fuel additive in the form of commercially available nanoparticles of size 10 to 20 nanometers and density of 4.26 g/ml. They had tried dosing level of nanoparticle in base fuel set to 500mg/L, 250mg/L and 80mg/L. The positive result was obtained for dosing level of 80mg/L and all the experiment was done with this value. Engine performance and emission tests were performed at constant speed of 1500 rpm and for Compression ratio 17.5:1. There was 0.9% increase in BTE when TiO_2 nanoparticles are used as fuel additive in diesel fuel at maximum load. There was 21.28% decrease in BSFC value and 32.2% of NOx emissions at the maximum load. However, there was 18.36% in HC and of

25% in CO emissions decrease at the maximum load. There is a 16% increase in Carbon dioxide emissions at maximum load when TiO_2 nanoparticles are used as fuel additive.

Ranaware A. A.et al. [56] investigated on correlation between effects of cerium oxide nanoparticles and ferro fluid on the performance and emission characteristics of a C.I. engine. The BSFC decreases with an increase in the engine load for the diesel cerium oxide and ferro fluid blends than neat diesel at all the BMEP due to the positive effects of nanoparticles on physical properties of fuel and also reduction of the ignition delay time, which lead to more complete combustion. In addition, it could be due to effects of nanoparticles on fuel propagation in the combustion chamber. The addition of cerium oxide further decreases the CO emission when comparing with neat diesel then increases with higher ppm of cerium oxide. The NO_x emission is lower for the neat diesel when comparing to all the fuel blends containing Cerium oxide. Adding water-based ferro fluid to diesel fuel of 0, 0.4, and 0.8 ferro-fluid/diesel ratios by volume at 2200 rpm not only improves engine performance (increasing BTE and decreasing BSFC) but also reduces NO_x emissions. However, CO emissions increase. Furthermore, the results showed that increasing ferrofluid concentration will magnify the results. If both CeO_2 & ferrofluid are added to the neat diesel then we can combine favorable effects of both additives in order improve performance & emission characteristics of CI engines.

Gnanasikamani Balaji et al. [57] investigated on the influence of alumina oxide nanoparticles on the performance and emissions in a methyl ester of neem oil fuelled direct injection diesel engine. The Al_2O_3 nanoparticles were mixed in various dosing levels (100 to 300ppm) with methyl ester of neem oil. The test was done in a single cylinder computerized, 4-stroke, stationary, water-cooled Diesel engine of 3.5 kW rated power. The brake thermal efficiency increased by 4.23% and NO emissions reduced by 7.81% for MENO+ALN200 blend compared to neat biodiesel. The NO, HC, CO, and smoke emissions were reduced by adding Nano additive to the neat biodiesel. The performance parameters like BTE increased and BSFC decreased by adding Nano additive. Generally, results show that the Nano additive is effective in increasing the performance and controlling the NO emissions of methyl ester of neem oil fueled Diesel engines.

N Karthik, et al. [58] had an experimental that conducted in a constant speed (1500rpm), 4stroke single cylinder DI diesel engine for diesel(D100), B20 (Jatropha 20%+Diesel 80%), B20ZO (Jatropha 20%+Diesel 80%+Zinc oxide), B20CE(Jatropha 20%+Diesel 80%+Cerium Oxide) to investigate the performance and emission characteristics. The tests were conducted with the condition of 220 bar injection pressure and 21° BTDC ignition timing. Nano particles (Zinc Oxide (ZnO) and Cerium Oxide (CeO_2) mixed with Jatropha blended fuel in mass fraction (100 ppm) with assist of an ultrasonicator.

Performance results revealed that brake thermal efficiency (BTE) of Jatropha blended Cerium Oxide (B20CE) is 3% and 11% higher than Jatropha blended zinc oxide (B20ZO) and Jatropha blended fuel (B20) 4% lower than diesel fuel (D100) at full load conditions. Emission result shows that HC and CO emissions of Jatropha blended Cerium Oxide (B20CE) was (6%, 22%, 11% 6%, 15% and 12%) less compared with Jatropha blended Zinc Oxide (B20ZO), diesel (D100) and Jatropha blended fuel (B20) at full load conditions. NOx emissions of Jatropha blended Cerium Oxide is 1 % higher than diesel fuel (D100) and 2% and 5% lower than Jatropha blended Zinc Oxide, and jatropha blended fuel.

Karthikeyan et al. [59] used cerium oxide nano-particle that was added grape seed methyl ester (GSOME)-diesel blend in a 1 cylinder, 4 stroke diesel engines for performance and emission analysis. The result showed that the BTE increased for B20+$CeO_2$100 at constant BEMP and the CO emission was decreased for B20+$CeO_2$100. Exhaust gas temperature (EGT), hydrocarbon (HC) and nitrogen oxide (NOx) decreased for B20+$CeO_2$100 blended fuels. Moreover, it was observed that the brake specific fuel consumptions (BSFC) of the cerium oxide nanoparticles blended fuels decreased while compared to the B20.

Ajin C. Sajeevan and V. Sajith [60] experimental investigations were carried out by varying the dosing levels of CeO_2 nanoparticles in the fuel (from 5 to 35 ppm). The performance tests were conducted on naturally aspirated four stroke single cylinder water cooled ignition compression engine operated at rated speed 1500rpm. The results of the load test on the diesel show that the efficiency is increased up to 5% and a reduction of HC and NOx emissions by 45% and 30%, respectively, especially at higher load and the reduction in the emissions is proportional to the dosing level of nanoparticles in the diesel and optimum dosing level of 35ppm of catalytic nanoparticles was observed.

R. Sathiyamoorthi et al. [61] studied the performance, emission and combustion characteristics using Neem oil biodiesel with nano additive CeO_2. Shows break thermal efficiency for nano particles blended BN20 is higher than that of BN20 and diesel fuels and the harmful gases like, CO, HC, smoke and NOx emissions reduce significantly due to the addition of nano additive in the BN20 fuel blend. The cerium oxide additive influences the better combustion process which yields the peak pressure and heat release rate than BN20 and diesel fuel blends.

C.Srinidhi, Dr.A Madhusudhan. [62] investigated with Nickel Oxide nano fuel-methyl ester. They observed that the rise in brake thermal efficiency due to nano particles was on average of 6.2% with respect to original base blends (i.e. B10, B20 and B30). The rate of specific fuel consumption was lowest for B20 blend of Diesel-palm oil methyl ester and NiO nanoparticle dosing level of 40ppm. The usage of nanoparticle depreciated the brake specific energy consumption by 5.119% and B20 blend with Nickel Oxide nanofuels with dosing level of 40ppm proved a better alternative to conventional fuel for diesel engine.

K. Krishna et al. [63] investigated the effects of Alumina Nano Metal Oxide Blended Palm Stearin Methyl Ester Bio-Diesel. The test was performed at constant speed of 1500 rpm using different Nano Biodiesel fuel blends (psme+50ppm, psme+150ppm, and psme+200ppm). Results showed that the break thermal efficiency was almost same for diesel and palm stearin methyl ester blended with alumina (50ppm), the carbon monoxide (CO) emissions were decreased by 39.21% blended with 50ppm compared to diesel. The NO_X emissions were decreased by 9.70% for 50ppm alumina nano particle blended with palm stearin methyl ester compared to diesel and 50ppm alumina can be used as additive with biodiesel which showed reduction in emissions as well as compatible performance characteristics with diesel.

Arul Mozhi Selvan et al. [64] analyzed the performance and emission characteristics of a single cylinder four stroke DI diesel engine fuelled with cerium oxide nanoparticle added diesel and biodiesel fuels. The results showed an improvement in BSFC and BTE of diesel-biodiesel-ethanol blend with the addition of cerium oxide nanoparticles. The addition of ethanol in diesel increases the ignition delay whereas the addition of cerium oxide decreases the ignition delay. The heat release rate increases with the addition of ethanol in diesel but addition of cerium oxide accelerates earlier initiation of combustion and cause for the lower heat release rate when comparing with diesel-biodiesel-ethanol blends. The CO and HC emission decreases with the use of cerium oxide nanoparticles in diesel-biodiesel-ethanol blends and neat diesel. The NO emission is lower for the neat diesel than the oxygenated blends. The addition of cerium oxide nanoparticles in neat diesel and diesel-biodiesel-ethanol blends decreases the smoke further.

Generally from the review literatures, numerous works in the utilization of fuel additives especially the nanoparticle form in neat diesel, biodiesel and diesel biodiesel blends in diesel engines have been done. Many researchers have used nano-particles as additives in diesel as well as biodiesel as new hybrid fuel blends. The use of fuel-borne catalyst has the advantage of increase in the fuel efficiency and reducing harmful greenhouse gas emissions by enhancing the fuel properties. The addition of nanoparticles in the fuel increases the surface area to volume ratio that enables rapid oxidation process. However, the stability of liquid-based fuels with the metal additives was a major concern because of the rapid settling of the metal particles. Finally the intention in this work is testing the performance of argemone Mexicana seed biodiesel with cerium oxide (CeO_2) in diesel engines to improve the engine performance.

3. MATERIALS AND METHOD

In order to efficiently accomplish the general and specific objectives of the study there was a combination of materials and methods intended to use. These are extraction of oil from argemone mexicana seed, production of biodiesel from extracted oils, blending with diesel fuel in different proportions to get different samples, characterizing the produced biodiesel blended fuel samples, performance and emission testing for blended fuel samples adding of additive with two different dosing levels to the best output samples and testing for performance and emissions in the diesel engine.

3.1. Materials Required

The argemone Mexicana seed, Methanol, Potassium hydroxide, Sodium hydroxide, Phenolphthalein ($C_{20}H_{14}O_4$), distilled water; cerium oxide Nano particles, Cetyltrimethyl Ammonium Bromide (CTAB) and diesel fuels was used in my research work. Additional equipment for this research work is list in the tables below.

Table 3-1 List of equipment required for biodiesel production

NO	ITEM
1	Glass ware
2	Thermometer
3	Hot plate with magnetic stirrer
4	Digital balance
5	Beaker different size
6	Fuel flow meter
7	Glove
8	Gratuated glass cylinders for measurments
9	Burette
12	Ultrasonic cleaner

Table 3-2 List of equipment required for testing produced samples

NO	ITEM
1	Single cylinder, 4-stroke air cooled diesel engine
2	Engine Dynamometer
3	Exhaust gas analyzer

3.2. Methodology of the Research

Basically, since all the engineering researches are experimental this research work was done with the experimental based work. There would be a combination of materials and methods to overcome the work and planned to use. These were the extraction of the oil from Argemone Mexicana seed, titration of crude oil with phenophetaline indicator, production of biodiesel from extracted oil through trans-esterification methods with methanol alcohol and potassium hydroxide catalysis, making samples by blending with diesel fuel, characterizing the properties of the produced biodiesel and samples those are with and without nanoparticle additives. Moreover, the performance and emissions of biodiesel and diesel blended fuel samples testing were conducted in a four stroke, single cylinder diesel engine.

This research was conducted primarily based on the following experimental procedures shown in the figure 3.1 below.

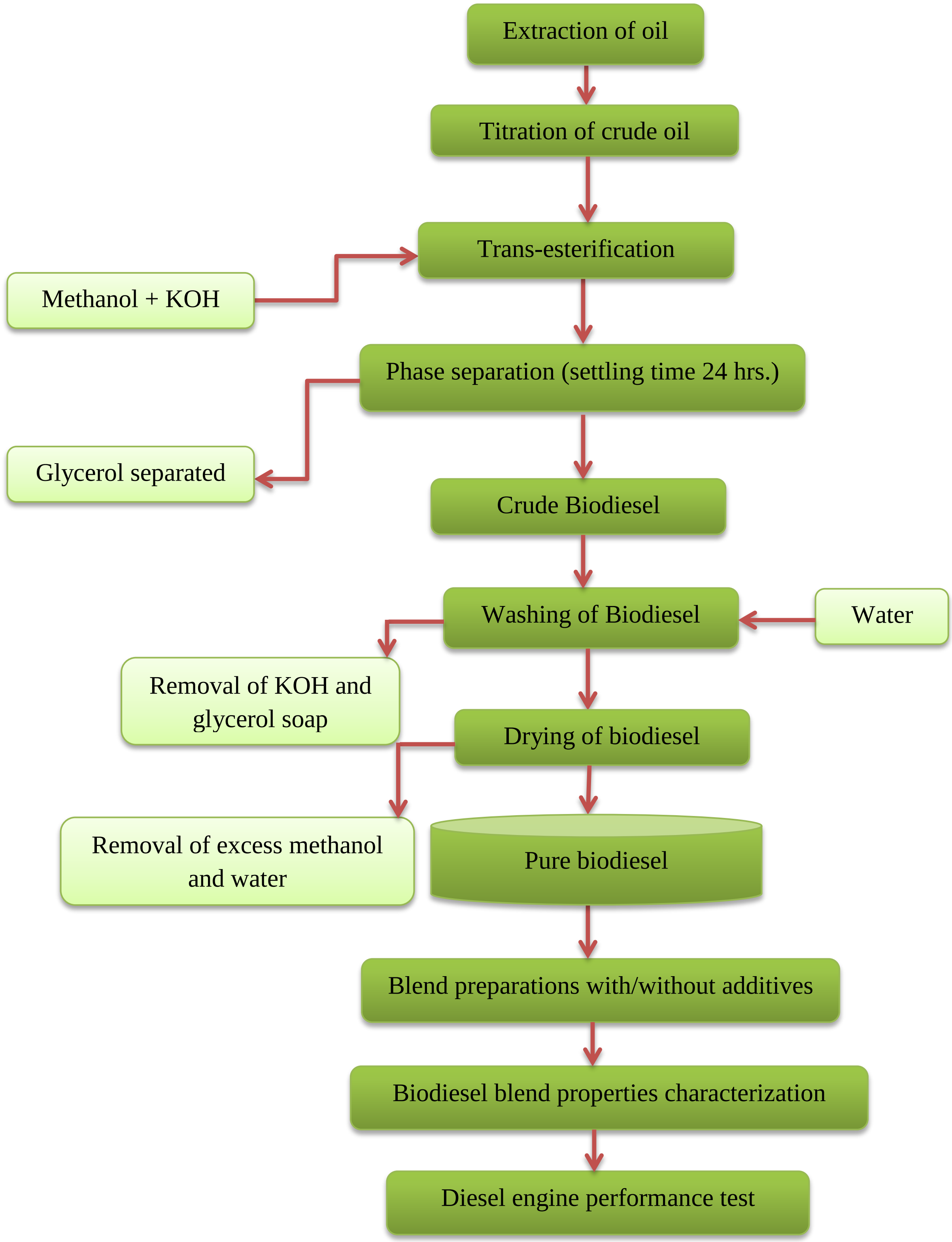


Figure 3-1 General method to conduct the experiment

3.2.1. Collection and preparation of seed

The Argemone Mexicana seeds were collected from the village around Adama and Wonji towns and prior to the extraction process of Argemone mexicana seeds was dried with sunlight to remove the excess moisture and the impurities was removed by handpicking.

3.2.2. The extraction of oil

After the seeds dried well with appropriate temperature the seed oils was obtained by mechanical press machine at Adama Town. The following (Figure 3.2) shows 38 kg of seed extracted by mechanical oil press machine and the amount of argemone oil extracted were calculated by (Eq.3.1). In total 10.5 litters of oil was extracted by using mechanical press machine in the Ayisha oil factory (Fig.3.2).

Figure 3-2 Mechanical extraction of argemone Mexicana oil

The amount of oil extracted was calculated by:

$$\%\ \text{oil} = \frac{\text{mass of oil}}{\text{mass of seed}} * 100 \qquad \text{Eq. 3-1}$$

3.2.3. Titrations of crude oil

From a chemical point of view, oils from different sources have different fatty acid compositions. Acid values of seed oil were determined as the percentage of free fatty acid present in oil which is estimated by titrating it against NaOH in presence of phenolphthalein as indicator [16, 17]. The fatty acids vary in their carbon chain length and in the number of unsaturated bonds they contain. The percentage and type of fatty acids composition relies mainly on the plant species and their growth conditions. The fatty acid composition and distribution of some non-edible oils are generally aliphatic compounds with a carboxyl group at the end of a straight-chain.

The presence of FFA is widely considered also as a limiting factor in oil conversion because of the tendency to consume the catalyst and produce soap. The high FFA content (>1%w/w) will cause soap formation and the separation of products will be extremely difficult and as a result, low yield of biodiesel product would be obtained. It is important to first determine the FFA content of oil.

Steps used during titration of argemone Mexicana seed oil is given below:-

a) Take 10ml of ethanol alcohol in the 250ml flask and mix with 3 drops of phenolphthalein indicator.
b) Measure 5gm of argemone oil with highly precision digital balance as (Fig. 3-3 (b))
c) Take 100ml of distilled water in 500ml measuring flask.
d) Measure 10gm of NaOH with 0.0001gm precision digital balances and swirled until the sample was entirely dissolve with measured distilled water.
e) Fill the solution of NaOH up to 15ml in the measuring burret vessel.
f) Add 3 drops of phenolphthalein solution into measured oil.
g) Titrate the measured oil with solutions of NaOH until pink color is formed (Fig. 3-3 (c)).
h) Record the measured values of NaOH solution in (ml) Table 3-3 from the burret but, the pink color solutions must stay for the next 15minutes.

Table 3-3 Titration results

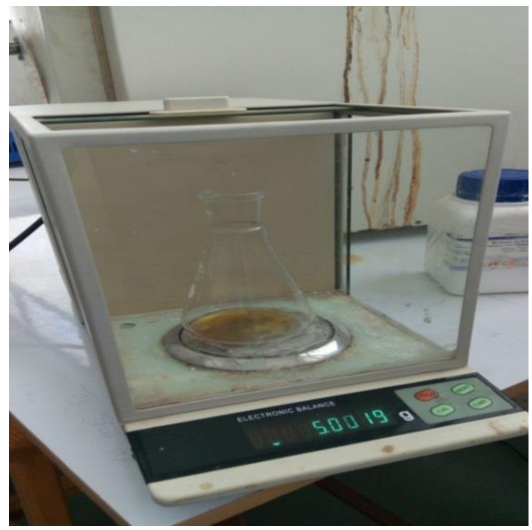
Trials	NaOH (gm)	Argemone oil (gm)	NaOH solution in (ml)
1	10	5	0.8
2	10	5	0.6
3	10	5	0.7

$$\text{Acid value} = \frac{NaOH\ Solution\ in\ ml * N * 40}{Mass\ of\ the\ oil} \quad \text{.....................................Eq. 3.2}$$

Where, N= normality of NaOH, (i.e. 0.5)

$$\%FFA = \frac{Acid\ value}{2} \quad \text{...Eq. 3.3}$$

a. List of materials for titration



b. Measuring of argemone oil

c. Titrate the oil with NaOH solution

d. Titrated oil

Figure 3-3 Titration Materials and Processes

3.3.Laboratory Preparation of Biodiesel

3.3.1. Transesterification

Transesterification of the extracted oil comprises making triglycerides of the Mexicana seed oil to react with methyl alcohol (methanol) in the presence of a catalyst (KOH) to produce glycerol and fatty acid ester. This step was carried out at Adama Science and Technology University, in Materials Science and Chemistry departments' laboratory.

The step by step approach used in transesterification production of biodiesel from Mexicana seed is given below:

1. 1000ml argemone mexicana seed oil was measured with beaker and heated to the temperature of 60^0c (Fig.3.4 (a)).
2. The solution of potassium methoxide was prepared in volumetric flask using 14gm of KOH catalyst concentration and 200 ml of methanol alcohol that is the molar ratio of oil to methanol of 1:5. Then, the solution was stirred until the KOH was completely dissolved in methanol.
3. After the KOH was totally dissolved, the potassium methoxide solution was poured into the warm oil (i.e. at 60^oc of argemone oil) and stirred vigorously for 50 minutes using magnetic stirrer with 600rpm stirrer speed. During this transesterification process the mixture of argemone oil and methoxide solution were covered by Aluminium foil to prevent the escaping of methanol because its boiling point is closer to 60- 65^oc (Fig.3.4 (c)). When the reaction time reaches around 40 minutes glycerin starts to separate and settle at the bottom and a clear solution appears at the top. Then the mixture was allowed to settle for 24 hours in a separating funnel to separate glycerol from methyl ester (Fig.3.4 (d)).
4. The lower layer which comprises of glycerol and soap was collected from the bottom of the separating funnel and the biodiesel was then poured in separate beaker.
5. The next step was washing of biodiesel with the hot distilled water that was heated at 50^oc and the water equivalent to one third volume of the biodiesel was taken and filled to a spray gun to remove any excess glycerol, soap, alcohols and catalysts that may be left in the biodiesel. This was done until the water is mostly clear that would be seen below the biodiesel in the separating funnel (Fig.3.5 (d)).

Finally, the washed biodiesels was dried by placing it on the hot plate for 45 minutes about150^{o}c to remove trace of alcohol and water in the biodiesel (Fig.3.5 (e)). Then, the amount of the biodiesel collected was measured and yield of the biodiesel was calculated (Fig.3.5 (f)).

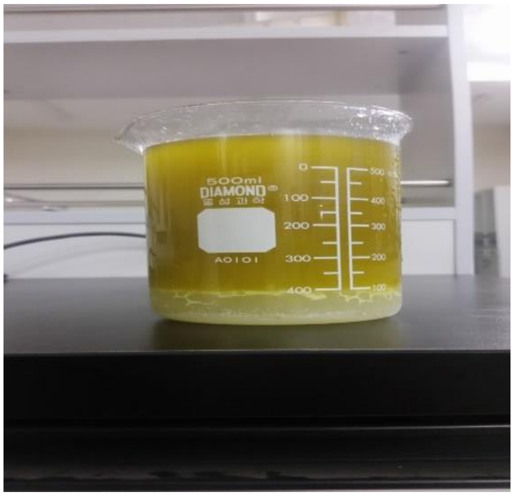
a. preheating of the oil

b. preparation of methanol and KOH

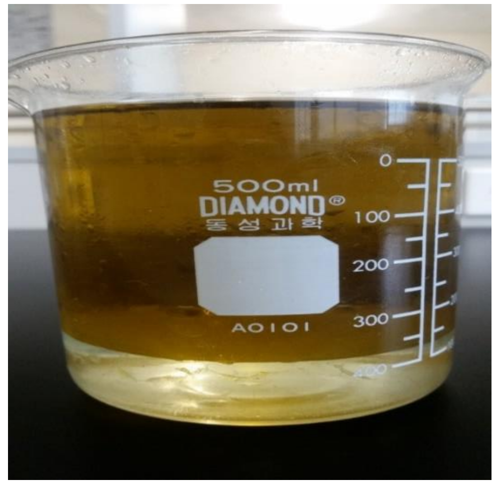
c. Trans-esterification reaction of argemone oil

c. separation of the glycerol

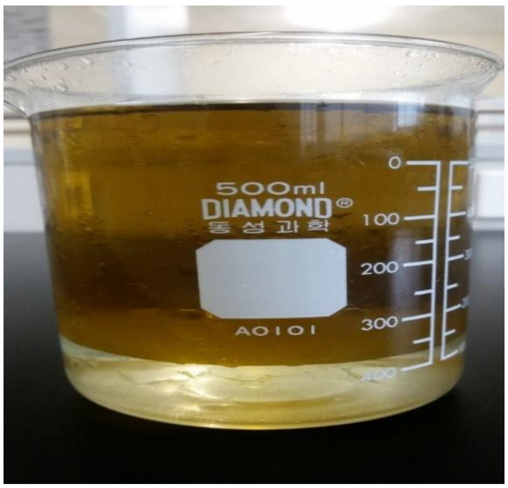
Figure 3-4 Trans-esterification processes



a. First washing process

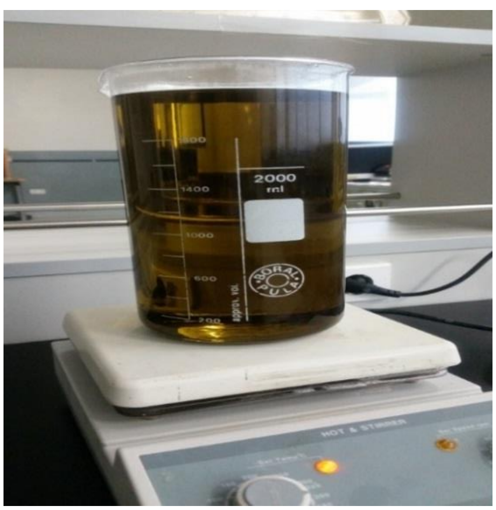


b. Second washing process

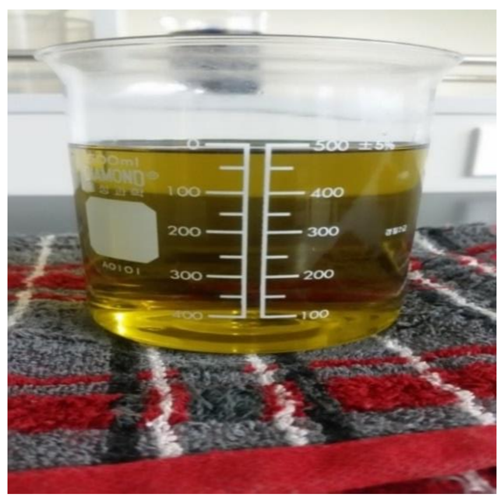


c. Third washing process

d. The last washing process



e. Biodiesel drying process



f. The final pure biodiesel after dried

Figure 3-5 Washing processes and drying steps of biodiesel

3.4. Kinematic viscosity test for pure biodiesel

This test method specifies the determination of the kinematic viscosity v of liquid petroleum products both transparent and opaque, by measuring the time for a volume of liquid to flow under the gravity through calibrated viscometer. The kinematic viscosity is the measured flow time calibrated constant of the viscometer.

The kinematic viscosity of the produced pure biodiesel (B100) was measured with viscometer according to DIN 51 562 that is with constant ($K = 0.005278\ mm^2/s^2$). The viscometer tube was used in viscometer bath and the sample was kept in the bath for some minutes until to reach the equilibrium temperature of $40^o c$. The time (t) was measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer and that can be under the closely controlled and known temperature. The kinematic viscosity v within mm^2/s of a liquid can be calculated using the instrument constant for the tube,

$$v = K*t \qquad \text{Eq. 3.4}$$

Where, ‘t’ is the flow time in seconds.

3.5. Biodiesel Blend Preparation

As it is known a lot of research work has already been carried out to use vegetable oil both in a pure form and also in blended forms. Studies have shown that the usage of vegetable oils in its pure form is possible but not preferable as the blended one. Because, biodiesel can be blended with petro-diesel in any proportions, with ratio of B_5 (5% biodiesel and 95% diesel fuel) to B_{20} (20% biodiesel and 80% of diesel fuel) being the most common one. Therefore, for biodiesel blends at a range of B_{20} and lower no part modifications (alterations) are required.

In this study the Argemone mexicana biodiesel mixed with conventional diesel in different proportions namely at AB_{15} (15% biodiesel and 85% diesel fuel), AB_{20} (20% biodiesel and 80% diesel fuel), AB_{25} (25% biodiesel and 75% diesel fuel) all these were without the additions of cerium oxide (CeO_2) nanoparticle additives.

Figure 3-6 AB15, AB20 and AB25 blended fuel samples

3.5.1. Nano-Biodiesel Fuel Blends Preparation

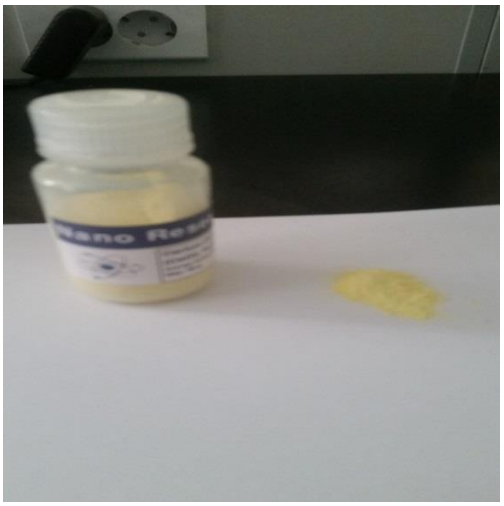
For the present study Argemone oil was selected as an alternative fuel for diesel as it was locally and abundantly available non edible feedstock. It was then subsequently converted into its biodiesel using trans-esterification method. The fuel additive used in this investigation is cerium oxide, in the form of commercially available nanoparticles of size 20 to 30 nanometers and density of 6.5g/cm^3 Appendix-E. The dosing level of the cerium oxide nanoparticle samples (by weight) in the base fuel was varied with 50ppm and 100ppm.

3.5.1.1. Blending Methodology

The nano-particles blended with argemone Mexicana biodiesel fuel is prepared by mixing the AME and cerium oxide nano-particles with the aid of an ultrasonic cleaner Fig.3.7 (f). The ultrasonicator technique is the suitable method to disperse the cerium oxide nano-particles in the blended fuel, as it accelerates possible agglomerate nanoparticles back to nano-meter range.

The required quantity of the nanoparticle for each sample was accurately weighed Fig. 3.7 (c) to a predefined mass fraction (i.e. for 50ppm and 100ppm) using a precision electronic digital balance and first it was mixed with the diesel fuel in small amount by means of hot plat magnetic stirrer Fig. 3.7 (d). Moreover, finally after preparing the sample it was mixed with an ultrasonic cleaner for a time period of 30 minutes with a high frequency level to produce a uniform suspension.

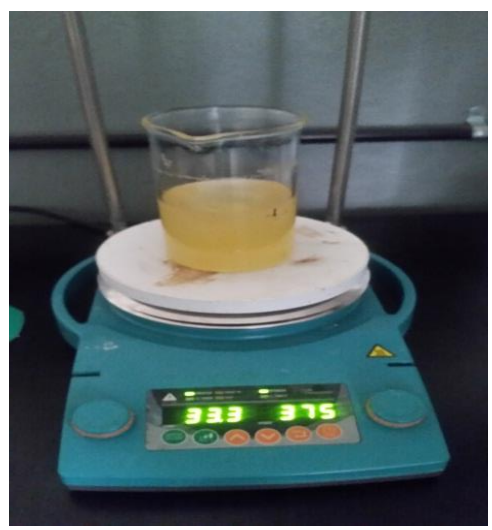
By using Cetyl-Trimethyl Ammonium Bromide (CTAB) Fig.3.7 (b) the nano particle sedimentation is organized. CTAB is a cationic surfactant; it is covered on the surface of cerium oxide nano particles and produces a negative charge. Then nanoparticle is disperse to blended fuels magnetic stirrer procedure was followed. Finally, fuel blends were prepared by volume as shown in the table 3.4 below. The resulting nanoparticles blended Argemone Mexicana biodiesel is named as AME+50ppm Cerium oxides and AME + 100ppm Cerium oxides.



a. Cerium Oxide nano-particle

b. Cetyl-Trimethyl Ammonium Bromide (CTAB)

c. Measuring CeO_2 and CTAB with electronic digital balance



d. String of CeO2 & CTAB with diesel

e. B20 + 50 & 100ppm CeO2 blends

f. Mixing of cerium oxide Nano-particle with ultrasonic cleaner

Figure 3-7 Nano particle blended fuel preparation materials and process

Table 3-4 Blend Proportions of Test Fuels

Fuel type	Petro diesel	Argemone biodiesel	CeO_2 dosing	Total
B0	2000 ml	-	-	2000 ml
AB15	1700 ml	300 ml	-	2000 ml
AB20	1600 ml	400 ml	-	2000 ml
AB25	1500 ml	500 ml	-	2000 ml
AB20 +50ppm	1600 ml	400 ml	+50ppm	2000 ml
AB20 +100ppm	1600 ml	400 ml	+100ppm	2000ml

Table 3-5 Specificactions of Cerium oxide nanoparticle [Appendix-E]

S.N	Parameters	Cerium oxide nano-particles
1	Manufacturer	Nano Research Lab (India)
	Chemical Name	CeO_2
3	CAS No	1306-38-3
4	Atomic Weight	172.1148 g/mol
5	Average particle size (APS)	20-30nm
6	Specific surface area	40-45 m^2/g
7	Appearance	Light yellow
8	Bulk density g/cm^3	1.3
9	True density g/cm^3	6.5
10	Purity	99.9%

3.6. Characterization

Characterization is the process of determining the physiochemical properties of petroleum products and non-petroleum like biodiesel fuels and blends. The physio-chemical properties were evaluated for the blended samples of biodiesels in the laboratory found in Ethiopian institute of petroleum supply enterprise at Addis Ababa, whether or not it satisfy the ASTM standards as per the procedure of the enterprise for biodiesel testing without the interference of the researcher. The samples that brought for characterization was a blend of argemone Mexicana biodiesel and diesel fuel with different ratios (AB15, AB20, AB25) and the other fuel blend prepared for characterization is AB20 with two different amount of cerium oxide (CeO_2) nanoparticles as additives (AB20 + 50ppm CeO_2 and AB20 + 100ppm CeO_2).

3.7. Engine Performance Test

Engine performance was measured in terms of brake torque, brake power and brake specific fuel consumptions (bsfc). The experimental test was done with a diesel engine with a power output of approx. 5.5KW at 3500rpm (Figure 3.8). To perform the experiments, the engine is placed on the CT 110 Test Stand for Small Combustion Engines of maximum power output 7.5kw (Fig.3.8). Exhaust emissions are measured with an Infralyt smart gas analyzer (Figure 3.8).

3.8. Experimental Test Setup

The experiments were carried out in automotive laboratory, of mechanical and automotive department, at Dilla University, Odaya Branch. In order to study the effect of different diesel and biodiesel fuel blends on small diesel engine performance parameters a test set up unit (Gunt model CT 110, Germany) was used in this study Figure 3.8. The set up stand consists of three main components including a CT 110 for mounting of the engine and as a control unit, a universal drive and brake unit or dynamometer as a load unit, and a four-stroke diesel engine (CT 100.22). The main function of CT 110 is to mount the engine, supply it with fuel and record and display relevant measurement data. The CT 100.22 engine is an air cooled, single cylinder, 4-stroke diesel engine was used to conduct the performance and emission studies. The flywheel fitted with fan blades is used for cooling the engine Appendix-C. The engine is started using the asynchronous motor in the CT 110 as a starter motor and equipped with a temperature sensor for the measurement of the exhaust gas temperature. This is connected to the CT 110 test stand as the connections for electrical shut down and the fuel supply. The lower section of the mobile frame contains fuel tanks and a vessel for the intake air. A measuring tube for fuel consumption is also included in the test unit. The speed and torque are adjusted and displayed on the test stand.

The diesel engine brake power, torque and brake specific fuel consumption was measured at different engine speed levels ranging from (1550 up to 3050 rpm) for the diesel-biodiesel fuel blends. The fuel flow rate, speed, load, exhaust gas temperature, and gas flow rate are dis-played on a personal computer through engine software. Moreover in all the cases the emissions of gases such as HC, CO, CO_2 and O_2 are noted down for specified speeds and the results are displayed on the exhaust gas analyzer. The specifications of the direct injection diesel engine to carry out the tests are given in Table 3.5 and a schematic block diagram of the experimental test facility is illustrated in Fig. 3.9.

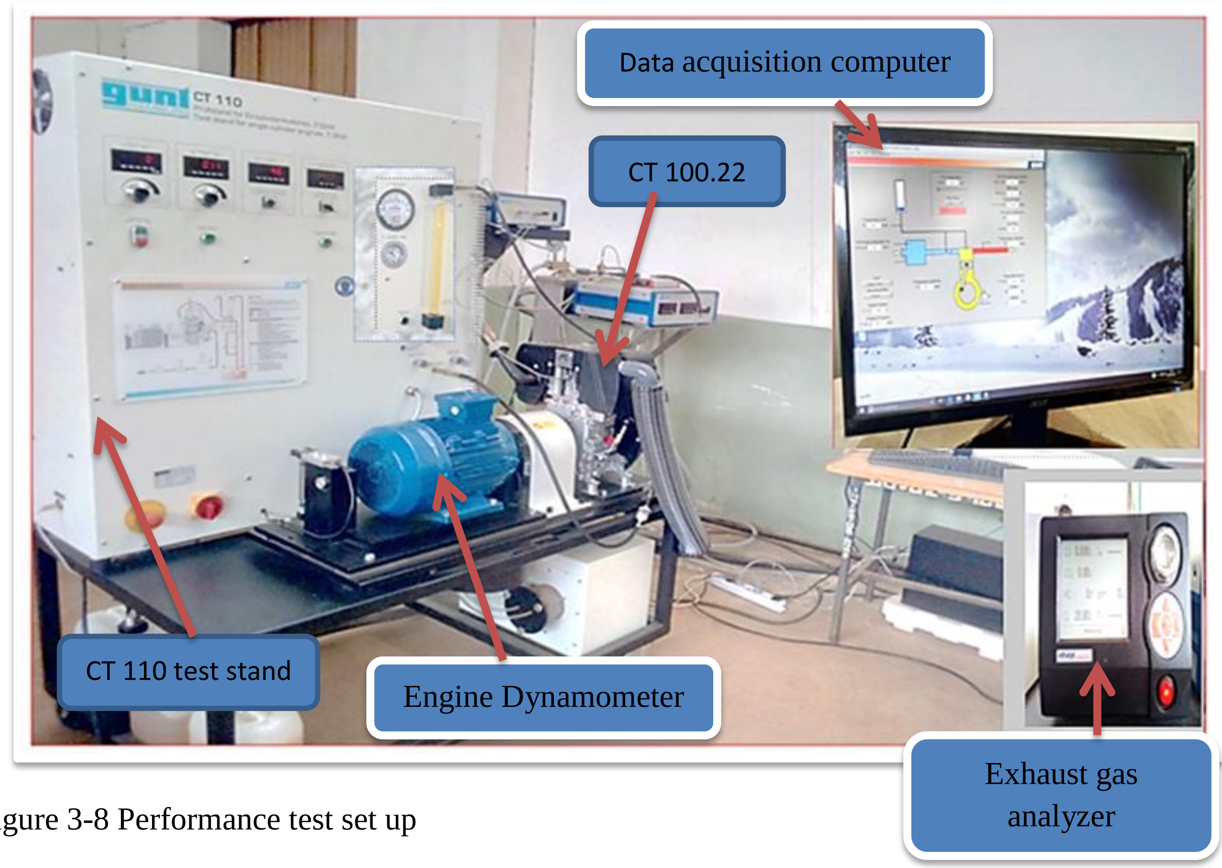


Figure 3-8 Performance test set up

Table 3-6 The test engine specifications

S.N	Parameters	Values
1	Company	Hatz (German)
2	Type	1B30-2
3	Output power at 3500 min-1	5.5kw
4	Compression ratio	22: 1
5	Bore	80 mm
6	Stroke	69 mm
7	Stop solenoid	12V
8	Method of loading	Electrical load
9	Method of cooling	Air cooled
10	Type of ignition	Compression ignition
11	Rod length	114.5mm
12	Crank length	34.5 mm

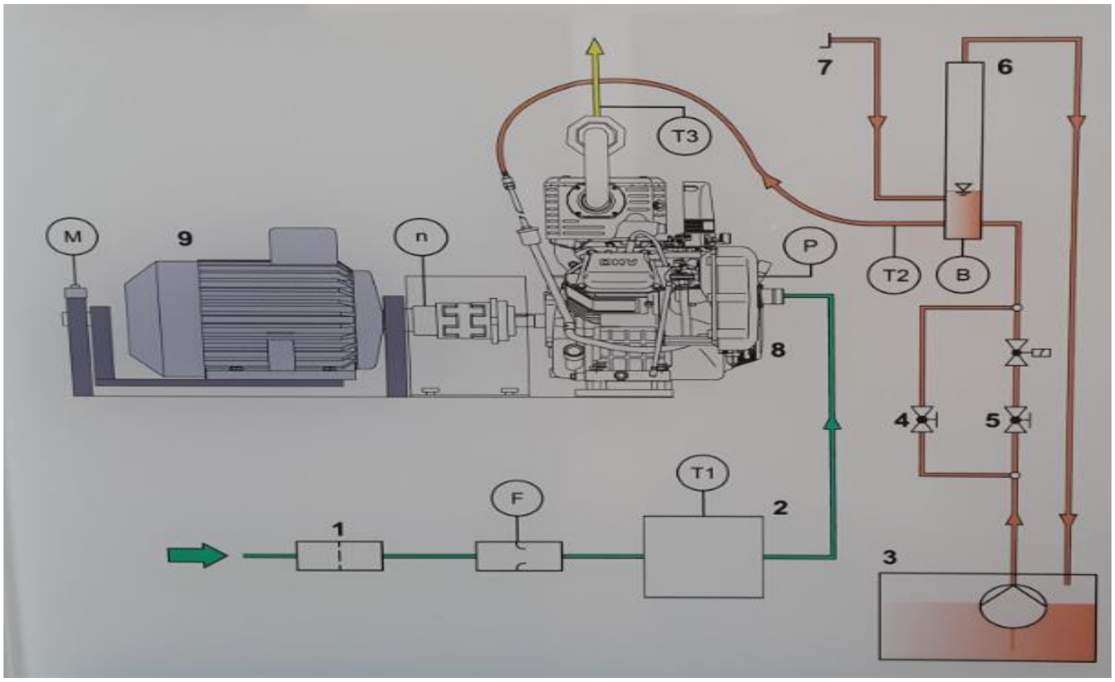


Figure 3-9 Schematic of test engine setup (From test engine manual)

Main component parts of test setup	**Instrumentation and control**
1. Air filter	B. Fuel consumption
2. Settling tank	F. Air flow rate
3. Fuel tank with pump	M. Torque
4. Drain valve	n. Speed
5. Filling valve	P. Intake pressure
6. Fuel measurement tube	T1. Intake temperature
7. Diesel return line	T2. Fuel temperature
8. Combustion engine	T3. Exhaust temperature
9. Asynchronous motor for starting and loading	

3.9. Experimental Test Procedure

The base plate with the engine is placed in the CT 110 Test Stand and the engine is aligned with the braking device (dynamometer). After alignment the fixing bolts for the engine are tightened. The fuel pipe and also the return pipe for the engine are connected to the supply connections on the CT 110 test stand (beside the measuring tube). Air hose and exhaust hose are connected to the engine. After the experimental test engine connected, the following procedure was followed:

1. Connect it to the mains electricity and Check that the EMERGENCY STOPS (A) is released then turns on the master switch (B).
2. All connections between the engine and the test stand must be set up and the air hose and exhaust hose must be connected, and the outlet of the exhaust hose must be outdoors.
3. Make sure that the safety cover for the coupling and is bolted to the test stand base plate and check the engine oil level.
4. The fuel line to the engine and the fuel measuring tube on the CT 110 test stand must be filled and the fuel valve for draining the measuring tube must be closed.
5. The engine stop solenoid must be released by operating the "Ignition" switch on the CT 110 test stand.
6. The speed regulator must be set to "Start", ("Start" = full load).
7. Set the speed adjusting knob (D) for the asynchronous motor to approx. "5" and the torque adjusting knob (F) to a maximum torque of "10".
8. Turn on the ignition with the push button (E).
9. Turn on the asynchronous motor by pressing the "Starter/Brake" button (C) (green) on the CT 110 test stand.
10. When the C engine starts up, turn off the asynchronous motor with the "Starter/Brake" (C) (red) button.
11. The engine now runs at idle speed and experiments were carried out on the engine first by the use of pure diesel to provide baseline readings. After the engine warmed up the dynamometer acts as a brake for applying resistant load to the engine.
12. Allow the engine to warm up without load for approx. 5 minutes.
13. After the base line reading is recorded followed by the application of the blends AB15, AB20, AB25, AB20 + 50ppm CeO_2 and AB20 + 100ppm CeO_2. The measured values are transmitted directly to a personal computer via USB and the data acquisition software.
14. When the fuel level in the measuring tube is lowered top up fuel using the button (G).

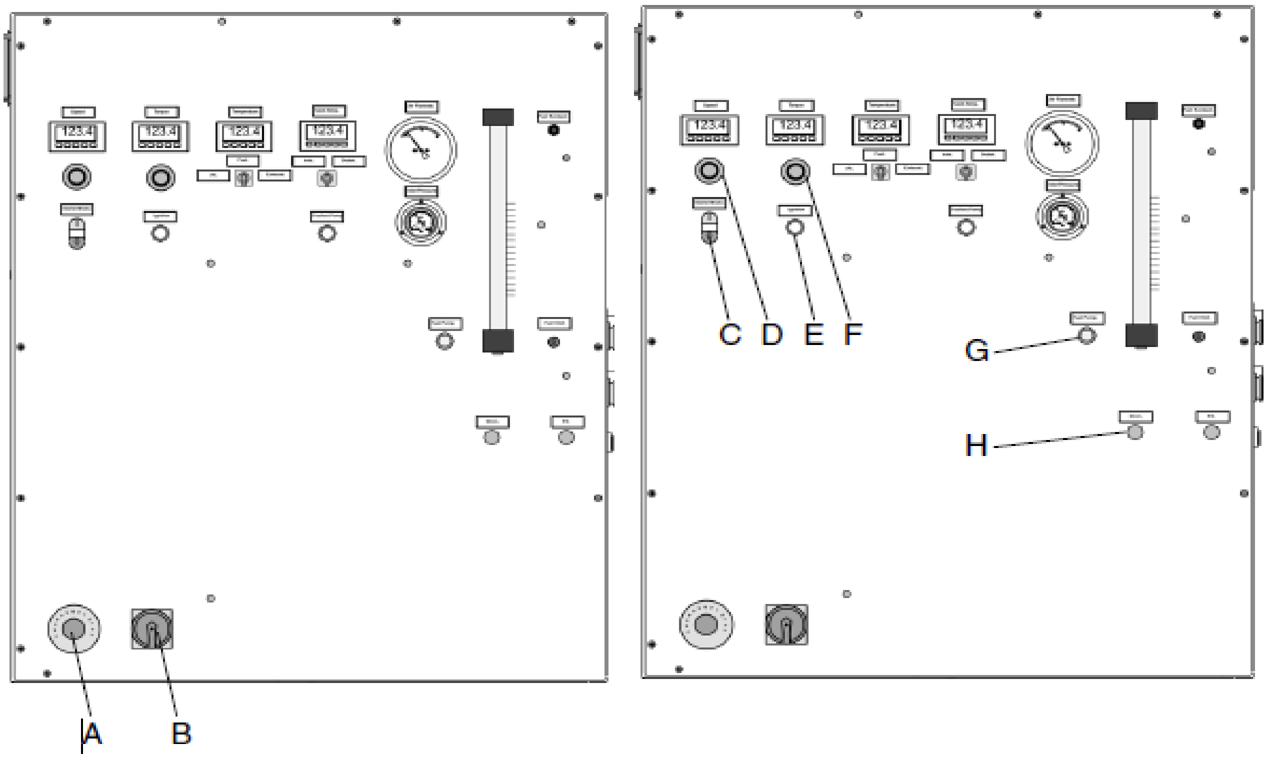


Figure 3-10 Controlling units

3.10. Data Analysis

i. **Brake Torque (Tb)** is the torque available at the fly wheel that by using the dynamometer on the CT 110 test stand, the engine is then loaded by turning the speed potentiometer to maximum. By reducing the speed set on the potentiometer in steps, torque values are displayed on the CT 110 test stand.

ii. **Brake Power (Pb)** is the net power at the fly wheel. It can be calculated by using the formula:

$$P = Tb*2\prod n \quad \text{......Eq. 3.5}$$

Where: n is engine speed,(in KW)

iii. **Brake Specific Fuel Consumptions (bsfc)**: is the ratio of the amount of fuel consumed by the engine that the consumption is measured at the measuring tube on the test stand using stopwatch.

$$be = \frac{mB}{P} \quad \text{......Eq. 3.6}$$

where: m_B fuel flow rate (Kg/KWh), p is power (W) and *be* (g/kWh)

3.11. Measuring Principle of Exhaust Gas Analyzer

The measuring principle of CO, CO_2 and HC is based up on the interference correlation filter principle. Infrared light is radiated through the measuring chamber and is detected by a sensor that operates an interference correlation filter. The Sensor signals are processed by a microcontroller directly. Oxygen is measured using chemical sensors.

Table 3-7 Functional requirements of exhaust gas analyzer

components and ranges	CO= 0-10.00 % vol. CO2= 0-20.00 % vol. HC =0-2500 ppm vol. (C6H14) O2 =0-22.00 % vol. NO =0-5000 ppm vol. (an option) NOx =0-5000 ppm vol. (an option)
Measuring components absolute tolerances	CO ±0.03 % vol. CO2 ±0.5 % vol. HC ±10 ppm vol. (C6H14) O2 ±0.1 % vol. NO ±25 ppm vol. (an option) NOx ±25 ppm vol. (an option)
Measuring components relative tolerances	± 5 %

4. RESULT AND DISCUSSION

4.1. Extraction of Argemone Mexicana Oil

The amount of oil extracted from the argemone seeds by the mechanical press oil extraction machine was calculated by the formula given in the methodology (Eq. 3.1). From 38 kg of argemone seeds the crude oil extracted was 10.5 kg which means about 27.63 % (V/ m) ratio of oils were obtained.

4.2. Titration Results

As the free fatty acid causes saponification, instead of biodiesel production it’s important to know the FFA content within an oil weather it’s necessary to take steps to reduce the contents to success in trans-esterification process. From the titration results in Table 3-3 the acid value is calculated by Eq. 3.2 and the result were 2.79 mgNaOH/gm. The percentage of free fatty acid (%FFA) from Eq. 3.3 was 1.39%. From this result it is possible to conduct the trans-esterification processes.

4.3. Biodiesel Production yield

The biodiesel production was done by trans-esterification reaction process by using KOH catalyst and methanol as an alcohol. Finally after washing four times with distilled water and drying the biodiesel the production yields found to be about 83% argemone mexicana biodiesel. From the table below (table 4.1) that shows the trans-esterification reaction conditions and biodiesel yield from argemone mexicana oil was 83%.

Table 4-1 Reaction condition and biodiesel yield

Sample	Molar ratio	Oil sample (ml)	Methanol (ml)	KOH (%w/v)	Reaction temp. (^{o}c)	Reaction time (minutes)	Yield (%)
Argemone M.	1:5	1000	200	0.7	65 - 70	50	83

4.4. Characterization Results

The characterization was done to know the properties of the produced biodiesel blended fuel samples whether or not it satisfied the ASTM standards for biodiesel earlier to testing its performance on the existing diesel engines without doing any modifications. The characterization of biodiesel produced from argemone seed oil that blended with the diesel fuel with different ratio and moreover, two blends with cerium oxide (CeO_2) nanoparticle by varying the dosing levels were shown in the table 4.2 or in Appendix- A. From the table 4.2 below, the densities of all the prepared fuel samples were within the range given by European standards (EPSE Diesel limits) for Diesel fuels. The flash point of all the diesel biodiesel blend fuels was within the standard because the fuel with the flash point more than 60^oc is considered as safe, therefore, the result of the entire sample of biodiesels are considered to be safe to store and to use it in the engine. Higher flash point temperatures are desirable for safe handling of the fuel. In this context, and because of its higher flash point temperature, the fuels modified with cerium oxide nanoparticles are inherently safer than the base fuels. The copper strip corrosion values were the same for all blend samples and that is equal with the EPSE Diesel limits. The B25 and B20 + 50ppm CeO_2 fuel samples had the lower cloud point that indicates it could operate under lower temperatures than B15, B20 and B20 +100ppm CeO_2 fuel samples.

Table 4-2 properties of blended biodiesel fuels [Appendix- A]

SN.	Property	Test Method ASTM	EPSE Diesel limits	Test results				
				B15	B20	B25	B20+ 50ppm CeO_2	B20 + 100ppm CeO_2
1	Density@ 15^oc,g/ml	D4052	Report	0.8461	0.8487	0.8518	0.8491	0.8517
2	Density@ 20^oc,g/ml	D4052	Report	0.8425	0.8452	0.8487	0.8456	0.8482
3	Flash point(PMCC)^oc	D93	Min.60	88	86	84	87	88
4	Copper strip corrosion 3hr@100^oc	D130	Max.No.1	1a	1a	1a	1a	1a
5	Cloud point, ^oc	D2500	Max.+5	+2	+1	0	0	+1
6	Kinematic viscosity@40^oc	D445	2.0-4.5	3.86	3.89	3.99	3.93	3.93
7	Water & sediment,V/V%	D2709	Max. 0.05	<0.05	<0.05	<0.05	<0.05	<0.05
8	Total acidity, mg KOH/g	D974	-	0.1203	0.1323	0.1697	0.144	0.145
9	Ash, %Wt	D482	Max 0.01	0.007	0.0095	0.01	0.0041	0.0094

Generally, no significant differences were observed in all fuel samples as due to the addition of CeO_2 nanoparticle additives while, there was a change with some of properties.

The Kinematic viscosity of the pure A. Mexicana biodiesel was measured with viscometer according to DIN 51 562 at 40^0c and the value was calculated according to the given (Eq.3.4). The average time measured after 3 trials during this measurement was 915.6sec and the value of the kinematic viscosity was 4.8mm^2/s.

4.5.Engine Performance and Emission Test

The following section illustrates the results obtained from the performance and emission characteristics of the CI engine.

4.5.1. Evaluation of Engine Performance Curve's

The brake torque or engine torque, brake power and brake specific fuel consumptions obtained at different engine speeds were shown in table 4-3 to table 4-8 below for all test fuel samples. Figure 4-1 to 4-6 shows brake torque, brake power and brake specific fuel consumptions relative to engine speeds for all tested fuel samples of B0, AB15, AB20, AB25, AB20 + 50ppm CeO_2 and AB20 + 100ppm CeO_2. Those figures show the performance curves for all tested fuel samples. As shown from the performance curve the trend of the curve were similar for all tested fuel samples even thought their values were varies as given in the tables. The figure shows that at lower engine speed brake torque and power are lower, while the brake specific fuel consumptions of the engine were slightly higher. As the engine speed increases the values for brake torque and power increases up to some point maximum but further increase in speed shows that the values falls down. Whereas for Bsfc as the speed of the engine increased, it starts to decreased up to the brake power and brake torque values are become equal then it starts to increase as the engine increased further.

Table 4-3 B0 performance test results

Engine Speed (n)	Brake Torque	Brake Power	Brake Specific Fuel Consumption
1/min	Nm	kW	g/kWh
1550	15.19	2.81	329
1800	16.14	3.31	306
2050	16.93	3.79	288
2300	17.11	4.11	277
2550	18.52	4.52	271
2800	15.06	5.21	333
3050	13.12	3.81	357

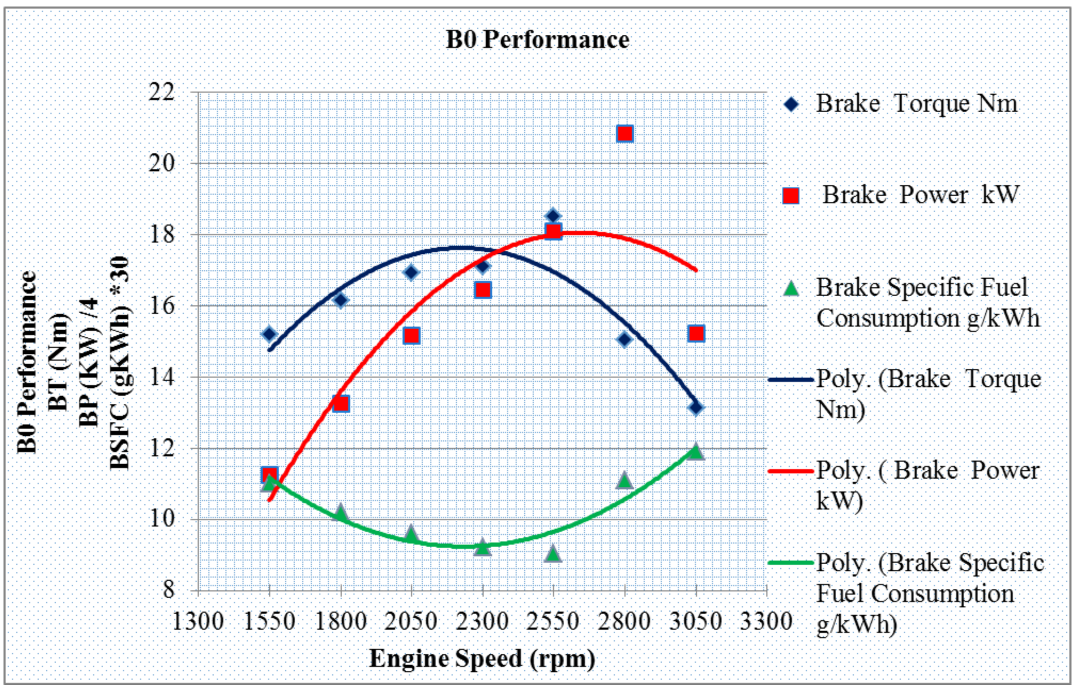


Figure 4-1Variation of Performance vs. engine speed of B0

From Fig.4-1 the maximum brake torque observed by B0 was 18.52 Nm at 2550rpm, brake power 5.21 KW at 2800rpm and the minimum brake specific fuel consumption was 271g/KWh at 2550rpm of engine speed. The figure shows that at lower and higher engine speeds brake torque and power are lower, while the brake specific fuel consumptions of the engine were slightly higher.

Table 4-4 B15 performance test results

Engine Speed (n)	Brake Torque	Brake Power	Brake Specific Fuel Consumption
1/min	Nm	kW	g/kWh
1550	15.06	2.71	337
1800	15.97	2.91	313
2050	16.74	3.55	296
2300	16.96	3.85	280
2550	18.51	4.19	274
2800	14.07	4.70	323
3050	13.11	3.61	335

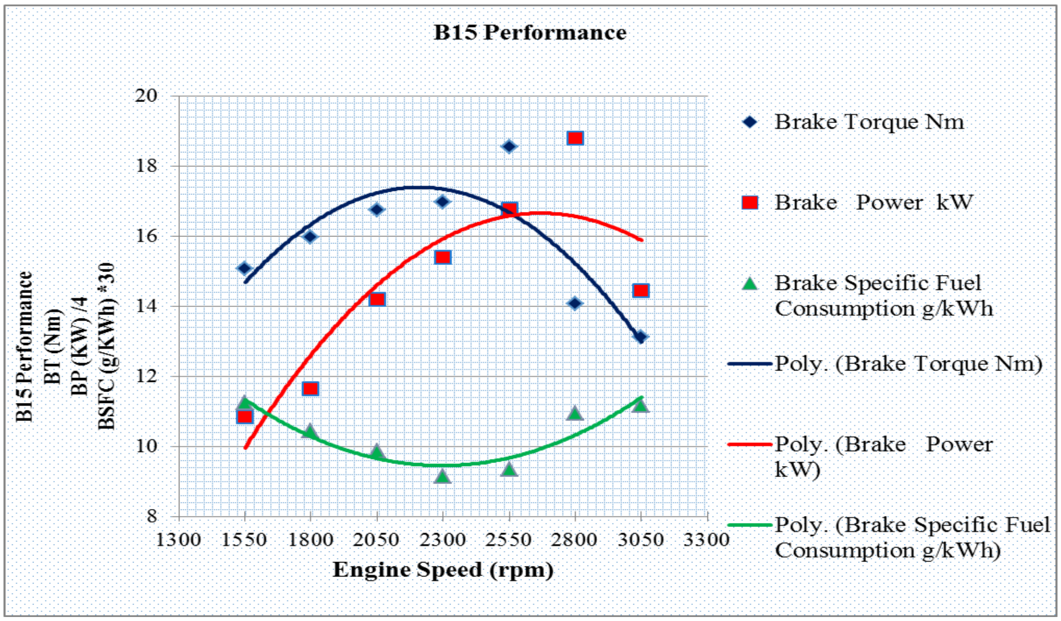


Figure 4-2 Variation of performance vs. engine speed of (B15)

From Fig.4-2 the maximum brake torque observed by B0 was 18.51 Nm at 2550rpm, brake power 4.70 KW at 2800rpm and the minimum brake specific fuel consumption was 274g/KWh at 2550rpm of engine speed. The figure shows that at lower and higher engine speeds brake torque and power are lower, while the brake specific fuel consumptions of the engine were slightly higher. But the values for brake torque and power observed by AB15 was lower than B0, but higher than AB20 and AB25, whereas the brake specific fuel consumptions was higher than B0 and lower than AB20 and AB25.

Table 4-5 B20 performance test results

Engine Speed (n)	Brake Torque	Brake Power	Brake Specific Fuel Consumption
1/min	Nm	kW	g/kWh
1550	15.01	2.64	339
1800	15.77	2.75	319
2050	16.31	3.43	298
2300	16.67	3.72	282
2550	18.03	4.12	285
2800	13.94	4.66	338
3050	12.89	3.55	343

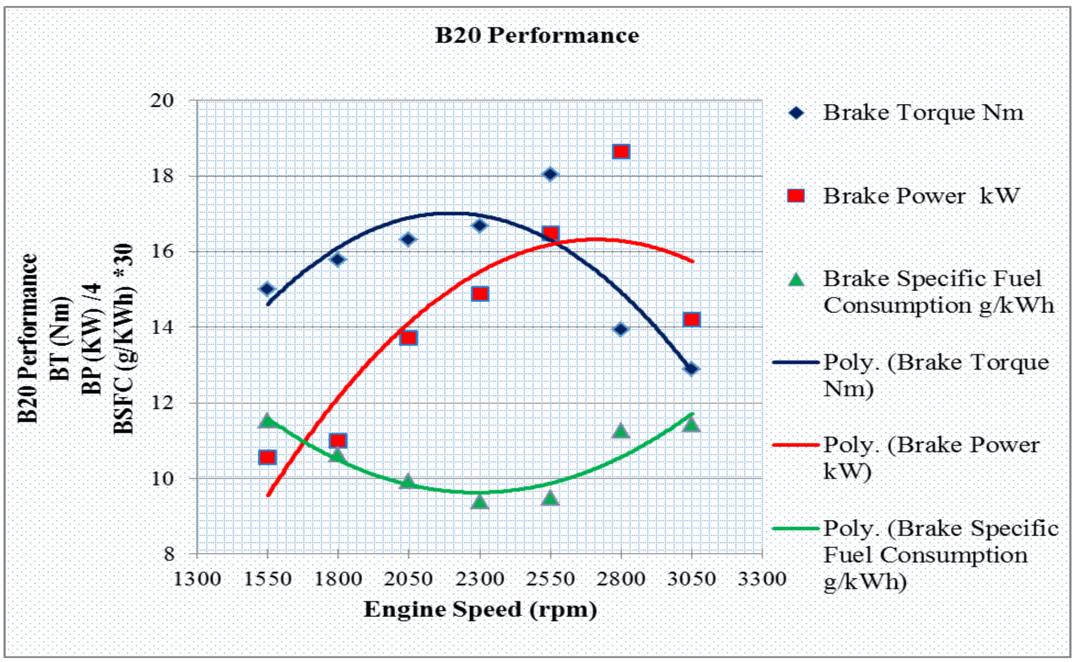


Figure 4-3 Variations of Performance vs. engine speed of (B20)

From Fig.4-3 the maximum brake torque observed by B0 was 18.03 Nm at 2550rpm, brake power 4.66 KW at 2800rpm and the minimum brake specific fuel consumption was 282g/KWh at 2300rpm of engine speed. The figure shows that at lower and higher engine speeds brake torque and power are lower, while the brake specific fuel consumptions of the engine were slightly higher. Compared to B0, AB15, AB20 + 50ppm and AB20 +100ppm the brake torque and power were lower but the brake specific fuel consumption was higher as observed from the values. Because, the density and viscosity increased as the biodiesel ratio increased while the calorific value decreased.

Table 4-6 B25 performance test results

Engine Speed (n)	Brake Torque	Brake Power	Brake Specific Fuel Consumption
1/min	Nm	kW	g/kWh
1550	14.87	2.61	345
1800	15.61	2.69	320
2050	16.27	3.37	307
2300	16.41	3.71	286
2550	17.72	4.01	289
2800	13.43	4.36	327
3050	12.03	3.22	322

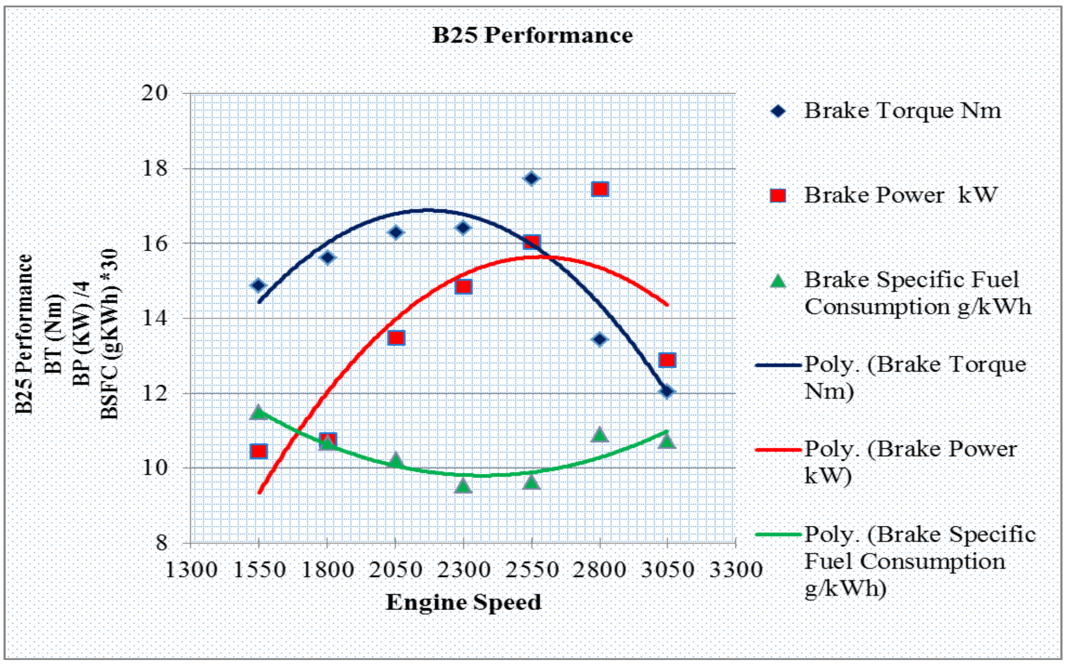


Figure 4-4 Variations of performance vs. engine speed of (B25)

From Fig.4-4 the maximum brake torque observed by B0 was 17.72 Nm at 2550rpm, brake power 4.36 KW at 2800rpm and the minimum brake specific fuel consumption was 286g/KWh at 2300rpm of engine speed. The figure shows that at lower and higher engine speeds brake torque and power are lower, while the brake specific fuel consumptions of the engine were slightly higher. Compared to the other fuel samples AB25 showed the lowest of all in brake torque and power and it has maximum fuel consumption due to lower calorific values and higher in viscosity and density due to higher ratio.

Table 4-7 B20 + 50ppm CeO_2 nanoparticle performance test results

Engine Speed (n)	Brake Torque	Brake Power	Brake Specific Fuel Consumption
1/min	Nm	kW	g/kWh
1550	15.02	2.74	331
1800	15.97	3.04	310
2050	16.61	3.57	289
2300	16.92	3.87	269
2550	18.67	4.37	277
2800	14.03	4.93	321
3050	12.95	3.58	354

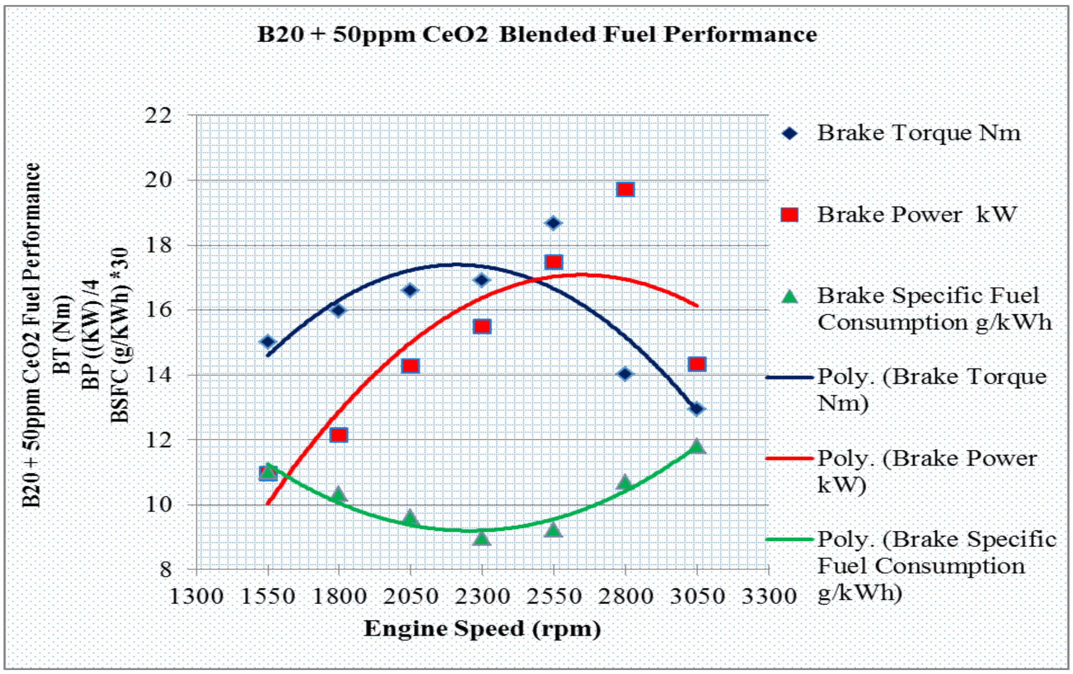


Figure 4-5 Variation of performance vs. speed of (B20 + 50ppm CeO_2 nanoparticle)

From Fig.4-5 the maximum brake torque observed by B0 was 18.67 Nm at 2550rpm, brake power 4.93 KW at 2800rpm and the minimum brake specific fuel consumption was 269g/KWh at 2300rpm of engine speed. Compared to B0 showed improvement in brake torque and brake specific fuel consumption but brake power was lower. However, when compared with AB15, AB20 and AB25 showed improvement in performance but with AB20 + 100ppm CeO_2 showed lower.

Table 4-8 B20 + 100ppm CeO_2 nanoparticle performance test results

Engine Speed (n)	Brake Torque	Brake Power	Brake Specific Fuel Consumption
1/min	Nm	kW	g/kWh
1550	15.37	2.80	332
1800	16.12	3.17	308
2050	16.92	3.73	281
2300	17.33	4.13	277
2550	18.71	4.49	271
2800	14.88	5.14	325
3050	13.03	3.62	353

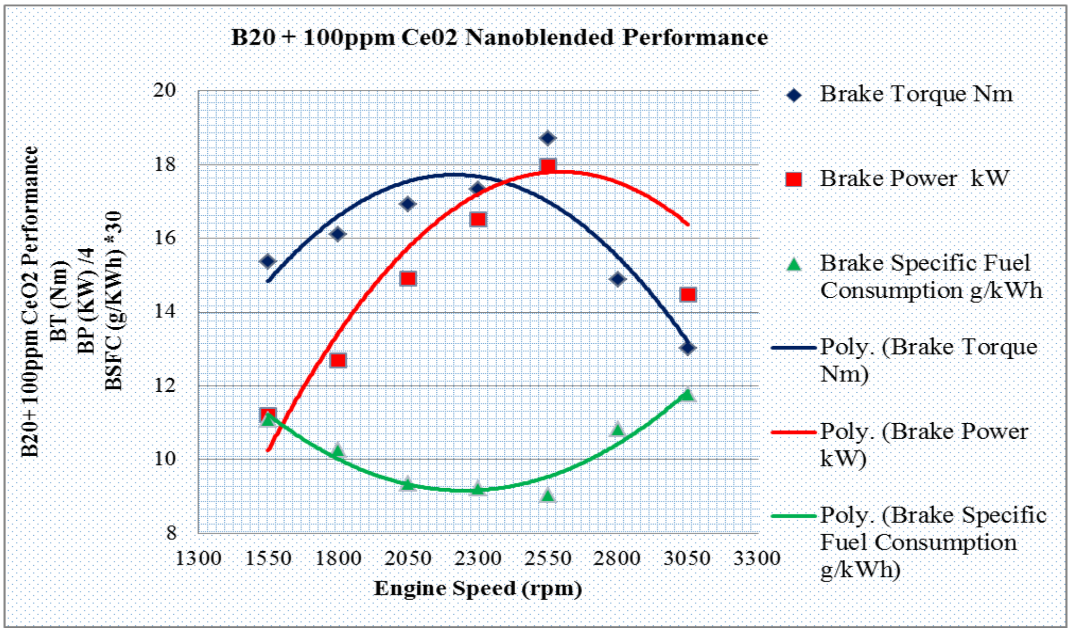


Figure 4-6 Variation of performance vs. speeds of B20 + 100ppm CeO_2 blended fuel

From Fig.4-6 the maximum brake torque observed by B0 was 18.71 Nm at 2550rpm, brake power 5.14 KW at 2800rpm and the minimum brake specific fuel consumption was 271g/KWh at 2550rpm of engine speed. The table above shows that the AB20 +100ppm fuel sample showed an improvement in all aspects when compared with the B0, AB15, AB20, AB25 and AB20 + 50ppm fuel samples.

Generally, from the above shown graphs the brake power and brake torque of B0 shows more than all the other fuel samples, which is due to the higher calorific value, lower viscosity and density of B0 fuel. But the fuel consumptions with diesel biodiesel (AB15, AB20, AB25, AB20 + 50ppm CeO_2 and AB20 + 100ppm CeO_2) fuels show higher than the B0.

4.6.Brake Torque for all tested Fuel Samples

Table 4-9 Brake torque for all samples performance test results

Brake Torque (Nm)						
	Fuel Sample					
Engine Speed (rpm)	B0	AB15	AB20	AB25	AB20 + 50ppm CeO_2	AB20 + 100ppm CeO_2
1550	15.19	15.06	15.01	14.87	15.02	15.37
1800	16.14	15.97	15.77	15.61	15.97	16.12
2050	16.93	16.74	16.31	16.27	16.61	16.92
2300	17.11	16.96	16.67	16.41	16.92	17.33
2550	18.52	18.51	18.03	17.72	18.67	18.71
2800	15.06	14.07	13.94	13.43	14.03	14.88
3050	13.12	13.11	12.89	12.03	12.95	13.03

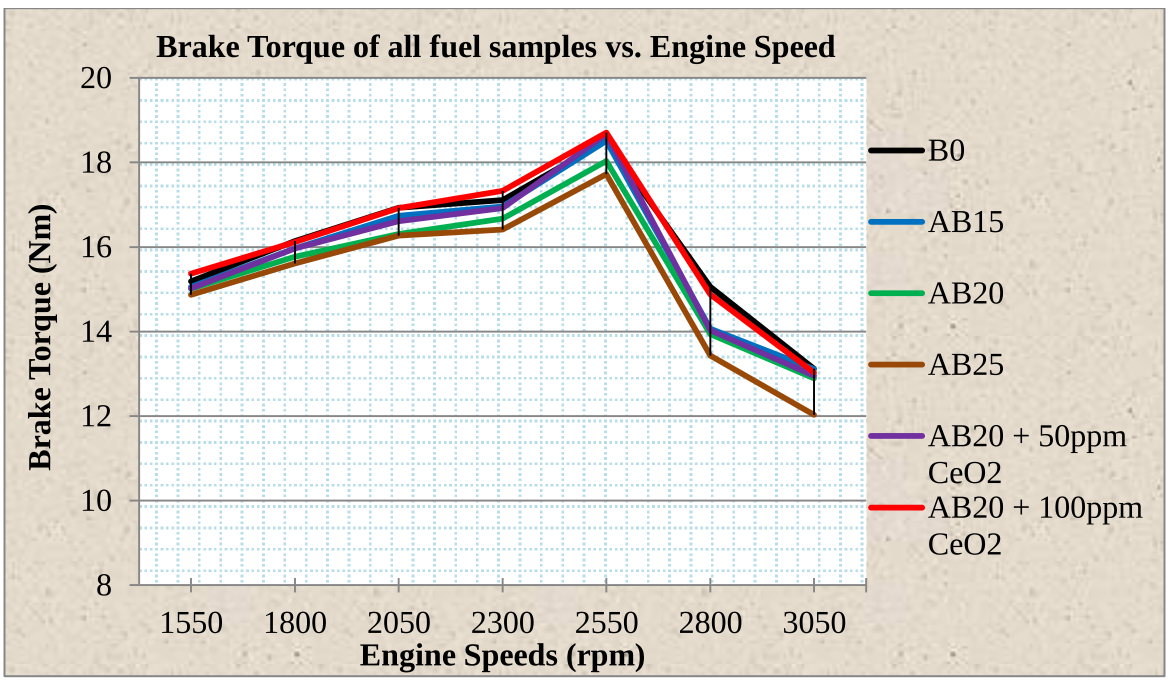


Figure 4-7 Variation brake torque of all diesel biodiesel blended fuel samples vs. speed

From figure 4-7 above shows that the variations of engine torque versus engine speed that almost similar trend for all tested fuel samples. It shows that at lower speeds slightly torques are lower and increases as engine speed increases while, as engine speed increaes further torque reaches a maximum and starts to decreases. In very high speeds, breathing time is lesser and consequently the cylinder is not filled fully. As a result, combustion pressure become lesser, inertial forces of mobile parts of the engine increase, and finally the real torque of the engine decreases. The brake power of the argemone Mexicana ester blends was lower than the diesel fuel due to the lower calorific value and also higher viscosity and density. However, there was an improvement in brake torque that was found when addition cerium oxide nanoparticles to the blended fuels. The cerium oxide nanoparticles present in the fuel promote longer and more complete combustion, because it acts as an oxygen buffer and thus increases the efficiency. It has also been observed that the improvement in the efficiency generally increases with the dosing level of nanoparticles.

Generally, it can be seen that the brake torque of the AB20 +100ppm CeO2 blend fuel is higher than other samples. The average torque incrment for AB20 + 100ppm CeO2 blend fuel as compared to B0 was 0.26%. The average engine torque reductions for AB15, AB20, AB25 and AB20 + 50ppm CeO2 as compared to B0 was 1.47%, 3.08%, 5.11% and 1.67% respectively. The reason of reductions of engine torque with blended fuels without nano particles is due to higher viscosity, density and lower calorfic value of biodiesel fuel. Also, the mixture of nanoparticle has lower value than B0 because the dosing levels affect the torque out put.

4.7.Brake Power of all tested fuel samples

Table 4-10 Brake power of all samples performance test results

Engine Brake Power (KW)						
Engine Speed (rpm)	Fuel Sample					
	B0	B15	B20	B25	B20 + 50ppm CeO_2	B20 + 100ppm CeO_2
1550	2.81	2.71	2.64	2.61	2.74	2.80
1800	3.31	2.91	2.75	2.69	3.04	3.17
2050	3.79	3.55	3.43	3.37	3.57	3.73
2300	4.11	3.85	3.72	3.71	3.87	4.13
2550	4.52	4.19	4.12	4.01	4.37	4.49
2800	5.21	4.70	4.66	4.36	4.93	5.14
3050	3.81	3.61	3.55	3.22	3.58	3.62

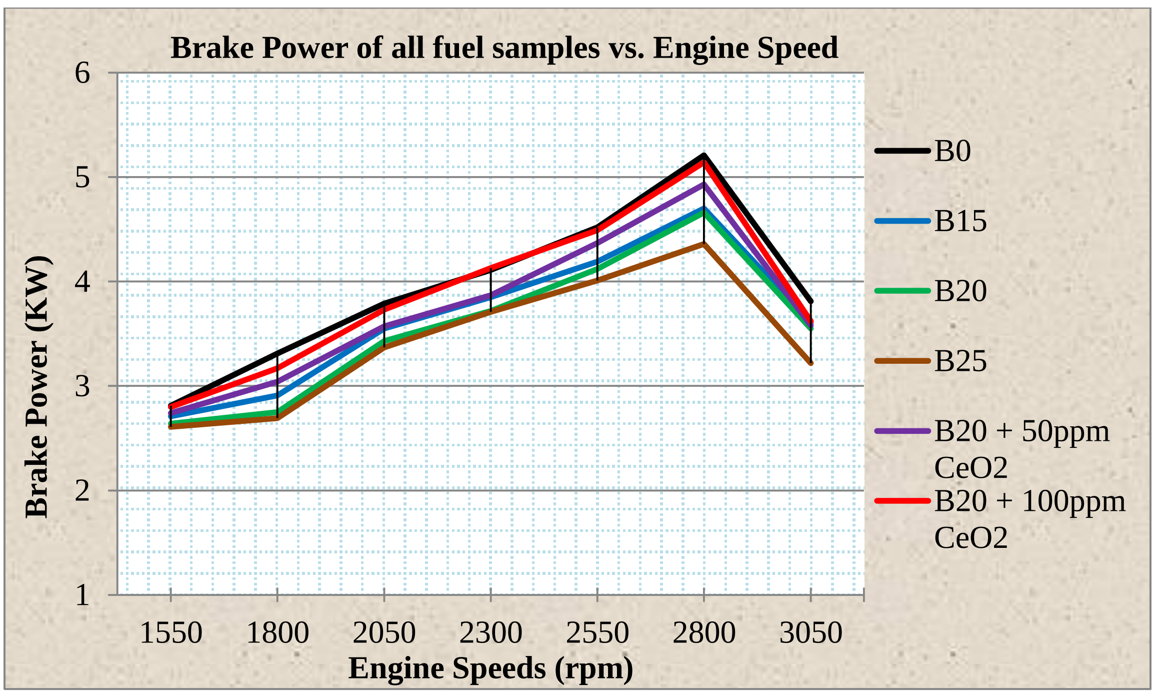


Figure 4-8 Comparison of brake power vs. engine speed of all tested fuel samples

Figure 4.8 above shows that the trend of the curves is almost similar for all fuel samples. However, the power output from diesel fuel (B0) is higher than all the other except B20 + 100ppm CeO_2 sample in medium engine speeds. The reason is that B0 fuel has higher heating value than the other diesel-biodiesel blended fuel samples. This is due to the heat of combustion (MJ per kg or liter) is a measure of the amount of energy available to produce work. As engine speeds increases the brake power increases and reaches to its peak however the friction power starts to increase at greater rate that results with reduction in brake power values. In general in almost all speeds, power resulted from pure diesel (B0) fuel is greater than the power of biodiesel-diesel blended and nanoparticles fuels, though the B20 + 100 ppm CeO_2 nanoparticle fuels has relatively equal power. The reason is in addition to the oxygenated nature of the biodiesel fuels, the addition of nanoparticle also has oxygen buffering nature that can increase the surface area of the fuels which increases the combustion efficiency. Here also the dosing level of nanoparticle additive has an effect; even if the B20 +50ppm CeO_2 nanoparticles blended fuels improve the performance than the biodiesel blended fuels it was lower than pure diesel. Selecting optimal range of nanoparticle addition is a key to get good results on enhanced performance and reduced emission in a CI engine.

Generally, the reason for the lower brake power of biodiesels blended fuels compared to diesel can be attributed to their lower heating value, higher viscosity and density causing poor atomization of the fuel. Therefore, the average brake power reduction for AB15, AB20, AB25, AB20 + 50ppm and AB20 + 100ppm CeO2 in compared to B0 fuel is 7.4%, 9.76%, 13.03%, 5.30% and 1.38% respectively.

4.8. Brake specific fuel consumption of all tested fuel samples

Table 4-11 Brake specific fuel consumption of all samples performance test results

Brake Specific Fuel Consumption (g/KWh)						
	Fuel Sample					
Engine Speed (rpm)	B0	AB15	AB20	AB25	AB20 + 50ppm CeO_2	AB20 + 100ppm CeO_2
1550	329	337	339	345	331	332
1800	306	313	319	320	312	308
2050	288	296	298	307	289	281
2300	277	274	282	286	269	277
2550	271	280	285	289	277	271
2800	333	328	338	337	321	325
3050	357	335	343	352	354	353

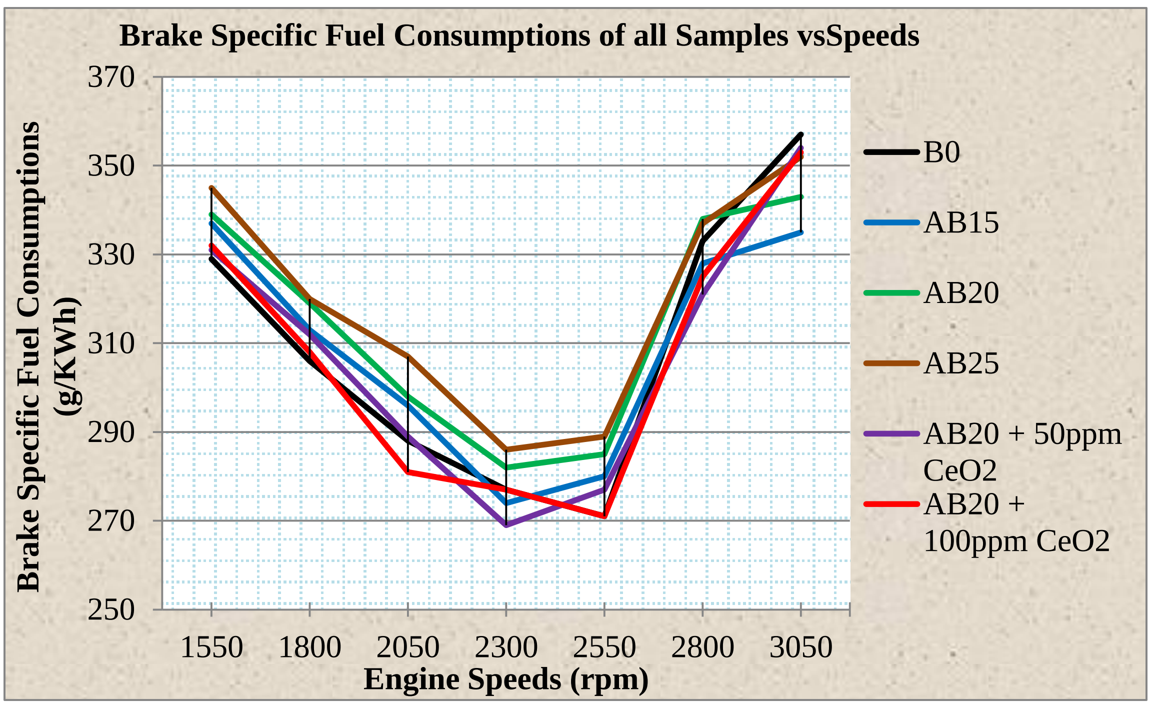


Figure 4-9 Variation of brake specific fuel consumptions vs. speed of all tested fuel samples

Figure (4.9) shows the variation of brake specific fuel consumption with engine speeds of all tested fuel samples. The non-additive biodiesel blend showed maximum fuel consumption. It's clear that the addition of cerium oxide nanoparticle (CeO_2) had made a positive impact on bsfc. Fuel consumption rate had decreased with the addition of (CeO_2) had altered the fuel properties and had reduced the ignition delay which leads to the complete combustion of fuel. Also the introduction of nanoparticle in fuel may have altered the momentum of fuel entering and its propagation in the cylinder which might have increased combustion effect. It was reported that the fuel consumption of a CI engine fueled with biodiesel was higher than diesel fuel due to the loss of heating value that leads to bsfc increases with the increase in the biodiesel content. This is due to the lower calorific value, higher viscosity and density of the diesel biodiesel blends than neat diesel; more quantity of fuel is consumed to maintain the engine speed constant.

Generally, it was show that the brake specific fuel consumptions (bsfc) of biodiesel blend fuels are higher when compared to diesel fuel. But the nano-blended fuels can improve the (bsfc) than even diesel fuel due to the nature of surface increment of nanoparticle and oxygen buffering natures. The average brake specific fuel consumptions increment for AB15, AB20 and AB25 when compared to B0 is 0.093%, 1.99% and 3.47% respectively. While for fuels with cerium oxide additive, there is a reduction with 0.37% and 0.65% for AB20 + 50ppm and AB20 + 100ppm CeO_2 nanoparticles respectively.

4.9.Exhaust Emissions

Emission standards are requirements that set specific limits to the amount of pollutant that can be released into the environment. Many emission standards focused on regulating pollutant released by automobile and other powered vehicles but they can also regulate emissions from industry, power plants and diesel generators. The emission output of fuel samples are measured, they are for CO, CO_2, HC and excess O_2 emissions with reference to diesel fuel emissions.

4.9.1. Exhaust emissions of carbon monoxide (CO % Vol.)

The CO emission depends on the oxygen content, carbon content and combustion efficiency of a fuel. During combustion, the carbon present in the fuel oxidezes to form CO emission, which is then converted into CO_2. However, if the available oxygen is lower, it causes incomplete combustion and hence comes with higher CO value. Figure 4-10 shows the variation of CO emissions for all the blended fuels at different engine speeds. The result indicated that the CO emission increased at higher engine speeds because of less time available for combustion and rich mixture especially for biodiesel blend increased due to viscosity and density increment, but the reduction is higher for 100ppm CeO_2 nanoparticle blends. This is related to the shorter ignition delays, degree of mixing intensity and uniform burning could be improved in the presence of CeO_2. For biodiesel blended fuels due to its higher cetane number and has 10 to 11% oxygen content by weight and this combinations reduce the ignition delay.

Generally, the average CO emission reduction for AB15, AB20, AB25, AB20 + 50ppm and AB20 +100ppm blended fuels when compaered to B0 fuel is 3.18%, 1.06%, 6%, 8.3% and 8.66%, respectively.

Table 4-12 CO exhaust emission test results of all tested fuels

Exhaust gas Emission (CO) in %Vol.						
Engine Speed (rpm)	Fuel Sample					
	B0	AB15	AB20	AB25	AB20 + 50ppm CeO_2	AB20 + 100ppm CeO_2
1550	0.079	0.076	0.071	0.074	0.07	0.076
1800	0.075	0.074	0.071	0.067	0.067	0.063
2050	0.08	0.078	0.075	0.077	0.075	0.069
2300	0.083	0.078	0.079	0.081	0.077	0.073
2550	0.091	0.087	0.083	0.083	0.082	0.079
2800	0.109	0.108	0.108	0.102	0.102	0.098
3050	0.131	0.119	0.114	0.113	0.109	0.104

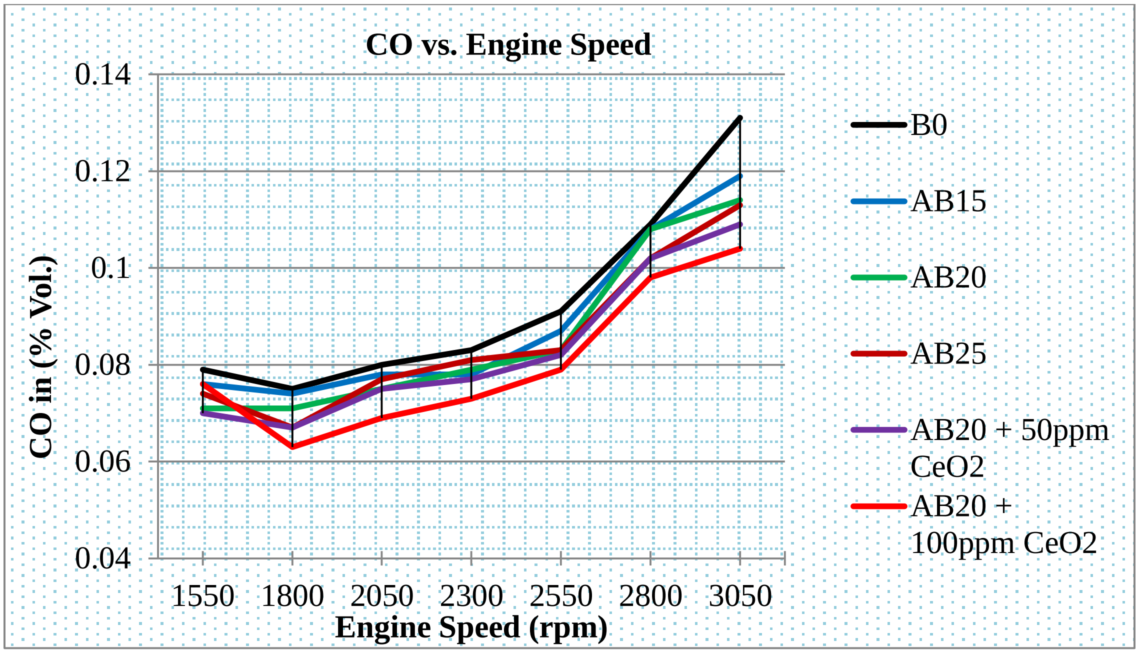


Figure 4-10 Variations of CO emissions vs. engine speed of all tested fuel samples

4.9.2. Exhaust emissions of oxygen (O_2 in %Vol.)

Table 4-13 O_2 exhaust emissions test result of all tested fuel samples

Exhaust gas Emission (O_2) in %Vol.						
Engine Speed (rpm)	Fuel Sample					
	B0	AB15	AB20	AB25	AB20 + 50ppm CeO_2	AB20 + 100ppm CeO_2
1550	17.51	17.57	17.61	17.67	17.69	17.73
1800	17.42	17.51	17.51	17.51	17.54	17.68
2050	17.2	17.29	17.31	17.36	17.48	17.49
2300	17.17	17.22	17.22	17.29	17.29	17.37
2550	17.05	17.1	17.09	17.11	17.11	17.19
2800	16.67	16.65	16.71	16.79	16.83	17.03
3050	16.19	16.37	16.42	16.61	16.67	16.62

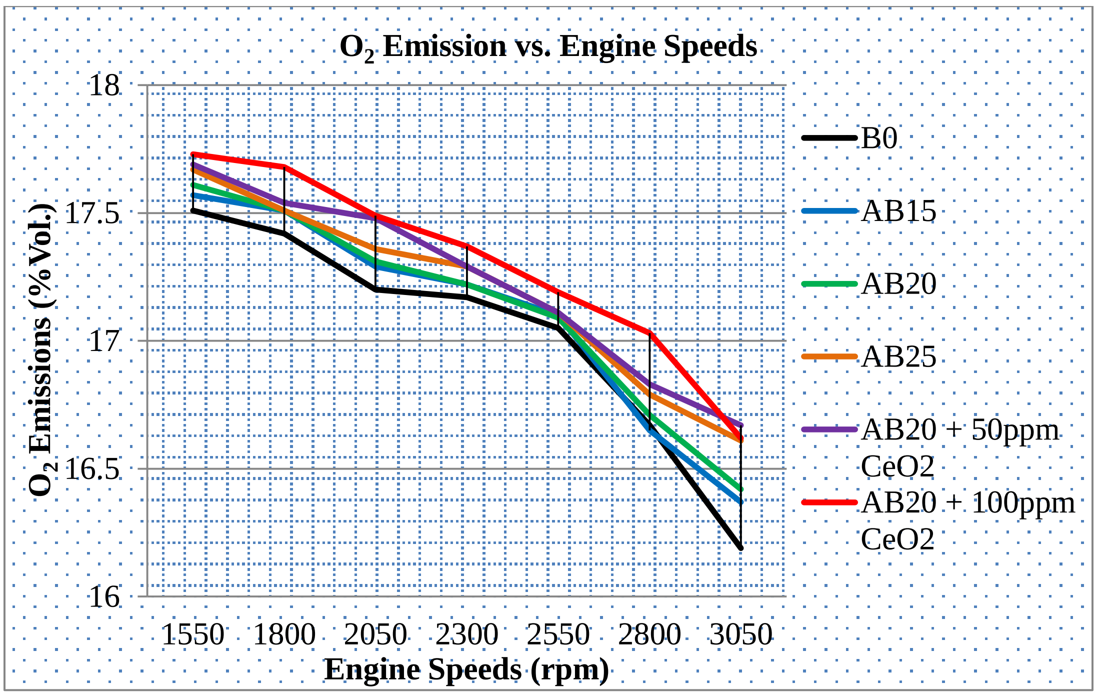


Figure 4-11 Variations of O_2 emissions vs. engine speeds of all tested fuels

As the experimentation revealed, the trend of unused oxygen released with the exhaust gas increased as percentage volume of biodiesel increased. The implication is that, even though the amount of air which entered to the engine cylinder at each rpm varies, the variation of unburned oxygen in the structure of the biodiesel has a role of combustion reaction. Figure 4-11 shows that as percentage of biodiesel blend increased excess oxygen released increased but it is below diesel fuel while the nanoparticle blended fuels shows that further reduction of O_2 emissions because, due to it has a nature of increasing the surface area for better activating the combustion reactions.

4.9.3. Exhaust emissions of carbon dioxide (CO_2 in %vol.)

Table 4-14 CO_2 test results of all tested fuel sample

Exhaust gas Emission (CO_2) in %Vol.						
Engine Speed (rpm)	Fuel Sample					
	B0	AB15	AB20	AB25	AB20 + 50ppm CeO_2	AB20 + 100ppm CeO_2
1550	2.27	2.43	2.45	2.59	2.71	2.74
1800	2.22	2.49	2.49	2.57	2.58	2.58
2050	2.47	2.61	2.57	2.61	2.65	2.71
2300	2.53	2.67	2.71	2.69	2.72	2.72
2550	2.61	2.71	2.72	2.77	2.79	2.89
2800	2.69	2.79	2.9	2.94	2.96	3.04
3050	2.93	3.07	3.17	3.17	3.14	3.21

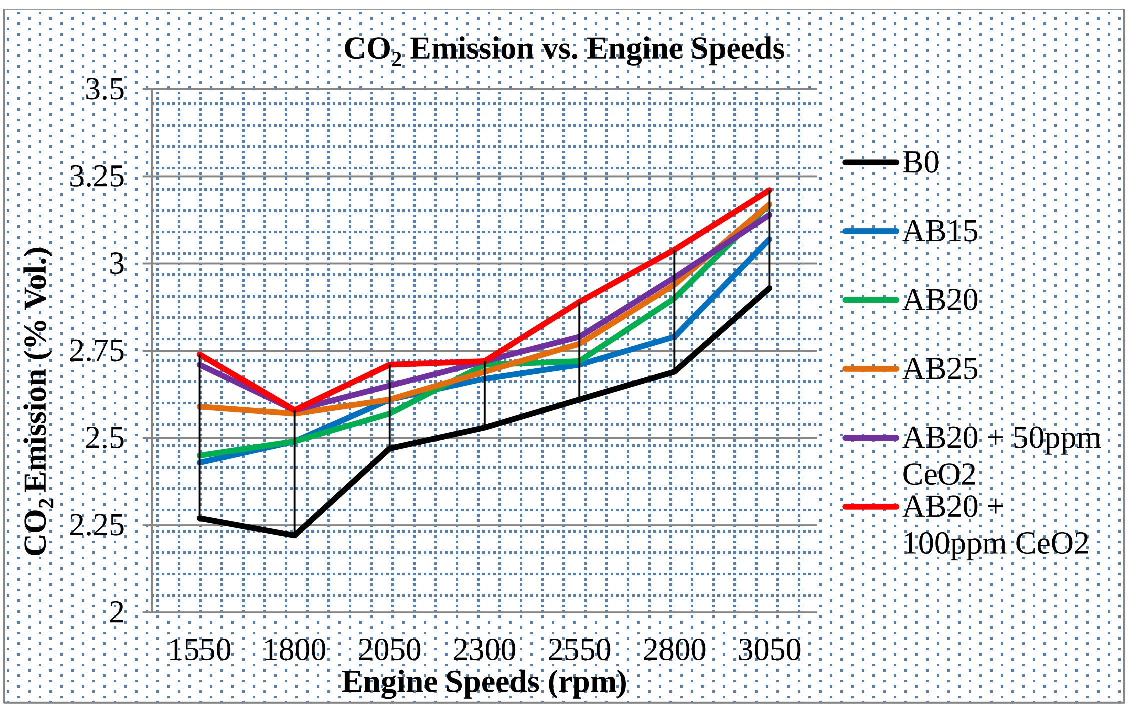


Figure 4-12 Variation of CO_2 emissions vs. engine speeds of all tested fuels

Figure 4-12 shows the CO_2 emission with engine speeds. The CO_2 emission increases with speed for all the fuel blends due to higher fuel consumption at lower and higher engine speeds to maintain the constant. The inbuilt oxygen content of biodiesel promotes oxidation which intern results in increased CO_2 for biodiesel than diesel. For cerium oxide nano-fuels CO_2 emission further increased compared to the non-additive fuel. This may be due to the improved combustion in the engine cylinder. The average CO_2 emissions increment of blended biodiesel fuels, AB15, AB20, AB25, AB20 + 50ppm and AB20 +100ppm to B0 was, 5.93%, 7.84%, 9.54%, 8.07% and 8.86% respectively.

4.9.4. Exhaust emissions of hydrocarbons (HC in ppm Vol.)

Figure 4-13 shows the emission of HC with respect to load for various fuel blends. As shown from figure below the hydrocarbon emissions first decreased with engine speed due to increase in cylinder temperature. When increased with increase in engine speed as less time is available for combustion at higher speeds. The Unburned hydrocarbon emission affects the engine performance unfavorably due to incomplete combustion of fuel. As shown in the figure below at lower and maximum speeds the HC exhaust emissions were slightly maximum. As the biodiesel ratio increases, unburned hydrocarbon (HC) increased for all engine speeds. The addition of nanoparticle improves the air fuel mixture during the fuel injection as well the nanoparticle propagation leads to complete combustion in the chamber leading to reduced emission of HC at the exhaust.

The average HC emissions reduction of blended biodiesel fuels, AB15, AB20, AB25, AB20 + 50ppm and AB20 +100ppm to B0 was, 1.96%, 6.86%, 10.78%, 29.41% and 32.35%, respectively.

Table 4-15 HC test results of all tested fuel samples

Exhaust gas Emission (HC) in ppm Vol.						
Engine Speed (rpm)	Fuel Sample					
	B0	AB15	AB20	AB25	AB20 + 50ppm CeO_2	AB20 + 100ppm CeO_2
1550	19	19	17	17	16	15
1800	19	18	14	13	13	12
2050	17	18	13	13	13	13
2300	18	17	14	15	14	13
2550	19	19	14	16	13	15
2800	21	20	17	15	17	15
3050	22	21	20	19	20	19

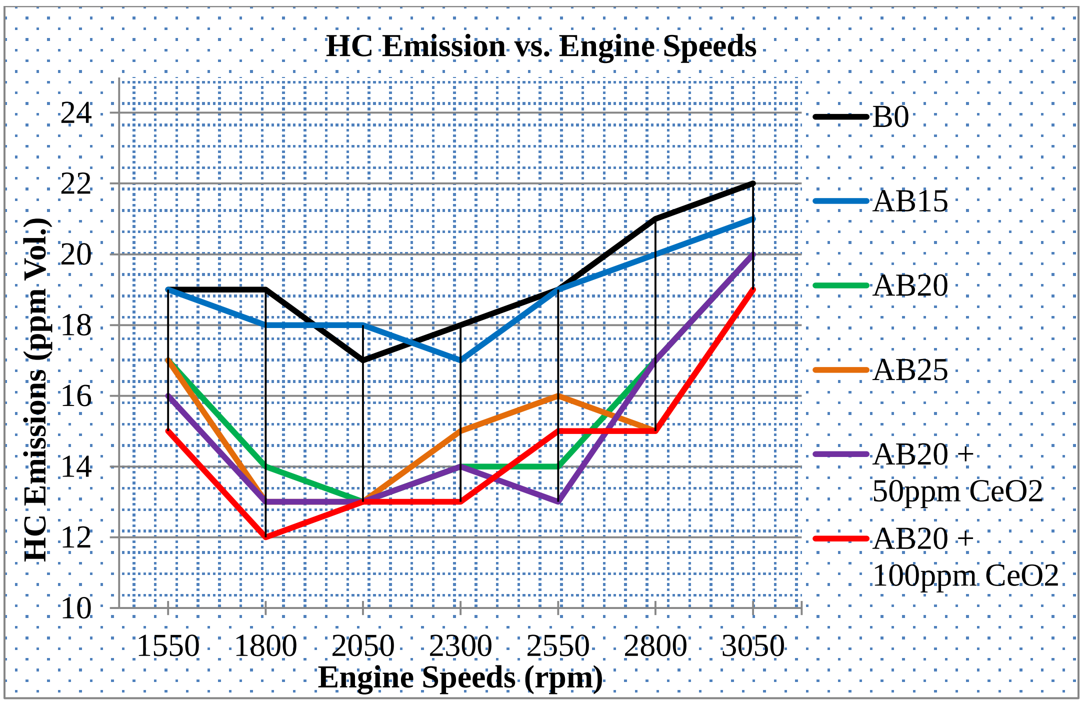


Figure 4-13 Variation of HC emissions vs. engine speeds of all tested fuels

5. CONCLUSION AND RECOMMENDATIONS

5.1.Summary

The main objective of the study was based on extraction, production of biodiesel, characterizations and evaluating the performance and emissions characteristics of biodiesel produced from argemone Mexicana by blending with different ratios with and without cerium oxide nanoparticls. ASTM standard tests for the fuel property measurements and engine performance tests were reported in this paper for blended biodiesel modified by the addition of cerium oxide nanoparticles. Experiments were carried out at two dosing levels of the nanoparticle additives, to investigate the influences on the physicochemical properties, engine performance and emissions.

5.2.Conclusion

Based on the result the following conclusions were found out:-

- The oil extracted from the argemone Mexicana seed was about 27.63 % ratios of oils were obtained and the produced biodiesel from argemone Mexicana oil shows about 83% of biodiesel yield.
- The characteristics of blended biodiesel fuel samples found in the specified values for using in the diesel engines without engine modification.
- The biodiesel shows an increasing trend for the flash point with the dosing level, which indicates a successive decrease in the volatility of the fuel with increase in the quantity of the fuel additive this increase, is nearly linear. Higher flash point temperatures are desirable for safe handling of the fuel. In this context, and because of its higher flash point temperature, the fuels modified with cerium oxide nanoparticles are inherently safer than the base fuels.
- The copper strip corrosion test serves as a measure of possible difficulties with copper, brass parts of the fuel system components. The copper strip corrosion of the biodiesel blended fuel samples and diesel fuel was found to be the same. Therefore, the degree of corrosivity of the samples to the fuel system component is the same to the diesel fuel.

- Density of the fuel increases with an increase all dosing levels. The change in the viscosity of the fuel affects the engine performance as well as the hydrocarbon emissions. The fuel atomization is affected by the fuel density. But the cloud and ash values are decreasing with the dosing levels of the nanoparticles.
- The kinematic viscosity of pure biodiesel produced from argemone Mexicana was found, $4.8mm^2/s$ that is higher than diesel fuel which indicates that due to the higher in viscosity of biodiesel blended fuel the fuel consumptions was found higher than diesel.
- From the performance test result it is seen that the torque and power performance gets reduced and fuel consumptions increased for biodiesel blends when compared to diesel fuels. This is because of even though biodiesels are oxygenated fuel and hence has less energy content compared to the diesel fuel. But this minimum reduction in performance can be compensated with the additions of nanoparticle to improve these draw backs.
- The addition of nanoparticle fuel additives has a significant increase in performance efficiency when compare to biodiesel without additives due to its high surface area to volume ratio of nanoparticle promoting better combustion by improved atomization, better mixing of air-mixture and rapid evaporation of the fuel.
- AB20+100ppm blend has the highest amount of power and torque increase, while its specific fuel consumption is almost the same when compared to pure diesel fuel.
- It shows the amount of changes in specific fuel consumption of the engine in each of the samples compared to the pure diesel fuel. It is observed that AB20+100ppm fuel has the highest specific fuel consumption reduction compared to others.
- The reduction in CO emission by using biodiesel fuels shows good results especially, AB20+100ppm is optimum when compare with diesel. The HC emissions are obtained minimum for AB20+100ppm when compared with diesel and other biodiesel nanoparticle fuel additives.
- The carbon dioxide emissions of all fuels increases from lower engine speed to higher engine speed and the nanoparticle blended fuel shows slight difference compared to biodiesel blended fuels.
- The HC emissions shown decreased for biodiesel blended fuels and that would decreased with biodiesel blend ratios as it has more oxygen the combustion efficient and total combustion is shown.

- Among the diesel, biodiesel blended and nanoparticles dispersed test fuels AB20+100ppm shows significant improved of performance and emission characteristics of the engine.

Generally, the performance, combustion and emission characteristics of a DI diesel engine are improved by incorporation of cerium oxide nanoparticles as additive in biodiesel diesel blend without any engine modification. The cerium oxide nanoparticle additive blended fuel samples show slightly an effective result when compared to the other fuel samples.

5.3.Recommendations

In the present study the characteristics were only carried out for some properties of the argemone biodiesel blended fuels. To have a better comparison the characteristics for all properties of biodiesel and blends should have to be carried out.

In this study due to absence of analyzer there was only focused on the emissions of CO, CO_2, HC and O_2 but for future to have a better investigation on the effects of CeO_2 nanoparticle on NOx emission test should have to be carried out.

In the present study, since only one blend ratio (i.e. AB20) with 50 and 100ppm Cerium oxide nanoparticle is conducted. For comparison it is recommended to conduct further research on different blending ratios and nanoparticles dosing level to have better evaluations.

AB20+100ppm fuel has the best performance and emission characteristics, so it is recommended to substitute diesel fuel with it.

Finally, I recommended the Department of Mechanical Systems and Vehicle Engineering of Adama Science and Technology University to have set-up of biodiesel laboratory which is very important to make a research work on renewable energy sources.

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APPENDICES

Appendix-A

The below data show the results of the fuel samples characterized by Ethiopian Petroleum Supply Enterprise (EPSE).

Telefax 251- (0)11 - 551 29 38
251- (0)11 - 55179 56
251 - (0)11 - 5541905
Email – eth-petroleum@ethionet.et

Telephones:
P.B.X. (251) 011 551 32 88
Direct: (251) - 011 - 551 00 45,
(251) - 011 - 552 60 30,
(251) – 011 – 5541904,
P. O. Box 3375
Addis Ababa - Ethiopia

የ ኢ ት ዮ ጵ ያ ነ ዳ ጅ አ ቅ ራ ቢ ድ ር ጅ ት
ETHIOPIAN PETROLEUM SUPPLY ENTERPRISE

Ref. No. 079/6.1.3.4.4/2010
09 ሐምሌ 2010

አዳማ ሳይንስና ቴክኖሎጂ ዩኒቨርስቲ
ለመካኒካል፤ኬሚካልና ማቴሪያልስ ኢንጂነሪንግ ዲ/ት
አዳማ

በቀን 15/10/2010 ዓ.ም በቁጥር SOMCME/17/4187/10 በተፃፈ ደብዳቤ በተመራማሪ አቶ ደረሰ ፍሬው፤ አቶ ገረመው ብርብርሳ፤ አቶ ራሚሽ ባቡ እና አቶ ፀጋዬ ተፈሪ በምርምር ያመረቱትን የባዮዲዝል ናሙና የላብራቶሪ የጥራት ፍተሻ እንድንሠራላቸው በጠየቃችሁት መሠረት የፍተሻው ውጤት እንደሚከተለው ቀርቧል፡፡

SN.	Property	Test Method AS TM	EPSE diesel Limits	Results				
				B15	B20	B25	B20+ 50ppm ceo2	B20+100ppm ceo2
1.	Density @ 15°C,g/ml	D 4052	Report	0.8461	0.8487	0.8518	0.8491	0.8517
2.	Density @ 20°C,g/ml	D 4052	Report	0.8425	0.8452	0.8487	0.8456	0.8482
3.	Flash Point (PMCC), °C	D 93	Min. 60	88	88	84	87	86
4.	Copper strip corrosion 3 hrs @100 °C	D 130	Max No. 1	1a	1a	1a	1a	1a
5.	Cloud point, °C	D 2500	Max. +5	+2	+1	0	0	+1
6.	Kinematic viscosity @ 40 °c	D 445	2.0-4.5	3.86	3.89	3.99	3.93	3.93
7.	Water and sediment, V/V %	D 2709	Max 0.05	<0.05	<0.05	<0.05	<0.05	<0.05
8.	Total acidity, mg KOH/g	D 974	-	0.1203	0.1323	0.1697	0.144	0.145
9.	Ash , %Wt	D 482	Max 0.01	0.007	0.0095	0.01	0.0041	0.0094

- The results in this report related only to the samples tested.

Remark- The test results of the above parameters are satisfying the diesel specifications.

Liability

Ethiopian Petroleum Enterprise, its Laboratory, its Servants or agents Shall not be held liable for any damages, loss, claims or expenses direct or indirect howsoever caused, arising in connection with the laboratory test carried out on biodiesel samples submitted to it for analysis whether in tort or in contract, due to any act, omission or error of whatever nature, whether or not negligence and howsoever caused. Furthermore all expenses and implied warranties are specifically disclaimed.

ከሠላምታ ጋር

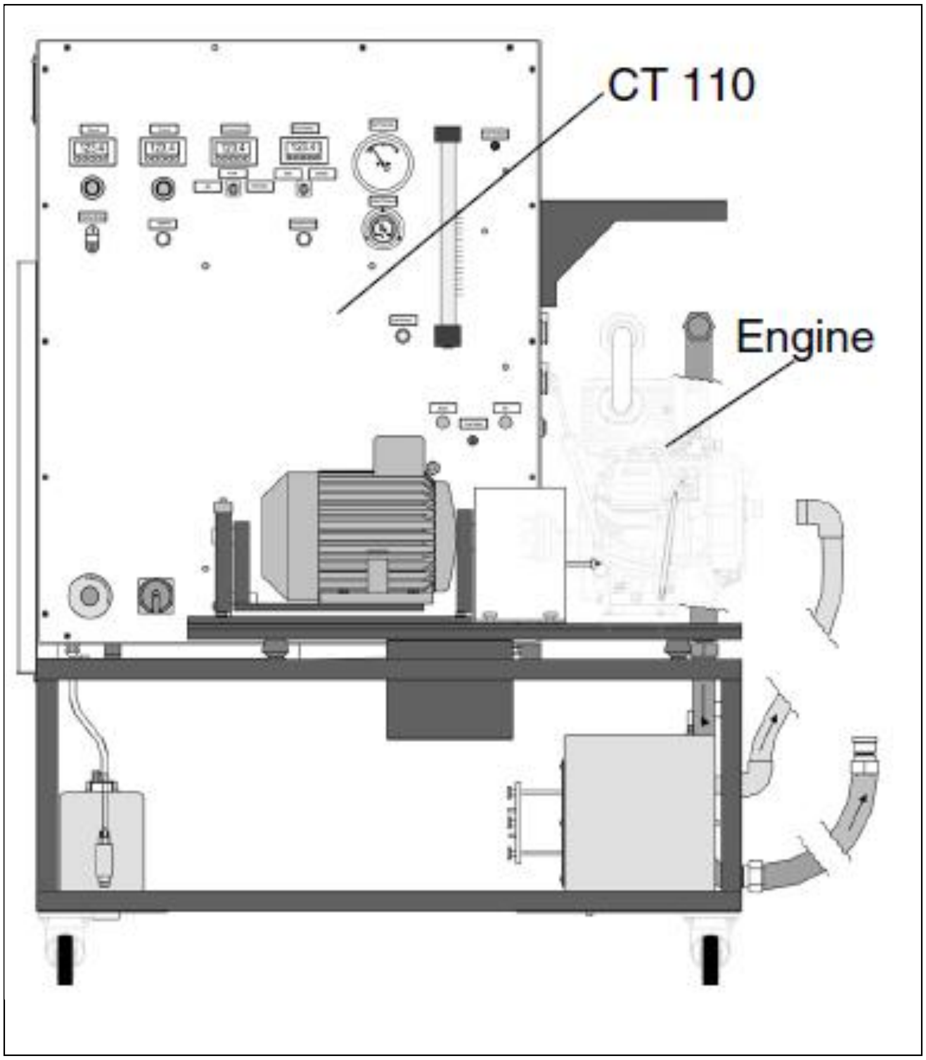
ሰዩም አራጋው
የነዳጅ ጥራት ማረጋገጫ

1959
1966
Ethiopian Petroleum Supply Enterprise

ጥራቱን የጠበቀ የነዳጅ ምርት በማቅረብ የአገራችንን ልማት ለማፋጠን በሚደረገው ርብርብ ውስጥ የድርሻችንን እንወጣለን!

Appendix-B

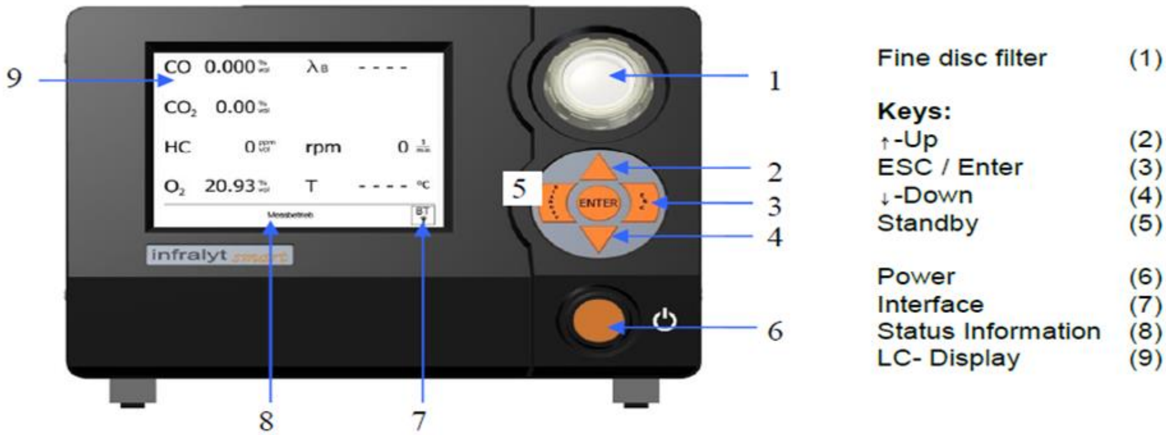
Appendix-C

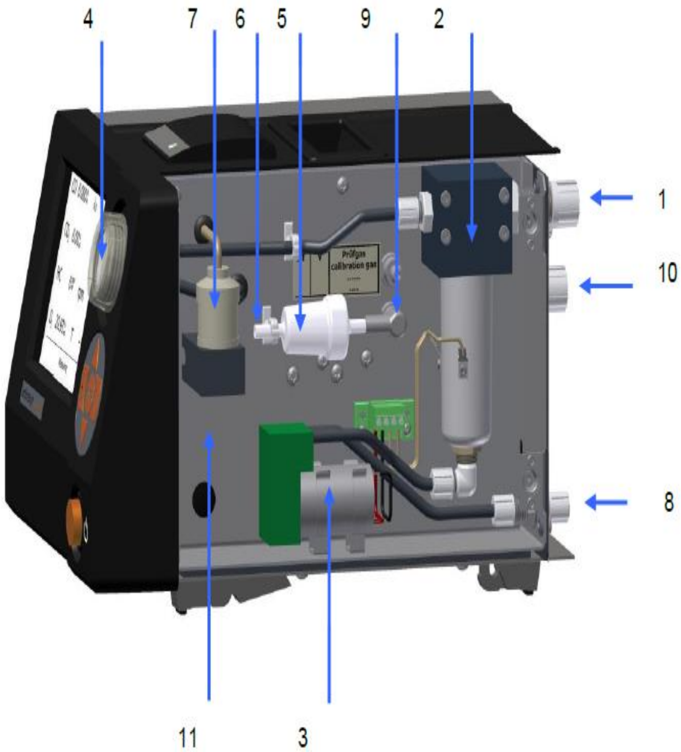


Figre C-1 Functional Experimental set up

Appendix-D

Exhaust gas analyzer operating principle.





Sample gas input (1)
Condensate separator (2)
Condensate pump (3)
Front filter (4)
Charcoal filter (5)
Input zero gas (6)
Oxygen (O2) sensor (7)
Outlet condensate (8)
Input calibration gas (9)
Input leak test (10)
No sensor (optional) (11)

Figure D-1 Exhaust gas analyzer

Appendix-E

NRL Nano Research Lab

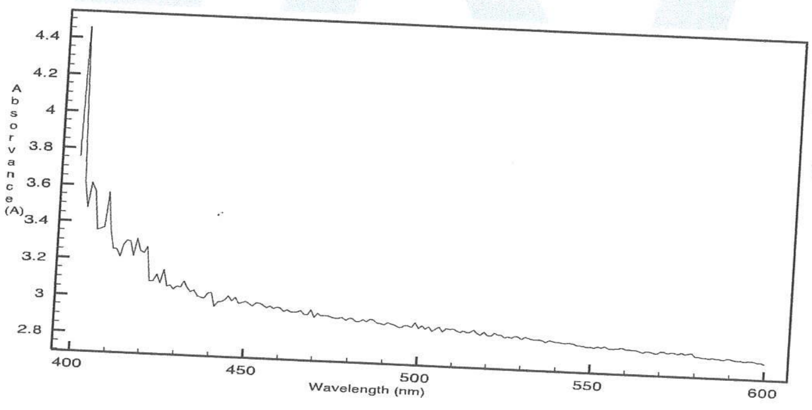
GSTIN: 20AAOFN2135R1Z0

Certificate of analysis

Cerium Oxide Nanoparticles (CeO_2, 20-30nm, Purity 99.9%)
CAS: # 1306-38-3
Purity: 99.9%
APS: 20-30nm
SSA: 40-45 m2/g
Color: light yellow
Bulk Density: 1.3 g/cm3
True Density: 6.5 g/cm3
Crystallographic Structure: spherical
Atomic Weight: 172.1148 g/mol
Cerium dioxide Nanoparticles Certificate of Analysis--%

CeO_2:	≥99.9
SiO_2:	≤0.05
TiO_2:	≤0.06
MgO:	≤0.06
Al_2O_3:	≤0.05

UV Spectrophotometer analysis



H 21, Gopalpur, Jadugoda, (E) Singhbhum, Jamshedpur, Jharkhand 832102 India,
http://www.nanolabs.co.inemail nanolab@live.com , nanolabs@hotmail.comPh (91) 8757368901

NRL

Nano Research Lab

GSTIN: 20AAOFN2135R1Z0

Cerium Oxide (CeO2) Nanopowder
Material Safety Data Sheet

---

1 Identification of substance:

Product details:

Trade name: Cerium oxide Nanoparticles (CaO)

Stock number: SKu 52119

Manufacturer/Supplier:

Nano Research Lab, H 21 Gopalpur, PO Jadugoda (E) singhbhum Jamshedpur Jharkhand-832102, www.nanolabs.co.in

---

2 Composition/Data on components:

Chemical characterization:

Description: (CAS#) 1306-38-3

Identification number(s):

EINECS Number: 215-150-4

---

3 Hazards identification

Hazard description: Xn Harmful

Information pertaining to particular dangers for man and environment

Harmful by inhalation.

Limited evidence of carcinogenic effects.

not restricted

NANO RESEARCH LAB ★ H-21, GOPALPUR ★ EAST SINGHBHUM(JH) PIN:- 832102
