Major Project II

“STUDIES OF NANO ADDITIVES FOR DIESEL FUEL PERFORMANCE ENHANCEMENT”

Submitted in partial fulfillment
of the requirement for the award of the Degree of

Master of Technology
In
Thermal Engineering

By

ROBINSON

2K11/THE/15

UNDER THE SUPERVISION OF

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DECLARATION

I, hereby declare that the work embodied in the dissertation entitled **“STUDIES OF NANO ADDITIVES FOR DIESEL FUEL PERFORMANCE ENHANCEMENT”** in partial fulfilment for the award of degree of MASTER of TECHNOLOGY in “THERMAL ENGINEERING”, is an original piece of work carried out by me under the supervision of Prof. Naveen Kumar, Mechanical Engineering Department, Delhi Technological University. The matter of this work either full or in part have not been submitted to any other institution or University for the award of any other Diploma or Degree or any other purpose what so ever.

(ROBINSON)

M.Tech (Thermal Engineering)

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CERTIFICATE

This is to certify that the work being presented in major project II entitled "STUDIES OF NANO ADDITIVES FOR DIESEL FUEL PERFORMANCE ENHANCEMENT" *by* ROBINSON (2K11|THE|15), is an authentic record of work carried out under my guidance and supervision and refers other researcher's work which is duly listed in the reference section.

It is also certified that this dissertation has not been submitted to any other Institute/University for the award of any diploma or degree.

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ACKNOWLEDGEMENT

Apart from personal effort, the success of any project depends largely on the encouragement and guidance of many others. I take this opportunity to express my gratitude to the people; their guidance, support, encouragement and all the above blessing that have been instrumental to achieve this endeavour.

First and foremost, I would like to thank the almighty and my parents for creating, nurturing and enabling me up to this level of intellectual, spiritual and academic maturity. I would like to show my greatest appreciation, heartfelt sense of gratitude and indebtedness to Prof. Naveen Kumar. I can’t say that the word “thank you” is enough for his tremendous support and help. I feel motivated and encouraged every time I attend his company. Without his encouragement and guidance this project would not have been materialized.

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ABSTRACT

Nano additives are added to propellants and explosives to improve ignition and combustion performance. In particular, aluminium has been used as an energetic material in solid-based propellant rockets and explosives for many years due to its high combustion enthalpy and low cost. With the recent development in nanotechnology, a lot has been achieved in the field of energetic materials or rightly called the secondary energy carrier materials. Due to their large surface area and unique thermal properties, nano particles are known to exhibit many advantages over conventional micron sized particles. However, the current mechanism of nano aluminium ignition and combustion is not fully understood. Also the studies encompassing suspensions of nano materials in a diesel fuel are very limited. Therefore, an experimental study of nano additives for diesel fuel combustion enhancement was performed, with a primary focus on alumina.

The first experimental study involved the preparation & characterization of the alumina nano particles produced during the course of investigation. The nano particles are made by solid state reaction of aluminium nitrate and citric acid by heating it in a microprocessor controlled furnace. Both the reagents on heating up to a temperature of 445^{O}C in a controlled environment yielded the alumina nano particles. Mechanical grinding of the alumina nanoparticles was further carried out so as to ensure that the nano particles thus obtained should not agglomerate. The SEM analysis of the particles reveal that the average diameter of the aluminium nanoparticles obtained is about 40–60nm.This provides a large contact surface area with diesel and high activity for the combustion process.

The alumina nanoparticles were then dispersed in the diesel fuel to make a suspension of the nanoparticles in the diesel fuel. The study of calorific value of the alumina nano particles blended diesel was fuel was carried out using Parr 6100 calorimeter. The experiments were carried out with mass fraction of 1%, 2%, 3% & 4% alumina nano particles. The results show that the amount of heat liberated from diesel combustion increases with addition of the alumina nano particles. The maximum increment in the

calorific value was observed in case of the 4% blend with a percentage increase of 4.5 %. After the property testing, the performance and emission study was carried out on a four stroke, vertical, naturally aspirated, single cylinder, air cooled, direct injection diesel engine. The combustion experiments of the alumina nanoparticles blended diesel fuel showed the following phenomena:

The Brake Thermal Efficiency and the Brake Specific Energy Consumption of the Alumina nano particles blended diesel fuel are improved significantly showing much better results than the diesel fuel. Initially with load below 20 % almost same pattern in the brake thermal efficiency was observed but with increasing loads the blends started showing markable increase in the efficencies. For the 1 % and 2 % blends an increased brake thermal efficiency was noticed at all loads as in comparison to diesel with the highest value of 28.96 % with the 2 % blend.

Furthermore in case of emissions, the NO_X and CO emissions showed a considerable reduction at all load conditions thereby resulting in an overall emission reduction from the engine. Along with energy density enhancement, achieving precise control over the reactivity of nano fluids is an opportunity for future nano energetic fuel applications.

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Nomenclature

AIT	Auto Ignition Temperature
ALICE	Aluminium Ice Composite
AP	Ammonium Perchlorate
APS	Average Particle Size
ASTM	American Society for Testing and Materials
CEA	Chemical Equilibrium with Applications
CNT	Carbon Nanotubes
Da	Damkohler Number
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EDS	Energy Dispersive X-Ray Spectroscopy
EPA	Environmental Protection Agency
FGS	Functionalized Graphene Sheet
HMX	Octogen
HoC	Heat of Combustion
HTPB	Hydroxyl-Terminated Poly-Butadiene
JANAF	Joint Army Navy Air Force
MDM	Melt Dispersion Mechanism
MIC	Metastable Intermolecular Composites
n-Al	Nanoaluminium
n-Al2O3	Nanoaluminium Oxide
NM	Nitromethane
SAM	Self-assembled Monolayer
SEM	Scanning Electron Microscopy
SHS	Self-Propagating High Temperature Synthesis
SRM	Solid Rocket Motor
SSA	Specific Surface Area
TEM	Transmission Electron Microscopy
TDI	Toluene Di-isocyanate
TGA	Thermogravimetric Analysis
TNT	Trinitrotoluene
W	Watt
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
GDP	Gross Domestic Product
NOAA	National Oceanic and Atmospheric Administration
p.a.	per annum
UNFCCC	United Nations Framework Convention on Climate Change
GHGs	Greenhouse gases
N_2O	Nitrous Oxide
O_3	Ozone

CFCs	Chlorofluorocarbons
IC	Internal Combustion
CO	Carbon monoxide
NOx	Nitrogen oxides
PM	Particulate matter
UBHC	Un-burnt hydrocarbon
SCR	Selective catalytic reduction
CI	Compression Ignition
DI	Direct Injection
g	Grams
kwh	Kilowatt hour
° K	Degree Kelvin
atm	Atmospheric
psi	Pounds per square inch
° C	Degree celsius
TDC	Top dead centre
rpm	Revolutions per minute
SVO	Straight vegetable oil
WVO	Waste vegetable oil
TDI	Turbocharged Direct Injection
° F	Degree Fahrenheit
THC	Total hydrocarbon
EGR	Exhaust gas recirculation
DPF	Diesel particulate filter
m/s	Meters per second
Btu/lb	British thermal unit/ pound
Gal	Gallon
SCF	Standard cubic foot
NREL	National Renewable Energy Laboratory
~	Nearly
LPG	Liquefied petroleum gas
v/v	volume/volume ratio
ASTM	American Society of Testing and Materials
KJ	Kilojoules
mm	Milli meter
KVA	Kilovolt ampere
AC	Alternating current
Min	Minutes
nm	Nanometer
D100	Neat diesel
BTE	Brake thermal efficiency
BSEC	Brake Specific Energy Consumption

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CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION

The modern concept of nanoscience and nanotechnology is credited to Professor Richard Feynman who gave a seminal talk in 1959, ‘There is plenty of room at the bottom’. The prefix, nano, then becomes a common vocabulary word in research domain boosted by the development of experimental tools such as Atomic Force Microscope (AFM), Scanning Tunnelling Microscope (STM) and advanced simulation methods conducted on high-performance computers. Nanoscale materials are known to exhibit different physical, chemical, electrical, and optical properties compared to their counterparts at the macroscale.

As fundamentally most of the energy conversion, energetic reaction and storage processes occur at atomic or molecular level, it is natural to adopt nanotechnology to solve today’s big issue: the energy challenge, *i.e.* the challenge to secure our clean energy future under the scenario of a sharp increase in energy demand *vs.* the depletion of fossil fuels together with increasing concerns about carbon emission and global warming. The motivation of today’s energy research in respect of material approach is double sided: find alternative cleaner energy sources and conversion processes to secure our future energy supply and find new materials for converting or collecting the harmful emissions to tackle the climate change. The use of nanotechnology is a potential solution to contribute both sides in various energy applications including photovoltaic cells, hydrogen (storage, transport and distribution), carbon capture and storage, fuel cells, heat transfer and combustion applications, hot rock drilling system, power transmission, catalyzing chemical processes, as well as improving the efficiency of oil and natural gas systems, and solar and renewable energy systems.

Nanoparticle is referred to any solid material whose length scale typically in the range of one to several hundred 10-9 m. Due to their unique physical, chemical and thermal properties associated with their large specific surface area, nanoparticles have been found extensive applications in many energy related fields as catalyst, nano composites or energetic materials. Compared to their counterparts at macroscale, theses nanoparticles are shown to have increased reactivity (Guczi, 2005), increased catalytic activity (Schlogl and Abd Hamid, 2004), super paramagnetic behavior (Gupta *et al.*, 2004), super plasticity (Xu *et al.*, 2004), lower melting temperatures (Mei and Lu, 2007)

Understanding the thermodynamics of nanoparticles is a key step for the bottom-up approach for nano design and nano machining. The utilization of metallic nanoparticles in combustion and energetic materials communities advances the application of future fuels, propellants, pyrotechnics, explosives and reactive materials with nanoscale features or ingredients (Yetter *et al.*, 2009). Some nanostructured composite particles, *i.e.* mixtures of nano sized reactant particles; undergo exothermic reactions after being activated, possessing features such as high burn rates and high temperature accompanied by low volume expansion, which have wide range of defense and commercial applications (Zhao *et al.*, 2006, 2007a, 2007b).

Recently some energetic nano materials such as aluminium, iron and silicon have been proposed as an alternative secondary energy carrier where the fundamental scientific challenge is to understand and control the oxidation, ignition and combustion process of these energetic nanoparticles (Wen *et al.*, EPSRC Project: EP/F027281/1, 2007). In many of these applications, proposed materials need to be nano-structured or functionalized with one or two other materials, in order to utilize the distinct properties of both materials at both nano and macro-scales. These nanostructured functional particles do not only improve conventional properties of energy materials related to their bulk counterparts but also promote other novel applications such as future fuel for outer space exploration and self-propagating high-temperature synthesis (SHS) of materials.

Metal additives have been utilized in solid propellants and fuels for some time and have been shown to dramatically increase combustion enthalpies and quality. These metalized additives in fuels combust to significantly heat up and expand the surrounding gases, providing a larger specific impulse, the impulse per unit amount of propellant and fuel. Common metallic materials of interest, including aluminium, boron, magnesium, and zirconium [1], offer increases in the overall energy density of the fuel and effectively reduce the tank storage volume. In the current state of the art implementation, energetic additives offer a high volumetric enthalpy of combustion, facilitating transportation of more payload per given fuel volume. Furthermore, in liquid-based fuels, a major challenge of dispersing metal additives is the settling of solid particles in the fuel. Consequently, conventional liquid fuels may need to be remixed or processed before use, due to the rapid settling of energetic additive particles.

This has led to new approaches to mitigate several of the disadvantages of larger metal particle additions in fuels. New advances in nanotechnology are being developed to understand and enhance energy interactions in various fuel formulations. Fundamental research on nano materials, such as nanoparticles suspended in fluids (nano fluids) and oxide reduction reactions between nanoscale metals (super thermites), have led to entire new classes of energetic materials. By taking advantage of the new functionalities offered by nanoparticles, the reactivity and efficiency of propulsion vehicles has proven to be substantially improved. For instance, nanoscale materials containing nano meter Al particles, can theoretically release more than twice as much as energy as the best molecular explosives [1, 2, 3]

Utilizing aluminium nanoscale additives in solid-based composite propellants, it is possible to have faster burning rates and more complete combustion [3, 4, 5], thus improving the performance of aluminized propellants. In liquid propellants, nanoparticles, due to their high specific surface area, can be successfully suspended in fuels much longer than micron-sized particles without precipitation out of the solution [9, 10]. In addition, recent studies have reported reduced ignition delays in nano aluminium suspended in ethyl alcohol [6, 7], and JP-8 [4], increased catalytic activity in cerium oxide suspended in diesel [5].Based on these developments, the research on energetic nano materials has become a topic of immense significance, and has led to a relatively new area of research named nano energetics.

Current investigations are underway to further characterize the energy contributions of nanoparticles, and to develop a unified understanding of the relationships between nanoparticle additives and fuel performance.

1.2 RESEARCH MOTIVATION

With recent advancements in nanoscale material production techniques, there has been renewed interest in metal particle combustion and their energetic applications. The energy consumed and cost to produce nanoparticles is reduced with the development of new manufacturing technologies, offering nanoparticle additives that are increasingly affordable [11, 12, 13]. As a result, it is now possible to routinely synthesize and characterize nanoparticles, for instance, nano aluminium is now commercially available as an electro explosively produced material named ALEX [5, 12, 13].

Further development in this area is expected to make these additives more available and affordable in the near future. Presently, there are relatively few practical applications that are taking advantage of nanoparticles ignition and combustion enhancements, and this opens up a large window of opportunity for the research of new viable energetic fuels and their future applications of nanoscale additives, including as advanced weapons, combustion synthesis materials, and propellant enhancers [5].

There are many practical applications of nanoenergetic additives that have attracted worldwide attention and given rise to new fuel formulations, however, there has been considerable debate over the mechanism of nanoparticle ignition, and the conditions at which nanoparticles burn. For example, considering aluminium, the most commonly used metallic additive [4, 7, 13], current theoretical models cannot fully explain nano aluminium ignition in certain environmental conditions and particle size ranges. In particular, bulk aluminium ignition is typically associated with the melting of the ambient oxide layer at 1700-2400ºC, while the ignition temperatures of nanoscale aluminium has been determined to be well below the bulk material value at 660 ºC [13]. A number of experimental investigations on aluminium additive combustion have reported a wide range of ignition temperatures even within the same particle distribution [6, 7, 15]. Furthermore, the phenomena of the growth of the aluminium oxide layer, effect of mechanical stresses or strains, and phase changes of the surrounding oxide layer and core solid-liquid of core are not completely understood [13, 14, 15]. Consequently, more experimental studies are needed to fully characterize nano aluminium and along with other metals as nanoenergetic materials. While there are a number of combustion enhancements resulting from the addition of nanoparticles to gelled and solid-based propellants, there has been relatively little investigative work on the combustion properties of nanoparticles suspended in liquids (nano fluids). Nanoscale structures (< 100 nm) stably suspended in fluids give rise to exciting new properties and phenomena.

Recent attention has focused on the concept which proposes that pure nanoenergetic materials or suspensions of nanoenergetic materials in a liquid medium can be controllably ignited to provide a secondary release of thermal energy. The combustion products can then be captured and reprocessed into their original nanoparticle form for repeated use. Very few studies currently in press or within the last few years have investigated nano fluid combustion phenomena, and there is currently a need for more insight into their behaviour, particularly in alternative energy systems. [4-5, 8, 9, 10]

A projected decline in the world‘s oil production and concern of greenhouse gas emissions have led to a recent push for increased propellant performance and environmental sustainability. Current propellants in use, such as hydrazine, have many negative health and environmental effects to human and animals. According to the Environmental Protection Agency (EPA) [11], short term exposure to hydrazine can result in permanent damage to the central nervous system, kidneys, and liver. In addition, there is also concern about the occupational exposure of kerosene-based fuels, such as military JP-8 and civilian equivalents Jet-A [16]. As a result, several alternative propellants with nanoenergetic additives have been proposed such as graphene sheets or nano aluminium suspended in nitromethane [11, 12], and nano aluminium suspended in liquid or frozen water formulations [5, 11, 13, 14].

Thus, Nano Energetics offer a range of benefits, and it is of interest to explore other promising fuel candidates that minimize the formation of greenhouse gases, ozone-forming pollutants, and harmful or toxic emissions.

1.3 RESEARCH OBJECTIVES

The primary aims in this study were to make and characterise nano aluminium particles to be used as in the development of nanofuels and to study the effect of aluminium nano energetic additives (basically nanofluids thus developed) on emission & performance characteristics of diesel.

As a result ,this experimental study characterizes the combustion of alumina nanoparticles which are being developed in the lab(CASRAE) to gain a better understanding of aluminium oxidation in a multi-component heterogeneous system, and as a secondary energy carrier suspended in diesel.

This study is one of the first studies investigating the combustion nature of this fuel formulation. The basic combustion studies here may be extended to more complex nanoenergetic systems, such as bimodal (combination of micron and nanoscale) aluminium compositions, mechanically alloyed metals, or metastable intermolecular composite (MIC) materials.

1.4 METHOD OF APPROACH

Chapter 1 provides a brief introduction on nanoenergetic particle combustion, particularly the work done on micron-sized and nanoscale aluminium, and the current applications that utilize the unique features of the nanoscale additives.

Chapter 2 describes the extensive literature review regarding nano energetic material, nano fluids and their applications in fuel systems etc currently accepted by Nanoscale Research Letters.

Chapter 3 describes the experimental setup and the procedures which are being followed while working on the nano particles, including their, preparation and then dispersion and the stabilisation of the nanoparticles in the fuel

Chapter 4 summarises the results as well as the discussions part related to the various performance parameters thus calculated.

Chapter 5 summarizes the conclusion and challenges which are being faced during the process of making the nano fuels.

Chapter 6 describes the future research work that need to be carried out in the field of nanofuels in the near future and its shows the future research work that will be taken in the upcoming time for further research in the field of nano fuels.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

The combustion process of nano energetic materials is a multidisciplinary subject, and due to their propellant performance enhancing abilities, there has been a large body of research in order to effectively model and understand the mechanism of nanoscale metal ignition and combustion. A brief review of metal particle combustion is provided in section 2.2. As shown in section 2.3, a better theoretical understanding of the thermodynamics and reaction kinetics of micron-sized and nanoscale aluminium particles can lead to improved combustion models and prediction capabilities. Ultimately, as reviewed in section 2.4, this can lead to practical nano energetic applications that utilize the unique features of micron and nanoscale energetic materials.

Nanofluids, as a kind of new engineering material consisting of nano meter-sized additives and base fluids, have attracted great attention of investigators for its superior thermal properties and many potential applications. Many investigations on nano fluids were reported and especially some interesting phenomena, new experimental results and theoretical study on nano fluids, in which consistent and inconsistent even contrary conclusions were reported, have been presented in literature. The aim of this report is to summarize recent development in research on synthesis and characterization of stationary nano fluids and try to find some challenging issues that need to be solved for future research. The report will cover the experimental study of performance and emission characteristics of the various nano fuel samples made in the lab and issues related to it.

With progress of thermal science and thermal engineering, it is of a strong interest to develop micro-scale liquid flow devices, which have compactness and high surface-to-volume ratio. Thus giving an important role in many diverse industries, including transportations, microelectronics, chemical engineering, aerospace and manufacturing.

In the past several years, some review articles [1-8] involved in the progress of nano fluid investigation were published. Although these review papers have generally covered the current aspects of experimental and theoretical studies of nano fluids, the state-of-the arts on nano fluids need to be re-surveyed due to a great number of new papers on nano fluids published, in those some new phenomena and new findings are reported. The purpose of this report focuses on the preparation &characterization and to test the various samples in accordance to different concentrations. To perform these all following aspects are involved for the preparation, characterisation and engine testing of the various samples:

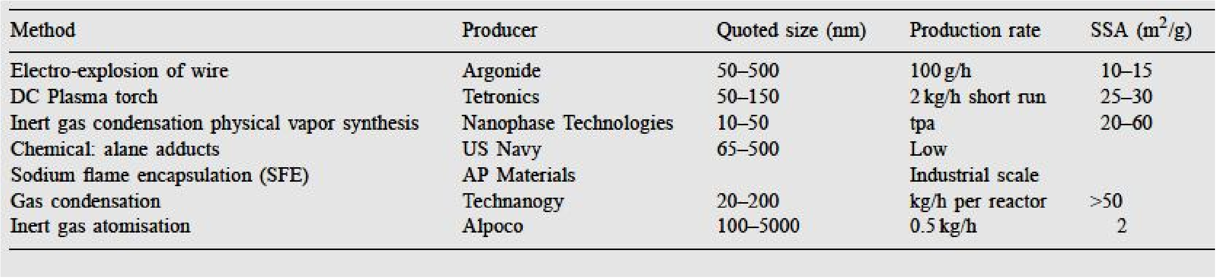
- Selection of a nano fluid system
- Synthesis of nano fluids
- Stability of nano-liquid–solid suspension
- Engine testing for performance & emission parameters

At present, investigation on different nano fluid systems is in experimental stage, and as for engineering application of a special nano fluid system is rarely reported. For example, a system of nano fluids applicable to an advanced vehicle with special properties has not been proposed.

2.2. PREPARATION OF NANO PARTICLES

Several techniques are being developed today for the manufacture of nano aluminium. With the exception of gas atomisation, exploding wire and plasma wire fragmentation, most methods seek to grow powders from an induced gaseous phase (a ‘bottom up’ approach rather than a fragmentation method).

Table 1 lists some of the leading practitioners:



Method	Producer	Quoted size (nm)	Production rate	SSA (m^2/g)
Electro-explosion of wire	Argonide	50–500	100 g/h	10–15
DC Plasma torch	Tetronics	50–150	2 kg/h short run	25–30
Inert gas condensation physical vapor synthesis	Nanophase Technologies	10–50	tpa	20–60
Chemical: alane adducts	US Navy	65–500	Low	
Sodium flame encapsulation (SFE)	AP Materials		Industrial scale	
Gas condensation	Technanogy	20–200	kg/h per reactor	>50
Inert gas atomisation	Alpoco	100–5000	0.5 kg/h	2

Alpoco’s ultrafine gas atomised powder is included for comparison. In general the methods break down into chemical/pyrolysis methods and high energy plasma or current-assisted methods. Typical production rates for nano aluminium are quoted at between ∼200 g/h and 2 kg/h. The fastest production route appears to be flame pyrolysis which is claimed to be capable of delivering 1000–5000 tpa from a single reactor for oxides and carbon black.

AP Materials claim a unique sodium flame and encapsulation technology for pyrolysis and subsequent encapsulation of particles before agglomeration occurs. They claim advantages in scale of production. The combustion of nanoenergetics is a multidisciplinary subject, and due to their performance enhancing abilities, there has been a large body of research in order to effectively model and understand the mechanism of nanoscale metal ignition and combustion. A brief review of metal particle combustion is provided in section 2.3. As shown in section 2.1, a better theoretical understanding of the thermodynamics and reaction kinetics of micron-sized and nanoscale aluminium particles can lead to improved combustion models and prediction capabilities. Ultimately, as reviewed in section 2.3, this can lead to practical nanoenergetic applications that utilize the unique features of micron and nanoscale energetic materials and low cost versus IGC.

Singhal et.al [23] quotes∼US$ 50 kg−1 production cost for a reactor with burner diameter of 12.5 cm scaled up to 100 tpa for oxides. Particle size can be controlled by controlling pressure in the reactor. Reduced pressure in flame pyrolysis leads to rapid quenching and fine particles, but at normal pressure there is an opportunity for coarsening by coalescence.

Nanophase Technologies employs plasma evaporation of a metal substrate followed by cooling with carrier gas and collection (physical vapour synthesis (PVS) or inert gas condensation (IGC)). The conditions in the carrier stage can determine size and level of agglomeration. Alumina with median size 10–50 nm can be produced with SSA of 15–90m2/g. Nano alumina is offered at ∼US$ 200 kg−1. The IGC method involves evaporation of the precursor followed by homogeneous nucleation/condensation of powder in a low partial pressure of inert gas. Importance is placed on control of the colloidal behaviour of nano aluminium and complementary coating technology enables subsequent dispersion.

Technanogy also operates an IGC method (reactor output ~lbs/h) and claim techniques for control of particle size within ±10 nm and control of oxide thickness between 1and 5 nm . They expect to deliver 200 t nano aluminium products in 2012. The SSA is >50m2/g and the main application is in propulsion where the goal is to increase effective payload of space vehicles.

IGC methods are also operated by Nano products Inc., who describes preparation of a precursor solution of the required stoichiometry which is then subjected to plasma evaporation.

Higa et al. [17] have a solution method for decomposition of solutions using transition metal catalysts. Choice of catalyst and concentration of reactants determines particle size. In general, chemical methods appear to be advantageous in giving tight size distributions and low impurity levels but production rates are relatively low.

Argonide operate a unique exploding wire method for making aluminium powders by passing high currents through fine wires. This is a semi-continuous process and the plasma formed subsequently condenses to form fine particles (~100 nm) in an argon gas environment. This requires expensive equipment and production rates are low.

Tetronics' DC Plasma route also has a wire feed, but the application of a plasma torch results in significantly finer particle sizes (see Table 2) and a noticeable level of carbon pick up (~2.4 w/o) and other significant impurity levels. The very high surface area of nanopowders generally means that they are prone to adsorb impurities from the manufacturing environment. Other highly energetic sources such as spark discharge are also being applied to production of nanopowders (e.g. CyTerra Corp., Advanced Materials and Processes, November 2001).

2.3 COMBUSTION OF METAL FUELS

Early works by von Grosse and Conway [18, 19], and Glassman [19, 20 , 26], serve as general framework for current metal combustion models. The combustion of metal-oxygen systems typically involves a significant release of energy, and the products of combustion are usually condensed when at room temperature. Thus, the general equation for metal oxidation reactions is

$$xM(s) + yO_2 \rightarrow M_xO_{2y}(s)$$

Due to their high reactivity, they are rarely found in their free (unbound) form in nature. Metals may react in the presence of an oxidizer to form an oxide passivation layer - a thin 25Å (~2.5 nm) protective layer that surrounds the metal particle, prevents spontaneous combustion, and impedes against further oxidation of the metal. There are many of contributing factors that determine which materials are best suited for a given application, including the enthalpy of combustion (energy content), toxicity, chemical stability, cost and availability, and properties of the metal and its oxide.

2.3.1 ENTHALPY OF COMBUSTION

Metal additives are evaluated, in part, by the amount of energy they release for a given mass or volume. As shown in Fig. 2.1, the heats of combustion for various energetic

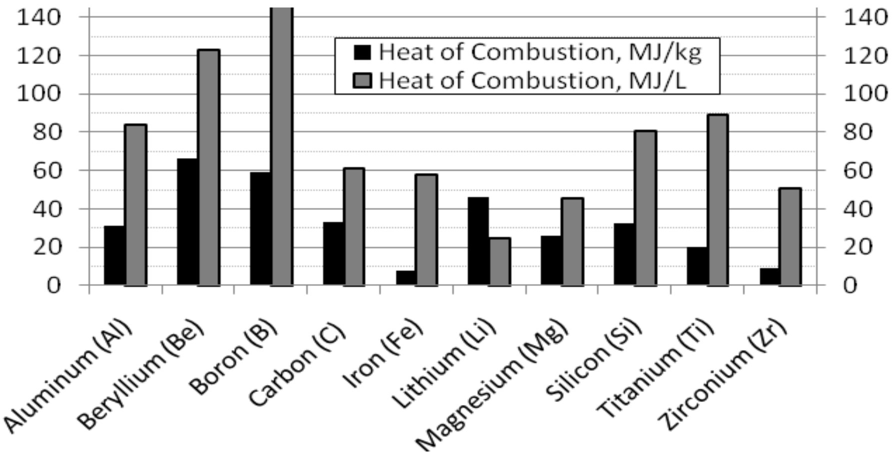


Fig 2.1 Heat of combustion of various metals. Ref (21)

materials are illustrated for comparison. Aluminium, boron, and beryllium offer the highest energetic content in comparison to the other materials. Carbon has the advantage of participating energetically, typically in the form of graphene sheets or carbon nanotubes (CNT), without producing any residual solid oxide material [28]. In theory, boron (a metalloid) has demonstrated to be an excellent energetic material, with the highest volumetric heat of combustion of any known element. Furthermore, as shown in Fig. 2.1, compared to hydrocarbon fuels boron has approximately 4D100 higher energy density on a gravimetric basis and more than three times higher on a volumetric basis.

Unfortunately, the use of boron-based propellants has thus far resulted in poor combustion efficiency and low energetic performance [22]. The combustion of boron is limited due to its inhibitive oxide coating, and energy trapping due to the formation of HBO2 species within a hydrogen containing atmosphere [28]. As a result, for the efficient combustion of boron particles, the oxide layer must first be removed, and the formation of HBO2 reduced. Recent attention has focused on the potential large scale implementation of nanoparticles as viable secondary energy carriers [18, 19]. This concept proposes that pure nanoenergetic materials or suspensions of nanoenergetic materials in a liquid medium can be controllably ignited to provide a secondary release of thermal energy. In addition to energetic content, a critical consideration is the toxicity and chemical stability of the metal reactants and products. The present concern for reduced toxicity significantly restricts the application of certain metals. For instance, the high energy content of beryllium is particularly attractive; however it is extremely hazardous to humans and animals even in small doses [16, 28]. For engineering applications, magnesium also has been used in fuel systems; though due to its reaction with water and humid air, it is fairly unstable to handle. Other considerations include the cost to produce, flame temperatures, material abundance, and burning characteristics of the metal and its oxide, respectively.

Recent attention has focused on the potential large scale implementation of nanoparticles as viable secondary energy carriers [5, 7, 9]. This concept proposes that pure nanoenergetic materials or suspensions of nano particles in a liquid medium can be controllably ignited to provide a secondary release of thermal energy. In addition to energetic content, a critical consideration is the toxicity and chemical stability of the metal reactants and products. The present concern for reduced toxicity significantly restricts the application of certain metals. For instance, the high energy content of beryllium is particularly attractive; however it is extremely hazardous to humans and animals even in small doses [16, 28]. For engineering applications, magnesium also has been used in fuel systems; though due to its reaction with water and humid air, it is fairly unstable to handle. Other considerations include the cost to produce, flame temperatures, material abundance, and burning characteristics of the metal and its oxide, respectively.

Powdered spherical aluminium is the most widely used metal in energetic materials [6, 8, 9, 13], and the primary focus of the present study. Aluminium additives have been utilized foremost in solid propellants and fuels for many years, and have been shown to dramatically increase combustion enthalpies and quality. Aluminium is used due to its low cost, high combustion enthalpy, high thermal conductivity, excellent surface absorption, and low melting and ignition temperatures

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There are many materials that have generated interest in regards to their applications as energetic materials. Aluminium and magnesium have been used as energetic additives to chemical rockets, mostly solid propellants, while boron has been used for air breathing (jet engine) applications such as in ramjets. When considering energetic additives, there are many factors that determine which material to use. In existing metalized propellants, aluminium is the leading additive used in combustion systems due to its unique combination of low cost, commercial availability, and heat of combustion. As a result, the primary focus of this work is on aluminium ignition and combustion.

Nanoscale energetic materials, due to their surface area and unique thermal properties, are known to exhibit many advantages over conventional micron sized particles. New combustion regimes are being reported that have significant practical applications. There has been a good amount of research on micron-sized aluminium combustion, as recently reviewed by *Beckstead*. However, for nanoscale aluminium combustion, there currently has been considerable debate over the mechanism of nanoparticle ignition, and the exact conditions under which the particle burns. Similar to very fine coal particles, nanoscale aluminium has the ability to burn on its surface. Nano aluminium synthesis and combustion have been reviewed and describe the first nano aluminium applications being explored [9, 12, 14, 18]; however, there have been recent advances that deserve attention.

Other considerations for nanoscale additives are presence of an ambient metal oxide layer, which is significant in determining the fuel additive energy potential. Depending on the metal and layer thickness, the enthalpy of combustion and combustion rate may be decreased, or oxidation may be inhibited altogether. For nanoparticle diameters of 20 nm or less, the oxide layer becomes a more prominent part of the particle volume, accounting for approximately 6D100 energy loss per volume (26). Therefore, it is expected that nanoparticles release more energy when taken as a whole, due to more complete combustion; however, there may be a lower limit of the particle diameter on the energetic enhancement of nanoparticles. As a result, to prevent any oxidation, the metal must be first be synthesized and then stored in an inert atmosphere, such as argon. Furthermore, post-processing techniques can selectively coat the outer layer with another material altogether, such as with organic self-assembled monolayers (SAMs). For example, a recent study investigated alkyl-substituted epoxide capping on the surface of aluminium, and determined that the particles were effectively passivated, but were no longer pyrophoric [26]. Nonetheless, the development of surface modifying and synthesis techniques needs to be considered when utilizing nanoscale materials. As will be described more, these unique configurations of increased surface to volume ratio, temperature uniformity, melting point depression, and oxide layers have many practical applications in nanoenergetic materials. An increase in surface area can lead to increased chemical reactivity, allowing more fuel to be in contact with the oxidizer. For instance, catalytic activity is essentially a surface area phenomenon, and the active surface at which the reaction takes place is increased when the surface to volume ratio is increased.

In gaseous micron aluminium combustion, the ignition event is typically associated with melting or cracking of the ambient oxide layer at approximately 2350 K (2070 ºC), that protects the metal. In the case of cracking, the particle is first heated up, and the core aluminium melts to form liquid aluminium. Liquid aluminium has a density of 2.4 (g/cm3) and solid aluminium has a density of 2.7 (g/cm3), therefore there is an approximate 1N2 volumetric expansion of the core, leading to cracking [68]. Ignition is then initiated on the exposed aluminium with a heterogeneous surface reaction, the interior metal begins to evaporate and diffuse towards the surrounding oxidizer, and the product aluminium oxides (primarily ALO) condense as an oxide cap (Al2O3) on the particle.

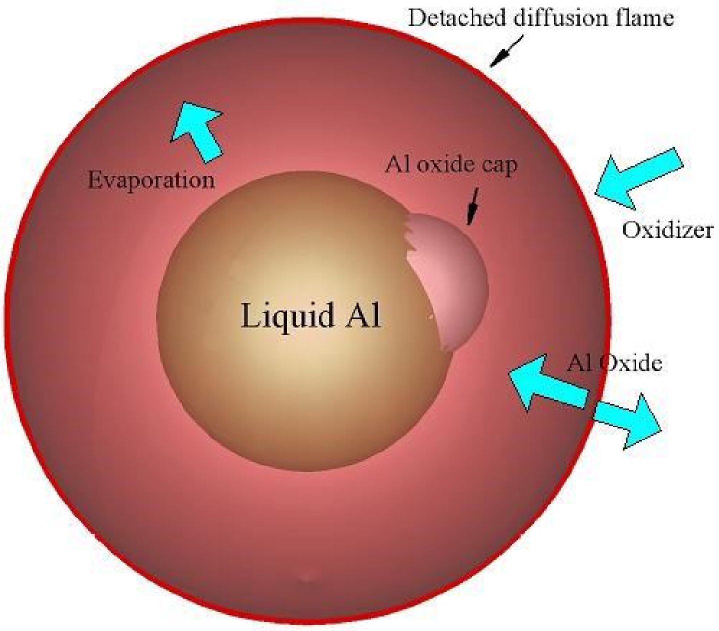

Fig 2.2 . Aluminium vapor phase particle combustion [19, 20, 24]

In nanoscale aluminium combustion, the conditions at which particles combustion takes place and the cause of ignition are still unclear. Due to limited information on the burning of nanoparticles, there is no current suitable model

Rai et al. [37] proposed that aluminium nanoparticle oxidation occurs in two distinct regimes. At temperatures below the melting point of aluminium, a slow oxidation occurs with oxygen-limited diffusion through the aluminium oxide shell. At temperatures above the melting point of aluminium, a fast oxidation occurs with both aluminium and oxygen diffusing through the oxide shell, followed by a hollowing of the aluminium core [37] at temperatures above 1000 °C. In the case of oxidation through the shell, it is a surface phenomenon with transport of reactants through the oxide shell, as shown in Fig. 2.2.

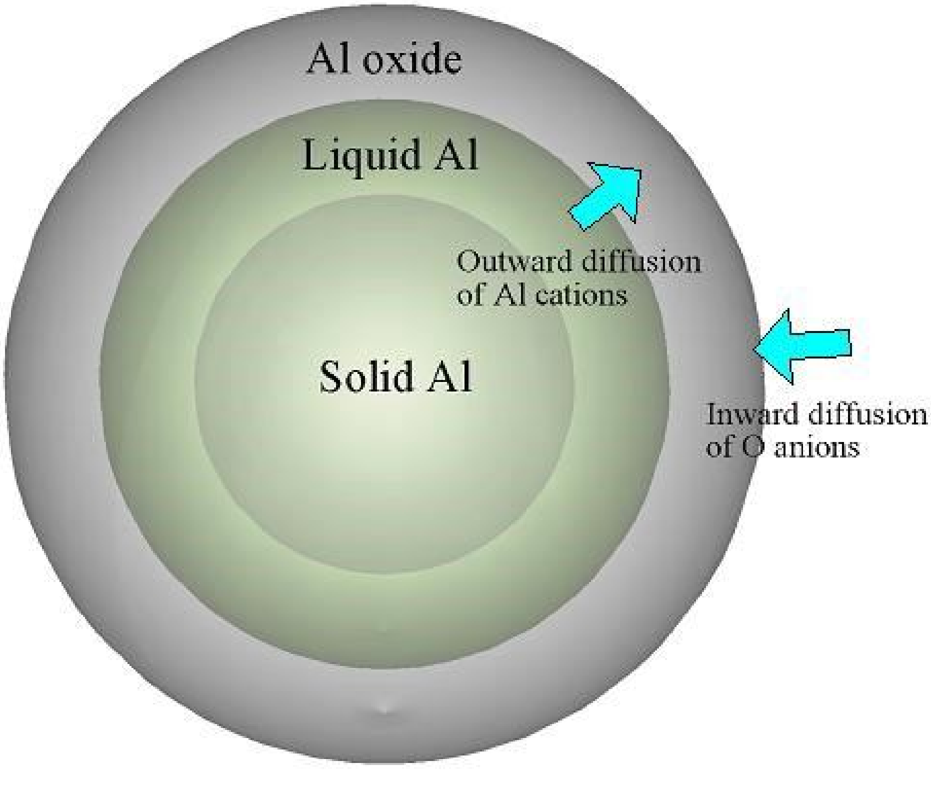

Fig. 2.3 Nanoscale aluminium heterogeneous surface combustion, where the surface is between Liquid Al and Al oxide [22].

2.4 NANOENERGETIC APPLICATIONS

There are many practical applications to nanoenergetic additives that have attracted worldwide attention and given rise to new fuel formulations. Because aluminium has been the most applied and experimented metal additive, the focus of this section will be on aluminium. With recent advancements in nanoscale aluminium production techniques, there has been renewed interest in metal particle combustion and their energetic applications. Presently, there are relatively few practical applications are taking advantage of nanoparticles ignition and combustion enhancements, and this opens up a large window of opportunity for the research of new viable energetic fuels and their future applications of nanoscale additives, including as advanced weapons, combustion synthesis materials, and propellant enhancers [25]. Due to the relatively limited studies involving nanoenergetics suspended in liquid fuels, other currently applied formulations such as condensed metal reactions and solid-based composite fuel applications are also reviewed.

Originally proposed for micron particles, un passivated aluminium and steam (H2O) can react to produce hydrogen, with three possible reactions [22],

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2$$

$$2Al + 4H_2O = 2AlO(OH) + 3H_2$$

$$2Al + 3H_2O = Al_2O_3 + 3H_2$$

By carrying and reacting in-situ hydrogen from an Al/H2O mixture, as opposed to 21 carrying cryogenic hydrogen along with a fuel delivery system [23], this offers new capabilities to make H2 on demand without storage or transport of hydrogen. This has great interest to offer more non-toxic alternatives to the currently deployed hydrazine propellants and in underwater propulsion applications, where the oxidizer does not need to be carried on board the vehicle. Building upon this research, latest fuel research with nano aluminium and frozen water (ice) composites, offer increased handling and safety to the fuel.

2.5. NANOFUELS

In contrast with solid propellants, gelled and liquid propellants can be throttled in the engine, allowing longer range flight missions than SRM powered vehicles. Recent attention has focused on nanoenergetic additives dispersed in liquid fuels, which offer numerous capabilities and advantages to liquid fuel combustion. However, thus far there have been relatively few advances in the ignition of colloidal suspensions. In addition, there may be combustion instabilities in both liquid-fuelled and solid-fuelled systems due to unsteady acoustical waves in the combustion chamber. These traveling waves can result in high-frequency, or screech oscillations, can result in pressure variations that can sometimes result in catastrophic motor failure. Agglomerated metal particles have also been shown to dampen acoustic vibrations that may lead to these combustion instabilities. The magnitude is dependent on the mass fraction of particles in the chamber, and generally, larger particles have the ability to damp lower frequencies, while smaller particles can damp out higher frequencies [7, 9]. It may be interesting to see what applications nanoparticle additives have to offer in this area. Recent attention has focused on the potential large scale implementation of nanoparticles as viable secondary energy carriers [15]. This concept proposes that pure nanoenergetic materials or suspensions of nanoenergetic materials in a liquid medium can be controllably ignited to provide a secondary release of thermal energy.

2.5. SUMMARY

There has been a considerable amount of research on the combustion of micron and nanoscale aluminium metal. As expected, the current costs of implementation may be an obstacle; however, further development in this area is expected to make these additives more available and affordable in the near future. Nonetheless, a fundamental understanding of micron and nanoscale aluminium combustion is critical to the design and implementation of practical propulsion systems that use aluminium additives. Nanocomposites, solid-based, gelled, and liquid fuels all have demonstrated available benefits to nanoparticle additives. However, relatively little investigative work has been performed on nanofluids. More experiments on the feasibility of these fuels, especially the combustion of nanofluid fuels, are needed to explore novel applications of nanoparticles.

Concluding from the literature review, a variety of nano energetic materials are present in the market, which can act as a secondary energy carrier and can be put to use as a viable fuel to propel the diesel engines. Now from the economic point of view and as well as the rapidly growing pollution, such material needs to be chosen which have very less or no contribution to pollution. So, here alumina is chosen as the desired nano energetic material, which can be put to use to enhance the performance and as well as to reduce the emission levels coming after burning of diesel fuels.In this thesis, the use of commonly available alumina is prompted. An experimental study for preparation & characterisation of nano alumina is carried out to prepare the desired nano particles using the solid state reaction in a controlled temperature conditions.

CHAPTER THREE

EXPERIMENTAL PROCEDURES

3.1 INTRODUCTION

The experimental method involves the production, characterisation and the engine testing of the samples thus prepared in the laboratory. Each section is discussed separately for the better understanding of the behaviour of the nano particles at various conditions. The first section involves the preparation of the nano particles. The second part discusses the preparation of nano fuel by adding the nano particles into the diesel fuel and to stabilise it. Last section deals with the engine testing part and the tools ad methods implied in following up the experimental procedure.

Solid state reaction is used in making the nano sized alumina particles. The reaction involved is as

$$\mathrm{Al(NO3)3 + C(OH)(COOH)(CH2COOH)2 = n\ (Al_2O_3) + NO_2}$$

Based upon this reaction aluminium nanoparticles are being prepared experimentally.
The experimental setup involved in the making of alumina nanoparticles involved a micro processor based furnace, which help in determining the required temperature range for the reaction to proceed. The reaction being an endothermic reaction requires external heat for the reaction to proceed. In the reaction approximately 450 degree Celsius temperature is required for the completion of the reaction. The furnace is fed with 3 different gases, used for providing the sufficient amount of air for combustion, among these gases; one is acting as a fuel and getting consumed and the other being the oxidiser for the same. While the third being an inert gas, which simultaneously assist in the proper functioning of the apparatus used.

Plate 1 shows the micro processor controlled furnace.

Plate 1 Micro- processor Controlled Furnace (NST_DTU)

3.2.EXPERIMENTAL SET UP FOR PREPARATION OF NANO PARTICLES

Firstly all the reactants involved in making of the alumina nano particles are thoroughly mixed together after taking the proper measured values of the aluminium nitrate and the citric acid solution. If needed some distilled water ca be put to use for the mixing of the particles. Once they form a uniform mixture, the reactants are put in a crucible and finally inserted into the micro processor based furnace from the inlet end. It is then heated in temperature increments of 50^0 Celcius. When it reaches 400^0 Celcius, the reactants finally start showing up signs of completion of reaction and at a temperature of 450^0 C, brown colored fumes starts coming out from the exhaust side of the furnace. This marks up the completion of the reaction. The crucible is then taken out with the help of tongs and the sample is then made to cool to room temperature conditions.

Plate 2 Micro Controller Furnace

Plate 3 Cylinders connected to the furnace which assists in heating of reactants

Plate 4 Gas Cylinder Controllers

The chemicals which are being used for making the nanoparticles are as aluminium nitrate, citric acid, acetone, distilled water, D2O etc. Following pictures show the major chemical which are being used in the making of the desired nano aluminium particles.

All the chemicals used were of analytical grade and need not to be required for further purification to be used further in the making of the desired nano particles. Further equipments such as test tubes, silver foils, scrapper, crucibles, baking tube are also used for further carrying out the experimental work.

Chemicals are, tested for the corrected weights of the reactants to be used further in the furnace. Chemicals are properly mixed with each other and some distilled water is poured into it, to make the mixture in a paste form , so as to ensure proper heating of the reagents while put into the micro controller based furnace.

Plate 5 Weighing machine used for checking weights of various samples

Chemicals used for making of Aluminium in the lab for the making of the desired nano aluminium particles are shown below

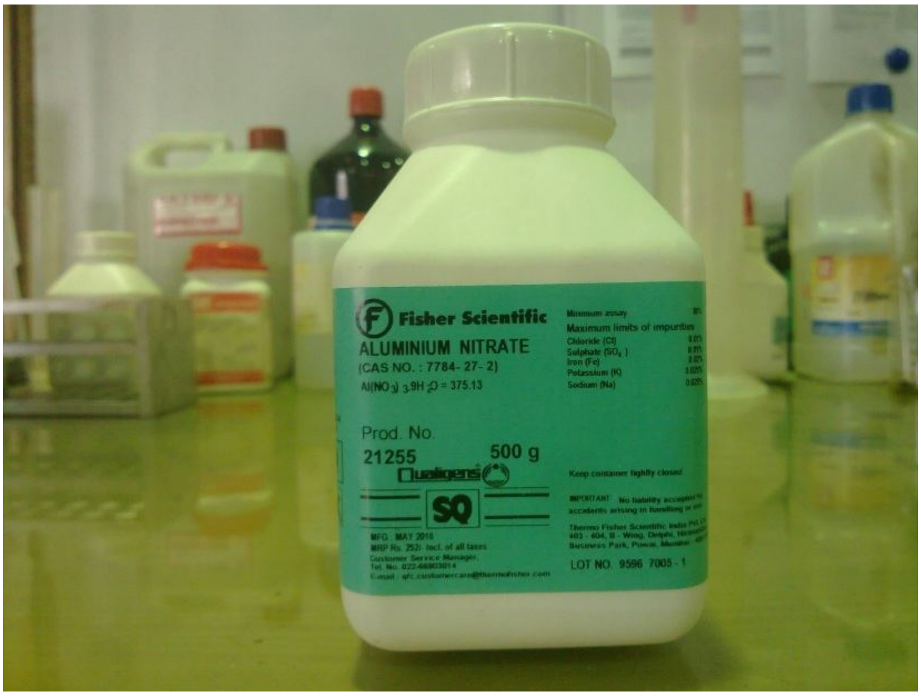

Plate 6 Aluminium Nitrate (Hydrous)

Plate 7 Citric Acid Anhydrous

3.3. PREPARATION OF NANO PARTICLES

The making of nano aluminium particles involves a controlled heating of the mixture of aluminium nitrate and citric acid in a microprocessor controller furnace upto a temperature of approximately 450 ^{O}C.

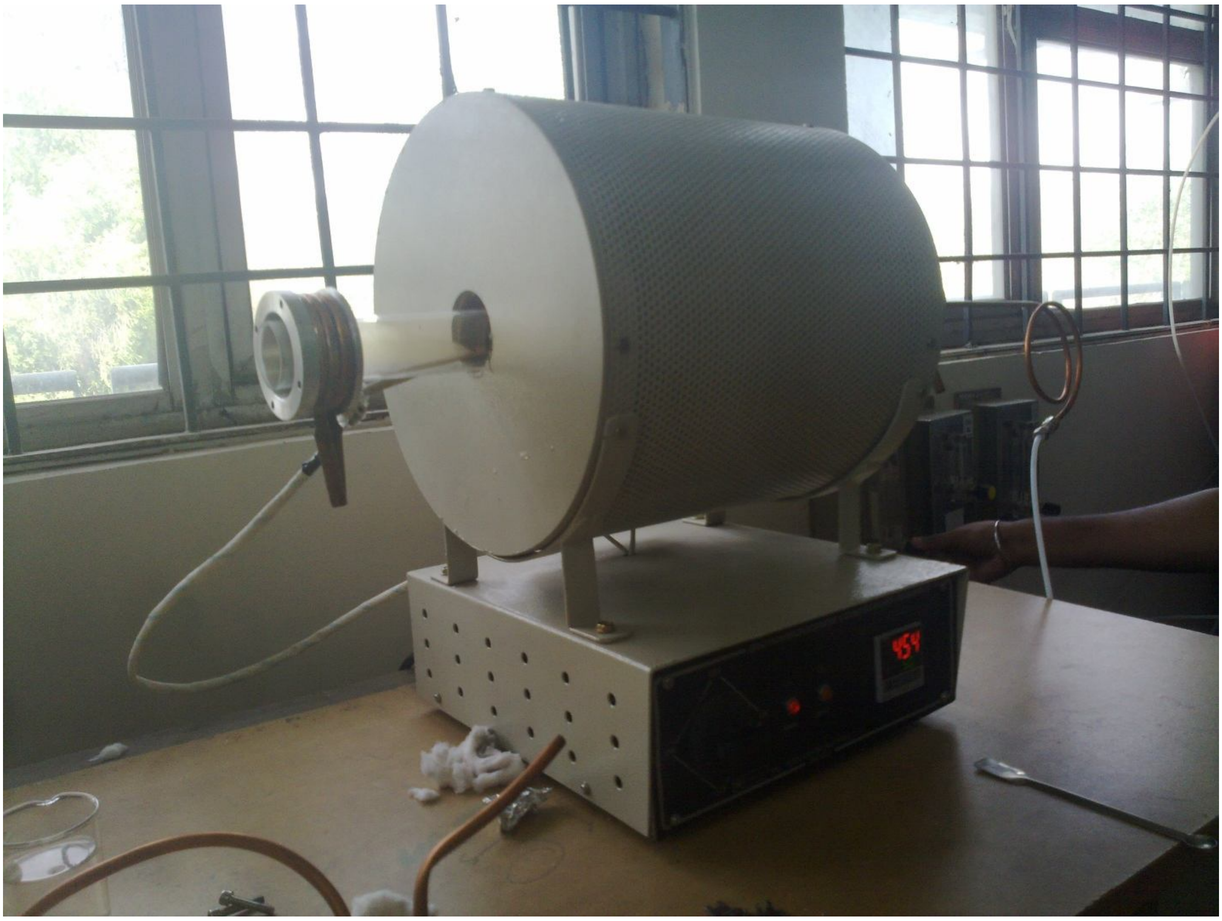

Plate 8 Micro Controller Furnace Showing readings towards completion of reaction

At the temperature of 454 degree Celsius, NO2 fumes of brown colour were reported at the left edge of the glass tube, showing the completion of the reaction. Special care must be taken while this reaction is taking place, especially about the nitrogen dioxide gas which is being produced towards the completion of the reaction, which is a laughing gas and can produce serious effects on the temperament of the people surrounding it.

The furnace being used here is a furnace giving control over the temperature range of up to 1000 degree Celsius. Temperature coming into the range can be easily regulated by this furnace.

Plate 9 Micro Processor Controlled Furnace Inlet section

The appearance of brown colored fumes of NO_2 , acts as a marker towards finalisation of the reaction. Special care must be taken while the reaction is coming towards the completion as the Nitrogen Dioxide gas which is produced during the reaction has a great hallucinating effect on human beings. Also , special care must be taken while dealing with the various types of nano energetic materials which are being made in the lab using the furnace. As these are the secondary energy carriers , hence the reactions can be highly exothermic at times , hence the experiment needs to be performed within the given conditions range.

Plate 10 Inlet end of the Furnace showing the end products of the reaction

The appearance of brown colored smoke shows the NO_2 gas coming out towards the finishing of the reaction. Plate 10 shows the nano alumina particles obtained from the reaction.

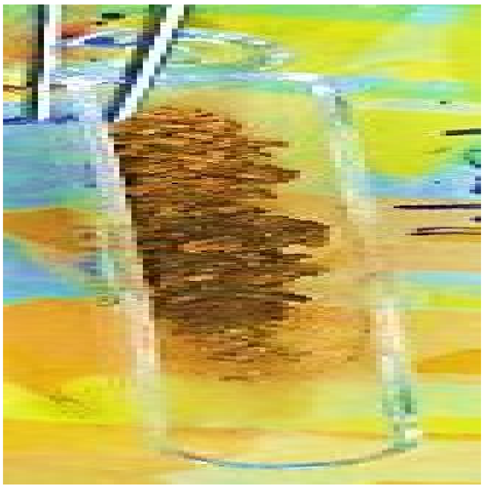

Plate 11 Alumina nano particles

Plate 12 Alumina Nano particles during grinding

A novel sol-gel approach has proven successful in preparing nanostructured metals or their oxides. By introducing a fuel metal, such as aluminium, into the nanostructured metal oxide matrix, energetic materials based on thermite reactions can be fabricated. Furthermore, organic additives can also be easily introduced into the nano composites for the production of nanostructured gas generators. The resulting nanoscale distribution of all the ingredients displays energetic properties not seen in its micro-scale counterparts due to the expected increase of mass transport rates between the reactants. The unique synthesis methodology, formulations, and performance of these materials will be presented. These energetic Nano composites have the potential for releasing controlled amounts of energy at a controlled rate. Due to the versatility of the synthesis method, a large number of compositions and physical properties can be achieved, resulting in energetic nanoparticles that can be fabricated to meet specific safety and environmental considerations.

3.4. PREPARATION OF NANOFUEL

After mechanical grinding has been done for around half an hour the desired nano alumina particles are produced. After grinding, the nanoparticles are then mixed with any base fluid, usually an energy producing fluid like diesel or kerosene etc. The nano alumina thus produced after passing through a series of processes and reactions is poured into the diesel fuel and mixed thoroughly into it with the help of a stirrer. The stirrer is made to run at above 5000rpm rate for the thorough mixing of the nano particles into the diesel fuel.Now for dispersion there are a variety of methods stated as below.

There are currently two methods available to disperse nanoparticles in the base fluid:

- **Two step technique**
- **Single step technique**

In current experimental study the two step technique is used for the dispersion, firstly the nanoparticles are made and then they are then dispersed into the base fluid. Now to disperse the alumina nano particles into the diesel fuel an ultrasonic vibrator was used. The results obtained were satisfactory as it finally resulted into a stable suspension of the particles in the base fluid. The sample stability was checked and the results obtained were adequate. Yet some more work is required to be done in regards of the sample stability of higher concentration blends.

Plate 13 Showing the stable suspension of alumina nano particles in the diesel fuel

Dispersion experiments show that stable suspensions of oxide and metallic nanoparticles can be achieved in the common base fluids.

3.5. METHODS OF STABILISATION

The methods of stabilisation include a variety of methods for the stability of the nano particles. The most common methods used in the stability experiments include changing the pH value of the nanofluid, using dispersants and by using ultrasonic vibration

Ultrasonic vibration which has been relatively successful in eliminating agglomerated nanoparticles.

In the current study an ultrasonic vibrator was used for dispersing the nano particles into the base fluid i.e. the Diesel fuel. The samples were checked for stability for few days and the results obtained were satisfactory.

3.6 PHYSICO-CHEMICAL PROPERTIES:-

3.6.1 DENSITY AND SPECIFIC GRAVITY:-

Density of a fluid may be defined as the mass per unit volume of the fluid at the given conditions. There are a number of instruments available which can be used for the determination of density and specific gravity of various fuel sample made. This investigation uses DMA 4500 Anton Paar density meter to determine the density and specific gravity of the fuel samples thus prepared. The measurement is based on the proven oscillating U-tube principle ensuring highly accurate density values. The determination of density is carried out at room temperature. The density of the nano fluid samples were measured and then compared with that of the diesel fuel.

Plate 14 DMA 4500 ME density measuring

3.6.2 KINEMATIC VISCOSITY:-

Viscosity is the measure of the resistance of a fluid is being induced by either shear stress or tensile stress. Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. The viscosity of the fuel affects atomisation and fuel delivery rates. It is an important property because if it is too low or too high then atomisation and mixing of air and fuel in combustion chamber gets affected. The different samples are prepared and are investigated for viscosity at room temperature using a kinematic viscometer as per the specification given in ASTM D445. A suitable capillary tube was selected, and then a measured quantity of sample was allowed to flow through the capillary. Efflux time was measured for calculating Kinematic Viscosity using the formula given below.

The kinematic viscosity of different fuel blends can be calculated as:

$$V = k \times t$$

Where,

V= kinematic viscosity of sample;

k = constant for viscometer;

t = time taken by the fluid to flow through capillary tube

Plate 15 Petrotest viscobath viscometer

3.6.3 CALORIFIC VALUE

Calorific value of a fuel is defined in terms of the number of heat units liberated when unit mass of fuel is completely burnt in a calorimeter under specified conditions. Higher calorific value of the fuel is the total heat liberated in KJ per Kg or $m^{3.}$ To measure the calorific value of the various samples, numerous calorimeters are available in the market. In general higher is the calorific value of fuel; better is the performance of fuel sample in internal combustion engine. The calorific value of various fuel samples in this investigation is calculated using Parr 6100 Bomb Calorimeter. It is an oxygen bomb calorimeter used to measure the higher calorific value of the fuel as per the specification given in ASTM D240. The combustion of fuel takes place at constant volume in a totally enclosed vessel in the presence of oxygen. The sample of fuel was ignited electrically. The bomb calorimeter used for determination of calorific value is shown in Plate 3.5

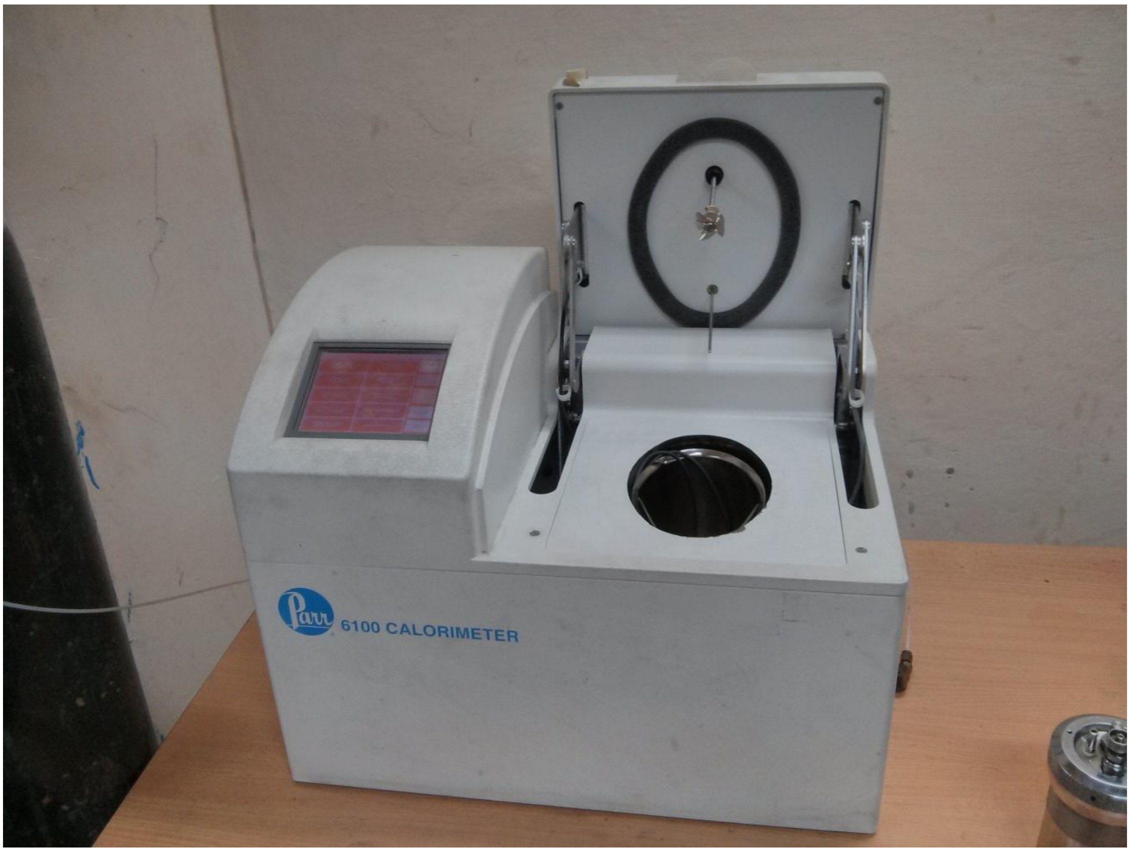

Plate 16 Parr 6100 calorimeter

3.7 ENGINE SELECTION

Diesel engines play an important role in transportation , agriculture and household power generation in India. Because of the increasing fuel consumption rate especially in the transportation and agriculture sector, India is going to face a severe crisis in future. The diesel engine continues to dominate the agriculture sector in our country in comparison to spark ignititon engine and always has been preferred widely because of its power developed, specific fuel consumption and durability. A thorough description of combustion mechanism in diesel engine is beyond the scope of this study. However it would be worth while to inform that the fuel is burnt in diesel engine by self ignition at higher temperature and pressure conditions of the order of 600 degree celcius and 40 bar pressure respectively. In India, almost all irrigation pump sets, tractors, mechanised farm machinery and heavy transportation vehicles are powered by direct injection diesel engines. Keeping the specific features of diesel engine in mind, a typical engine system , which is actually used widely in the Indian Agriculture Sector, has been selected for the present experimental investigation.

Plate 17 Kirloskar DAF 8 Diesel Engine

3.8 DEVELOPMENT OF AN EXPERIMENTAL TEST RIG

In the present investigation, the trials were conducted on a four stroke, vertical, naturally aspirated, single cylinder, air cooled, direct injection diesel engine which is primarily used in India for agricultural activities and household electricity generation and in small scale industrial applications. It was a Kirloskar make single cylinder, air cooled, direct injection, DAF 8 Model diesel engine. The engine is connected to an electric alternator which is used to produce electric current. This current thus produced is given to the electric loads. The engine can be hand started using decompression lever and is provided with centrifugal speed governor. The cylinder is made of cast iron and fitted with a hardened high-phosphorus cast iron liner. The lubrication system used in this engine is of wet sump type, and oil is delivered to the crankshaft and the big end by means of a pump mounted on the front cover of the engine and driven from the crankshaft. The inlet and exhaust valves are operated by an overhead camshaft driven from the crankshaft through two pairs of bevel gears. The fuel pump is driven from the end of camshaft. The detailed technical specifications of the engine are given in Table 3.3.

Table 3.3 Engine Specification

Kirloskar DAF 8 Diesel Engine	
Rated Brake Power (bhp/kW)	8/5.9
Rated Speed (rpm)	1500
Number of Cylinder	One
Bore X Stroke	95 X 110
Compression Ratio	17.5:1
Cooling System	Air Cooled
Lubrication System	Forced Feed
Cubic Capacity	0.78 Lit
Inlet Valve Open (Degree)	4.5 BTDC
Inlet Valve Closed (Degree)	35.5 ABDC
Exhaust Valve Open (Degree)	35.5 BBDC
Exhaust Valve Closed (Degree)	4.5 ATDC
Fuel Injection Timing (Degree)	26.0 BTDC

For conducting the desired set of experiments and together required data from the engine, it is essential to get the various instruments mounted at the appropriate location on the experimental setup.

The schematic diagram of the experimental setup is shown in Figure 3.3.

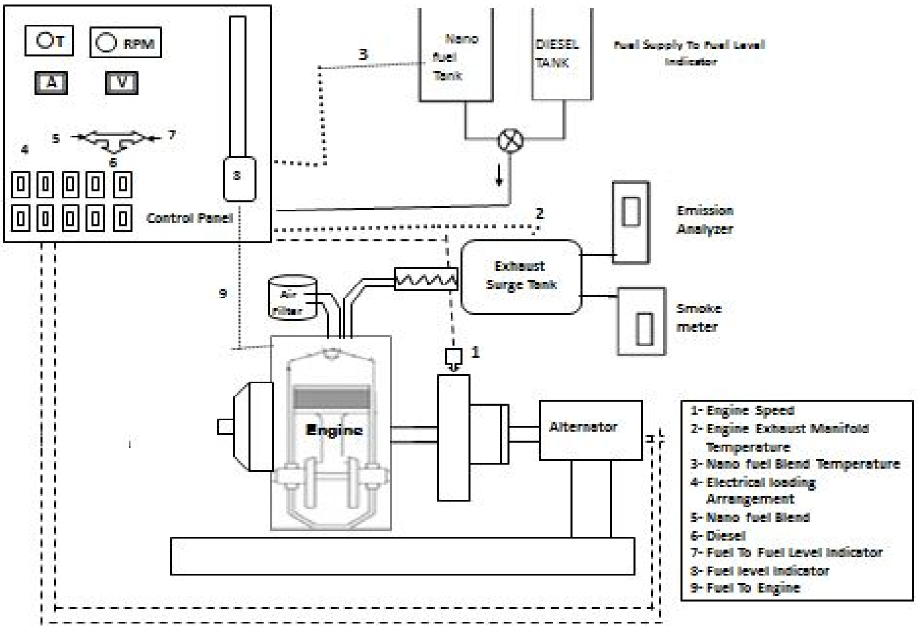

Fig 3.3. Schematic Diagram of the Experimental Set Up Test Rig

This test was carried out only after the preliminary run. After stable operating conditions were experimentally achieved, the engine was subjected to similar loading conditions. Starting from no load, observations were recorded at 20%, 40%, 60%, 80% and 100% of the rated load.

The Brake Specific Energy Consumption was calculated by using the relationship given below:

$$\mathrm{BSEC} = (\mathrm{Vcc} \times \ell \times 3600) / (\mathrm{hp} \times t) \tag{1}$$

Where,

BSEC = Brake Specific Energy Consumption, g/kW-h

Vcc = Volume of fuel consumed, cc

ℓ = Density of fuel, g/cc

hp = Brake horsepower, kW

t = Time taken to consume, cc of fuel, sec.

The brake thermal efficiency of the engine on different fuel blends at different operating conditions was determined using the equation as given below:

$$\eta_{th} = Ks / (HV \times BSEC) \quad (2)$$

Where,

η_{th} = Brake thermal efficiency, %

Ks = Unit constant, 3600

HV = Gross heat of combustion, kJ/kg

BSEC = Brake Specific Energy Consumption, g/kW-h

3.9 Control Panel Installation:

After developing the test rig the control panel is made and is connected to the engine. The control panel is mounted with ammeter, voltmeter, rpm indicator, temperature indicator switches, MCB, fuel lines, burette, electrical loads and control valves as shown in the plates.

Plate 18 Control panel meters

Two fuel tanks are also mounted at the back of the test rig at the highest position so as to provide a smooth and regular supply of fuel viz the diesel fuel or the nano fuel samples. The valves mounted at the control panels helps to regulate the fuel selection between the two tanks. Electrical load banks, i.e., 12 bulbs each of 500 watts, were mounted on the rear side of the control panel which is shown in Plate and their switches provided on the front side of the control panel.

Plate 20 Control panel for the experimental setup

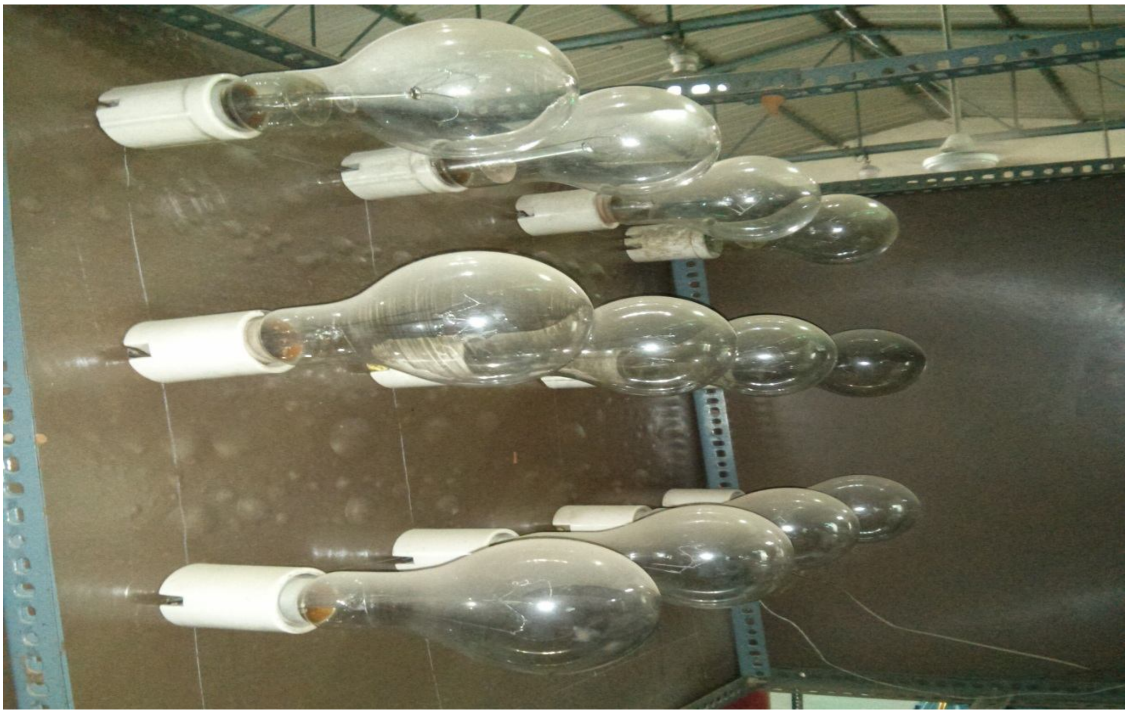

Plate 21 Load Bank for the Experimental Setup

Plate 22 Load Bank Switches mounted on the front of control panel

One burette with stop cocks and two way valves were also mounted on the front side of the panel for fuel flow measurements and selecting between either diesel fuel or nano fuel blend.

Plate 23 Fuel selector Valve (Two way Valve)

3.10 Exhaust Emission Analysis

The major pollutants appearing in the exhaust of a diesel engine are the oxides of nitrogen. Engine emission parameters like HC, NOx, CO etc. were recorded using AVL Di gas analyzer. Measurement of engine smoke was carried out using AVL 437 smoke meter. All the instruments used in the test rig were of standard quality and the error within the permissible range. The details of test rig instrumentation are shown in table 4.The engine trial was conducted as specified in IS: 10,000.

Table 3.4[Test rig specification]

S.N	Instrument Name	Range	Accuracy	Measurement Technique	Percentage Uncertainty
	AVL DIGAS Analyser				
1	Carbon Monoxide	0 – 10 % Vol.	±N1	Non dispersive infra-red sensor	±1
2	Hydrocarbons	0 – 20.000 ppm Vol.	±20 ppm	Flame ionization detector-FID	±0.20
3	Oxides of Nitrogen	0-10,000 Ppm	±10 ppm	Chemi-luminescence principle, electro chemical sensor	±0.20
	AVL SMOKE METER	**0 - 10D100**	**±1 %**	**Hatridge principle**	± 1

Plate 24 Smoke meter

Plate 25 AVL DIGAS ANALYSER

3.11 RPM Measurement of the Engine

A digital Tachometer of MTC company is used to measuring the rpm of the engine. The tachometer was mounted on a bracket near the flywheel at a distance less than 5 mm. And the display of the tachometer was mounted on the control panel board.

Plate 26 Digital Tachometer used for rpm measurement

3.12 PARAMETERS SELECTION

The selection of appropriate operating parameters is an utmost requirement for engine calculations. Hence the required parameters were selected astutely. Following are the main parameters desired from the engine testing.

1. Power produced by the engine
2. Fuel consumption
3. Temperature
4. Speed of engine
5. Engine Speed(rpm)

And now to calculate the above parameters, following readings were noted from the control panel of the test bench.

1. Voltage generated by the alternator
2. Current generated by the alternator
3. RPM of the engine
4. Exhaust gas temperature

5. Fuel consumption rate
6. AVL smoke meter readings
7. AVL DIGAS Analyzer readings

3.13 EXPERIMENTAL PROCEDURE

The engine was started using neat diesel at no load and allowed to attain stability for at least 30minutes before taking observations. After engine conditions stabilized and reached to steady state, the base line data were taken. Now with the help of fuel measuring burette and the stop watch the time taken by the engine for the consumption of 20cc of fuel was measured. In the similar manner the time elapsed for various loads for diesel and then the alumina blended nanofuel was measured. Power developed, current, voltage, exhaust temperature, rpm of the engine and the various emission related parameters were also measured. Short term performance tests were carried out diesel fuel and then comparative tests were followed up using the alumina blended fuel. All the performance and emission characteristics were noted upon and an extensive comparison of the related parameters was carried out.

CHAPTER FOUR

RESULTS & DISCUSSIONS

4.1 INTRODUCTION

An experimental investigation was carried out to study the effect of nano additives in combustion enhancement as well as to study the various performance and emission characteristics of the various blends. The present study was done on an unmodified diesel engine which was converted to run on a dual mode of operation.

4.2 STABILITY OF BLENDS

The various blends formed in the lab are examined over three month’s time and no significant changes were observed. The blends formed are stable and homogenous in their composition. No separation or sedimentation of the alumina nanoparticles in diesel fuel was observed. Visual inspection and centrifuge tests were used to determine the stability of blends.

4.3 PERFORMANCE CHARACTERISTICS

The performance characteristics of the test engine on Diesel and Alumina nano particles blended diesel fuel are summarised as belows.

4.3.1 BRAKE THERMAL EFFICIENCY (BTE)

The variation of brake thermal efficiency of the engine for the various test fuels with respect to BMEP is shown in figure 4.1 . From the figure, it is observed that the brake thermal efficency of the alumina nanoparticles blended diesel fuel is higher in comparison to that of the neat diesel fuel at all loads. Up to 20 % laod, variation in the brake thermal efficiency was insignficant but with increasing loads the blends started showing markable increase in the efficencies. For the 1 % and 2 % blends an increased brake thermal efficiency was noticed at all loads as in comparison to diesel with the highest value of 28.96 % with the 2 % blend. This could be possibly be attributed to better combustion characteristics of the nano particles such as higher surface area to volume ratio which inturn allows more amount of fuel to react with the air leading to an enhancement in the brake thermal efficency. The highest brake thermal efficiency was observed in case of 2 % blend of alumina nano particles. The maximum thermal efficiency for N1 , N2 , N3 & N4 were observed as 24.91 % , 28.96 % , 27.22 % & 25.61 % respectively whereas the peak thermal efficiency of the diesel was 24.02 %.

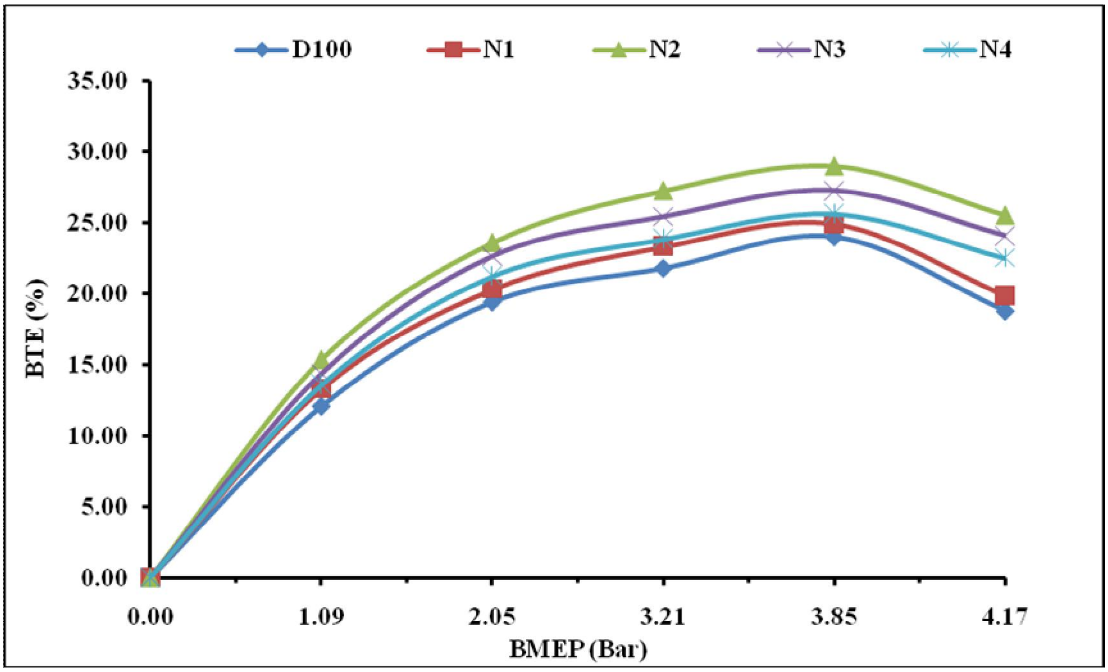

Fig 4.1 Variation of Brake Thermal Efficiency with respect to BMEP for various blends

4.3.2 BRAKE SPECIFIC ENERGY CONSUMPTION (BSEC)

Since the densities and calorific values of the various blends are significantly different from that of the diesel fuel , Brake Specific Fuel Consumption is not considered as a very reliable parameter to compare the performance of the different blends. Hence Brake Specific Energy Consumption was taken as a parameter to compare the energy requirement for producing unit power in case of various test fuels i.e. the different blends of alumina nano particles.

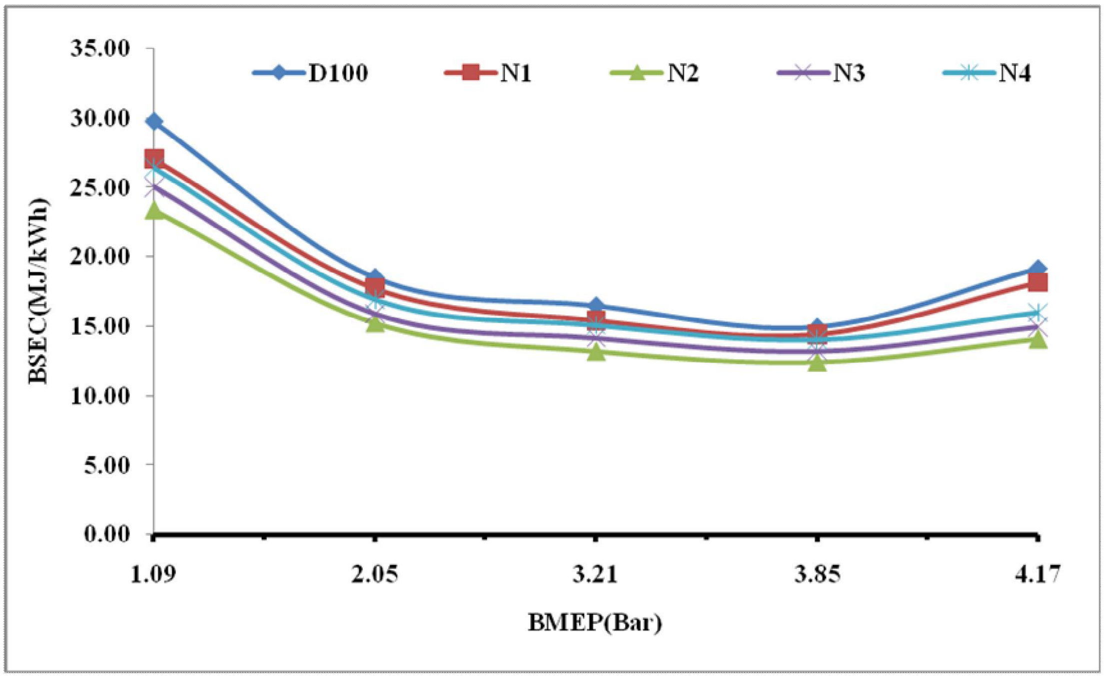

Fig 4.2 Variation of Brake Specific Energy Consumption with respect to BMEP of various blends

Brake Specific Energy Consumption is the ratio of mass of fuel consumed to the brake power. The variation in Brake Specific Energy Consumption for all test fuels is shown in Figure 4.2. There is a decreasing trend in the Brake Specific Energy Consumption with increase in the percentage of the alumina nano particles in the blends. Among the various samples tested the lowest BSEC was obtained with the 2 % alumina nano particle blend because of the lower fuel consumption rate. This could be possibly attributed to the presence of nanoparticles in the diesel fuel as it possesses enhanced surface area to volume ratio to ameliorate the catalytic effect and hence less fuel consumption in the unit volume of fuel during combustion in the engine. The highest BSEC was obtained with the neat diesel because of the higher fuel consumption rate. The lowest Brake Specific Energy Consumption observed is 14.12 MJ/kWh for 2 % alumina nanoparticle blend. At full load, the BSEC for the N1, N2, N3, N4 and neat diesel are 18.16 MJ/kWh, 14.12 MJ/kWh, 14.97 MJ/kWh, 16.02 MJ/kWh & 19.19 MJ/kWh respectively. The results are in consistence with the investigations made by J. Sadik Basha et. al.

4.3.3 EXHAUST TEMPERATURE

The variation in exhaust gas temperature of the engine with various fuels blends in reference with diesel fuel is shown in figure 4.3. The results show that the exhaust gas temperature increases with increase in brake power in all cases. The highest value of exhaust gas temperature of 465°C was observed in the neat diesel as in comparison to the different blends. Whereas a lowest exhaust gas temperature of 436°C is achieved with N2 alumina nanoparticle blend. In case of alumina nanoparticles blended diesel fuel the exhaust gas temperature is lower as compared to neat diesel because of the reduced ignition delay characteristics [15]. Hence due to shorten ignition delay less fuel is accumulated during the combustion which in turn leads to reduction in the exhaust gas temperature. Similar trends are observed in case of NO_x emissions reduction with the alumina nanoparticles blends in the diesel fuel. The corresponding values of the exhaust

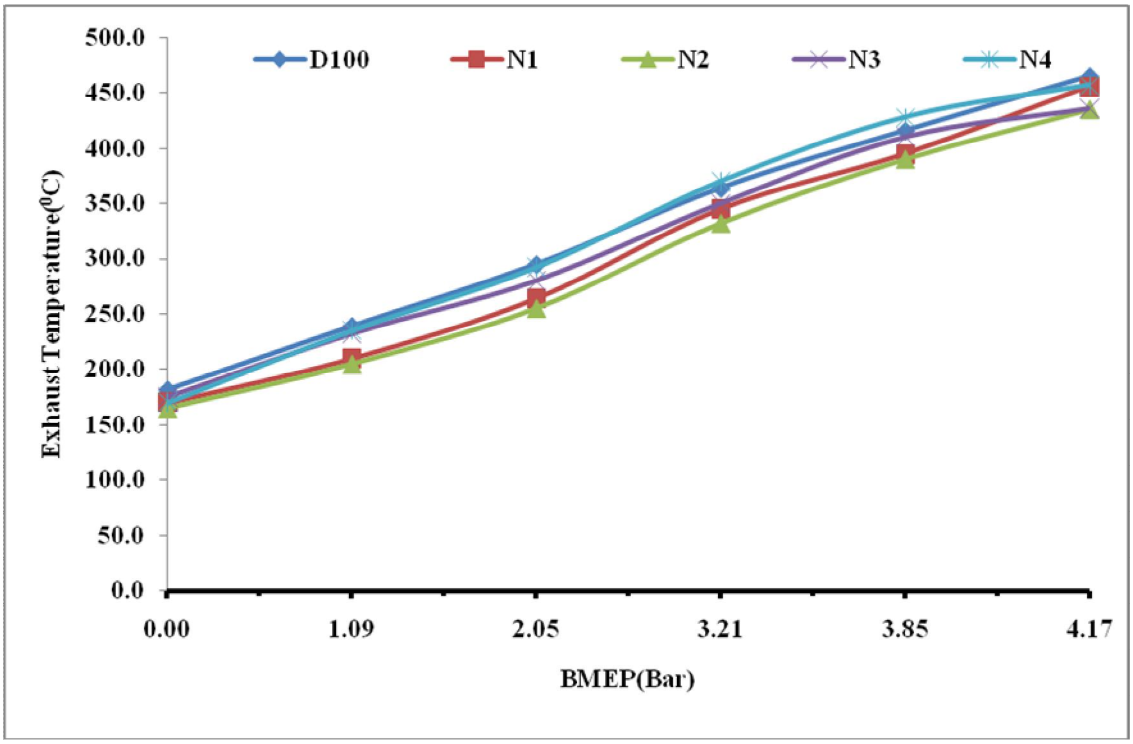

Fig 4.3 Variation in exhaust temperature of the engine with respect to BMEP for various blends

gas temperature of the D100, N1, N2, N3 & N4 alumina blends are 465^{o}C, 437^{o}C, 436^{o}C, 456^{o}C, 457^{o}C respectively.

4.4 EMISSION CHARACTERISICS

4.4.1 NO$_X$ EMISSIONS

The variation in NO$_X$ emission of the diesel engine with various fuel blends with reference to the diesel fuel are shown in figure 4.4. The NO$_X$ emissions increases with the increasing engine load, due to higher combustion temperature (Zeldovich thermal NO mechanism). This proves that the combustion temperature is the most important factor for the emission of NO$_X$ in the engine cylinder. However, in case of alumina nanoparticles blended diesel fuel the magnitude of NO$_X$ emissions is lower as compare to that of neat diesel fuel due to the reduced ignition delay characteristics [15]. Hence due to shorter ignition delay less fuel is accumulated during the combustion which in turn leads to reduction in NO$_X$ emissions. Similar trend was also observed in case of exhaust gas temperature for the nanoparticles blended diesel fuel compare to that of neat diesel as shown in figure 4.3.

The maximum reduction in NO$_X$ emissions is obtained with N2 alumina nanoparticle blended diesel fuel. The magnitude of NO$_X$ emissions observed are 788ppm, 720ppm, 650ppm, 764ppm and 667ppm for D100, N1, N2, N3 and N4 alumina nanoparticles blended diesel fuel at the full load respectively.

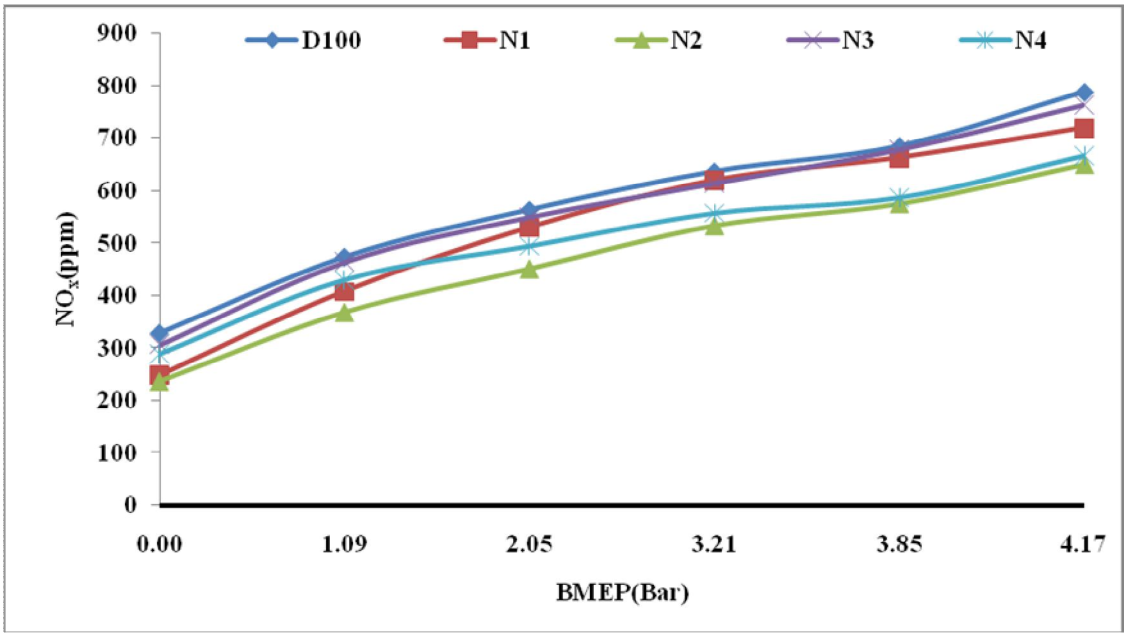

Figure 4.4: Variation of NO_X emissions with respect to BMEP for various blends

The result obtained from the experiment clearly show that using alumina nanoparticles blended diesel fuel results in reduction of NO_X emissions and these results are in agreement with Wang et.al and J.Sadhik Basha et.al

4.4.2 CO Emissions

Figure 4.5 shows the comparison of CO emissions for all the fuels at different engine loads. The magnitude of CO emissions for the alumina nanoparticles blended diesel fuel are marginally lower as compared to that of neat diesel fuel as shown in the figure. This could be probably because of the short ignition delay and improved ignition characteristics of alumina nanoparticles. The higher catalytic activity of the alumina nanoparticles is due to their higher surface to volume ratio and it enhances fuel air mixing in the combustion chamber respectively. It was found that at lower loads the variation in CO emissions was insignificant. However, at peak loads the CO emissions increase drastically. The minimum value of the CO emissions at full load is noted in N1 alumina nanoparticles blended diesel fuel with the value of 0.7ppm. The magnitude of CO emissions observed are 0.9ppm, 0.7ppm, 0.75ppm, 1.2ppm and 1.4ppm for D100, N1, N2, N3 and N4 alumina nanoparticles blended diesel fuel at the full load respectively.

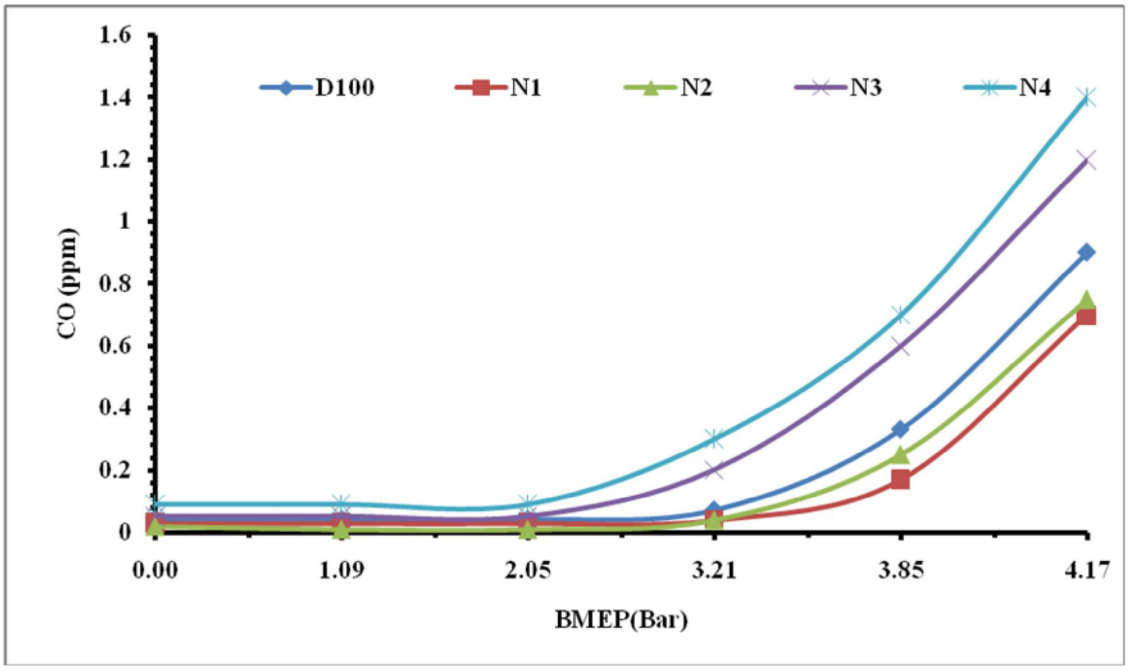

Figure 4.5 Variation of CO emissions with respect to BMEP for various blends.

4.4.3Hydro Carbon Emission (HC)

The variation of un burnt hydrocarbon (HC) emissions for diesel fuel and the nano alumina blended diesel fuel are shown in Figure 4.6. The HC emissions of all the fuels are lower in lower loads, but it increases as the engine load is made to increase. This is due to relatively less amount of oxygen fuel available for the reaction when more fuel is injected to the engine cylinder at higher engine loads. Figure 4.5 shows that the HC emissions of the nano alumina blended diesel fuel are bit higher as in comparison to the neat diesel fuel.

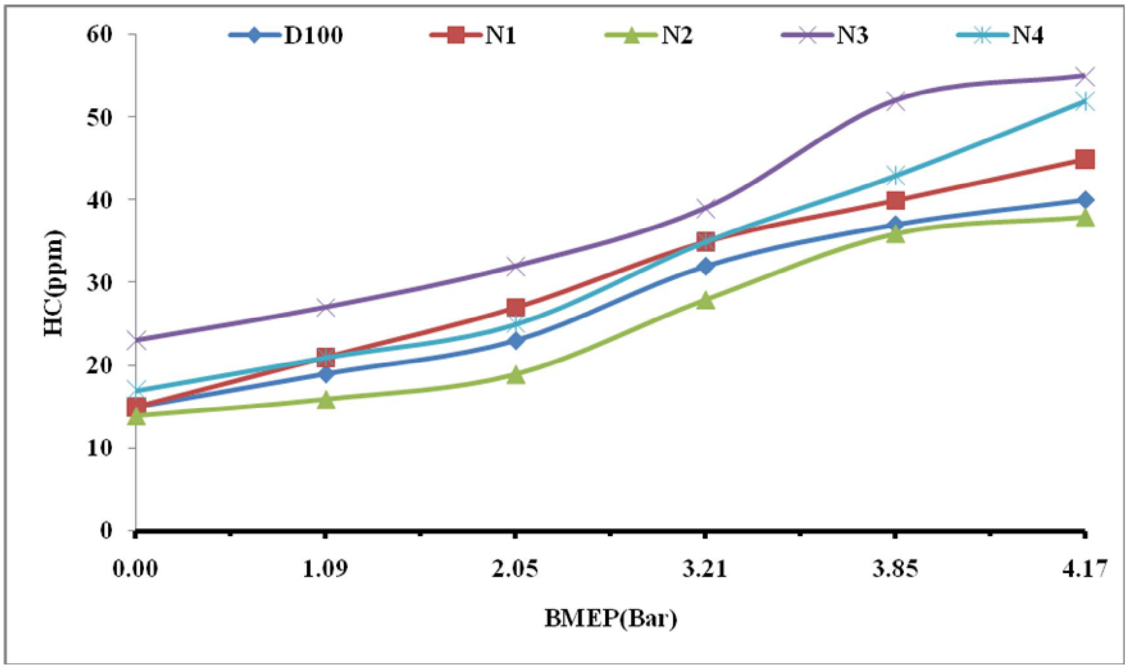

Fig 4.6 Variation of HC emissions with respect to BMEP for various blends

HC emissions are formed as an outcome of incomplete combustion that may occur due to lack of sufficient availability of air, in sufficient combustion duration and poor cetane rating of the fuel. In the present case a lower proportion of oxygen and as well as a lower cylinder temperature can be attributed as the major reason behind it. Insufficient combustion duration may be a plausible reason subjected to further investigation of the combustion phenomenon.

CHAPTER FIVE

CONCLUSION & CHALLANGES

5.1 CONCLUSION

In the present investigation, the trials were conducted on a four stroke, vertical, naturally aspirated, single cylinder, air cooled, direct injection diesel engine which is primarily used in India for agricultural activities and household electricity generation and in small scale industrial applications. The combustion, performance and emission tests of the alumina blended nano fuel were carried out for different blends of nano alumina in diesel fuel. The experimental results reveal that the engine performance is much better with the use of alumina nano particles blended fuel as is comparison to the neat diesel fuel. Further conclusions drawn from the experimental study can be enumerated as follows:

1. Alumina nano particles dispersed in the diesel fuel yield a stable suspension of the particles. However it needs to checked extensively for further domestic and commercial applications.
2. The brake thermal efficiency and the Brake Specific Energy Consumption of the alumina blended fuel are improved significantly showing much better results than diesel fuel.
3. The NO_X emissions and the CO emissions are reduced considerably at all loads conditions, which plays an important role in the overall emission reduction as compared to diesel fuel.
4. However, there was slight increment observed in the case of un burnt hydrocarbons in the emissions, which could be attributed to the lower cylinder temperature causing incomplete combustion of the fuel. The complete combustion behavior of the nano particles in the blended fuel is still required to be explored.

Finally it can be concluded that adding a particular quantity of aluminium nanofluid to diesel fuel not only reduces fuel consumption, but also improves the exhaust emission concentration from the diesel engine.

5.2 CHALLANGES

In general, nanofuels show many excellent properties promising for engineering application. But there are still several important issues that need to be solved for applications of nanofuels in engineering.

1. Although many nanofuel systems have been prepared, nanofuels systems that can meet practical engineering requirement have not been developed.
2. The long term stability of nanofuel is a key issue for both scientific and practical applications.
3. Factors influencing the enhancement of heat of combustion need to be investigated systematically.
4. No uniform standard as presented for experimental research on Nano fuels, including the preparation of Nano fuel and the stability evaluation of Nano fuels.

CHAPTER SIX

FUTURE RESEARCH

Nanofuel is potentially a new topic of research and a lot needs to be explored in this area. As this is in the beginning stage of research and development, new methods and instruments for making and characterisation of the properties of the nanofuel thus produced experimentally need to be developed. Although SEM, XRD etc techniques are available for the characterisation of the particles size and symmetry of the cluster of the particles and the dispersed fuel, but still new methods for the characterisation need to be developed.

Moreover the dispersion techniques and as well as the stabilisation of the particles in the base fuel needs to be worked upon. All the future research which needs to be done is summarised as

- Development of new experimental methods for characterizing Nano fluids which includes the imaging techniques and the analysis subsequently.

- Engine testing of various fuel samples, which are made in the lab, engine setup needs to be prepared for testing for various fuel properties as well as the emission characteristics of the fuel coming after burning of the nanofuel.

- Nanoscale structure and dynamics of the fluids: using a variety of scattering methods:

- ➢ small-angle x-ray scattering (SAXS)
- ➢ small-angle neutron scattering (SANS)
- ➢ x-ray photon correlation spectroscopy (XPCS)
- ➢ laser based photon correlation spectroscopy (PCS)

- Development of computer based models of nanofluid phenomena including physical and chemical interactions between nanoparticles and base-fluid molecules.
- Experimenting new methods for preparation of other Nano Energetic Materials
- To perform the XRD analysis of the sample

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