

**SOME EXPERIMENTAL STUDIES ON NO_x REDUCTION IN CI ENGINE USING
WATER IN DIESEL EMULSION**

A major thesis submitted in the partial fulfillment of the requirement
for the award of the degree of
Master of Technology
In
Thermal Engineering



Submitted by

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ROLL NO. 2K15/THE/02

SESSION 2015-17

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JUNE-2017

CANDIDATE’S DECLARATION

I, hereby declare that the work which is being presented in this dissertation, titled “**SOME EXPERIMENTAL STUDIES ON NO_x REDUCTION IN CI ENGINE USING WATER IN DIESEL EMULSION**” towards the partial fulfillment of the requirement for the award of degree of **Master of Technology** with specialization in THERMAL ENGINEERING from Delhi Technological University Delhi, is an authentic record of my own work carried out under the supervision of **Dr. Naveen Kumar**, Professor, Mechanical Engineering Department, Delhi Technological University, Delhi.

The matter embodied in this dissertation record has not been submitted by me for the award of any other degree.

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CERTIFICATE

This is to certify that the report entitled “**SOME EXPERIMENTAL STUDIES ON NO_x REDUCTION IN CI ENGINE USING WATER IN DIESEL EMULSION**” submitted by **Ankit Kumar (2K15/THE/02)** in partial fulfilment for the award of Master of Technology in Thermal Engineering, is an authentic record of student’s own work carried out under my guidance and supervision.

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ACKNOWLEDGEMENT

It gives me immense pleasure to acknowledge my indebtedness and great sense of gratitude to **Dr. Naveen Kumar**, Professor, Mechanical Engineering Department, Delhi Technological University, Delhi for providing me an opportunity to work on this very relevant topic their able guidance, sympathetic and encouraging attitude throughout the project work, is acknowledged with core of my hearts. In spite of their busy schedule, he could find time to provide me priceless guidance.

I would like to extend my deep sense of gratitude towards all the staff of Center for Advanced studies and research in automotive engineering (CASRAE) especially Sh. Kamal Nain, Sh. Manoj Kumar and Sh. Surendra Kumar for their constant help. I further extend my gratitude to my seniors Mr. Parvesh, Mr. Roshan Raman and my friends Swapnil Anand, Sumeet Rewalia for their technical, moral and physical support all the time just as a constant companion for the successful completion of this project.

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ABSTRACT

Diesel engines have high fuel efficiency and long record of reliability but these engines emit a significant amount of Oxides of Nitrogen (NO_x) and Particulate Matter into the atmosphere. NO_x is a combined term for the Mono-nitrogen oxides NO and NO₂ (nitric oxide and nitrogen dioxide). These are produced from the reaction of Nitrogen, Oxygen and even Hydrocarbons (during combustion), especially at high temperatures. At high temperature usually above 1600 °C molecular Nitrogen (N₂) and Oxygen (O₂) in the combustion air disassociate into their atomic states and participate in a series of reactions.

Technologies such as Exhaust Gas Recirculation (EGR) and Selective Catalytic Reduction (SCR) can be used to reduce the NO_x emission. But to achieve the present emission norms without increasing the cost of the vehicles water in diesel emulsion is the most suitable strategy. In this strategy, some modification in the fuel is done and this can be used along with EGR or SCR to achieve the present emission standards.

Water in Diesel emulsion (WiDE) fuel has potential to significantly reduce the formation of NO_x and PM in the diesel engine. The emulsion fuel contains water, diesel fuel, and surfactants, to stabilize the system. Reduction of NO_x is originated from the reduction of local high temperature due to vaporized water during combustion. The reduction of local high temperature may cause the reduction of reaction rate, which has a possibility of affording a mixing time for better combustion for reducing PM. Formation of Hydroxyl (OH) radical is also helpful to reduce the NO_x in the case of water in diesel emulsion. In this study WiDE fuels are prepared by using surfactants (sorbitan monolaurate, polyoxyethylene sorbitan monolaurate, sorbitan monopalmitate, sorbitan monooleate), a major concern is the long-term stability of the emulsion. Emulsion fuels were prepared by using 1%, 2%, 4% of water and 0.5% of surfactant by weight. The Physico-chemical properties were evaluated and experimental procedure conducted using a Kirloskar single cylinder diesel engine. The results are presented by using the graphs which shows the comparison of the emulsion fuels properties with baseline data. Recommendations are given for further studies, including improving the emulsion fuels and considerations for long-term testing as well.

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NOMENCLATURE

O/W	Oil in water
W/O	water in oil
WiDE	water in diesel emulsion
BTDC	Before top dead centre
BSFC	Brake specific fuel consumption
BMEP	Brake mean effective pressure
BP	Brake power
CO	Carbon Monoxide
EGR	Exhaust Gas Recirculation
SCR	Selective Catalytic Reduction
HLB	Hydrophilic Lipophilic Balance
HC	Hydrocarbon
NO	Nitric oxide
NO _x	Oxides of nitrogen
PPM	Part per million
RPM	revolution per minute
SO _x	Oxides of Sulphur
VVT	Variable valve timing
EU	European Union
EEA	European Economic Area

BSES	Bharat stage emission standards
BS	Bharat Stage
PM	Particulate matter
SO ₂	Sulfur dioxide
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter

CHAPTER-1

INTRODUCTION

1.1 Introduction

Compression Ignition engines play a major role in shipping, farming, and electricity generation due to the high thermal efficiency and long record of reliability. These are easily repairable, economical to operate, and very durable. Compression Ignition (CI) engines have many advantages but these engines emit a large amount of PM and NO_x into the air. Health experts concluded that these pollutants critically affect human health and are main cause of lung damage, respiratory problems and cancer in humans ^[1].

In order to reduce these emissions from the existing CI engines, EGR and SCR are such technologies which can be been used but the cost associated with these technologies is very high and these technologies can not fit the existing engines without any additional retrofitting. Water in diesel emulsion is a strategy which can be used to reduce the NO_x emission in CI engines. Apart from reducing the NO_x, it has a number of possible benefits ^[2]. NO_x is produced at very high temperature; this strategy has an influence on decreasing the temperature which stops the formation of NO_x. Water in diesel emulsion is a strategy which can be used to reduce the NO_x emission in CI engines.

Prof. B. Hopkinson in 1913 used water to make better internal cooling of the gas engine and to increase the engine output. Furthermore, various techniques were developed by introducing water into the combustion chamber for improving the thermal efficiency and reducing exhaust emissions from the CI engines. Owing to the increasing pollution, the Government of India has mandated the reduction of exhaust emissions from the CI engines. All light and heavy-duty diesel engines must meet the Bharat Stage emissions standards by 2020, reducing PM and NO_x to near zero levels. The available technologies alone cannot achieve the required emission standards and some technologies are very costly as per the Indian economy.

1.2 Emission Standard

1.2.1 European emission standards

These emission standards are applicable in the European Union and European Area member states. Euro 1, Euro 2, Euro 3, Euro 4, Euro 5 and Euro 6 are used for light duty vehicles standards. Similarly, Euro I, Euro II, etc. are used for heavy-duty vehicles ^[3,4]. The comparison for NO_x and PM reduction is shown below.

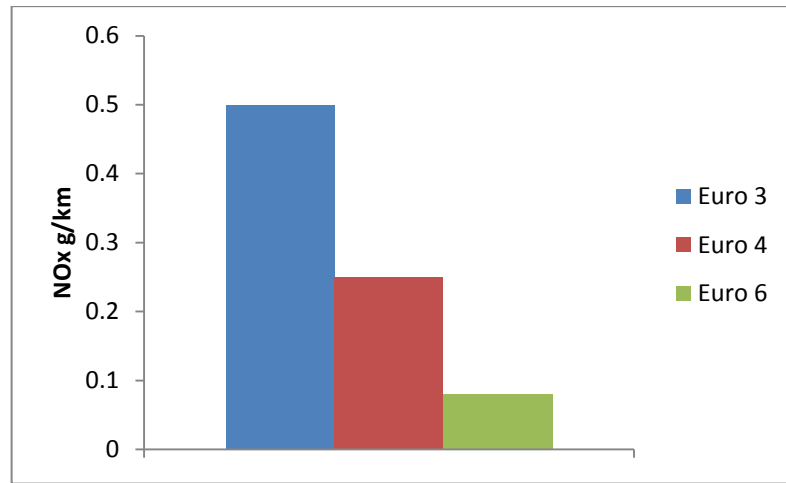


Fig.1.1: Reduction of NO_x emission ^[5]

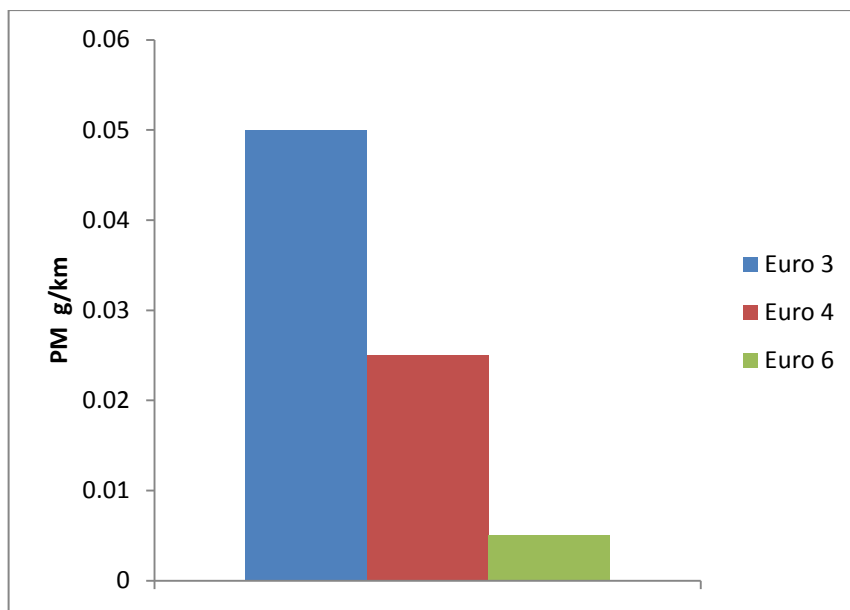


Fig.1.2: Reduction of PM emission ^[5]

Table 1.1: European emission standards for different vehicles, g/km ^[5]

Vehicles category	Tier	Date	NOx	PM
passenger and light commercial vehicle ≤1305 kg	Euro 4	January 2005	0.25	0.025
	Euro 6	September 2014	0.080	0.005
light commercial vehicles 1305–1760 kg	Euro 4	January 2006	0.33	0.04
	Euro 6	September 2015	0.105	0.005
light commercial vehicles >1760 kg	Euro 4	January 2006	0.39	0.06
	Euro 6	September 2015	0.125	0.005

1.2.2 Bharat stage emission standards

Bharat stage emission standards (BSES) are based on European emission standards. These standards are regulated by the Central Pollution Control Board which comes under Ministry of Environment and Forest and Climate change ^[6]. All new vehicles manufactured should fulfill these norms . In India BS-III norms have been enforced Since October 2010. Mumbai, Kolkata, Chennai, Bengaluru, Hyderabad, Ahmedabad, Pune, Surat, Kanpur, Lucknow, Sholapur, Jamshedpur, and Agra are the 13 cities in which BS IV was implemented and these emission norms were enforced for the whole country since April 2017.^[7]

Implementation of Indian emission standards is shown in Table 1.2.

Table 1.2: Implementation of Indian emission standards ^[8]

Standard	Reference	Date	Region	NOx g/km	PM g/km
BS IV	Euro 4	April 2010 April 2017	NCR, 13 Cities Nationwide	0.25-0.39	0.025-.06
BS VI	Euro 6	April 2020 (proposed)	Entire country	-	-

NCR-National Capital Region (Delhi)

1.3 Pollutant Formation

The air pollutant emitted by the CI engines varies with the Design as well as operational parameters. Apart from these the other factors which affect the exhaust emissions from CI engines include ignition and valve timing. These exhaust emissions can be characterized as gaseous and non-gaseous emissions.

1.3.1 Gaseous emissions

Oxides of nitrogen (NO_x) and Carbon monoxide (CO) are the major gaseous pollutants emitted from the diesel engine. The mixtures of Nitric oxide (NO) and Nitrogen dioxide (NO₂) are called as NO_x. In diesel engines, SO₂ emissions are due to fuel-bound Sulfur and can be reduced by decreasing sulfur in the fuel.

1.3.2 Non-Gaseous emissions

Unburned hydrocarbons (HC) are primarily called as non-gaseous pollutants. Based upon their role in photochemical smog formation these are divided into reactive and nonreactive categories.

1.3.3 NO_x formation and reaction

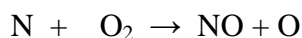
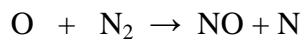
The mixture of nitric oxide and nitrogen dioxide is referred as NO_x. These emissions should be controlled because these emissions contribute to the formation of low-level ozone, smog, and causes an environmental and human health hazard.

Other oxides of nitrogen such as N₂O, NO₃, N₂O₄, and N₂O₅ are also called as NO_x. But these are insignificant in the emissions from CI engines and readily react to NO and NO₂. Over 90 percent of the total NO_x emissions from diesel fuel combustion is generally due to NO, and the remainder due to NO₂.

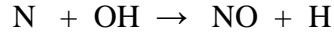
The NO formation occurs by these three different mechanisms ^[9]:

1. The Extended Zeldovich mechanism, or thermal NO, in which O, OH, and N₂ are in equilibrium concentrations.
2. Other mechanisms with NO formation rates above that predicted by the Extended Zeldovich mechanism, including
 - a. Fenimore CN and HCN pathways
 - b. N₂O-intermediate route
 - c. “Super-equilibrium” concentrations of O and OH in combination with the Extended Zeldovich mechanism
3. Fuel nitrogen mechanism, in which fuel-bound nitrogen is oxidized to NO.

The atmospheric molecular nitrogen (N₂) is oxidizing to form NO through the thermal or Zeldovich mechanism:

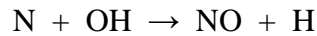
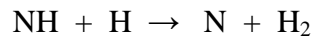
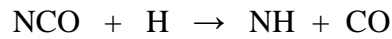
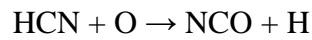
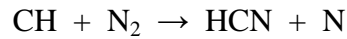


Lavoie et al. in 1970 proposed the thermal NO formation mechanism when hydroxyl radical reacts with nitrogen :



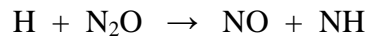
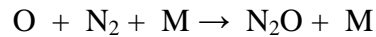
It was concluded from various studies that the Thermal NO formation rate is unimportant below 1800 K.

Fenimore mechanism is also referred as Prompt NO. Hydrogen cyanide is formed as an intermediate to NO formation when Hydrocarbon radicals react with molecular nitrogen. The related equations are given in the following steps:

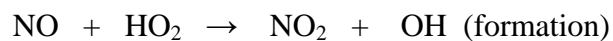


Owing to the thin flame fronts, short residence times, and high pressures in the combustion chamber, Prompt NO formation is insignificant in IC engines.

Whereas when $\phi < 0.8$ and temperature are less than 1800 K the formation of NO through an N_2O intermediate mechanism is important. This formation occurs in these three steps:



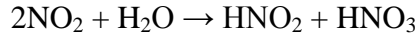
Here, M represents a third body collision molecule. The last mechanism is formation of NO_2 :



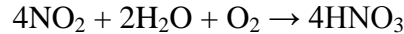


1.3.4 Formation of Nitric acid and Acid rain from NOx

When mono-nitrogen oxides react with atmospheric moisture, it eventually forms nitric acid. Nitric acid is the main component of acid rain. Nitrogen dioxide reacts with water to form HNO₂ and HNO₃. The related equation is as follows:



On combining these equations a single equation comes which explain the aerobic conversion of nitrogen dioxide to nitric acid:

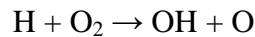
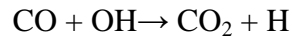
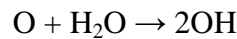
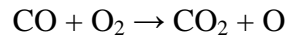


1.3.5 Carbon monoxide (CO) formation

CO emissions from CI engines are a distress from toxicological effects on people. Carbon monoxide is formed by the combustion of the hydrocarbon radical (R):



After formation, the oxidizing rate of CO to CO₂ is very slow. Water works as a primary oxidant source:



1.3.6 Particulate matter formation

Particulate matter (PM) is the major cause of black smoke associated with CI engine powered by diesel fuel. The particulates from Diesel engine form a very complex aerosol system. Despite various researches the formation of PM in the engine cylinder and its

physical and chemical properties or human health effects are not still understood. PM is one of the major harmful emissions produced by diesel engines.

Diesel particulates are subject to diesel emission regulations worldwide and, along with NO_x, have become the focus in diesel emission control technology.

1.4 Environmental Effects

Nitric acid vapor and related particles are formed when oxides of nitrogen react with ammonia, moisture, and other compounds. These particles can penetrate deeply into sensitive lung tissue and cause respiratory diseases, such as emphysema or bronchitis, or may also aggravate existing heart disease. These can cause untimely death in some cases. Inhalation of such particles may cause or worsen.

Ozone is also formed by the NO_x when it reacts with volatile organic compounds in the presence of sunlight. Ozone causes damage to lung tissue and reduction in lung function mostly in susceptible populations.

It can be transported by wind streams and causes health impacts far from the original sources. It is estimated by the American Lung Association that approximately 50 percent of US populations live in countries that are not in ozone compliance.

1.5 Approaches for Reducing Diesel Emissions

The emission controls manufacturing companies have responded to the challenge of decreasing air pollution from compression ignition engines. Through their efforts, they have developed various cost-effective technologies to reduce emission from the diesel engines. In the transportation, agriculture, mining, materials handling, ports, construction, and power generation industries these emission control technologies have proved their ability to considerably reduce harmful emissions at very fewer costs without decreasing vehicle performance.

1.5.1 Engine Controls

To develop cleaner diesel engines various technologies has been used. These technologies include advanced common rail fuel injection, electronic engine controls,

combustion chamber modifications, air boosting, improved air/fuel mixing, and reduced oil consumption.

Engine manufacturers are focusing on ways to control engine operation to reduce the exhaust emissions as low as possible and reduce the burden on the exhaust emission control systems.

Variable valve timing (VVT) is being used to introduce some fraction of exhaust gas into the combustion process and reduce HC and NO_x emissions. NO_x and PM have opposite reactions to combustion temperature. If the temperature decreases then NO_x also decreases but the emissions of particulate matters increases.

1.5.2 Exhaust controls

In this section, a brief description of the available CI engines exhausts control technologies, their operating characteristics, control capabilities, and operating experience is provided.

Diesel oxidation catalysts (DOC) are installed on the vehicle's exhaust system. These can reduce Particulate Matter typically by 25-50% by mass. DOC can also reduce smoke emissions, 90% of the CO and HC emissions and more than 70% of the toxic hydrocarbon emissions in diesel exhaust.

Diesel particulate filters (DPF) are used to meet the U.S. Tier 2 light-duty and 2007 heavy-duty on-highway emission limits for PM. DPFs can achieve up to 90 percent reduction in PM.

Exhaust gas recirculation (EGR) is the method by which a small amount of the engine exhaust gases is re-circulated back to the combustion chamber through the inlet system by using a control valve. By doing this some of the fresh inlet oxygen is displaced by the diluents (CO₂ and H₂O) to reduce the NO_x formation. These diluents have higher heat capacity which results in lower combustion rate and temperature rise. This will reduce the peak cylinder gas temperature. EGR is capable of achieving up to 50% reduction in NO_x emissions. In EGR due to a reduction in temperature PM emission increases.

Selective catalytic reduction (SCR) is the most effective technology for reducing NO_x emissions. In this a liquid-reductant agent usually automotive-grade urea is injected through a catalyst into the exhaust stream of a CI engine. The reductant source is also known as Diesel Exhaust Fluid (DEF).

The DEF sets off a chemical reaction that converts nitrogen oxides into nitrogen, water and tiny amounts of carbon dioxide (CO₂), natural components of the air we breathe, which is then expelled through the vehicle tailpipe. This technology reduces NO_x up to 90% while simultaneously reducing Hydrocarbon emissions by 50- 90 percent and Particulate Matter emissions by 30-50 percent.

1.5.3 Fuel modification (Introduction to Water in Diesel Emulsion)

Initially, water is introduced into the CI engine combustion zone to improve the thermal efficiency, reduce the exhaust emissions and make better inter cooling of the gas engines. It can be introduced in a diesel engine by the three major techniques. These are as follows:

- (i) Water can be directly injected into the combustion chamber through a normal injector
- (ii) Fumigation
- (iii) In the form of emulsion

From the experimental investigation, it is confirmed that emulsion fuel can simultaneously reduce the emissions of NO_x and PM. These fuels can be used without engine retrofitting this is the major advantage of this strategy ^[10].

CHAPTER-2

LITERATURE REVIEW

2.1 Emulsion

An emulsion is a mixture of two or more liquids immiscible in nature, one present as a droplet, or dispersed phase distributed throughout the other, or the continuous phase ^[11]. It is generated by means of a mechanical agitation in the presence of surface active agents, sometimes called emulsifiers or surfactants, for stability. As far as the smoke and NO_x emissions are concerned, ultrasonic and supersonic vibrations have a negative impact compared to emulsions prepared by mechanical homogenization ^[12].

2.2 Surfactants

The surfactants possess a polar, or hydrophilic head and a nonpolar, or hydrophobic tail ^[13]. It is incorporated to weaken the surface tension of the medium in which it dissolves. When it is placed in a water-oil mixture, the polar groups orient towards the water and the nonpolar group orients towards the oil as it lowers the interfacial tension between the oil and water phases. The fact that emulsion is used as a fuel in a diesel engine, it is recommended that it should be stable and this can be realized with the help of suitable surfactants. Surfactants should easily burn with no soot and free of sulfur and nitrogen ^[14]. Furthermore, they should have no impact on the physiochemical properties of the fuel. Usually, the amount introduced in the emulsion process is in the range of 0.5–5% by weight ratio.

2.2.1 Classification of surfactants

From the commercial point of view, surfactants are often classified according to their use. However, this is not very useful because many surfactants have several uses, and confusions may arise from that. The most accepted and scientifically sound classification of surfactants is based on their dissociation in water. Surfactants are classified into cationic, anionic, and nonionic based on the type of polar group on the surfactant.

Anionic Surfactants are having negatively charged head and a carbohydrate tail. Surfactants contain anionic functional groups at their head, such as sulfate, sulfonate,

phosphate, and carboxylates. Prominent alkyl sulfates include ammonium lauryl sulfate, sodium lauryl sulfate (sodium dodecyl sulfate, SLS, or SDS), and the related alkyl ether sulfates sodium laureth sulfate (sodium lauryl ether sulfate or SLES), and sodium myreth sulfate.

Nonionic Surfactants are a distinct type of surfactant with an uncharged polar head. In horticultural contexts, nonionic surfactants may be known as wetting agents because they help hydrophobic, or water repelling, soils to quickly and evenly absorb water by breaking the water's surface tension, allowing water molecules to spread for greater and faster water penetration. According to the University of Georgia (UGA), nonionic surfactants are the most popularly used surfactants in the horticulture industry, and though these surfactants can cause damage to plants, they are safe if used in the proper quantity.

Cationic surfactants are basically soaps or detergents, in which the hydrophilic, or water-loving, end contains a positively-charged ion, or cation. Typical examples are trimethyl alkyl ammonium chlorides and the chlorides or bromides of benzalkonium and alkyl pyridinium ions. All are examples of quats, so named because they all contain a quaternary ammonium ion.

All soaps or surfactants, short for surface active agents, work by the same basic principle, based on the fact that most substances in nature are either hydrophilic, or water-loving, or lipophilic, or fat-loving. Hydrophilic substances dissolve readily in water, and lipophilic substances dissolve in hydrocarbons, which are organic compounds containing a lot of carbon and hydrogen.

The most common surfactants used in the water-in-diesel emulsion are sorbitan monooleate and polyethylene glycol sorbitan monooleate mixture, polyethylene glycol sorbitan monooleate (polysorbate 80) and sorbitol sesquioleate (SSO) mixture, sorbitan monolaurate, Gemini, polyoxyethylene nonyl phenyl ether, solgen 40 and noigen TDS-30 (dai-ichi kogyo seiyaku), polysorbate 20 (commercially known as tween 20), detergent/liquid soap, and t-octylphenoxy polyethoxy ethanol.

Gemini surfactants

Gemini surfactant is the family of surfactant molecules possessing more than one hydrophobic tail and hydrophilic head group. These surfactants usually have better surface-active properties than corresponding conventional surfactants of equal chain length. Geminis are used as promising surfactants in industrial detergency and have shown efficiency in skin care, antibacterial property, metal-encapped porphyrine and vesicle formation, construction of high porosity materials, etc.^[15].

Conventional emulsions are thermodynamically unstable systems that tend to break down due to a variety of physicochemical mechanisms, such as Ostwald ripening, flocculation, coalescence, and creaming. The emulsion stability and the initial droplet size of emulsions depend on many factors such as the type and concentration of emulsifiers, composition (e.g., oil and water phase)^[16,17]. Surfactants can be used as emulsifiers to increase the stability of emulsions. The type of surfactant and its physical-chemical properties (HLB) play a very important role in emulsion stabilization. Showing many interesting physical-chemical properties, Gemini surfactants have drawn considerable attention from academia and industry since 1991^[18-19]. These surfactants are normally composed of two identical monomeric surfactants that are chemically linked by a spacer at the level of their hydrophilic head groups. Compared to their single chain surfactants, Geminis have higher surface activity and they can reduce the surface tension of water more efficiently.

The conventional surfactant has a single hydrophobic tail connected to an ionic or polar head group, whereas a Gemini has in sequence a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail.

A schematic representation of Gemini is given in Figure 2.1. Related surfactants with more than two tails are also known. To provide greater surface activity, chemists have been in search of newer surfactants and the preparation started with bis-surfactants, which were later renamed as ‘Gemini’ surfactants. Geminis are considerably more surface-active than conventional surfactants.

Menger and Littau et al. ^[20] assigned the name Gemini to bis-surfactants with a rigid spacer (i.e. benzene, stilbene). The name was then extended to other bis or double-tailed surfactants, irrespective of the nature of spacers.

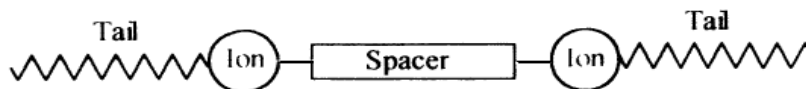


Fig. 2.1: Schematic representation of Gemini surfactant.^[20]

Examples of Gemini surfactants are 1,2-ethane bis(dimethyl alkyl (C_nH_{2n+1}) ammonium bromide), sodium dilauroyl cystine (SDLC) and sodium didecamino cystine (SDDC)

Comparison between Conventional and Gemini surfactants

M. Nadeem et al.^[21] studied Diesel engine performance and emission evaluation using emulsified fuels stabilized by conventional and Gemini surfactants.

Emulsified Fuels containing 5–15% water contents were prepared using conventional and Gemini surfactants and studied in an engine bed XLD 418 (Ford) to clarify the changes in the main pollutant emissions (NO_x, CO, and PM). The experimental results can be summarized as follows. The emission of NO_x, CO and PM was reduced using the emulsified fuels instead of neat diesel; however, the emulsified fuels containing Gemini surfactant were most prominent in the reduction of PM. In addition, emulsion fuels have higher specific fuel consumption and produced less torque, power, and brake mean effective pressure but the difference is insignificant. By considering the obtained data it can be concluded that water and diesel emulsions can be used in internal combustion engines without modification.

Instead of conventional, Gemini surfactants are much better emulsifiers. Amongst the analyzed emulsion fuels 15% water–diesel emulsion was found to be the best-emulsified fuel in controlling the engine's emission. Generally, the use of the emulsified fuel reduces the adsorption of the hydrocarbons.

Water emulsification has a potential to significantly reduce the formation of thermal NO_x, CO, SO_x, soot, hydrocarbons, and PM in the Diesel engines. Further, experimental

work for optimizing the emulsion formulation using Gemini surfactants and evaluation of internal structure is highly recommended.

2.2.2 Hydrophilic-Lipophilic Balance

William Griffin, in the late 1940s, introduced the Hydrophilic-Lipophilic Balance system (HLB) as a way of figuring out which emulsifier would work best with the oil phase of an emulsified product. All emulsifiers have a hydrophilic head (water loving) that is generally composed of a water soluble functional group and a lipophilic tail (oil loving) generally composed of a fatty acid or fatty alcohol.

The proportion between the weight percentages of these two groups in a surfactant molecule is an indication of the behavior that may be expected from that product. An emulsifier that is lipophilic in character is assigned a low HLB number and an emulsifier that is hydrophilic in character is assigned a high number.

For the best formation of an appropriate surfactant, hydrophilic-lipophilic balance, or (water liking-oil liking) score is developed. Low HLB tends to make water-in-oil-emulsion while those with a high HLB are more hydrophilic and tend to make oil-in-water-emulsion. The value of HLB ranges from 1 to 20.

2.2.3 Determination of HLB by calculation

Calculation of HLB value of a surfactant is very important in product quality and yield points of view. HLB values can be calculated theoretically or may be determined by experimentally. The experimental method is very long and laborious and was described long back ago by William Griffin in 1949. Formulas for calculating HLB values may be based on either analytical or composition data. For most polyhydric alcohol fatty acid esters approximate values may be calculated with the formula^[22].

$$HLB = (1 - S/A)$$

Where S = saponification number of the ester

A = acid number of the acid

Many fatty acid esters do not give good saponification data; for example, tall oil and rosin esters, beeswax esters, lanolin esters. For these a calculation may be based on the formula:

$$HLB = \frac{E+P}{5}$$

Where E = weight percentage of oxyethylene content

P = weight percentage of polyhydric alcohol content (glycerol, sorbitol)

2.2.4 Determination of HLB “Requirement”

HLB “requirement” is the amount of surfactant required to make an oil to remain in solution. Variation of the proportion of the blended emulsifiers has been preferred to obtain best results. When two emulsifiers of known HLB are thus blended for use with a given oil there is an optimum ratio that gives the best emulsification and the HLB at this ratio is said to be the required HLB for the oil (to give that type of emulsion, whether O/W, W/O solubilisation, etc.). This is expressed by the given equation ^[22].

$$HLB_{oil} = \frac{W_A \times HLB_A + W_B \times HLB_B}{W_A + W_B}$$

Where, W_A = the amount (weight) of the 1st emulsifier (A) used.

W_B = the amount (weight) of the 2nd emulsifier (B) used at the optimum ratio giving the best emulsion.

HLB_A , HLB_B = the assigned HLB values for emulsifiers A and B.

HLB_{oil} = the “required HLB” of the oil for the type of emulsion being studied.

Table2. 1: Calculated HLB values ^[23]

Surfactant	Common name	HLB value
Sorbitan monooleate	Span 80	4.3
Sorbitan monostearate	Span 60	4.7
Sorbitan monopalmitate	Span 40	6.7
Sorbitan monolaurate	Span 20	8.6
Polyoxyethylene sorbitan trioleate	Tween 85	11
Polysorbate 60	Tween 60	14.9
Polysorbate 80	Tween 80	15
Polysorbate 40	Tween 40	15.6
Polysorbate 20	Tween 20	16.7

Table 2.2: Application of surfactants depending on HLB range ^[23]

HLB Range	Application
4-6	w/o emulsifiers
7-9	wetting agents
8-18	o/w emulsifiers
13-15	detergents
10-18	solubilizers

2.3 Types of Emulsions

Diesel-water emulsions are classified based on the relative spatial distribution of diesel and aqueous phases. In general, there are two types of emulsification techniques, namely, two-phase and three-phase emulsion. The formation of three-phase emulsion is in need of two-stages of emulsification process with different surfactant and a result of increases in process cost. In addition, the stability period of three-phase and variation in physico-chemical properties are not clear in the previous literatures. A further study on the physico-chemical properties variation, combustion and emission behaviors is recommended with three-phase emulsion.

Diesel-water emulsions are classified based on the relative spatial distribution of diesel and aqueous phases. Depending upon the nature of the dispersed phase and dispersing medium, the emulsions are classified into two types:

2.3.1. Oil-in-water emulsions (O/W)

The emulsions where oil is the dispersed phase and water is present as the dispersion medium (continuous phase) is called oil in water emulsion. Milk is an example of oil in water emulsion. In milk fat globules are dispersed within the water.

2.3.2 Water- in- oil emulsions (W/O)

The emulsion in which water forms the dispersed phase and the oil is present as a dispersing medium (continuous phase) is called water in oil emulsion. They are also termed as oil emulsions. Butter, cold cream, cod liver oil etc. are examples of this emulsion. In addition to the above emulsion, few researches included concepts of introducing three-phase emulsions and comparative studies on the effect of two-phase and three-phase on the diesel engine performance also available. Irrespective of method of production either by mechanical homogenizing or by ultrasonic vibrating, the oil-in-water-in- oil (O/W/O) emulsions were found to have a higher fuel consumption rate, brake specific fuel consumption, CO emission, and black smoke opacity than the W/O emulsions.

Surfactants used for the formation of water-in-diesel emulsion fuel should burn easily with no soot and should be free of sulphur and nitrogen as discussed in. Furthermore, they should have no impact on the physicochemical properties of the fuel

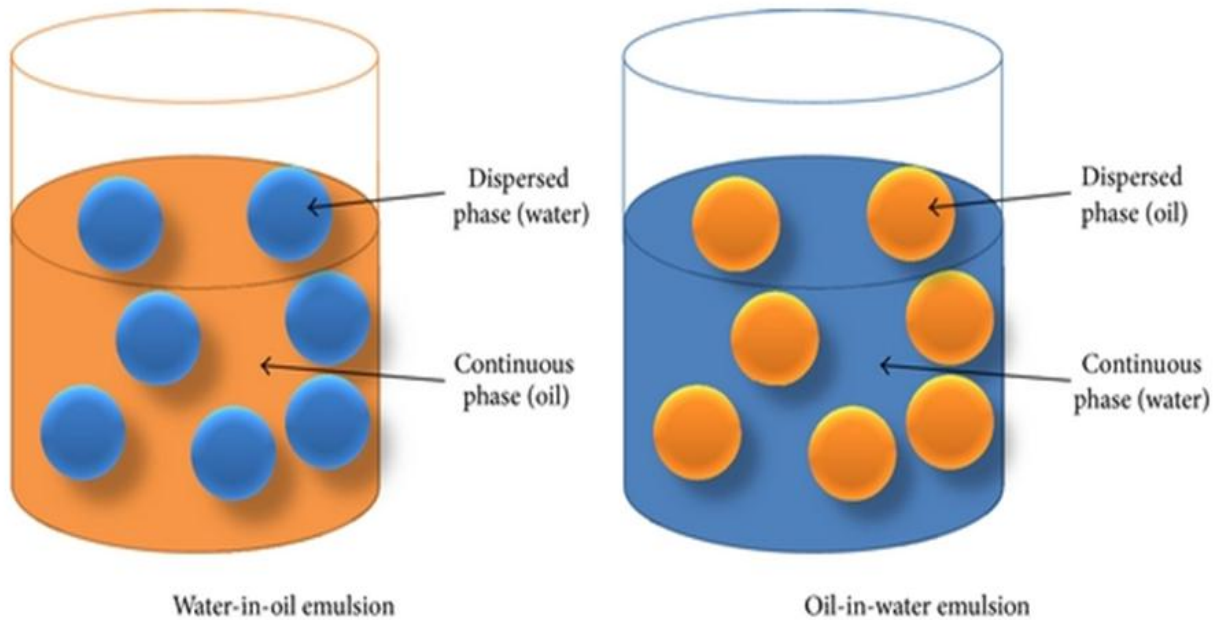


Fig.2.2: Concept of two-phase water-in-oil and oil-in- water emulsions.^[24]

Surfactants from the aliphatic hydrocarbon family are the best candidates to be used as emulsifiers. Usually the amount of surfactants used for emulsification is in the range of 0.5–5% by volume, as the surfactant concentration increased emulsion stability reduced.

2.4 Emulsion Characteristics

2.4.1 Stability

Among emulsion characteristics, the stability has great importance. The stability depends mainly on the type and quantity of surfactant that is used in the emulsion formulation, through the mode on how the surfactants adsorb to the newly created interfacial area^[25]. As soon as the emulsion is formed, it starts to change due to several time-dependent processes, among which creaming, sedimentation, Ostwald ripening, flocculation, and coalescence appear to be the most important^[26].

In the stability of water-in-diesel emulsion versus water concentration, surfactant concentration, mixing speed and time was investigated. For a given surfactant concentration and mixing speed and time, the percentage of separated water gradually increased with the water concentration shown in figure 2.3.

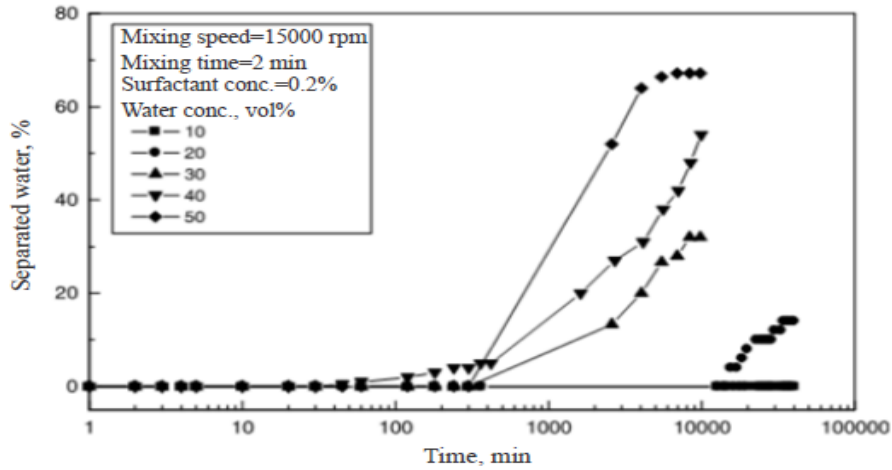


Fig. 2.3: Stability profile of a water-in-diesel emulsion for different water content ^[27].

The stability of the diesel emulsion is affected mainly by the emulsification technique, emulsification duration, volume fraction of water (dispersed phase), viscosity of continuous phase (diesel oil), stirring speed (or ultrasonic frequency), and concentration of surfactants. The experimental work by Chen and Tao et al. studied the effect of emulsifier dosage, oil water ratio, stirring speed, and emulsifying temperature on the stability of water in diesel emulsion using mechanical agitator. They reported that an increase in oil to water ratio, stirring speed, and duration had positive influence on stability, whereas an increase in emulsifying temperature showed negative impact. Two-phase W/O emulsion showed better engine performance with less CO emissions which were reported in with the application of ultrasonic vibrator compared to the emulsion prepared by mechanical agitation. In addition, the selections of suitable surfactants, the choice of a suitable agitator frequency, and agitation time have also been identified as equally important parameters in the formation of stable emulsified fuels.

Surfactant or emulsifier is the most important factor that affects the stability of an emulsion. Percentage of water in the emulsion, stirring intensity, stirring duration,

emulsifying temperature, and operational pressure also affect the stability of an emulsion. Chen and Tao et al. have experimentally studied the effect of emulsifier dosage, oil-water ratio, stirring speed, and time and emulsifying temperature on the stability of diesel-water emulsion. They have concluded that an emulsifier dosage of 0.5%, oil-water ratio of 1 : 1 by volume, stirring speed of 2500 rpm, and duration of 15 min and emulsifying temperature of 30°C have been optimum for the stability of the emulsion. They have also reported that while an increase in oil to water ratio, steering speed, and duration up to 15 min have positive impact on stability, increase in emulsifying temperature had negative impact.

Similar work has been done by Ghannam and Selim et al. on the stability of water/diesel emulsion fuel and they indicated the necessity of surfactant for the stability of the emulsion and possibility of getting stable emulsion of higher water percentage (>30%) by increasing the percentage of emulsifier agent (2%) and increasing speed up to 20000 rpm with mixing period of 30 min. To be a good fuel for a compression ignition engine, a water-in-diesel emulsion should possess most of the positive effects of petro-diesel fuel. As this type of engine is well established, complete alteration of fuel characteristics that requires engine retrofitting would not be feasible economically. A good CI engine fuel should hold characteristic features like short ignition lag, sufficiently high cetane rating in order to avoid knocking, suitably volatile in the operating range temperatures for good mixing and combustion, easy startup characteristics, limited smoke and odor, suitable viscosity for the fueling system, free from corrosion and wear, and ease of handling.

In diesel engines, fueling system must insure the fuel to be delivered into the engine cylinder economically and in an appropriate time so that it runs smoothly with minimal exhaust and noise. This is done by controlling the process of spray penetration, chemical and physical atomization, mixture ignition, and combustion and exhaust gas formation. These are mainly dependent on the physiochemical behaviors of the fuel and the injection system. Significant number of the literature could be found on the physiochemical behavior of water-in-diesel emulsion as well as their effect on the combustion behavior and stability. As the water content of the emulsion increases, physical properties like density, viscosity, bulk modulus of elasticity, and compressibility increased. A very close attention should have to be given to these changes as density has a pronounced effect on the mixing process and

viscosity in the injection system. It has also been reported that water addition reduces the heating value of the emulsion.

2.4.2 Viscosity

Viscosity is an important property of diesel fuel, which affects fuel combustion performance. The less the fuel viscosity, the better the fuel fluidity, which improves fuel atomized property so as to decrease fuel consumption and pollutant emission.

In general, water-fuel emulsions exhibit greater viscosity than pure liquid fuels, and both water content and size of the droplets dispersed in the emulsion significantly influence its viscosity (fig. 2.4) ^[28].

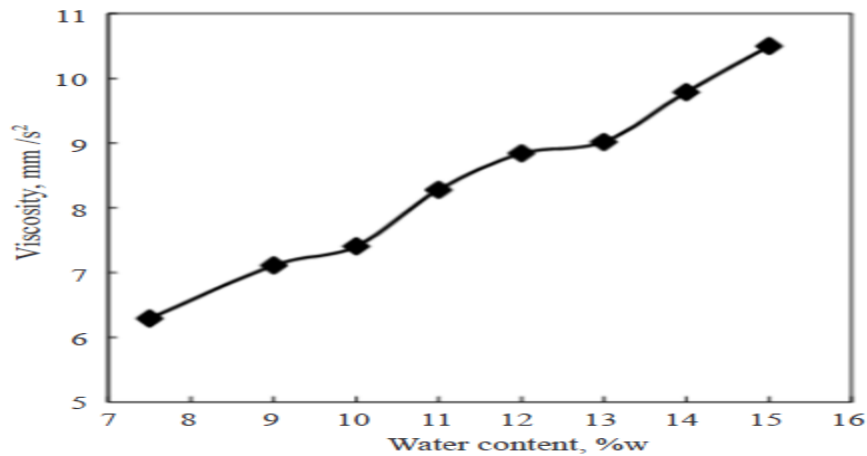


Fig. 2.4: Effect of the water content on the viscosity of a micro-emulsion diesel oil ^[29].

2.4.3 Heating value

In general, torque and power produced by emulsified fuels are lower as compared to the neat diesel fuel due to the lower heating values for emulsified fuels ^[30, 31, 32].

2.5 Water-in-diesel Microemulsions

Microemulsions are alternatives to emulsions as a means to incorporate water in a fuel. The terms “microemulsion” and “emulsion” seem to imply that such systems are very similar; differing just in the size of the dispersed component, but that is not the case. There are several fundamental differences between a microemulsion and an emulsion.

Microemulsion-based fuel formulations date back to 1976 when Gillberg et al. published a paper on the use of water-in-diesel microemulsions as fuel. Since microemulsions consist of much smaller domain sizes than emulsions, one may anticipate that they are superior to emulsions with regard to the atomization process but there are indications that the opposite holds true. As mentioned above, Qingguo et al. have reported that macroemulsions, i.e., normal emulsions, produced smaller drops in the flame than microemulsions.

In the experiments, they used 10% water in so-called Jet-A fuel in both types of formulations. The general characteristics of emulsions with regard to emission levels seem to hold true also for microemulsions, i.e., NO_x and CO emissions are reduced compared to neat diesel as fuel.

Attempts have also been made to add vegetable oils into water-in-diesel microemulsions, thus combining two approaches: replacement of hydrocarbons by triglyceride oils and introducing water into the fuel. Systematic studies have been made on combustion of microemulsions based on hydrocarbons of varying chain lengths. Special attention was paid to the vaporization behavior under dynamic heating conditions. The results indicated that the microstructure of the microemulsion played a role in the physical effects related to the microexplosion, and, thus, to the combustion process. Not much has been published on water-in-diesel microemulsions in recent years.

It is probably true to say that the advantages of the microemulsion approach, in particular, the thermodynamic stability, do not compensate for the drawback of the much higher loading of surfactants needed in a microemulsion formulation compared to an emulsion formulation. The microemulsion route is probably too costly for a very large scale application, such as fuels for vehicles.

Depending on the size of the droplets, the emulsions are classified into two types:

Table2.3: Macroemulsion vs Microemulsion^[33]

Macroemulsion	Microemulsion
Thermodynamically unstable	Thermodynamically stable
Direct oil/water contact at the interface	No direct oil/water contact
Multiple phases only	May be single or multiple phases
Cloudy colloidal systems	Optically transparent
Particle size >400nm	Particle size <100nm

2.6 Improved Combustion Efficiency

By investigating emulsion fuels with varying amounts of water Abu-Zaid et al. showed that the presence of water had a positive effect on the combustion efficiency of a single cylinder, direct injection diesel engine. Fig. 2.5 shows how water in the form of an emulsion affects the engine torque output for various speeds.

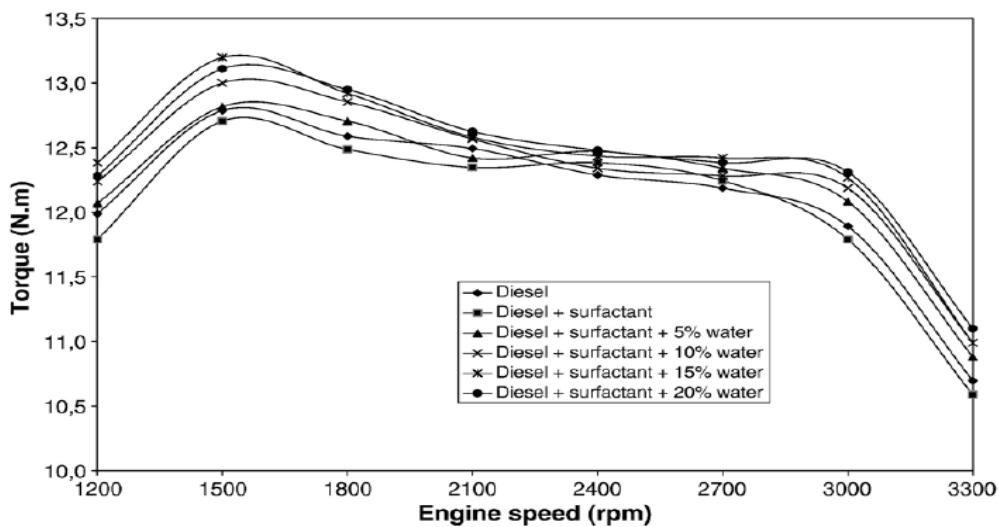


Fig.2.5: Engine torque output versus engine speed using water-in-diesel emulsions as fuel^[34].

The general appearance of the curves should be interpreted as follows. At low speed, the torque increases as the engine speed increases. At around 1500 rpm the torque starts to decrease because the engine is unable to ingest full charge of air. This effect becomes very pronounced at high speeds (above 3000 rpm in the figure).

It can be clearly seen from the figure that addition of water in the form of an emulsion has a positive effect on the combustion efficiency. The torque increases with water content over the entire rpm range. When the charge is fired in the cylinder, the water will turn to steam with high pressure. Another likely reason for the improved combustion efficiency is that the presence of water and, in particular, the presence of the oil–water interface with very low interfacial tension, leads to a finer atomization of the fuel during injection.

A finer dispersion of the fuel drops leads to higher contact with the air during the burning process, which is obviously advantageous for the combustion. It has been postulated that water in the fuel improves the combustion process owing to the simultaneous additional rupture of the drops, to the increase in evaporation surface of the drops, and to better mixing of the burning fuel in air.

When a water-in-diesel emulsion is heated, the water in the droplets is vaporized first because water is more volatile than diesel. The vaporization will cause the continuous hydrocarbon phase to “explode”. This occurs at a temperature much above the boiling point of water, around 270 °C, which is referred to as the superheat limit temperature. It is a general phenomenon that in order to make systems of a lower-boiling liquid immersed as droplets in a higher-boiling liquid “explode” one must reach a temperature far above that of the lower-boiling component.

2.7 Micro-explosion Phenomenon

Sangki Park et al.^[35] studied the characteristic of spray using diesel water emulsified fuel in a diesel engine. Diesel–water Emulsified Fuel (DE) used in this study means the water-in-oil (W/O) type fuel where water droplets are dispersed in diesel. Since W/O type fuel does not involve direct exposure of water upon fuel injection, the low risk of corrosion, enhancement of spray atomization characteristics through the micro-explosion phenomenon,

and combustion temperature decrease as a result of latent heat of water evaporation makes possible simultaneous reduction of NO_x and PM [36–41].

In the ‘micro-explosion phenomenon,’ as illustrated in Fig. 2.6, the difference in the boiling point between diesel and water upon fuel injection in a combustion chamber results in evaporation (explosion) of water droplets and more thorough splitting of fuel droplets. As a result, secondary atomization contributes to enhancing the air–fuel mixture and reducing the incomplete combustion [42–44].

The concept of DE, simultaneous reduction of NO_x and PM, was demonstrated already through the theory and experiment about 30 years earlier, but the research progress has been insignificant due to the limit of emulsion manufacturing technology (stability, homogeneity, miniaturization, production cost) [45–46]. In addition, DE has several expected problems.

The first issue is related to the low temperature solidification. According to previous studies, the emulsion has a low freezing point than pure materials.

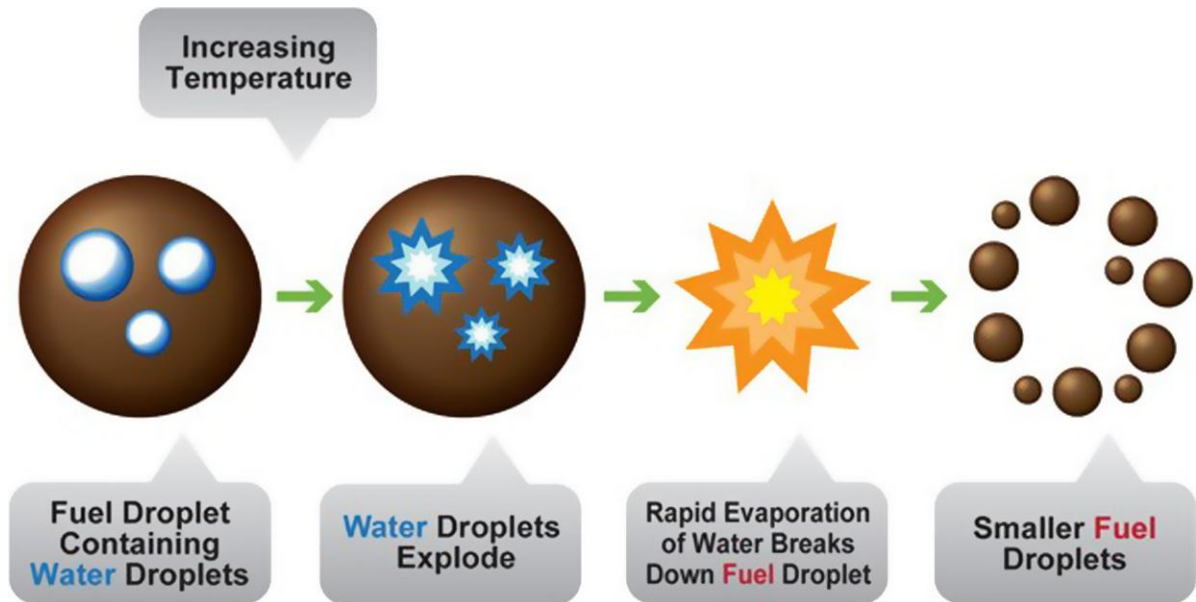


Fig. 2.6: Mechanism of micro-explosion phenomenon.[46]

The emulsion has a dispersed phase tiny water droplets present. Therefore, the solidification delays and water droplets are still observed under the freezing points of pure

material ^[47-48]. Because this phenomenon emulsion can be applied to diesel engine, even though the DE contains water droplets. The corrosion by containing the water is the second issue. This issue also occurs due to the water droplets in the DE. The surfactants used for the production of DE were the role of corrosion inhibitors.

The surfactants are proved to be one of eco-friendly corrosion inhibitor to protect material from the corrosion . Therefore, the corrosion issue was not considered in this study. From the earlier studies, it was well known that the microexplosion and latent heat of evaporation of DE enhance spray atomization characteristics and reduce NOx and PM simultaneously. To understand these steps, fuel properties need to be taken into consideration for accurate analysis of fuel spray, combustion, and exhaust emission characteristics.

Hence, this study investigated the water droplet size inside of DEs manufactured by means of 5 surfactants using particle size analyzer and analyzed the manufacturing performance. Moreover, the stability of DE was evaluated. Finally, two surfactants of superior performance were selected through the implementation of sample filtering. The kinematic viscosity, heating value, and flash point of selected DE were evaluated because fuel properties are essential in order to understand the fuel injection rate, spray behavior, and combustion characteristics.

2.8. Factors Influencing the Micro-explosion Behavior

The percentage of water concentration in the emulsion, size of dispersed water particle, droplet size, ambient pressure and temperature are the key factors that directly affect the strength of micro-explosion. Jeong and Lee et al. observed that the increase in water concentration in emulsion increases the intensity of micro-explosion and results in prolonged duration of explosion. They also reported that the strength of microexplosion is enhanced with increase in water concentration. However, too much increase in water concentration in emulsion led to premature failure of injection system as reported by Sheng et al. Fu et al. reported that the optimum level of water concentration in emulsion resulted in better explosion and shorter burnout time.

Marrone et al. reported that increase in water particle size of emulsion increases the ability of emulsified water to disperse in the oil droplet. Fu et al. observed the low strength of micro-explosion and weak expansion, with relatively small size of emulsified water particle. Concurrently, the larger size of emulsified particles also weakens the strength of micro-explosion due to much amount of water accumulated during the combustion. Fu et al. and Mura et al. reported that the dispersed water particles of size between 4.5 and 4.7 micrometer exhibit crucial explosion.

The small size of emulsion droplet at the entry of combustion process weakens the strength of micro-explosion due to the low residual mass of water. The increase in droplet size enhances the intensity of micro-explosion and results in earlier occurrence of explosion. Fu et al. concluded that the minimum droplet size should be twice the size of the dispersed water droplet or more. Sheng et al. observed that the increase in ambient pressure weakens the strength of micro-explosion due to the shorter penetration of the droplet at higher gas density. They also reported that vigorous explosion occurs at an ambient temperature of 773 K. At higher temperatures a weaker explosion is observed by the same authors due to partial attainment of super-heated state of water droplets. However, Tanaka et al. and Fu et al. stated that the increase in ambient pressure and temperature increases the intensity of microexplosion.

Similar to micro-explosion phenomena, ignition delay is another crucial factor in emulsion that can influence the combustion process. The water concentration in emulsion, fuel injection pressure and ambient temperature predominantly affect the ignition delay. Ghojel, Honnery and Armas et al. reported the increase in ignition delay with emulsion fuel due to lower flame temperature. Subramanian et al. also recorded similar trends in ignition delay. Ghojel and Tran et al. observed that the ambient temperature significantly affected the ignition delay. Hence, it is important to control the changes in ignition delay period with W/D emulsion fuel in order to keep smooth engine operations with desired combustion characteristics.

2.9 Water-in-vegetable oil (water-in-biodiesel) Emulsions

B. Tesfa et al.^[49] studied Water injection effects on the performance and emission characteristics of a CI engine operating with biodiesel. Biodiesel is one of the most promising renewable, alternative and environmentally friendly biofuels that can be used in diesel engine without any need for any modification in the engine. However, researchers have reported that the engines running with biodiesel emit NO_x in higher concentrations. To address this problem, in the present study an experimental investigation has been carried out on the combustion, performance and emission characteristics of a compression ignition (CI) engine running with biodiesel under steady state conditions with a novel NO_x reducing mechanism involving a water injections system.

The experimental work has been conducted on a four-cylinder, four-stroke, direct injection (DI) as well as turbocharged diesel engine. In this investigation, biodiesel (produced from the rapeseed oil by transesterification process) has been used. During the experiments the in-cylinder pressure, specific fuel consumption, water injection flow rate, fuel flow rate and exhaust emission (NO_x, CO, CO₂ and THC) were measured. The experimental results clearly indicate that water injection at a rate of 3 kg/h results in the reduction of NO_x emission by about 50% without causing any significant change in the specific fuel consumption. Furthermore, the water injection in the intake manifold has little effect on the in-cylinder pressure and heat release rate of the CI engine under different operating conditions.

The majority of water-in-fuel emulsions relate to diesel and other hydrocarbon fuels, but there are also a few papers that deal with the combustion characteristics and the emissions from emulsions of water-in-triglycerides, i.e., water-in-biodiesel. In a study where palm oil emulsions were compared with diesel emulsions, it was shown that engine performance, fuel consumption and wear resistance were all comparable for the two types of fuels. It was found that water-in-biodiesel fuels, containing 15% water, gave lower NO_x and smoke emissions than plain biodiesel, which is in line with comparisons of emissions from water-in-diesel emulsions.

In a series of papers Crookes et al. have investigated water-in-biodiesel emulsions and they compared the effect of the water in both diesel and biodiesel on the emission levels. It was found that NO_x emissions were generally lower for vegetable oils than for regular diesel and the values were reduced for both fuels when water was included in the form of an emulsion. CO emissions were higher for the vegetable oil emulsions than for the diesel emulsions although both values were low.

2.10 Role of Additives for Diesel and Emulsion Fuel

In order to improve the lubricity, stability and combustion efficiency, additives are incorporated with diesel, biodiesel and alternative fuels. These additives can be classified into pre flame additives, flame additives, and post-flame additives based on their application.

Pre-flame additives are used to overcome the drawbacks such as prior burning and higher pour point in biodiesel and alternative fuels. Flame additives are designed to improve the combustion efficiency, whereas, post-flame additives are used to reduce carbon deposits in the engine, smoke, and emissions.

Metal-based nano-additives have received much attention in eco-friendly fuel and W/D emulsion fuel. Metal-based additives effectively reduce the emission levels in diesel engines. The metal particles either react with water and enhance soot oxidation, or directly react with carbon atoms in the soot and lower the oxidation temperature.

2.11 Nanofuel in Combustion

Tyagi et al. recorded the enhancement in mass transfer properties, ignition temperature, and ignition delay period with nano-fuels using hot-plate ignition probability test. The high reactivity of nano-fuels due to high specific area and high potential of nano-size metallic powder to store energy can reduce the ignition delay and the soot emission in diesel engines.

Basha et al. conducted the experiments with different nanoparticles (CNT, Alumina) mixed emulsion fuel and observed significant improvement in combustion, performance and emission characteristics. Selva et al. conducted experiments with Cerium oxide nanoparticles as additive in biodiesel and noted marginal improvement in engine efficiency

and notable reduction in ignition delay, heat release rate, and emission levels. Marquis and Chibante et al. also carried out the experiments with CNT nanoparticles and recorded enhancement in surface area- to-volume ratio. The overall observations indicate improvement in combustion performance with nanoparticles incorporated diesel and W/D emulsion fuels.

However, no work has been focused in terms of insolubility and uniform dispersion of nanoparticles in the emulsion fuel. In addition, the effects of nanoparticle distribution to atmosphere through engine exhaust have to be studied, which are essential to improve environmental and human health.

2.12 Outcomes of the Literature Review

- The stability of the emulsion fuel depends on emulsification technique, process duration, the concentration of water, stirrer speed and surfactant concentration.
- The torque and engine power increases with increase in water percentage in the emulsion.
- The decrease in BSFC with an increase in water concentration has been recorded by many studies.
- Most of the studies reported that the BTE is increased with increase in water content.
- High latent heat absorption of water particle during the combustion will lower the local high temperature resulting in the reduction of NO_x Numerical study of Samec et al. reported a reduction of 20% NO_x emission with 10% water content in the emulsion.
- Lesser formation of soot and PM indicates more efficient combustion. The majority of the studies reported that soot and PM are reduced with an increase in water concentration.
- Many of the studies reported the increase in CO and HC emission with W/D emulsion fuel due to the lower combustion temperature that is not sufficient in emulsion fuel combustion to convert the CO into CO₂.

- Gemini surfactants can be ten to a thousand times more surface active than conventional surfactants with similar but single hydrophilic and hydrophobic groups in the molecules.
- Incorporation of nanoparticles with W/D emulsion fuel provides better combustion, performance and emission characteristics with shorter ignition delay period and complete combustion.

2.13 Gap in Literature

- There is not much information available about the Effect of temperature on the stability of the emulsion.
- Limited work has been done on Water in Diesel Emulsion with Gemini surfactants, span60 and span40.
- The mechanism which is taking place inside the combustion chamber is very complex, and there is not much literature available about this.
- Limited work has been done on water in diesel emulsion with Nanoparticles and Water in vegetable oil (water in biodiesel emulsions).

2.14 The Objective of the Present Study

- The objective of the present study is to find out the suitable surfactants to prepare an emulsion.
- To prepare water in diesel emulsion which can remain stable for a longer period.
- To reduce the emissions of NO_x.
- To improve Physico-chemical properties of W/D emulsion.
- To study Impact of water-in-diesel emulsion on engine performance.

CHAPTER-3

System development and Experimental procedure

3.1 Emulsion Preparation

A various fuel sample was prepared using different surfactants and by varying concentration of water. For all samples, the surfactant is added in a fix concentration of 0.5% by weight whereas water is added in a varying concentration of 1%, 2% and 4% by weight. A mixture of diesel-water-surfactant was mixed in a beaker using a magnetic stirrer. The careful measurement was done by the use of a pipette and pipette pump. The water in diesel emulsion fuel does not have a very high stability time period, therefore to stabilize the emulsion fuel surfactants (0.5%wt) are used. Stirring time for all fuels samples was taken 45 minutes. 6 samples were prepared using 1%, 2%, and 4% water by weight.

The nomenclature of fuel sample is given in Table 3.1.

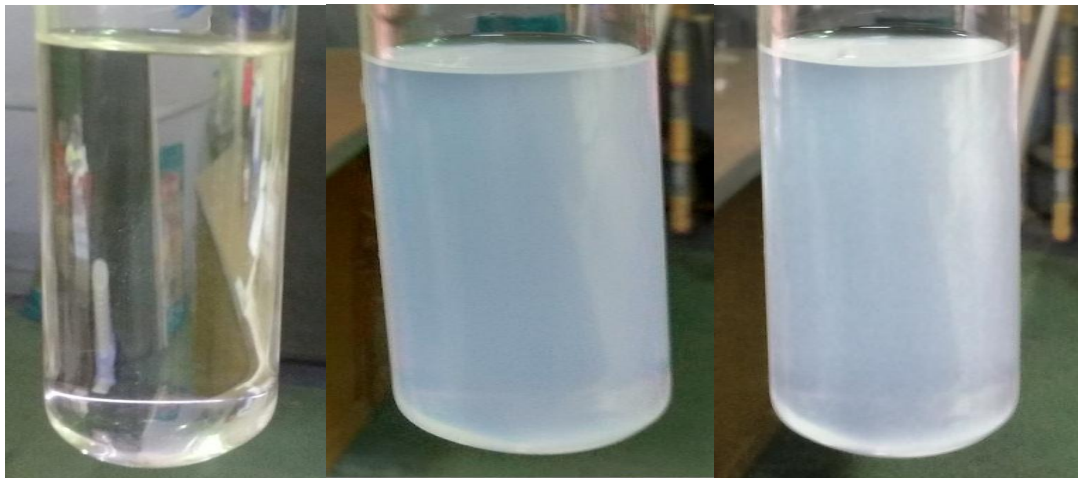
Table 3.1 The nomenclature of various water in diesel emulsion fuel

Sr. No.	Nomenclature	Diesel(%wt)	Water(%wt)	Surfactant(%wt)
1	D	100	0	0
2	DW1S20	98.5	1	0.5
3	DW1S40	98.5	1	0.5
4	DW1S80	98.5	1	0.5
5	DW1T20	98.5	1	0.5
6	DW2S20	97.5	2	0.5
7	DW4S20	95.5	4	0.5

where D = Diesel, W = Water

S20 = sorbitan monolaurate, T20 = poly oxyethylene sorbitan monolaurate

S40 = sorbitan monopalmitate, S80 = sorbitan monostearate



D

DW1S20

DW1S80



DW1T20

DW1S40

DW2S20

DW4S20

Fig3.1: Test fuel sample

3.2 Fuel Sample Characteristic

3.2.1 Homogeneity test

To check the uniformity of the samples homogeneity test is done. The term uniformity is used for phase separation. All the WiDE fuel samples were kept for more than three months to check for the phase separation and homogeneity of the emulsion.

3.2.2 Physico-chemical properties

Physico-chemical properties are important in respect of performance and emission characteristics. The physico-chemical properties of all the test fuel samples were evaluated and compared with diesel. In this investigation density, viscosity, and calorific value of the diesel and emulsion fuels were evaluated.

3.2.2.1 Density

Density is defined as the ratio of mass and volume. The density was measured at a constant temperature (15°C) with the help of a **U-Tube Oscillating True Density meter of make “Anton Paar”, model number “DMA 4500”**. The density of WiDE fuel was compared with the diesel fuel. To measure the density of fuel samples first of all 10cc of Toluene is injected into the injection port to rinse fuel pipeline. To provide a suitable value of density and specific gravity the measurement time was taken 7-8 minute. The same procedure was repeated 2-3 times to provide the satisfactory result. Further, the average of all the values was taken as the final result.

The U-Tube Oscillating True Density meter is shown in figure 3.



Fig. 3.2: U-Tube Oscillating True Density meter

3.2.2.2 Viscosity

When a fluid is subjected to external forces, it resists flow due to internal friction, this property of the fuel is known as the viscosity. The viscosity of the fuel affects atomization and fuel delivery rates. It is an important property because if it is too low and too high, atomization and mixing of air fuel in combustion chamber gets affected. Viscosity studies were conducted for different WiDE fuels. Absolute viscosity, sometimes called dynamic or simple viscosity is the product of Kinematic viscosity and density. The kinematic viscosity of WiDE fuel samples was measured using Kinematic Viscometer of make “Petrotest” as shown in figure 3.3 at a constant temperature (40°C) as per the specification is given in ASTM D445. For this, a suitable capillary tube was selected, and then a measured quantity of sample was allowed to flow through the capillary.



Fig. 3.3: Kinematic viscometer

3.2.2.3 Calorific value

The calorific value of diesel and emulsion fuels was measured with the isothermal bomb calorimeter as per the specifications are given in the ASTM D240. The calorimeter model was “Parr 6100 Calorimeter”. The combustion of fuel takes place in the presence of oxygen at constant volume in a totally enclosed vessel. The sample of fuels was ignited electrically. The oxygen was supplied from an oxygen cylinder which had compressed oxygen. The results were displayed when the sample had burnt completely, on the display.

The bomb calorimeter and oxygen cylinder are as shown in figure 3.4.



Fig. 3.4: Bomb calorimeter

3.3 Selection of Diesel Engine and Development of Engine Test Rig

A single cylinder Kirloskar DAF 8 industrial CI engine was chosen for the experiment. The engine runs on a 4stroke combustion cycle and is air cooled through the various ducts. There are a lots of reason to select this engine, the first one is, it is a light duty engine and can be taken anywhere easily in rural areas where energy sources are not available. This type of engine is used in agriculture and for power generation. But the problem with these engines is emission of NO_x and other harmful pollutant.

Development of Engine Test Rig

Setup contains hand cranked, single cylinder, four stroke, air cooled (radial cooled), vertical, totally enclosed, direct injection, cold starting, naturally aspirated, gravity feed fuel system with efficient paper element filter, force feed lubrication to main and large end bearing and camshaft bush diesel engine that is connected to dynamometer (eddy current type loading). The test rig is represented in fig.3.5 there is a provision with necessary instruments for measurement of combustion pressure and crank angle. It is also made for airflow, flow of fuel, temperature analysis and measurement of load. There is a panel box contains air box, two fuel tanks for fuel test, manometer, fuel measuring unit. There is a rotameter installed for measurement of flow rate of fuel. The final setup enables the measurements of various important parameters like brake thermal efficiency, brake mean effective pressure, frictional power, mechanical efficiency, specific fuel consumption, indicated thermal efficiency, A/F ratio, brake power and indicated power.

The technical specification of the corresponding engine are listed below in table 3.2

Table 3.2 Engine specification

Type	Vertical, 4 Stroke CI Engine
No of cylinder	1
Bore x Stroke	95 x 110 mm
Cubic capacity	0.78 L
compression ratio	17.5:1
Rated output as per BS5514/ISO 3046/ISO 10001	5.9KW(8.0 HP) at 1500 rpm
Starting	Hand Start with cranking handle
SFC at rated hp/1500 rpm	251g/Kwh(185 g/bhp-hr)
Lube Oil Consumption	0.8% of SFC max
Lube oil sump capacity	3.7 Lit
Fuel tank capacity	11.5 Lit
Fuel tank refilling time period	Every 6.9 hours engine running at rated output
Engine weight(dry) w/o flywheel	118 kg
Weight of flywheel	Genset-64 kg
Rotation while looking at flywheel	clockwise
Power Take-off	Flywheel end optional-Gear and half speed drive or full speed drive

The engine setup is shown in Fig.3.5

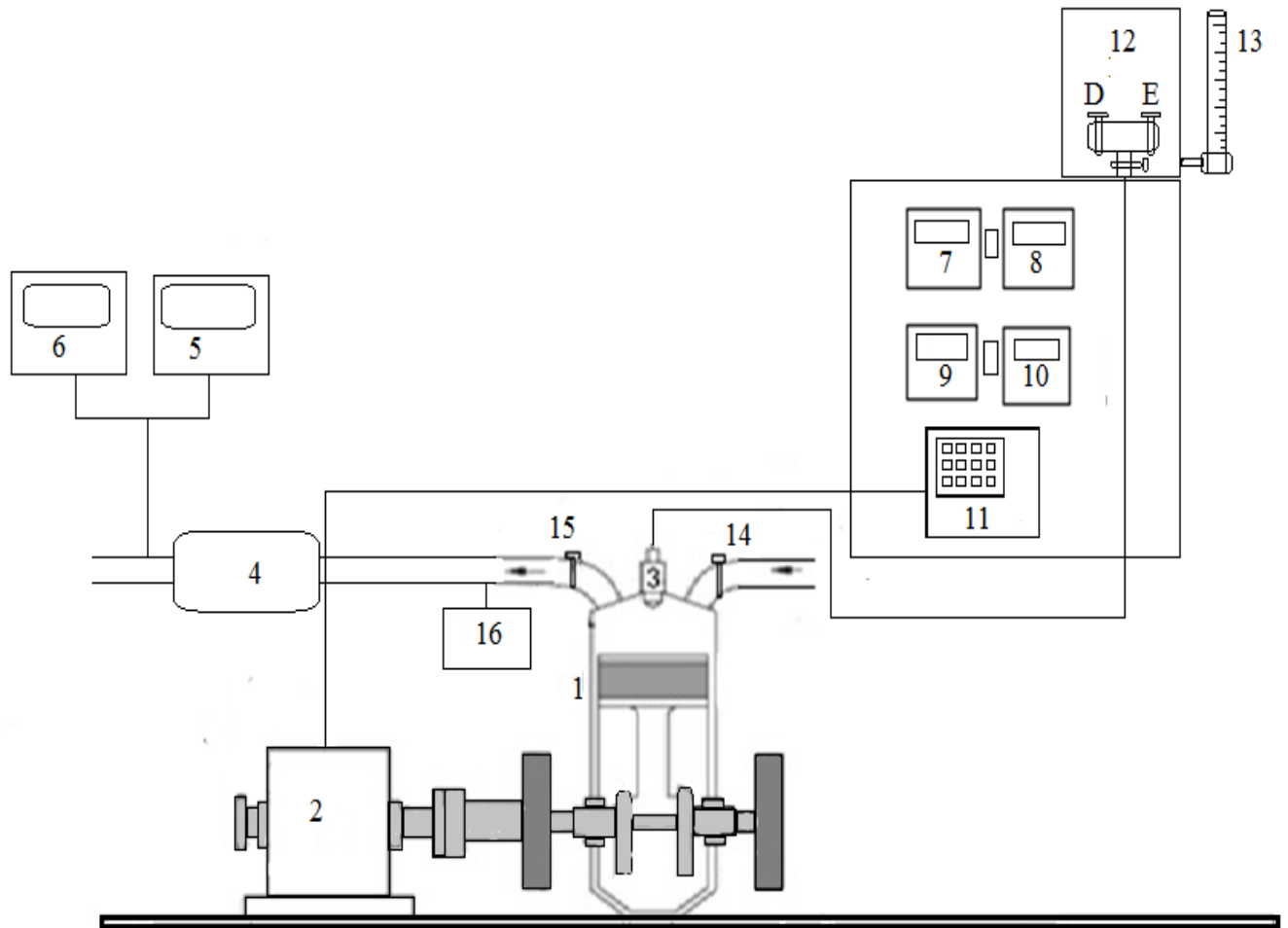


Fig. 3.5: Engine Setup

- | | |
|---|-------------------|
| 1. Kirloskar 4 stroke, single cylinder Engine | 10. Ammeter |
| 2. Dynamometer | 11. Load bank |
| 3. Injector | 12. Fuel tank |
| 4. Exhaust Silencer | 13. Burette |
| 5. AVL Gas Analyser | 14. Inlet valve |
| 6. AVL 437 Smoke Meter | 15. Exhaust valve |
| 7. Temperature Indicator | 16. Thermocouple |
| 8. RPM Indicator | |
| 9. Voltmeter | |

To measure the voltage and current, voltmeter and ammeter were connected between alternator and load bank. On the flywheel a nut was welded with the installation of photo reflective sensor that is mounted on the bracket which is linked to the engine. For measurement of the exhaust temperature, thermocouples were installed in the exhaust manifold. The AVL 437 Smoke Meter and AVL Di gas analyzer were also involved in the nearby region for analysis of temperature of various exhaust gases.

Thus a system is designed to study the theoretical as well as practical performance of emulsions and diesel fuel. Additionally it was easy to maintain and handle the engine because of presence of single cylinder. The experiment on the engine could be done on hot climate too because of air cooling system.

3.4 Parameter Selection

Engine calculations were done on the basis of specific parameters which were selected sensibly. The test performed on the engine is on the basis of IS: 10000. The fundamental parameters needed from the engine are enlisted below:

1. Engine RPM
2. Fuel consumed
3. Temperature analysis
4. Power output from the engine

The above parameters were calculated using the following signals from the test rig.

1. Alternator voltage
2. Alternator current
3. RPM sensor
4. Exhaust gas temperature at outlet
5. Fuel consumption rate
6. AVL 437 smoke meter
7. AVL Di gas analyzer

Essential instrument were installed for sensing these parameters in the set-up.

3.5 Emission Measuring Instruments

3.5.1 AVL 437 Smoke meter

This instrument is used to measure the smoke in the exhaust of the diesel engine and is shown in the fig. 3.6. The fundamental measurement of these instruments was recorder in terms of opacity. Light beam was projected across a flowing stream of exhaust gases; suspended soot particles absorbed the definite portion of light. The remaining part of light strikes on photocell, generating photoelectric current which defines smoke density.



Fig.3.6: AVL 437 Smoke meter

Table 3.3 Specifications of AVL Di-Gas 4000 light and AVL smoke meter

Emissions sensor	Measurement range	Resolution
CO	0-10 % vol	0.01 % vol
CO2	0-10 % vol	0.1 % vol
NOX	0-5.000 ppm % vol	1 ppm
HC	0-20.000 ppm % vol	1 ppm
AVL smoke meter	0-100 % vol	1 %

3.5.2 AVL Di Gas 4000 Light Exhaust Gas Analyser

It is a combined emission tester for emission analysis and diagnosis of petrol and diesel engines. There are a lot of exhaust emissions produced from the diesel engine which can be measured by the AVL Di Gas 4000 Light Exhaust Gas Analyser. Mainly CO and NO_x was measured. These instruments are calibrated regularly using standard gas mixture. Insertion of sampling probe for smooth flow of exhaust gas was done on the exhaust pipe. Additionally mounting of a surge tank at the engine exhaust to have consistent exhaust emissions.

AVL Di Gas 4000 Light Exhaust Gas Analyser is shown in Fig.3.7.



Fig.3.7: AVL Di Gas 4000 Light Exhaust Gas Analyser

3.6 Load Bank

The engine is loaded using a load bank comprising of two 300 W tungsten electrodes bulbs and Ten 500 W tungsten electrode bulbs. The load on the engine is varied through a series of individual switches.

The load bank comprises of a digital ammeter, a digital voltmeter, speed sensor, thermocouple to measure exhaust gas temperature, burette, and manometer. It also houses fuel tanks for the two fuels used- 42 cetane and 91 octane petrol.



Fig.3.8: Load bank



Fig.3.9: Control panel

3.7 Temperature measurement

To measure the exhaust temperature, a socket was welded on the exhaust pipe, before the muffler, and a chromel Alamel K-type thermocouple was mounted on it. Digital temperature display unit was mounted for getting the output of thermocouple attached for the measurement of exhaust gas temperature.



Fig.3.10: Temperature sensor

3.8 Methodology

The first step is the preparation of the emulsion fuel to be employed for experimentation work. After that, the engine is started with the prepared emulsion fuel by cranking the engine with the handle. The engine is made to run for some time to ensure that the older fuel which is used earlier, is completely drained off the system when the observations are being taken and the engine is running on the new fuel only.

In the case of any bubbles that may have entered the system during a change of fuel proper caution should be taken to ensure that the bubbles are released by turning the air release screw provided on the engine.

Observations are made on the engine which includes rpm, exhaust temperature, smoke opacity, NO_x, CO. A glass burette is used to measure the volumetric fuel consumption. A stopwatch is used to measure the time taken by the engine to consume a fixed volume. The volume divided by the time taken for fuel consumption gives the volumetric flow rate.

This test was carried out only after the preliminary run of the engine on diesel fuel. After stable operating conditions observations were recorded no load, 1kw, 2kw, 3kw, and 4kw of the rated load.

3.9 Measurement Methods

The fuel consumption measuring unit, electrical loading arrangement, voltmeter, ammeter, RPM meter, temperature indicator and emission measurement equipment are used to measure the performance and emission characteristics of the engine.

3.9.1 Brake power

Brake power is the most important parameter in the testing of the engine. The power developed by the CI engine was measured with the help of an electric alternator type of dynamometer. A flexible coupling is used to couple the dynamometer with the engine. The output load of this alternator was concerned to the control panel along with a voltmeter and ammeter of required range in series and thus by measuring voltage and current.

Lamp load was connected in series with the generator to act as a resistive load. It consists of 4 rows in parallel with 4 bulbs in series. The rating of each dynamometer used in this study was 220 volts, 7.5 KVA, single phase alternator. An ammeter, 0-30 ampere, and a voltmeter, 0-415 volts AC, were selected for measurements.

$$BP(W) = V \cdot I$$

Where, V = voltage recorded by voltmeter

I = current recorded by ammeter

3.9.2 Fuel flow measuring systems

The fuel consumption of the engine is measured by determining the volume in a given time interval and multiplying it by the specific gravity of the fuel. To get an accurate value it should be measure occasionally.



Fig.3.11: Fuel measurement system

3.9.3 RPM of the engine

For accurate measurement of speed, the best method is to count the number of revolutions in given time. In this study an ‘MTC’ make digital panel tachometer with proximate/photo reflective sensor was used for measurement of RPM of the engine. The magnetic pickup will produce a pulse for every revolution and a pulse counter will accurately measure the speed of the engine.

This instrument is capable of functioning in the range of 1 to 9.999 rpm with a sampling time of 1 second. A nut was welded on the flywheel face and sensor was mounted on a bracket near the flywheel in such a way that the distance was less than 5mm.

A digital display unit is mounted on the panel board. The tachometer used in this study is shown in the figure 3.12



Fig.3.12: Engine speed measurement

CHAPTER-4

RESULTS AND DISCUSSIONS

The results of series of experimental investigations of compression ignition engine fueled by diesel and emulsion fuels are presented here. The brake thermal efficiency, brake specific fuel consumption and exhaust gas emissions such as CO, NO_x, and smoke opacity are the performance parameters which were studied during exhaustive engine trials. The results obtained from emulsion fuels are compared with the baseline results obtained with the diesel as a fuel for comparative assessment.

4.1 Instability in Emulsions

4.1.1 Creaming

In Creaming the emulsion separates into two emulsions, one of which (the cream) is richer in the disperse phase than the continuous phase. It is not actual breaking; in this the disperse phase separates from an emulsion and is normally the herald to coalescence. Emulsions can also undergo creaming when a centrifuge is used. Due to the influence of buoyancy, or centripetal force one of the substance migrates to the top (or the bottom) of the emulsion.

4.1.2 Sedimentation

When water droplets falls from an emulsion due to the density difference between the diesel and water then this process is called sedimentation.

4.1.3 Ostwald ripening

Ostwald ripening is a detected occurrence in solid solutions or liquid sols that define the transformation of an inhomogeneous structure over time. In this the small crystals or sol particles dissolve, and redeposit onto larger crystals or sol particles.

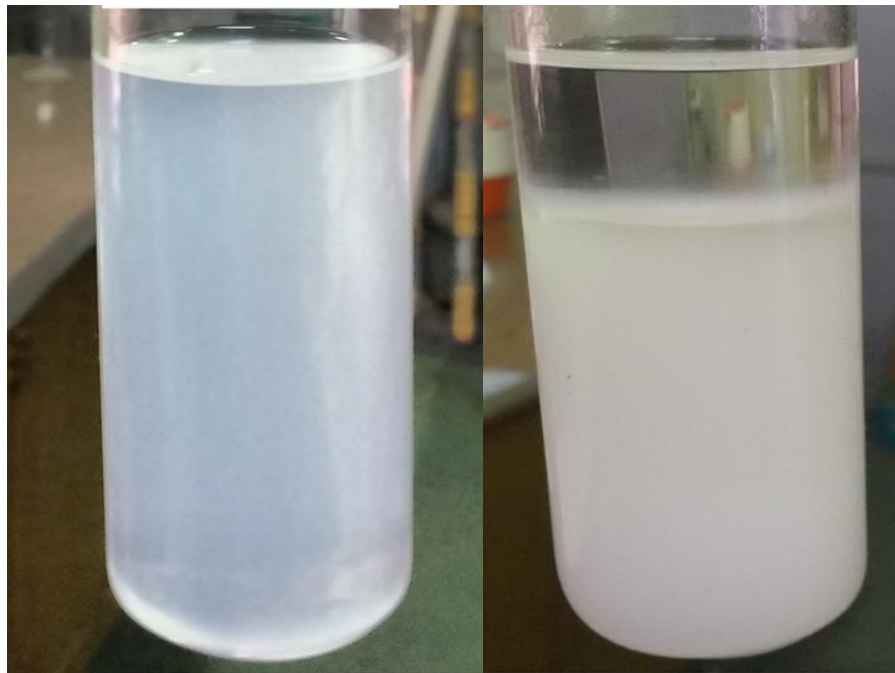
4.1.4 Flocculation

When dispersed phase comes out of suspension in the form of flakes then this is called as Flocculation.

4.1.5 Coalescence

In Coalescence very small droplets combine to form increasingly larger droplets.

The stable and unstable emulsion is shown in the figure 4.1.



Stable emulsion

Unstable emulsion

Fig. 4.1: Stable and unstable emulsion

4.2 Physico-Chemical Properties

The different physicochemical properties which were evaluated are presented in Table. 4.1. The result suggests that the density and kinematic viscosity of WiDE fuel are higher than the diesel fuel. Another important finding is that CV of the WiDE is higher than the diesel fuel on the addition of water up to 4% by weight.

Table 4.1 Physico-Chemical properties of WiDE

Properties	D	DW1S20	DW1S40	DW1S80	DW1T20	DW2S20	DW4S20
Density (g/cm ³)	0.82227	0.82474	0.82479	0.82476	0.82378	0.82490	0.82521
S.G	0.8230	0.8255	0.8254	0.8255	0.8245	0.8256	0.8260
Kinematic viscosity (mm ² /sec)	2.99264	3.2064	3.23312	3.23312	3.31328	3.34112	3.34260
C.V.(MJ/kg)	45.462	45.964	46.632	45.852	45.810	45.398	47.757
Stability period(days)	-	50	3	60	15	12	8

From the above table the measured value of different emulsion fuels are compared with the diesel fuel and it can be directly seen that the physico-chemical properties are nearly equal to the diesel. The stability period of DW1S20 is greater than all the other emulsion fuels samples. As we increase the water percentage in the emulsion then its stability decreases and it is lesser for DW4S20. Therefore to stabilize the emulsion fuels at higher water percentage other surfactants are required.

Emulsion fuel sample DW1S40 was stable for only 3 days therefore this surfactant is not suitable for our study.

4.2.1 Density

Oscillating “U” tube density meter was used to measure the density of fuel samples. The density meter was discussed in the previous chapter. The engine performance and emission behavior are directly related to the density of the fuel. Cetane rating of the fuel as well as heating value is linked to the density. But the effect of density is lesser than the viscosity.

Comparison of density of diesel fuel with emulsion fuels is done in the figure 4.2.

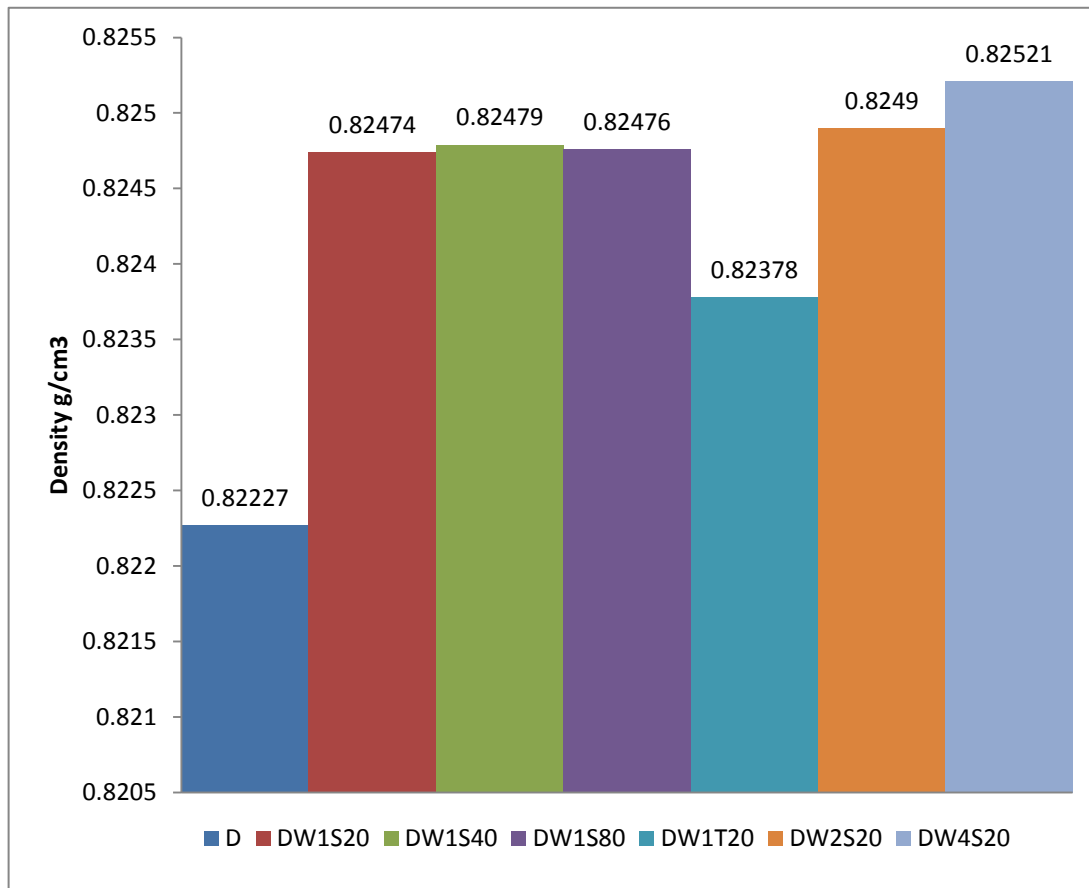


Fig.4.2: Comparison of density of diesel fuel with emulsion fuels

The density of the all emulsion fuel was measured and compared with diesel. Then from the study it was found that the density of the diesel fuel is lesser than the emulsion fuels samples.

The increase in density is due to the addition of water and surfactant in the emulsion because the density of both is higher than the diesel. The density of DW4S20 is higher than the other emulsion fuel samples.

4.2.2 Specific gravity

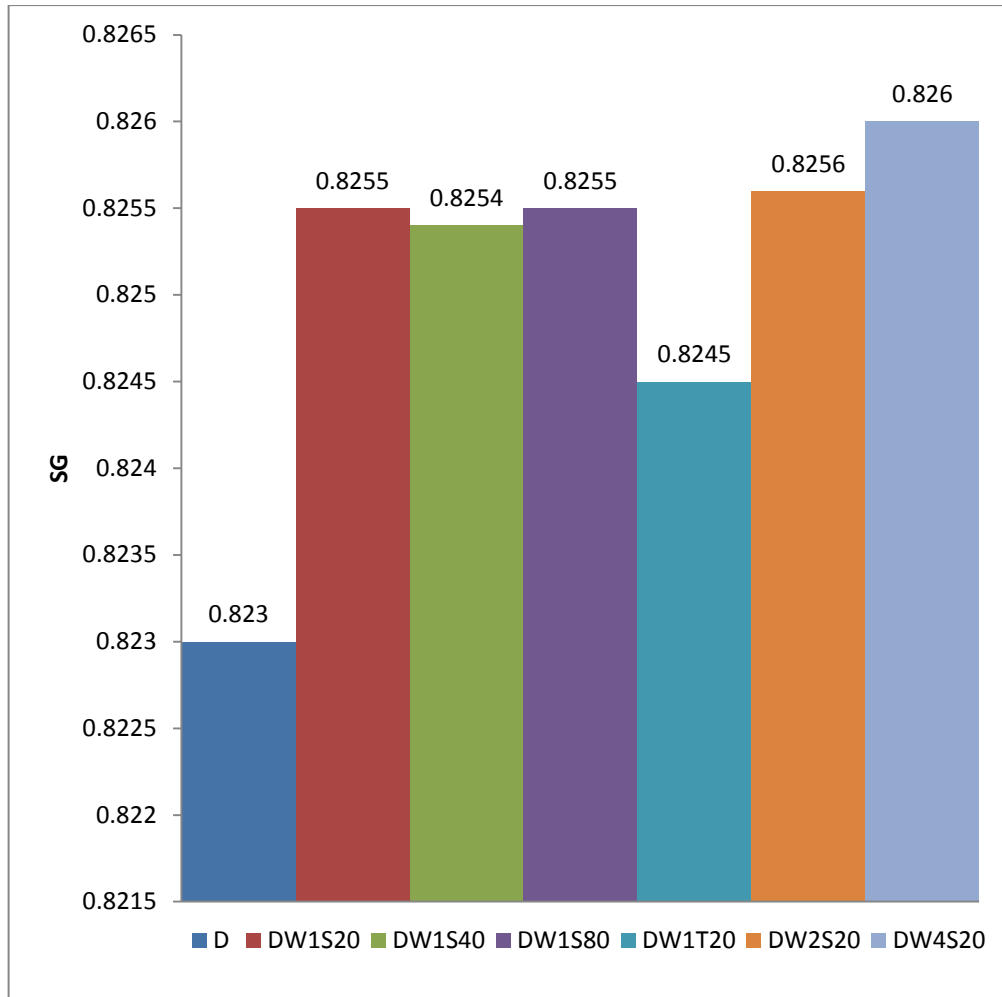


Fig.4.3: Comparison of SG of diesel fuel with emulsion fuels

4.2.3 Kinematic viscosity

Measurement of viscosity was done by using “Petrotest viscometer” which was discussed in the earlier section. During the measurement it was found that measurement time is directly related to the viscosity. If the viscosity of the fluid is more then it will take more time to flow from one end to the other.

The viscosity of diesel fuel is lesser whereas the DW4S20 has the higher viscosity in comparison to the other fuel samples. Comparison of viscosity of diesel fuel with emulsion fuels is done in the figure 4.4.

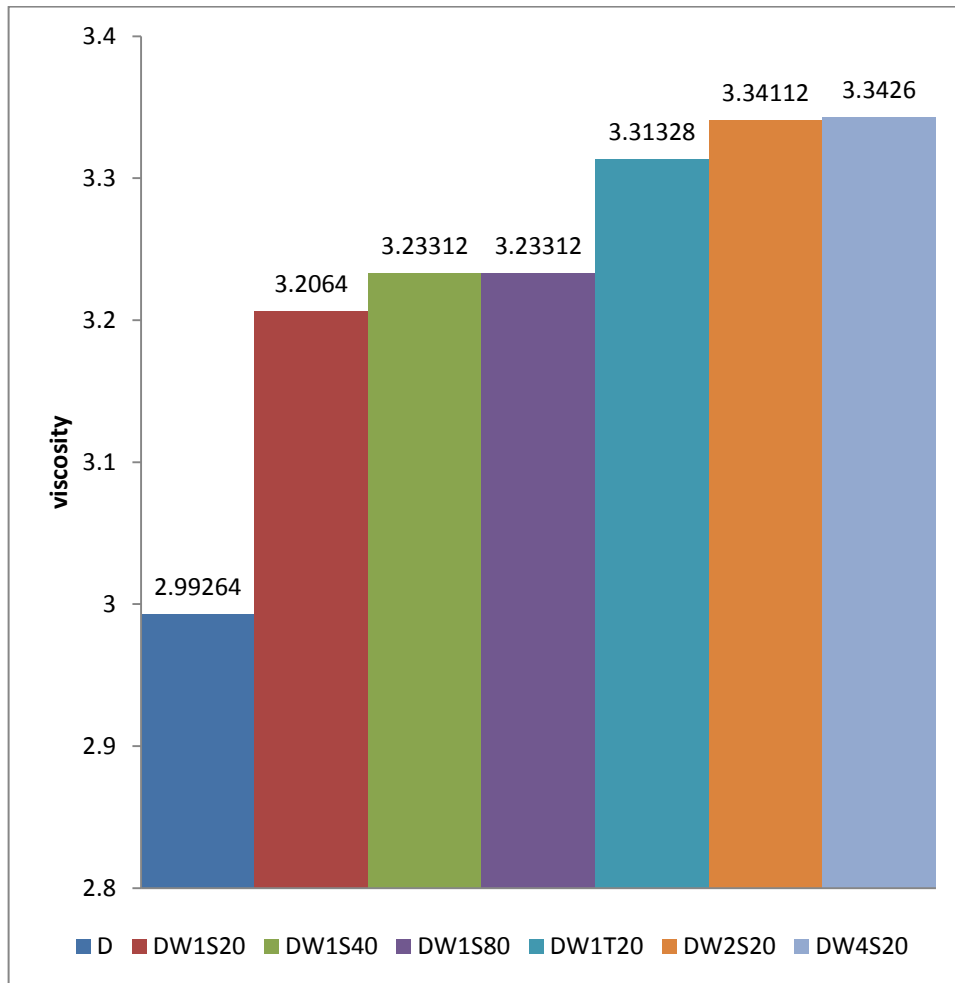


Fig. 4.4: Comparison of viscosity of diesel fuel with emulsion fuels

4.2.4 Calorific value

Calorific value is an important parameter regarding the engine performance and exhaust emission. NO_x emission is produced only at very high temperature. A bomb calorimeter which has been described in the earlier section was used to measure the calorific value of the test fuels.

When water is added in the fuel then its calorific value decreases. The vaporization of the liquid water and consequent dilution of the gas species decreases the temperature of the combustion products. Due to this the emission of NO_x decreases. But from the figure 4.5 it is found that the calorific value of fuel increases on addition of water upto the 4%. The calorific value of the diesel is 45.462 MJ/kg whereas the calorific value of the DW4S20 is 47.757 MJ/kg which is very high in comparison to the diesel fuel. The main mechanism inside the combustion chamber is very complex. Therefore it is very difficult to tell exactly the cause of rise in the calorific value of the fuel but microexplosion phenomenon may be the reason behind this increase in calorific value of the emulsion fuel.

Comparison of calorific value of diesel fuel with emulsion fuels is done in the figure 4.5.

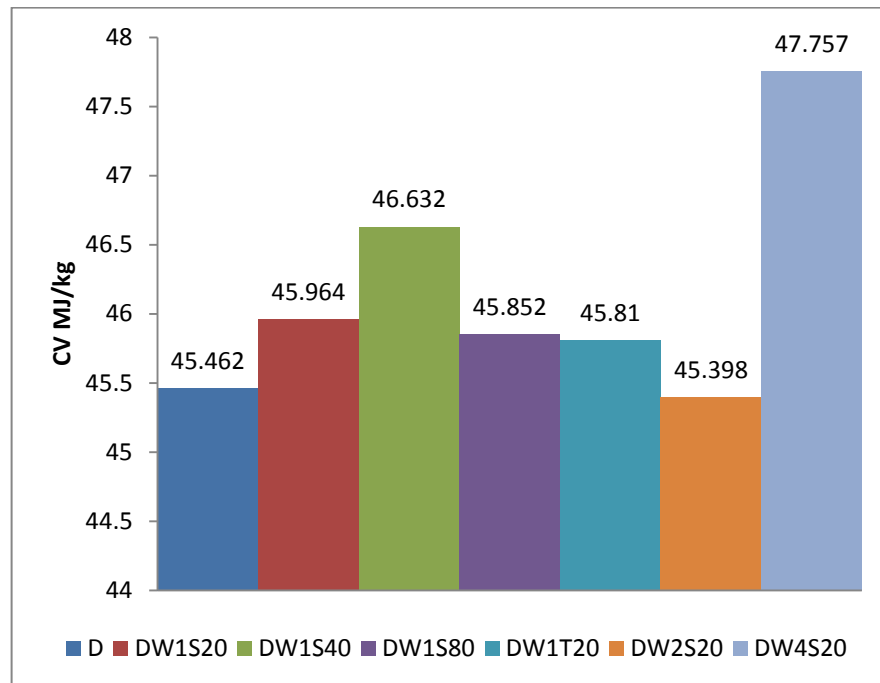


Fig.4.5: Comparison of calorific value of diesel fuel with emulsion fuels

4.3 Performance Characteristics

A series of engine test were carried out on a medium capacity Kirloskar diesel engine at a rated speed of 1500 rpm with water in diesel emulsion fuel. The performance characteristics brake thermal efficiency (BTE), Brake specific fuel consumption (BSFC) and the exhaust temperature was evaluated and results were compared with baseline data of the diesel fuel.

The performance characteristics as mentioned above are summarized below.

4.3.1 Brake thermal efficiency

Figure 4.1 shows the variation of BTE for different WiDE fuels on different loading conditions. It was observed that on increasing load, the BTE first tends to increase and then tends to decrease with further increase in load. It is also observed that maximum BTE occurs with DW4S20 followed by DW2S20, DW1S20, and D respectively.

The longer ignition delay and micro-explosion phenomena of emulsion fuel are the main cause to increase the brake thermal efficiency. The longer ignition delay leads to accumulating more amount of fuel which results in a higher heat release rate, higher fuel burning in the pre-mixed stage and better brake thermal efficiency.

Basha and Anand et al. ^[50] also noted 3.5 percent increase in brake thermal efficiency with 20 percent water in emulsion fuel. Alahmer et al. ^[51], and Wang and Chen et al. also reported improvement in BTE.

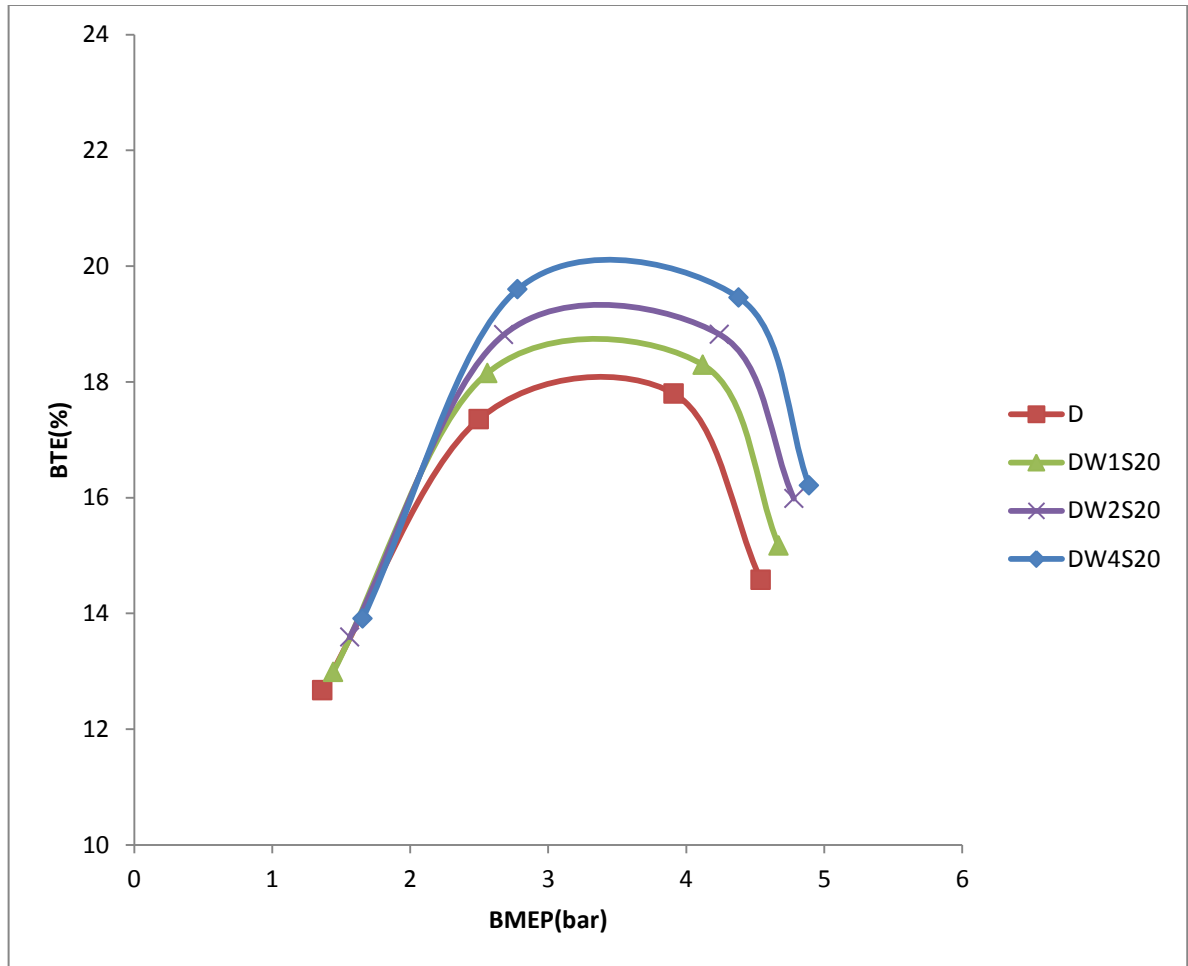


Fig.4.6: Variation of BTE vs BMEP for diesel and various WiDE fuel

4.3.2 Brake specific fuel consumption

Figure 4.2 shows the influence of the engine load on the brake specific fuel at a rated speed of 1500 rpm. Bsf_c is defined as the mass flow rate of fuel per unit of bp. From the experimental result it is observed that with an increase in load, the brake specific fuel consumption of all emulsion fuels decreases and then tends to increase with further increase in load.

The minimum bsfc was observed in the case of DW4S20, followed by DW2S20 and DW1S20 respectively. The intensity of micro-explosion behavior, improved air-entraining in the spray, higher premixed combustion, lower combustion temperature and more product

of combustion gas due to the presence of water in the emulsion are the main reasons to decrease the brake specific fuel consumption.

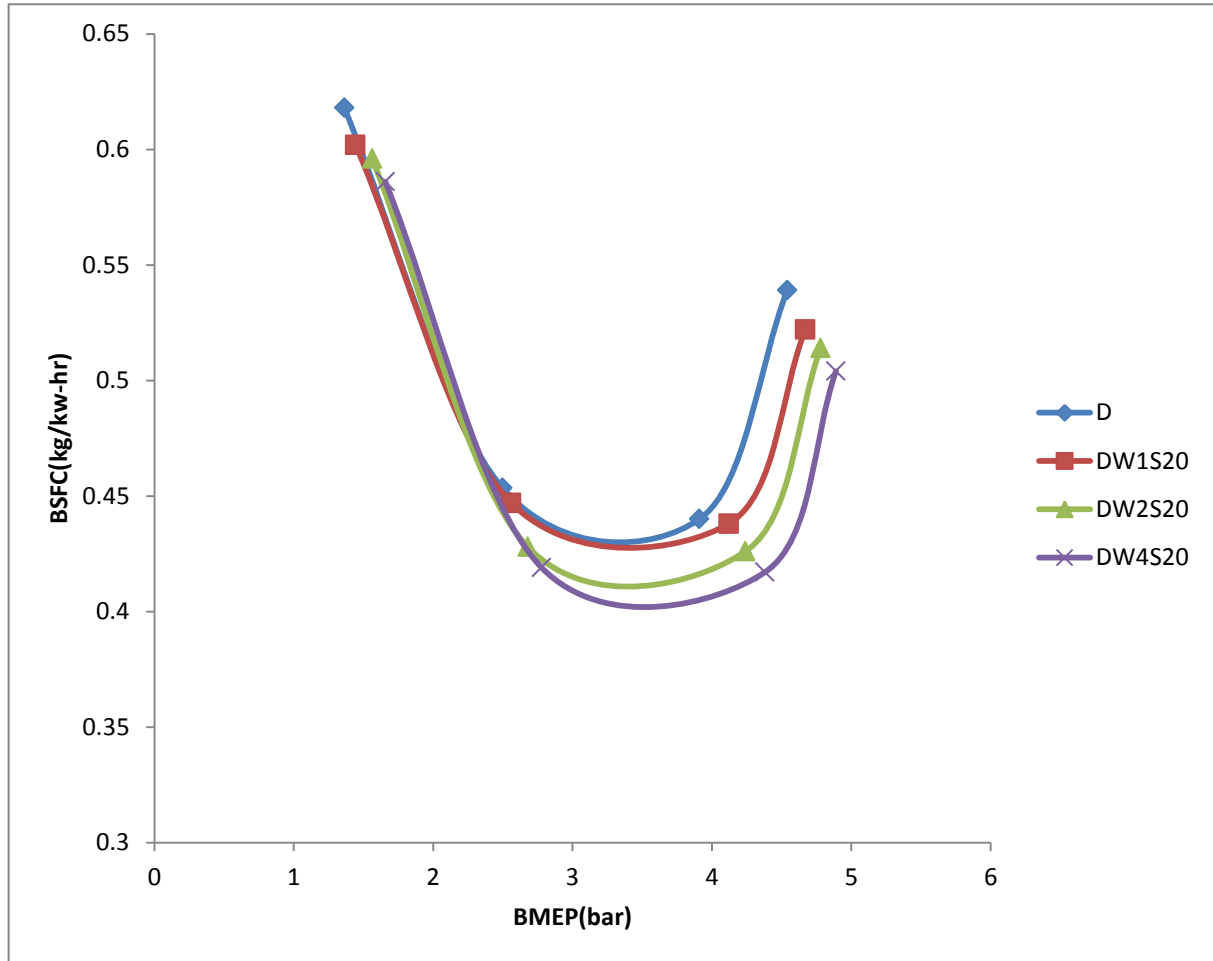


Fig. 4.7: variation of basic specific fuel consumption vs BMEP for diesel and water in diesel emulsion

Abu-Zaid et al. ^[52] also reported a decrease in brake specific fuel consumption with an increase in water in the emulsion.

4.4 Emission Characteristics

Engine test was carried out on a CI engine. Diesel and WiDE are used as a fuel to run the engine. The results of different emission characteristics are given below.

4.4.1 NOx emission

The variation of NOx emission for all test fuels is shown in figure 4.3. On increasing engine load the combustion temperature increases, therefore NOx will also increase. Therefore to control the emission of NOx, the temperature should be controlled. This can be done by adding the water in the diesel fuel. High latent heat absorption of water particle during the combustion will reduce the local high temperature which results in the reduction of NOx.

Water present in emulsion fuel increases hydroxyl (OH) concentration which leads to NOx reduction. Suresh and Amirthagadeswaran et al.^[53] also found 35 percent reduction in NOx. Attia et al.^[54] recorded 25 percent, whereas Park et al.^[55] recorded 20 percent reduction in NOx in their studies.

A numerical study is done by Samec et al.^[56] and he reported a reduction of 20 percent NOx emission with 10 percent water content in the emulsion.

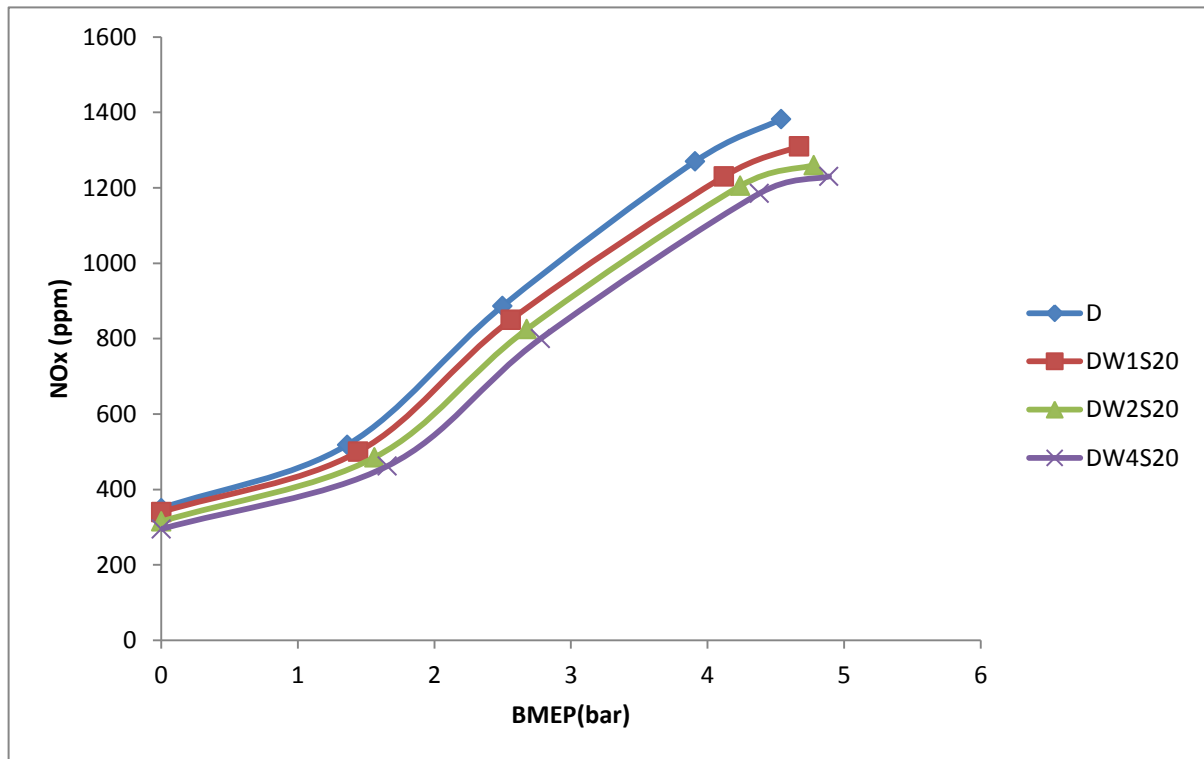


Fig. 4.8: variation of NOx vs BMEP for diesel and various WiDE fuel

4.4.2 Smoke opacity

The results suggest that on increasing the load on the engine smoke opacity also increases, smoke opacity is largely influenced by the engine load. Smoke opacity is highly reduced by DW4S20. The presence of water in diesel would increase the water vapour production in the exhaust gas. This will dilute the concentration of black smoke released from the diesel engine and thus smoke opacity will be less in comparison to diesel fuel. Apart from this water vapour produced from the combustion of the WiDE fuel may further be condensed to be liquid water, which could dissolve the part of the black smoke. This also resulted in significant reduction of black smoke opacity for burning the water in diesel emulsion fuel.

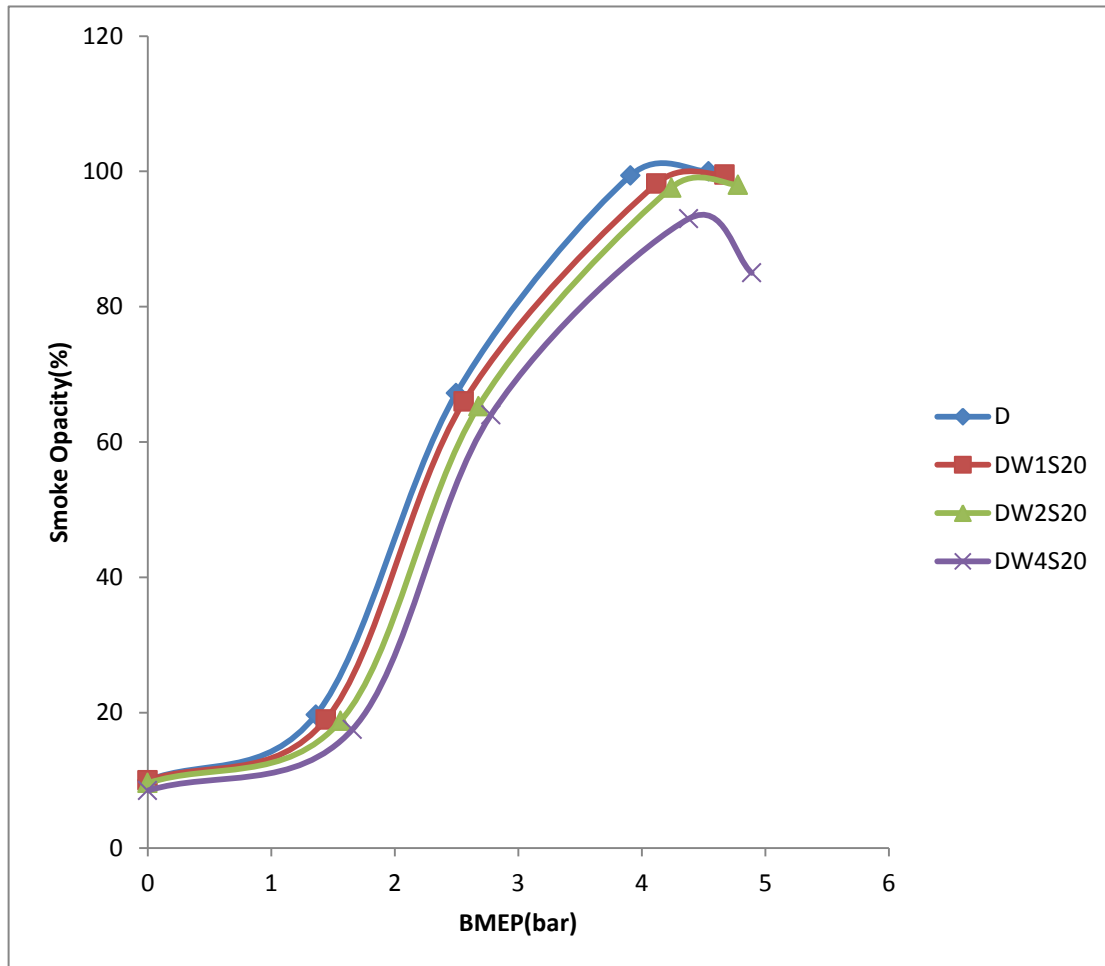


Fig.4.9: variation of smoke opacity vs BMEP for diesel and various WiDE fuel

4.4.3 CO emission

The results for CO emission is shown in figure 4.6. The CO emission increases on the addition of water in diesel fuel and it is highest for DW4S20. Carbon mono oxide (CO) and unburnt HydroCarbon (HC) in a CI engine are formed due to the Incomplete combustion, lack of homogeneity and slow burning of soot. The emulsion fuel decreases the combustion temperature that is not sufficient to convert the CO into CO₂.

Other factors which help in forming a higher level of emission in CI engine are increases in ignition delay and low flame temperature of emulsion fuel.

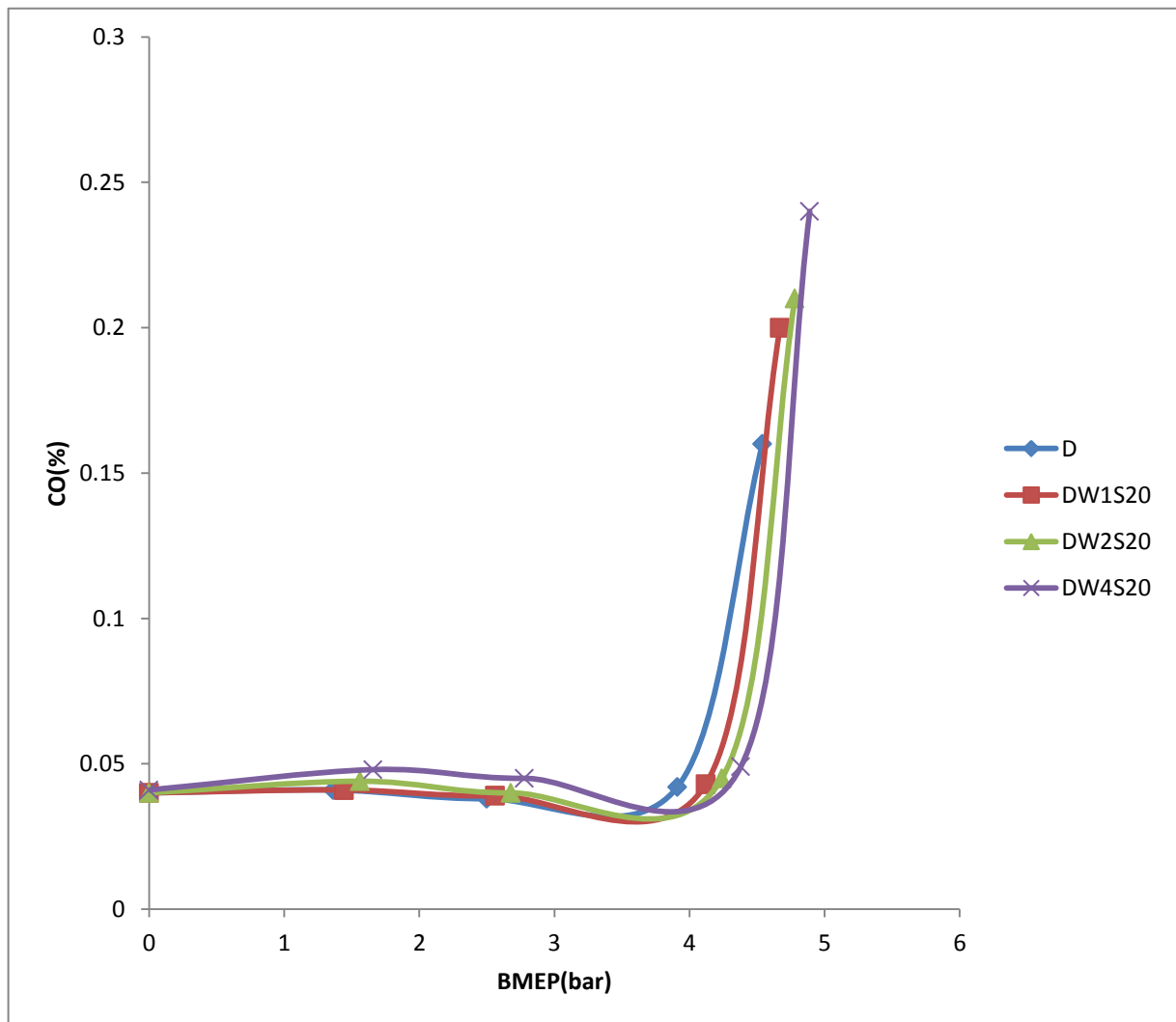


Fig.4.10: variation of CO vs BMEP for diesel and various WiDE fuel

Abdullah et al. ^[57] also observed the increase in CO and HC in emulsion fuel. The increase in these emissions is due to the high amount of OH contribution which results in better oxidation of carbon to carbonmono oxide.

CHAPTER-5

CONCLUSIONS AND FUTURE

RECOMMENDATIONS

5.1 Conclusions

The following conclusion can be made from this study:-

- The surfactants sorbitan monopalmitate (span 40) and sorbitan monostearate (span 4.7) have HLB value less than 7. Both the surfactants are in the greasy form. On stirring these are not properly mixed and some particles remain in the form of grease. These can choke the injector, therefore, these are not suitable to make emulsion fuels.
- For 1% water span 20, span 80, tween 20 have stability period for more than 15 days. But at 1% water concentration NO_x reduction is very less and it is nearly equal to 5%. Therefore if it is required to reduce more NO_x emissions from the diesel engines water percentage have to increase.
- For 4% addition of water NO_x reduction was 10% but the stability of emulsion was only for 8 days. Therefore these surfactants are not much effective to make water in diesel emulsion, and to increase the stability period other surfactants are required which can stabilize the emulsion for more than 90 days at 4-10% addition of water.
- Brake thermal efficiency increases with the addition of water and it was minimum for 1% and maximum for 4% water.
- Brake specific fuel consumption, NO_x emission, CO, Particulate matter emission decreases on increasing the water concentration and it was minimum for 4% of water.

5.2 Future recommendations

From the various studies, It is found that there is a conflict in the field of water in diesel emulsion fuel in terms of brake specific fuel consumption, brake power, hydrocarbon and carbon monoxide emissions due to the complication in combustion analysis. While all the studies report a reduction in oxides of nitrogen and Particulate Matter emission levels. Therefore to analyze the combustion and emission behaviour of CI engine running with WiDE fuel, an accurate numerical model is required.

Surfactant concentration, water concentration, stirrer speed can be optimized to obtain better physico-chemical properties with supreme stability.

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