

A
Dissertation Report
On
**Experimental studies on stationary single cylinder CI
engine operated on Jatropha-Diesel blended fuel with
Antioxidant to
minimize NO_x emissions**

Submitted in Partial Fulfillment of the Requirements for the Award of Degree of

Master of Technology

In

Thermal Engineering

By

DIGAMBAR SINGH

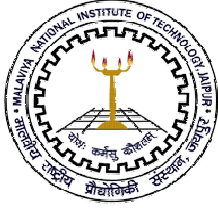
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CERTIFICATE

This is certified that the dissertation report entitled “**Experimental studies on stationary single cylinder CI engine operated on Jatropha-Diesel blended fuel with Antioxidant to minimize NOx emissions**” prepared by **Digambar Singh**(ID-2015PTE5046), in the partial fulfillment of the award of the Degree **Master of Technology in Thermal Engineering** of Malaviya National Institute of Technology Jaipur is a record of bona fide research work carried out by him under my supervision and is hereby approved for submission. The contents of this dissertation work, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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DECLARATION

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(Digambar Singh)

ABSTRACT

Biodiesel- diesel fuel made from animal or vegetable materials. Vehicle using biodiesel emit fewer pollutants as compared to diesel fuel. Biodiesel it is a renewable fuel, composed by fatty acid methyl (or ethyl) esters, produced by trans-esterification reaction between vegetable oils or animal fats and methanol (or ethanol). Vegetable oils can be used as alternative fuel in diesel engine. When vegetable oils are directly used as a fuel it is referred to as straight vegetable oils. Straight vegetable oils (SVO) have cleaner combustion properties as compared to diesel fuel. If we go for SVO it reduced PM, CO and HC emissions but NO_x emission slightly increases with SVO as compared with diesel fuel.

Use of antioxidant is one of the best methods to reduce formation of NO_x. Objective of this paper is experimental study on stationary single cylinder CI engine of 3.5kW rated power, operated on Jatropha-Diesel blended fuel with antioxidant p-phenylenediamine to minimize NO_x emission. Use of antioxidant is one of the best techniques. When antioxidant is used it donates an electron or hydrogen atom to free radical to inhibit oxidative process that is the main cause of NO_x formation. Antioxidant works by reducing the concentration of reactive radicals, chelating the transition metal catalyst, scavenging the initiating radicals and chain breaking reactions.

This report contains study of the effect of antioxidant of various concentrations on emission of engine which works on various load range. With different concentration of antioxidant (0.005%, 0.015%, 0.025%, 0.035% and 0.05% by mass) NO_x emission reduces for different loading condition and but emissions of HC and CO were found slightly increased. Maximum NO_x emissions reduction was found with 10% blend and with the concentration of 0.025% by mass of antioxidant.

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List of abbreviation

SVO - Straight Vegetable Oil

BD - Blend of Diesel and Jatropha

IC - Internal Combustion Engine

PM - Particulate Matter

CO- Carbon Mono Oxide

HC- Hydrocarbon

CV - Calorific Value

LPG- Liquid Petroleum Gas

CNG - Compressed Natural Gas

GHG - Green House Gas

CI- Compression Ignition

SI - Spark Ignition

Chapter 1

Introduction

The way towards energy sustainability includes the gradual adoption of available technologies, practices and policies which will fulfil the energy needs of the present population without compromising the ability of future generations to meet their energy demands. All countries are working to make themselves energy sustainable as energy is the basic entity for human to survive. A developing country like India, which has very large population, requires energy for its overall development. India is striving hard to solve problems related to energy such as energy supply security, emission control, economy and conservation of energy in the country etc. Generally, energy is consumed in agriculture, Industrial, transportation, residential sectors by a country for its development. In India, transport sector shares a high percentage of its overall energy consumption.

The emerging transport sector raises a big alarm for continuously depleting fossil fuels and increasing harmful emissions coming from the vehicles. The number of vehicles is increasing day by day which is offering a sound contribution to the degradation of quality of air in urban realms as well as at global level. Owing to high power density Internal Combustion Engines are extensively used in transportation and as a stationary power source. Continuously depleting petroleum reserves and prevailing rigorous emission norms have stimulated the researchers to evolve and instigate alternative fuels for automobiles with a thought of diminishing global emissions and lessening the consumption of fuels such as petrol and diesel.

1.1 Background

India is a developing country which has an increasing trend of crude oil production. India's crude oil production was 772.08 Thousand Barrel per Day in 2013[19]. Crude oil is a mixture of hydrocarbons which occurs in liquid state in natural underground reserves. It is passed through surface separating facilities and remained in liquid phase at atmospheric pressure after passing that. Depending upon the characteristic, Crude oil may also consists of small amounts of hydrocarbons which occur in gaseous state in natural

underground reserves but liquid at atmospheric pressure, small amounts of non-hydrocarbons (sulphur and various metals) produced with the oil, Drip gases, and liquid hydrocarbons produced from tar sands, oil sands, gilsonite, and oil shale. Crude oil is treated to get an extensive array of petroleum products, which includes heating oil's, petrol, diesel, jet fuels, asphalt, lubricants, ethane, propane, and butane and many other products which are used for their energy or chemical content. Appendix A shows crude oil production data of India from 1980 to 2013.

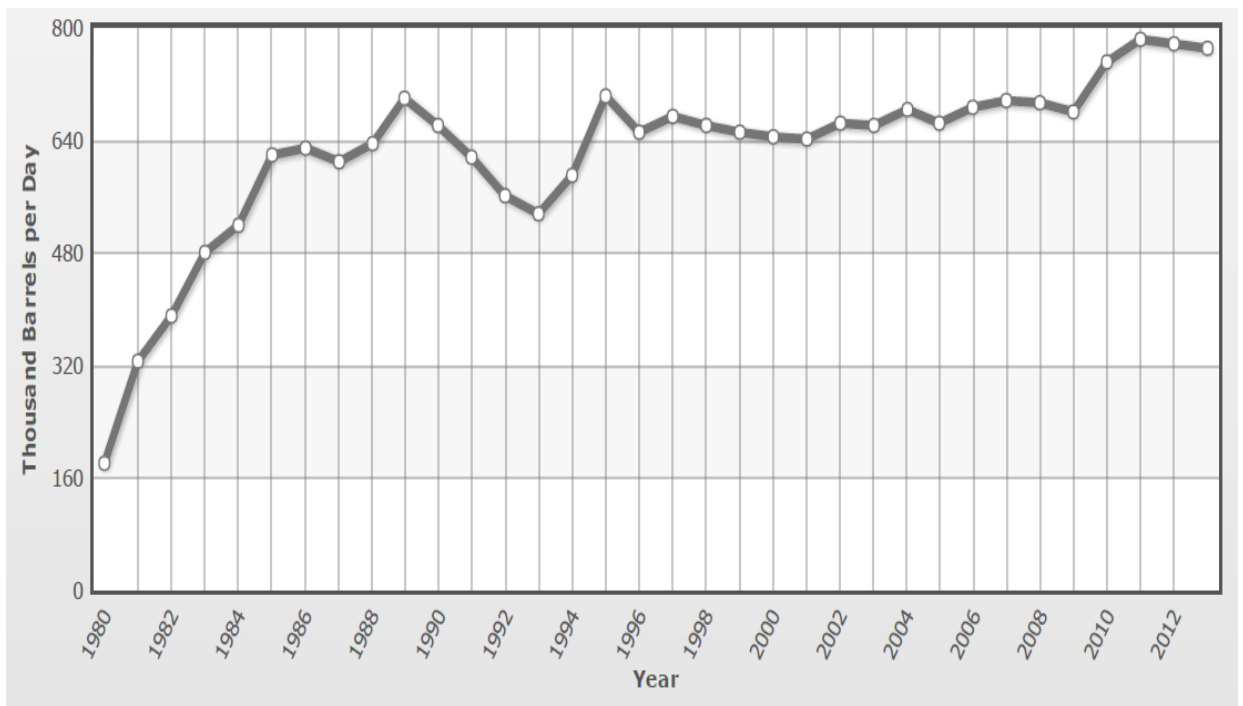


Figure 1.1 India's crude oil production by year [19]

India's crude oil consumption was having an increasing trend which had a value of 3509.00 Thousand Barrels per day in 2013[20]. It is clear from the data that there was a difference in Production and consumption of crude oil so crude oil was also imported in that era and which is continue to happen now days. As the data reveals, India heavily relies on crude oil imports in which petroleum crude is accounting for about 34% of the total inward shipments. India imports 80% of its oil demand. Presently, Saudi Arabia is

the biggest supplier of crude oil to India. After Saudi Arabia, India imports maximum crude oil from Iraq, Nigeria, Venezuela and Iran respectively. In 2010-11, Iran was the 2nd largest crude oil supplier tie India, after Saudi Arabia. India reduced its purchase from Iran in 2012-13 because western countries imposed sanctions on Iran. After that India had limited its crude oil supplies from Iran. Appendix B shows crude oil consumption data of India from 1980 to 2013.

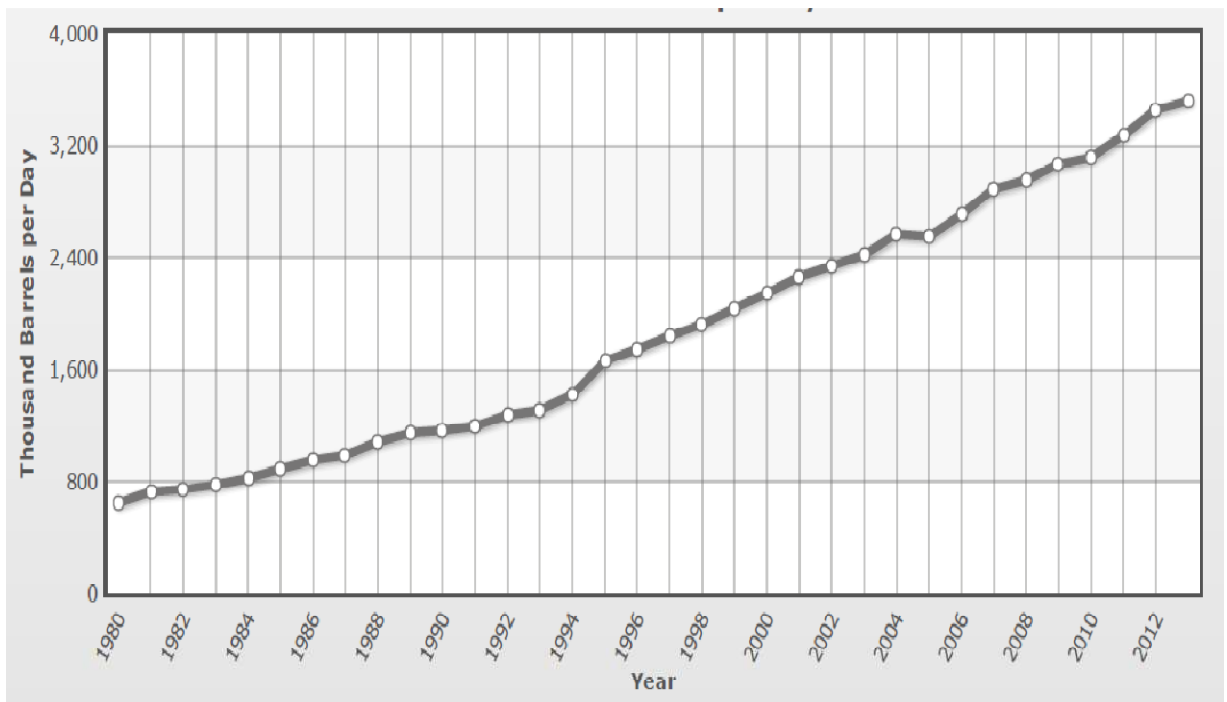


Figure 1.2 India's crude oil consumption by year [20]

1.2 Alternate Fuels

Alternate fuels are those which are substantially non-petroleum and produce energy security and significant environmental benefits. Alternative fuels that are used in engines for fueling are:

1.2.1 Alcohol

Although conventional fuels are the dominating energy resources for the present modern era, alcohol is a fuel which has been used throughout history. The four aliphatic alcohols (methanol, ethanol, propanol and butanol) are of great interest as alternate fuels because they can be produced biologically or chemically and their characteristics allow them to be deployed in presently working engines [18]. All four alcohols have high octane rating due to which fuel efficiency increases and it offsets the lower energy density of alcohol fuels to a great extent. So their fuel economy is comparable in terms of distance per volume metrics (kilometres per litre, or miles per gallon).

Methanol and ethanol can be synthesized from fossil fuels, biomass, or from carbon dioxide (CO₂) and water (H₂O). Generally, ethanol has been produced by fermentation of sugars and methanol has been produced by synthesis gas.

a) Fuel Economy and Performance

A litre of gasoline contains more energy than a litre of ethanol. Due to this is fuel economy is lower for ethanol. Energy difference amount varies according to the composition of the blend.

b) Emissions

The carbon dioxide (CO₂) is generated when ethanol is burned and this is compensated by the carbon dioxide (CO₂) captured when the crops are grown to make ethanol. On the other hand, petroleum is formed from plants that grew millions of years ago. On a life cycle analysis basis, GHG emissions are reduced on average by 40% with corn-based ethanol produced from dry mills, and up to 108% if cellulosic feed stocks are used, compared with gasoline production and use [18].

1.2.2 Biodiesel

Biodiesel is a renewable fuel which can be domestically produced from vegetable oils and animal fats. Physical properties of biodiesel are similar to petroleum diesel but it is a clean burning fuel in comparison to diesel.

a) Fuel Economy and Performance

Biodiesel has low calorific value in comparison to petroleum diesel owing to this biodiesel has less efficiency and power in comparison to diesel engine. Fuel consumption is also higher as compared to conventional fuel i.e. diesel. Biodiesel enhances fuel lubricity and increases the cetane number of the fuel. Lubricant of the fuel is required in diesel engine to keep moving parts from wearing prematurely [18].

Table 1.1 CV and Cetane number for Palm oil Biodiesel, Jatropha Biodiesel and Diesel [27]

Sr. No.	Fuel	Calorific Value (kJ/kg)	Cetane Number
1.	Palm Oil Biodiesel	36764	61.5
2.	Jatropha Oil Biodiesel	39340	58.4
3.	Diesel	43400	51.5

Generally, engine power will drop with the increase of content of biodiesel. For example, Carraretto et al. found that by increasing biodiesel percentage in its blends with diesel resulting in a slight drop in both power and torque over the entire range of speed for different blends (B20, B30, B50, B70, B80 and B100) of biodiesel in a 6-cylinder DI diesel engine. Aydin et al. found that the torque was reduced with the increase in CSOME (cottonseed oil methyl ester) in the blends (B5, B20, B50, B75 and B100). It was owing to lower heating value and higher viscosity of CSOME. Murillo et al. reported, by increasing the amount of biodiesel in the fuel, it dwindled engine power on a single-cylinder, four-stroke, DI and NA diesel engine [22].

b) Emissions

Using biodiesel in diesel engine reduces PM, HC and CO emissions significantly and it accompanies with an increase in NO_x emission as compared to conventional diesel engines with no or fewer modification. And it helps in reducing carbon deposit and wear of main engine parts. Hence biodiesel with small content in place of petroleum diesel can

help in maintaining air pollution at low level and easing the pressure on conventional resources without significantly effecting engine power and economy [24] [25].

Biodiesel lessens greenhouse gas (GHG) emissions because carbon dioxide released from the combustion of biodiesel is compensated by the carbon dioxide absorbed while growing the feedstock. Use B100 reduces carbon dioxide (CO₂) emissions by more than 75% in comparison with conventional diesel. Using B20 reduces carbon dioxide (CO₂) emissions by 15% [35].

1.2.3. LPG (Liquefied Petroleum Gas)

LPG is a mixture of many gases which are having varying proportions. Major constituents of LPG are propane (C₃H₈) and butane (C₄H₁₀) with minor amounts of propane (C₃H₈), various butanes (C₄H₈), iso-butane, and small amounts of ethane (C₂H₆) [27].

a) Fuel Economy and Performance

LPG (Liquefied Petroleum Gas) at primary infrastructure sites costs less per litre than petrol. It provides a comparable driving range in comparison to conventional fuel. LPG (Liquefied Petroleum Gas) has a higher octane rating than petrol and provides potentially more hp (horsepower) but it has resulted in lower fuel economy.

It has low carbon and low oil contamination characteristics which resulted in improved engine life in comparison to conventional petrol engines. The fuel and air mixture in case of LPG is completely gaseous which reduces the cold start problem that is generally linked with liquid fuels [33] [35].

b) Emissions

LPG in comparison with vehicles fuelled by conventional diesel and gasoline generates lower amounts of detrimental air pollutants and greenhouse gases (GHG). Emission mainly depends on vehicle type, drive cycle, and engine calibration.

1.2.4 Natural Gas

Natural gas is a domestically produced gaseous fuel. It is readily available through the utility infrastructure and it is a clean-burning alternative fuel. It should be compressed or liquefied for use in vehicles.

a) Fuel Economy and Performance

Natural gas vehicles (NGVs) are nearly similar to petrol vehicles in terms of power, acceleration, and cruising speed. The driving range of Natural gas based vehicles is generally less than that of gasoline. It is because by using natural gas, less amount energy content can be stored in the same size tank as compared to gasoline. Additional natural gas storage tanks or by using LNG (Liquefied Natural Gas) increase in the range can be obtained.

It can be used with higher compression ratio and it has high octane rating which results in a smoother engine operation as compared to conventional gasoline. In heavy-duty vehicles, dual-fuel, compression-ignited or CI engines are slightly more fuel-efficient than spark-ignited (SI) dedicated natural gas engines. Generally a dual-fuel engine increases the complexity of the fuel-storage system as it requires storage of two types of fuel [29].

b) Emissions

Natural gas has low emission as compared to conventional fuel. According to Argonne National Laboratory's Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model, light-duty vehicles which are running on natural gas can decrease life cycle greenhouse gas emissions (GHG) by 6% to 11%. Besides that vehicles use CNG produce no evaporative emissions because CNG fuel systems are completely sealed in those vehicles [29] [33] [35].

1.2.5 Hydrogen

Hydrogen can be obtained from many sources; most common is the water splitting or electrolysis. Electrolysis requires electricity to split the water, electricity can be generated

from fossil fuels, coal, natural gas, biomass, solar thermal techniques, exhaust gas of engine, nuclear fuels and other renewable energy techniques like Solar PV, hydro, wind energy. Trapping Sunlight for generating electricity for electrolysis is gaining popularity. Capturing solar energy is well suitable for countries like India. This also leads to a prominent green fuel.

a) Fuel Economy and Performance

Hydrogen is in gaseous state that reduces cold starting operation. It has following properties-

a) Lower minimum ignition energy

b) Higher burning rate

c) Higher diffusivity

d) Higher heating value

e) Higher octane number

f) Wider flammability range (4-75%) and ability to tolerate diluents delivers higher overall engine efficiencies when drawn with diesel and gasoline engines, this makes its use especially in high speed engines. It operates at leaner air-fuel mixtures than theoretical stoichiometric amount which improves the fuel economy of the system. Hydrogen has high Research octane number which makes the hydrogen powered engines less susceptible to knocks as compared to petrol engines. It is having high auto ignition temperature (585 °C) so for gasoline engines which are running on pure hydrogen, a gas mixer and gas injector may be employed to introduce the fuel into the combustion chamber and ignited by spark plugs. As Hydrogen is having high auto-ignition temperature so in diesel engines, it requires a pilot fuel (diesel 10 -30%) to be injected [29].

b) Emissions

Hydrogen has chemical and physical properties which makes it a good substitute for Petrol (SI) and diesel (CI) in IC engines. It is a clean fuel and doesn't emit hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO₂), sulphur oxides, volatile organic compounds and particulate matter (PM) because it has no carbon content which is related

to most fossil fuels. Hydrogen-powered fuel cell electric vehicles emit no detrimental substances. They have only water (H₂O) and warm air as emission. In engines little amounts of hydrocarbons and carbon oxides may be formed due to combustion of lubricating oils [33] [35].

1.3 Straight Vegetable oils

Straight vegetable oils contains no petroleum, but it can be blended at any level with petroleum diesel to create a blend. It can be used in compression-ignition (diesel) engines with little or no modifications. SVO can be used as a pure fuel or blended with petroleum in any percentage. B20 (a blend of 20 percent by volume SVO with 80 percent by volume petroleum diesel) has demonstrated significant environmental benefits.

Biodiesel is registered as a fuel and fuel additive with the EPA and meets clean diesel standards established by the California Air Resources Board (CARB). Neat (100 percent) biodiesel has been designated as an alternative fuel by the Department of Energy (DOE) and the US Department of Transportation (DOT).

1.3.1 Jatropha SVO

As per the National Biodiesel Policy, 2008 government of India aims that 20% of the diesel consumption from plants. To reach this targets we have to cultivate the biodiesel plants in 140,000 km² of land, presently in India fuel yielding plants cover less than 5,000 km² Most cultivated plant for biodiesel production in India is “JATROPHA” Dr.Kalam , was one of the strong advocates of Jatropha cultivation for production of biodiesel. As per statistics of Dr.Kalam, we have to use 300,000 km² out of 600,000 km² waste land in India for cultivation of Jatropha.

- It is an exotic plant for India and is species native to Mexico and Central America. In India, it is believed to have been introduced by Portuguese navigators in the 16th century.

Common Names : Ratanjyot, Purging net, physic nut.

Botanical Name	: <i>Jatropha curcas</i>
Family	: Euphorbiaceae
Availability	: Throughout India (mostly in dry/tropical areas)
Features	: Small tree or shrub, (3-5 m in height), smooth greasy bark which exudes whitish colored, watery latex when cut and large green to pale green leaves (deciduous), alternate but apically crowded
Gestation period	: Less than one year (minimum amongst all the tree borne oilseeds)
Productive life	: 30-35 years.

Table 1.2 various properties of Jatropha blend with Diesel

Property	Diesel	Jatropha oil	B5	B10	B15
Density (kg/l) At 30 ⁰ C	0.838	0.944	0.8433	0.8486	0.8539
Kinematic Viscosity at 30 ⁰ C [x10 ⁽⁻²⁾ strokes]	4-8	52.76	8.333	10.676	13.677
Cetane number	40-45	38	42.275	42.05	41.826
Flash point in ⁰ C	45-60	210	60.375	68.25	77.152
Calorific value (kJ/kg)	43400	39340	43197	42994	42791

1.3.2 Why Jatropha?

It is easy to cultivate Jatropha, it can grow on all the climatic conditions and soils hence it is cultivated in most of the places. It is less expensive to cultivate jatropha and most of the jatropha seed varieties are available of less cost. The percentage of yield is high and the extraction of oil is also maximum. Jatropha provides higher rate of output than any other crops. It is very easy to maintain the jatropha plant even at the seedling stage.

Jatropha stands as an ideal crop among the bio-diesel crops because of the following reason:

- a) Drought resistant
- b) Jatropha plant has the ability to grow well on poor and infertile soil, in marginal areas and can withstand any type of climate
- c) Needs only little amount water and maintenance
- d) The plant can be harvested for about 50 years

Advantages of the Jatropha plant

- a) Low cost seeds
- b) High oil content
- c) Small development period
- d) Grow on good and despoiled soil
- e) Grow in low and high rainfall areas
- f) Does not require any special maintenance
- g) Can be harvested in non-rainy season
- h) Size of the plant makes the collection of seeds convenient
- i) Multi products are developed using a single jatropha plant. The products include bio-diesel, soap, mosquito repellent, and organic fertilizer.

1.3.2 NO_x formation:

- a) The factors that cause diesel engines to run more efficiently than gasoline engines also cause them to run at a higher temperature. This leads to the creation of nitrogen oxides (NO_x).
- b) Fuel in any engine is burned with extra air and some of the oxygen is used to burn the fuel.
- c) When the peak temperatures are high enough for long periods of time, the nitrogen and oxygen in the air combines to form Nitrogen oxides.
- d) These are normally collectively referred to as “NO_x”.

NO_x reduction techniques:

- 1. In order to reduce NO_x a engine should run at a lower temperature than the normal temperature.
- 2. Reduced cylinder temperatures can be achieved in three ways.
 - a) Enriching the air fuel mixture
 - b) Lowering the compression ratio and retarding ignition timings
 - c) Reducing the amount of Oxygen in the cylinder

1.4 Fuel additives

Until the latter part of the twentieth century there was little or no use of diesel fuel additives. Due the versatility and robustness of the diesel engine, suitable diesel fuel could be produced from a blend of straight-run atmospheric distillation components. Where a refiner had a necessity to bias production towards gasoline then the diesel pool could often be supplemented with cracked gas oils from the gasoline refining process. As fuel sulfur levels were gradually reduced then additional processing could be required depending on the crude oil source. With the increasing fuel demand, changing demand mix and tightening specifications the refining processes have changed and with it the use of diesel fuel additives. Although there is no rigorous definition of what constitutes an

additive, as opposed to a blending component, it is generally accepted that an additive is something added at less than 1% w/w (i.e. 10,000 mg/kg or 10,000 ppm). Because of this low treat rate of additives the physical properties of the fuel, such as density, viscosity, and volatility are not changed significantly.

To increase the yield of diesel fuel the refiner must cut deeper into the crude feedstock; necessitating the use of flow improvers to restore the low temperature performance of the fuel. With increasing demand for improved ignition quality and increasing cetane number specifications the use of ignition improver additives has also risen. As legislation specifying ultra-lower fuel sulfur levels has spread, the ability of the diesel fuel to lubricate the fuel injection equipment has diminished; this has necessitated the use of lubricity additives. The additives discussed in this paper can be categorized as follows:

- Fuel handling and distribution additives
 - Low temperature operability additives
 - Flow improvers
 - Wax anti-settling additives
 - Cloud point depressants
 - De-icing additives
 - Other fuel handling additives
 - Antifoam additives
 - Drag reducing additives
 - Static dissipater additives
 - Biocides
 - Demulsifiers
 - Dehazers
 - Corrosion inhibitors for fuel distribution system
 - Marker dyes
 - Deodorants and re-odorants
- Fuel stability additives

- Antioxidants
- Stabilizers
- Metal deactivators
- Dispersants
- Engine protection additives
 - Corrosion inhibitors for vehicle fuel system
 - Injector cleanliness additives
 - Lubricity additives
- Combustion additives
 - Ignition improvers
 - Smoke suppressants
 - Combustion catalysts

1.4.1 Antioxidants

Antioxidants are those which reduces amount of oxygen content in combustion chamber to reduce formation of NO_x .Some of useful antioxidants are as follows:

- Butylated hydroxytoluene
- 2,4-Dimethyl-6-tert-butylphenol
- di-tert-butylphenol- Phenylene diamine,
- ethylene diamine
- p-phenylenediamine

1.4.2 Why p-phenylenediamine as antioxidant?

P-phenylenediamine selected as test additives as per the literature survey. Amines were chosen because they are active reductants for NO_x in a catalytic or gas phase systems. The chemical structure of the antioxidant and its specifications are given below. The free radicals formation during combustion determines the rate of reaction and prompt NO_x production. Free radical is a highly reactive molecule with one or more unpaired electrons. Examples include oxygen molecule, nitric oxide, superoxide ion and hydroxyl

radical. Antioxidant delays or inhibits oxidative processes by donating an electron or hydrogen atom to a radical derivative. Generally, antioxidants can reduce free radical formation by four routes; chelating the transition metal catalysts, chain breaking reactions, reducing the concentration of reactive radicals and scavenging the initiating radicals.

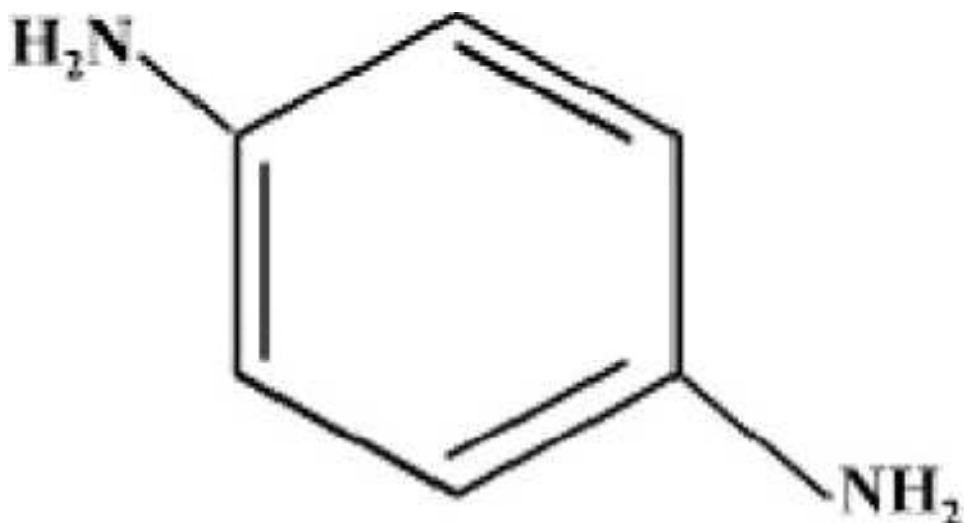


Figure 1.2 Chemical structure of P-phenylenediamine

Specifications - CAS number 106-50-3
Minimum assay 97%
Molecular weight 108.14
Melting point 141 _C
Sulphated ash 0.05%

1.5 Need of the study

With the increasing population demand of conventional fuels are increased but the resources of conventional fuels are limited. One day all the resources would be depleted. These issues motivate us for the use of alternative fuels with this all the above problems is resolved. One more issue that is related to environment is use of conventional fuels emit lots of harmful contents. The use of alternative fuel considerably decreases harmful exhaust emission like carbon mono oxide, carbon dioxide, particulate matter and sulfur

dioxide. But NO_x emission increases in the CI engine. There are too many problems that are associated with NO_x like health and environment problem. So the reduction in NO_x emission is required, there are different methods but use of antioxidant is one of it.

1.6 Objective of the study

To solve the problem of fuel scarcity due to depleting fossil fuels and rising prices alternative fuels are used. the main issue associated with SVO is NO_x emission that is harmful for health and environment.

- To analyse the performance of CI engine with Jatropha (SVO) with Diesel blend at various loads.
- To Measure the regulated NO_x emissions with using p-phenylenediamine antioxidant in Jatropha(SVO) with Diesel blend and compare with base diesel.
- To determine the optimum percentage of p-phenylenediamine to be mix for maximum NO_x reduction

1.7 Outline of thesis

The chapter plan of the thesis is as under:

Chapter 1: Introduction

The first chapter presents an overview of energy scenario of the world and India. It includes information like fuel economy and performance and emissions for presently used alternate fuels (Alcohol, Biodiesel, LPG, CNG and Hydrogen). It presents an introduction to Jatropha SVO and Why to use Antioxidant in Jatropha(SVO) with Diesel and what are the advantages and limits to that.

Chapter 2: Literature Review

In this chapter, an overview of the available literature corresponding to the Jatropha(SVO), Jatropha Biodiesel and Antioxidants are discussed. It includes experimental studies which are done on engines to evaluate the performance and emissions levels by using p-phenylenediamine antioxidant with blend of Jatropha(SVO) and Diesel.

Chapter 3: Methods and Materials

This chapter includes all information related to present research work. It includes the set-up details, fuel details and information about all the accessories which are used to attain the objectives of present work. It includes all the mathematical formulas which are used for the calculation of engine performance parameters.

Chapter 4: Results and Discussion

The results are summarized and discussed in this chapter. It includes the details about the performance and regulated emissions levels of all fuels which are tested in CI engine.

Chapter 5: Conclusion

This chapter includes the conclusion of the present research work. Challenges and limitations of the current study are discussed.

Literature Review

Lot of research work has been carried out by different researchers in the field of alternate fuels for past many years; Jatropha (SVO) with Diesel blend is one of them promising alternate fuel. Researchers worked to compare the performance and emissions of Jatropha (SVO) with diesel blend by use of Antioxidants. This chapter gives an overview about the works that have been performed by various researchers on reduction of NO_x by use of Antioxidants.

2.1 Studies on Jatropha SVO with Diesel

The main goal of this experiment was to investigate practical parameters through analysis and experiments that would increase the efficiency and effectiveness of SVO operated C.I. engine; ultimately resulting in quality end products. Therefore in this research, significant studies have been reviewed under the following main headings:

Diesel engine performance with straight vegetable oil (SVO).

- Production and processing of straight vegetable oils
- Fuel Properties.
- Chemical composition of fuels.
- Performance and exhaust emissions of diesel engine with Diesel and SVO Blends.
- Energy and Exergy analysis of C.I. engine with Diesel and SVO Blends.
- Optimal performance parameters.

A number of research works have been carried out with SVO. Some of the related articles on SVO are given below. It was observed that SVO posed operational and durability

problems when subjected to long term usage in CI engine. These problems can be attributed to high viscosity, low volatility and poly saturated characters of vegetable oil.

Barsic et al. (1981) conducted experiments using 100% sunflower oil, 100% peanut oil, 50% peanut oil with diesel. A comparison of the engine performance of Sunflower oil and peanut oil results showed that there was an increase in power and emissions.

Tadashi and Young et al. (1984) evaluated the feasibility of rapeseed oil and palm oil for diesel fuel in a naturally aspirated direct injection diesel engine. It was found that vegetable oil fuels gave an acceptable engine performance and exhaust emission levels for short-term operation. However, they caused carbon deposit build-ups and sticking of piston rings with extended operation.

Hammerlein et al. (1991) conducted experiments on naturally aspirated turbocharged air cooled and water cooled engines using rapeseed oils. Experiments were conducted using filtered rapeseed oil. It has been reported that the brake power and torque using rapeseed oil as fuel are 2% lower than that of diesel. The heat release rate is very similar for both fuels. With all the engines tested, maximum brake power was obtained with rapeseed oil. Lower mechanical stresses and lower combustion noise were observed. The emission of CO and HC are higher, whereas NO_x and particulate emission are lower in comparison with diesel fuel.

Z. Mariusz and J. Goettler et al. (1992) conducted experiments on sunflower oil and recommended incorporating dual fuel pre-heater for durability improvements of diesel engines. The durability of the engine increased through the prevention of engine operation at low load and low speed conditions, reduced exposure time of fuel injection system at very high temperature conditions during transition process from high to light loads and elimination of fuel injection of oil during shut down period.

S. Dhinagar and B. Nagalingam et al. (1993) tested neem, rice bran and karanja oil with a low heat rejection engine. An electric heater and exhaust gas was utilised for heating the oil. He observed that 1 to 4% lower efficiency was compared to that of diesel in case of without heating. However with heating the efficiency was improved.

Forson et al. (2004) conducted experimental investigation on pure jatropha, pure diesel and blends of jatropha and diesel in a direct injection single-cylinder diesel engine. The results obtained suggested that the above said oil exhibited similar performance and broadly similar emission levels under comparable operating condition. It was also observed that introduction of jatropha oil into diesel fuel appears to be effective in reducing the exhaust gas temperature.

Ramadhas et al. (2004) conducted experimental work by using rubber seed oil. He concluded that cold weather operation of the engine is not easy with vegetable oils. Raw vegetable oil can be used as fuel in diesel engines with some minor modifications. Results showed that the thermal efficiency was comparable to that of diesel with small amount of power loss. The particulate emissions of vegetable oils are higher than that of diesel fuel with a reduction in NO_x.

Agarwal et al. (2008) studied the performance and emission characteristics of linseed oil, mahua oil, and rice bran oil in a stationary single cylinder four stroke diesel engine and compare it with mineral diesel. Observed that straight vegetable oils posed operational and durability problems when subjected to long term usage in C.I. engine. These problems are attributed to high viscosity, low volatility and poly saturated character of vegetable oils.

Agarwal et al. (2009b) experimented with preheated karanja oil and blends. Performance and emission characteristics were found to be very close to mineral diesel for lower blend concentration. However for higher blend concentration, performance and emission were observed to be marginally low.

Sidibe et al. (2010) reviewed the state of the art for SVO use as fuel in diesel engines, based on a bibliographic study (literature review). The 1st section of the document examines the type and quality of vegetable oils for fuel use in diesel engines. The second section discusses the advantages and disadvantages of two options recommended for SVO use in diesel engines: dual fuelling and blending with diesel fuel. He concluded that SVOs can be used as a replacement of diesel oil in the agricultural diesel engines. They can be directly produced locally in a short supply chain and offer the extra fuel needed to

increase agricultural production. Their by-products can be used in agriculture and livestock production.

Acharya et al. (2011) conducted experiment on preheated SVO of karanja, kusum blends with diesel. Experiments were designed to study the effect of reducing kusum and karanja oil's viscosity by preheating the fuel, using a shell and tube heat exchanger. They concluded that, the engine performance with kusum and karanja oil (preheated), was found to be very close to that of diesel. The preheated oil's performances were found to be slightly inferior in efficiency due to low heating value. The performance of karanja oil was found better than kusum oil in all respects. The viscosity of kusum and karanja oil was reduced by preheating to 100–130°C. It was found that in the above cases the viscosity was close to that of diesel –which would be suitable for the engines.

Masjuki et al. (2015) used preheated palm oil to run a C.I. engine. Preheating reduced the viscosity of fuel. Torque, Brake Power, Specific fuel consumption, exhaust emission and Brake Thermal Efficiency were found to be comparable to that of diesel.

Gerhard Vellguth (2011) studied the performance of a direct injection single cylinder diesel engine with different vegetable oils. He reported that vegetable oils could be directly used as fuels in diesel engines on a short-term basis with little loss in efficiency. In long-term operation of engine with vegetable oils, he observed operational difficulties like carbon deposits, changes in the lubricating oil properties and ring sticking problems.

Varaprasad et al. (2010) investigated the effect of using jatropha oil and esterified jatropha oil on a single cylinder diesel engine. They found that the brake thermal efficiency was higher with esterified jatropha oil as compared to raw jatropha oil but inferior to diesel. They also reported low NOX emission and high smoke levels with neat jatropha oil as compared to esterified jatropha oil and diesel.

Parmanik et al. (2006) studied the properties and use of jatropha curcas oil and diesel fuel blends in compression ignition engine. The exhaust gas temperature was observed to be reduced due to reduced viscosity of the vegetable oil diesel blends. It was found that the fuel consumption was increased with a higher proportion of the jatropha curcas oil in the blends. Acceptable thermal efficiencies of the engine were obtained with blends

containing up to 50% (by volume) of jatropha oil. The tests were also conducted by Forson et al. [96] on a single-cylinder direct injection engine operated on diesel fuel, jatropha oil and blends of diesel and jatropha oil in proportions of 97.4% / 2.6%; 80% / 20%; and 50% / 50% by volume. The test results showed that jatropha oil can be conveniently used as a diesel substitute in a diesel engine.

2.2 Studies on antioxidants in C.I. engine

Varatharajan et al. (2011) investigated mitigation of NO_x emissions using different antioxidant additives in Jatropha biodiesel and observed that p-phenylenediamine is the more effective additive than other antioxidant additives such as ethylenedia-mine, a-tocopherol, butylated hydroxytoluene and ascorbic acid. It could reduce NO_x emissions by about 43.55% compared to neat biodiesel.

Palash et al. (2014) investigated experimental study on a four-cylinder diesel engine to evaluate the performance and emission characteristics of Jatropha biodiesel blends (JB5, JB10, JB15 and JB20) with and without the addition of N, N0-diphenyl- 1, 4-phenylenediamine (DPPD) antioxidant. The results showed that this antioxidant additive could reduce NO_x emissions significantly with a slight penalty in terms of engine power and Brake Specific Fuel Consumption (BSFC) as well as CO and HC emissions. When compared to diesel combustion, the emissions of HC and CO with the addition of the DPPD additive were found to be nearly the same or lower.

Palash et al. (2014) reviewed that the average reduction of NO_x emissions by using additives, EGR, WI & ET, ITR, ST and LTC are in the ranges 4–45%, 26–84%, 10–38%, 9.77–37%, 22–95% and 66–93% respectively, compared to biodiesel combustion without applying technologies. However, the average reduction of NO_x emissions by using those technologies for biodiesel are reasonable, 36–46%, 3–34%, 21–37%, 33–92% and 8.68–70% respectively, when compared to diesel.

Vedaraman et al. (2010) studied the effect of different blends of palm biodiesel with diesel on engine performance and emission characteristics and found B20 to be the optimum blend in terms of higher thermal efficiency and lower NO_x emission. B20 also

produced about 28% and 30% lower CO and HC emissions compared to baseline diesel, respectively

Ng et al. (2013) evaluated the suitability of PME-based biodiesel and its blends for on-road usage. They observed a reduction of tailpipe NO, UHC, and smoke opacity when neat PME was used, with maximum decreases of 5.0%, 26.2%, and 66.7%, respectively

2.3 learning from literature survey

From the literature survey we learn about the different alternative fuels that can be used in IC engine. We also learn about the advantages and disadvantages of these fuels when used in IC engine. When we go for the biodiesel NO_x emission become a severe problem in CI engine so in the literature we learn different techniques for the reduction of NO_x. One of the best techniques is use of antioxidant so we learn about the different types of antioxidants.

Chapter 3

Methods and Materials

In this chapter, methods followed and materials used are described which are to attain the objectives of present research. This chapter includes procurement of Antioxidant p-phenylenediamine, preparation of blend, experimental set-up and experimental Technique.

3.1 Procurement of Antioxidant

For the experiment, p-phenylenediamine is procured with help of Savita chemicals, Jaipur from Triveni chemicals, Mumbai.

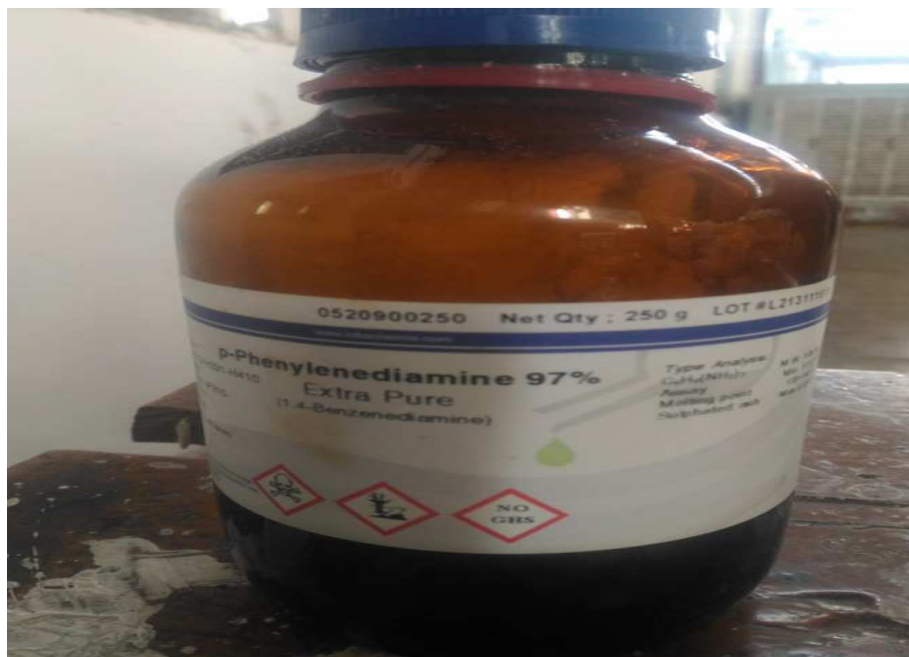


Figure 3.1 p-phenylenediamine(Antioxidant)

3.2 Preparation of blend

Preparation of blend for testing done in two processes, first different percentages of Jatropha(SVO) mixed with Diesel and after that different percentages of antioxidant mixed with blends.

3.2.1 Mixing of Jatropha (SVO) with Diesel

In this experiment test performed with different blends of 'Jatropha oil', i.e. 5% ,10% 15% and blends of Jatropha oil.

Steps to prepare blend:

1. Drop certain quantity of Jatropha oil into 500 ml beaker.
2. Fill rest of the beaker with diesel fuel.

Eg: for 10% blend 50ml Jatropha oil and 450 ml diesel in a 500 ml beaker.

3.2.2 Mixing of antioxidant

As p-phenylenediamine is in solid state and it is to be mix with liquid Jatropha (SVO) and Diesel blend. For homogenous mixing different methods tried i.e. direct mixing, magnetic stir, less RPM stir and mixer grinder of 20000 RPM. Only mixer grinder of 20000 RPM mixed antioxidant with fuel blend.



Figure 3.2 Mixing of antioxidant

3.3 Experimental Setup

Experiment set-up includes the details about the engine, mixer, Load arrangement, Gas Analyzer and other auxiliary equipment which were used in the research work.

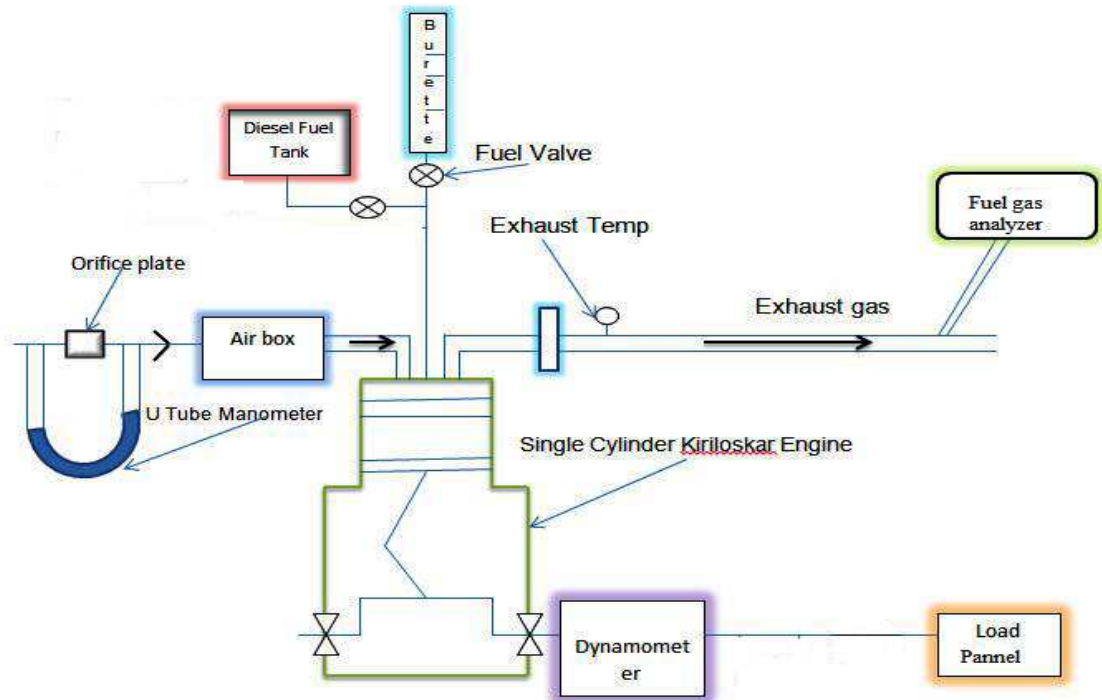


Figure 3.3 Schematic diagram of experimental setup

3.3.1 Engine

The engine being used in current project work is a single-cylinder 4-stroke water cooled C.I engine, coupled to a dynamo (generator) which converts mechanical shaft work of engine into electrical output with the help of alternator.



Figure 3.4 Single cylinder 4 stroke C.I. engine

Table 3.1 Engine specifications

PARAMETER	UNIT/TYPE	SPECIFICATION
Rated output	hp	4.7
No of cylinders		1
Bore x Stroke	mm	102 x 116
Compression Ratio		17
Type of engine		Compression Ignition
Fuel		High speed diesel
Injection type		Direct injection

Speed	Constant Speed	1500 rpm
Governor	Mechanical	Class B-1
Lubrication	Wet Sump	SAE 40
SFC	gms/kWhr	338

3.3.2 Alternator

The alternator being used in current project work, coupled to a 4 stroke single cylinder C.I. engine which converts mechanical shaft work of engine into electrical output.

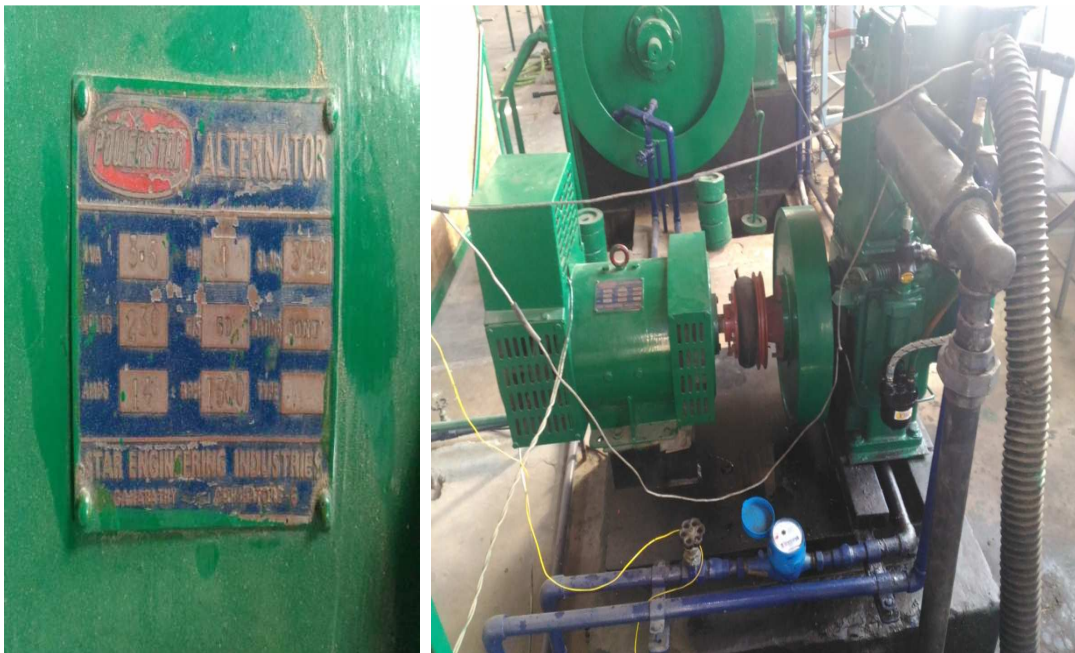


Figure 3.5 Alternator

Table 3.2 Alternator specifications

PARAMETER	UNIT/TYPE	SPECIFICATION
Type		Slip ring type
No of poles		4
Speed	RPM	1500
Max output	kVA	5
Frequency	Hz	50±5
Insulation class	H	180 °C
Phase		Single
Power Factor(P.F)		1
Efficiency	%	97@ full load

3.3.3 Fuel consumption rate measurement

Flow of fuel measured with the help of burette. Time noted down for every 10ml of fuel consumption with the help of stop watch and with this we find out fuel consumption rate.

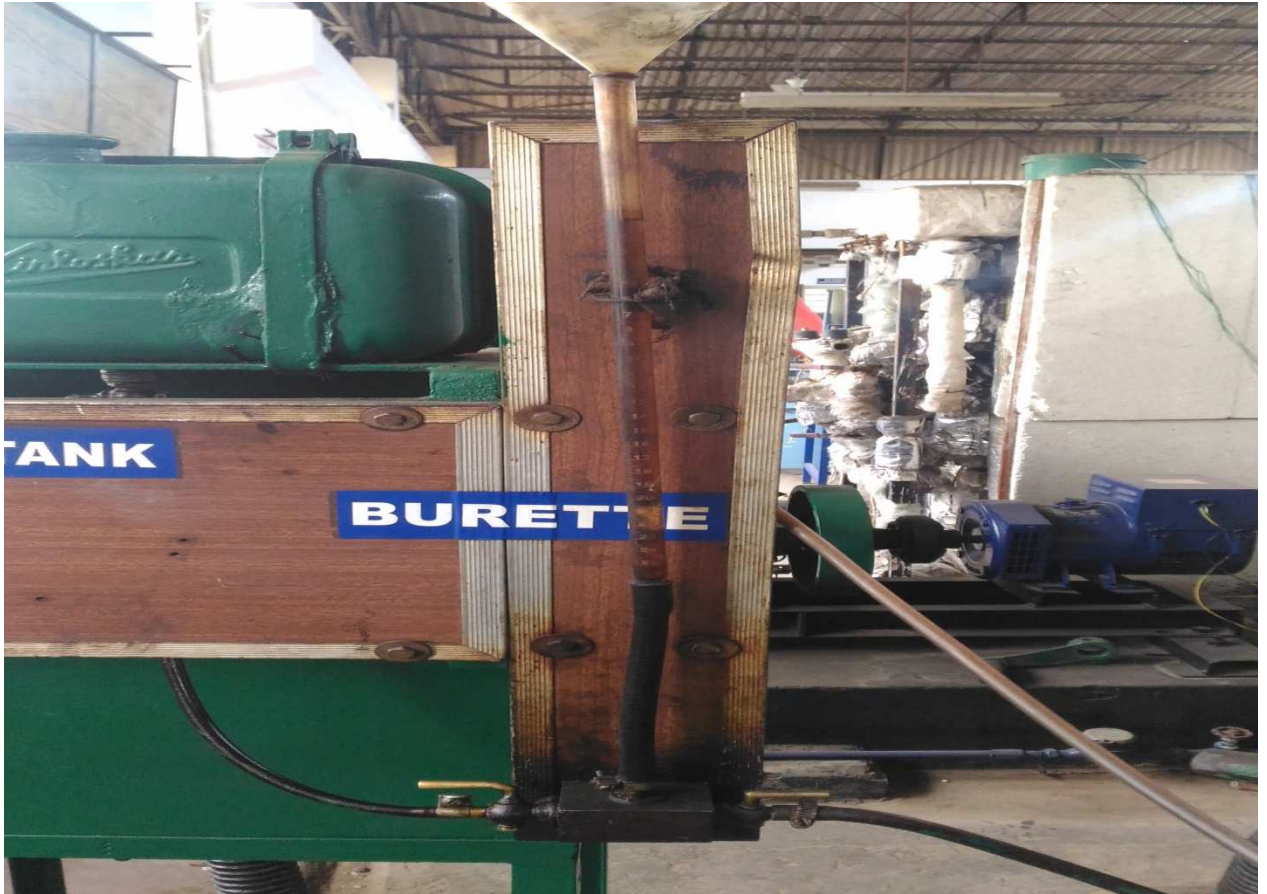


Figure 3.6 Burette for in feed of fuel

3.3.4 Air Supply

The air-box is connected to air-filter of engine through a 2.5'' pipe; this enables us to measure mass of air being utilized for combustion. Pressure of air entering the box is measure in terms of water column which is then converted into air-head and subsequently into air velocity which in turn helps determine mass flow rate of air.



Figure 3.7 Air supply system with measurement

3.3.5 Exhaust Gas Temperature Measurement

Exhaust gas temperature was measured with the help of a thermocouple. K type thermocouples was placed in the exhaust manifold to measure the temperature of exhaust gases The K type thermocouple is cheaper and a wide variety of probes are available in its $-200\text{ }^{\circ}\text{C}$ to $+1350\text{ }^{\circ}\text{C}$ range. Exhaust gas temperature is one of the important parameter which gives an indication about the potential available in the exhaust gas from heat recovery point of view.



Figure 3.8 Temperature indicator

3.3.6 Load arrangement

35 bulbs of rating 100 watt each were installed on the load bank. Arrangement was made to vary the load from zero to full at 3500 W.



Figure 3.9 load arrangement

3.3.7 Cooling arrangement

To make cooling more efficient, the engine is modified to water cooling system. The flow rate of cooling water is fixing to 6 litres per minute with the help of control valve. Figure 3.10 shows the cooling water flow rate measurement.



Figure 3.17 cooling water flow rate measurement

3.3.8 Gas Analyzer (NDIR type)

The gas analyzer is used to find out the exhaust gas emissions. In the experimental work the gas analyzer used, was supplied by AVL India private limited. It uses Non-Dispersive Infra-Red (NDIR) detector. Carbon monoxide (CO), Carbon dioxide, Oxygen, NO_x and Unburned Hydrocarbon are measured with the help of Gas Analyser. CO is measure in vol %, HC in ppm vol. Hex., CO_2 in vol %, O_2 in vol %, NO_x in ppm.



Figure 3.18 Gas analyzer

3.4 Experimental Techniques

Diesel and various blends of Diesel and Jatropha (SVO) with different percentage of p-phenylenediamine were used and study was done to measure the performance of engine. A sequence of experiments was done by varying the load on engine to compare the performance of neat Diesel and blends of Jatropha (SVO) and Diesel. During the experiment exhaust gas temperature and emissions were recorded at each load after allowing the engine to warm up and stabilize.

3.4.1 Variation of Load

The rated power output (full load) of the engine was 3.5kW. The different loads applied to the engine for all fuels (Neat Diesel, BD5, BD10, BD15) with 0.005%,0.015%,0.025%,0.035% and 0.05% (by mass) of p-phenylenediamine were 0.5 kW, 1.0 kW, 1.5 kW, 2.0 kW, 2.5 kW, 3.0 kW and 3.5kW. The loads were increased by switching on bulbs of appropriate wattage.

3.4.2 Variation of fuel

First engine was made to run on neat Diesel, BD5, BD10 and BD15 only to have a baseline data. Subsequently, it was made to run on various percentage of antioxidant mix with blends. The fuels for experiments were Diesel, BD5, BD10 and BD15.

Table 3.3 Range of investigation

Sr. No.	Parameters	Range
1.	Fuel	Diesel, BD5, BD10 and BD15
2.	P-phenylenediamine percentage	0.005%.0.015%,0.025%,0.035% and 0.05% by mass
3.	Load	0-3.5 kW
4.	Engine Speed	1500 rpm

3.5 Formulas for Calculation

Formulas for calculation of calorific value of blends, Brake Thermal efficiency (BTE), amount of p-phenylenediamine to be mix with different blends, Brake Specific Fuel Consumption (BSFC) and Brake Specific Energy Consumption (BSEC) are discussed below-

3.5.1 Calorific Value (CV) of Blends

It is the energy released per kg of the fuel, when the fuel is burned and the products of combustion are cooled back to the initial temperature of combustible mixture. The heating value so obtained is called the higher or gross calorific value of the fuel. The lower or net calorific value is the heat released by the fuel when water presents in the products of combustion is not condensed and remains in the vapour form.

1. Calorific value of the diesel = 43400 kJ/kg

$$= 36369.2 \text{ kJ/l}$$

2. Calorific value of the Jatropha oil = 39340 kJ/kg

$$= 37136.96 \text{ kJ/l}$$

{ Because Density of the diesel = 0.838 kg/l

Density of the Jatropha oil = 0.944 kg/l }

1. Calorific value of the 5% blend

$$= (0.05 \times 37136.96) + (0.95 \times 36369.2) = 36407.58 \text{ kJ/l}$$

2. Calorific value of the 10% blend

$$= (0.10 \times 37136.96) + (0.90 \times 36369.2) = 36445.97 \text{ kJ/l}$$

3. Calorific value of the 15% blend

$$= (0.15 \times 37136.96) + (0.85 \times 36369.2) = 36484.36 \text{ kJ/l}$$

Table 3.4 Calorific value of Diesel, BD5, BD10 and BD15

Sr. No.	Fuel	Calorific Value (kJ/l)
1.	Diesel	36369.2
2.	Jatropha oil	37136.96
3.	BD5	36407.58
4.	BD10	36455.97
5.	BD15	36484.36

3.5.2 Brake Thermal Efficiency (BTE)

Brake thermal efficiency is defined as the ratio of brake power of an engine to the energy supplied by the fuel. It is used to evaluate how well an engine is converting heat from a fuel to mechanical energy. It can be calculated for all fuels (Diesel, BD5, BD10 and BD15) by using following formula-

Brake Thermal Efficiency (BTE) = Brake Power/ Energy supplied by fuel

3.5.3 Amount of antioxidant

As we know

Density= mass / volume

$M_1 + M_2 + M_3 = 1\text{kg}$

Here,

M_1 = mass of antioxidant to be mix

M_2 = mass of Jatropha oil

M_3 = mass of Diesel oil

So,

$M_2 + M_3 = 1 - M_1$

$$\zeta_2 V_2 + \zeta_3 V_3 = 1 - M_1$$

Here,

$$\zeta_2 = 0.944 \text{ kg/m}^3$$

$$\zeta_3 = 0.830 \text{ kg/m}^3$$

$$V_2 = 5\%$$

So

$$(944 \times (5/100) + 830) \times V_2 = 1 - M_1$$

For $M_1 = 50\text{mg}$

$$V_2 = 56\text{ml}$$

Same procedure for 150mg, 250mg, 350mg and 500mg

3.5.4 Brake Specific Fuel Consumption (BSFC)

Brake specific fuel consumption is defined as the rate of fuel consumed per unit of brake power developed by the engine. Its unit is generally kg/kW-hr. It can be calculated for all fuels (Diesel, BD5, BD10 and BD15) by using following formula

Brake Specific fuel Consumption (BSFC) = Mass flow rate of fuel (kg/hr) / Brake Power (kW)

3.5.5 Brake Specific Energy Consumption (BSEC)

It is defined as a product of BSFC and Calorific value (CV) of fuel. It shows how efficiently fuel energy is obtained from fuel. It can be calculated for all fuels (Diesel, BD5, BD10 and BD15) by using following formula-

Brake Specific energy Consumption (BSEC) = BSFC * CV of fuel

Chapter 4

Results and Discussion

Engine was operated with neat Diesel and various blends) that were composed of Jatropha (SVO) and Diesel. In this chapter engine performance parameters i.e. Brake thermal efficiency (BTE), NO_x , CO and HC emissions are calculated and their variations with respect to load are plotted.

4.1 Engine Performance Parameters

These parameters are used for comparison of various engines. It includes Brake thermal efficiency, NO_x , CO and HC emissions.

4.1.1 Brake thermal Efficiency

Brake thermal efficiency (BTE) is a measure of net power developed by the engine which is readily available for use at the engine output shaft. Brake thermal efficiency (BTE) for all fuels increased with increase in load and reached its maximum at 2.5 kW load and then it dropped slightly at full load. Brake thermal efficiency in case of neat diesel was 19.25% which occurred at 2.5 kW load. As Jatropha (SVO) was used as a fuel in engine then its efficiency started decreasing. For BD5 (5% Jatropha (SVO) and 95% Diesel by volume) maximum brake thermal efficiency obtained was 18.86% at 2.5 kW load. For BD10 maximum brake thermal efficiency obtained as 18.03% which was at 2.5 kW load. For BD15 efficiency was lower than BD10 at all loads. At 2.5 kW load efficiency found 17.54%. Increasing Jatropha (SVO) will decrease peak pressure and temperature due improper combustion of blend and high density and viscosity of Jatropha (SVO). Figure 4.1 shows the variation of brake thermal efficiency with respect to load for all fuels used in the research work (Diesel, BD5, BD10 and BD15) without use of antioxidant.

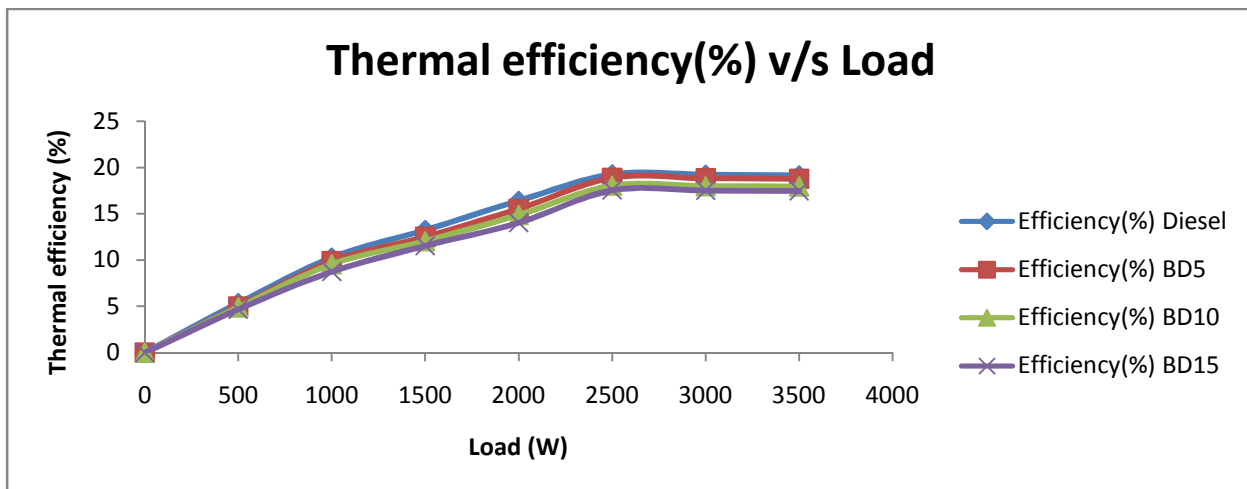


Figure 4.1 brake thermal efficiency with respect to load for Diesel, BD5, BD10 and BD15 without use of antioxidant.

For BD5 (Jatropha SVO 5%), BD10 (Jatropha SVO 10%) and BD15 (Jatropha SVO 15%) with different percentage (0.005%, 0.015%, 0.025%, 0.035% and 0.05% by mass) of p-phenylenediamine minor reduction in efficiency have observed. The main reason behind it reduction in availability of oxygen for complete combustion have reduced, this will lead to incomplete combustion of fuel. As we know Biodiesels are oxygenated fuels so there is no major reduction in efficiency of engine. Figure 4.2 shows the variation of thermal efficiency with loads for BD5. Figure 4.3 shows the variation of thermal efficiency with loads for BD10. Figure 4.4 shows the variation of thermal efficiency with loads for BD15. By these experimental results we can further move towards emissions reduction process because there is no major effect on efficiency by adding different percentage of p-phenylenediamine.

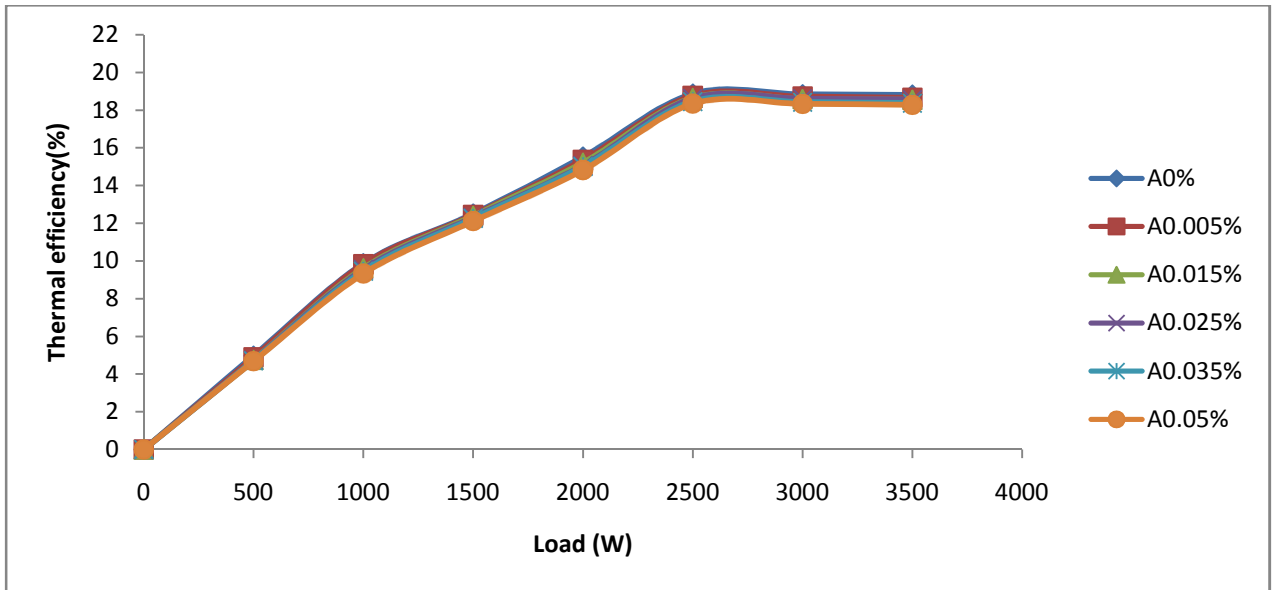


Figure 4.2 Variation of thermal efficiency with loads for BD5 with different percentage of p-phenylenediamine

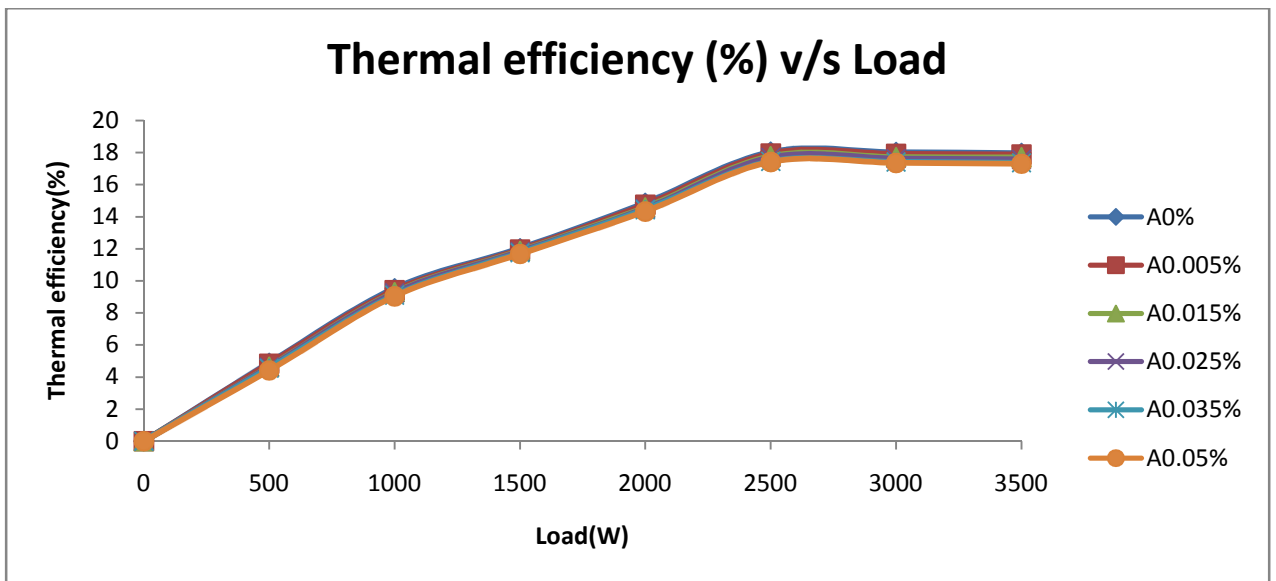


Figure 4.3 Variation of thermal efficiency with loads for BD10 with different percentage of p-phenylenediamine

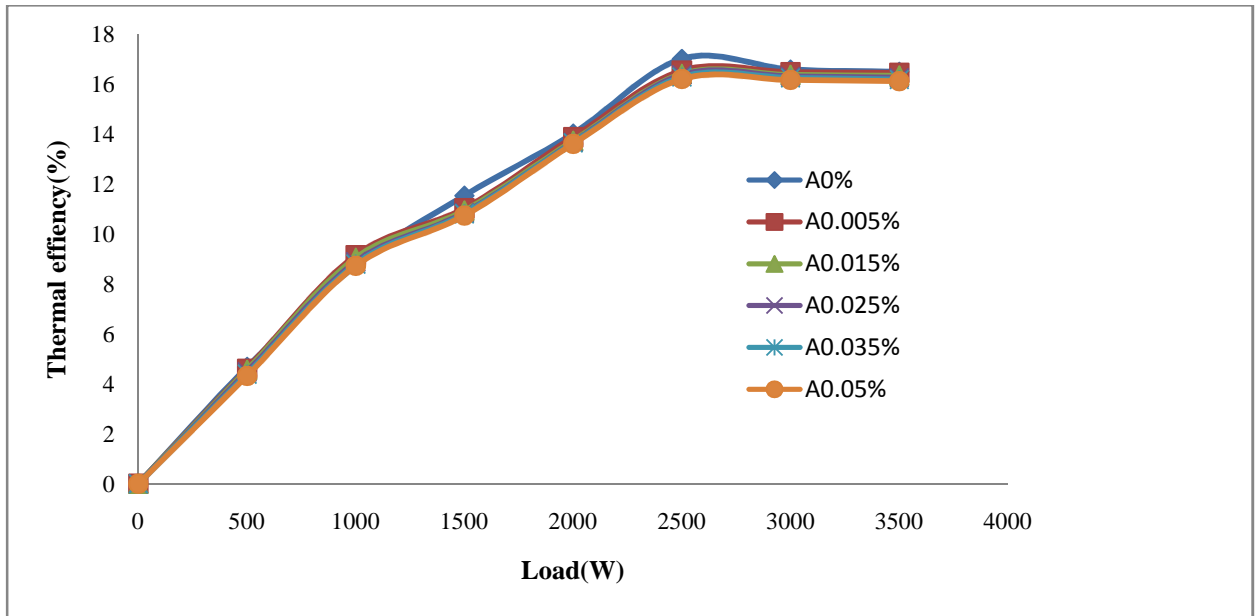


Figure 4.4 Variation of thermal efficiency with loads for BD15 with different percentage of p-phenylenediamine

4.2 Engine Exhaust Emissions

Tail pipe exhaust emissions are the vital source of emissions from the vehicle. NO_x (oxides of nitrogen), UBHC (un-burnt hydrocarbon) and CO (carbon mono oxide) are the main exhaust emissions.

Emissions can be classified into two categories-

a) Regulated emissions

b) Non-regulated emissions

a) Regulated emissions- Emissions for which there are certain norms and there is certain regulation on their quantity in exhaust gas, are called regulated emissions. UBHC (un-burnt hydrocarbon), CO (carbon mono oxide), NO_x (oxides of nitrogen), particulate matter (PM) and smoke are regulated emissions.

b) Non-regulated emissions- Emissions which are present in the engine exhaust and for which there is not any norm and there is no certain regulation on their quantity in exhaust gas, are called non-regulated or unregulated emissions. Ethanol, aldehydes, ketones, poly

nuclear aromatic hydrocarbons (PAH), nitro-PAH and soluble organic fraction of particulate matter are examples of non-regulated emissions.

4.2.1 NO_x emissions

Nitrogen and Oxygen reacts at relatively high temperature. NO_x formation in an engine depends on-

- a) Reaction temperature
- b) Oxygen availability and
- c) Duration of availability of oxygen

NO_x emissions are increasing by increasing load as increasing load will cause more fuel to enter in the combustion chamber due to this more NO_x emissions will be formed. NO_x emissions were found to increase in all blends in comparison to pure Diesel; it is due oxygenate nature of Jatropha (SVO) fuel. With increase in oxygen content in fuel proper combustion of fuel takes place. NO_x emissions variation with respect to engine load for all fuels is represented in the figures (4.4, 4.5, 4.6 and 4.7).

Antioxidant addition has been shown to reduce NO_x exhaust emissions. Figure (4.5, 4.6 and 4.7) shows the NO_x reduction percent of different antioxidants relative to neat Diesel, BD5, BD10 and BD 15 at full load based on observed data in ppm. Results indicate that significant reductions in NO_x were observed while using antioxidants and this reduction is not linearly correlated with the amount of antioxidants present in the biodiesel. Optimum reductions were found at 0.025%-m concentration of additives. The decrease in NO_x emissions are assumed to results from a reduction in the formation of free radicals by antioxidants.

The effect of antioxidants on NO_x emissions of Jatropha(SVO) fuel containing 0.025%-m of additives. It is important to note that the 0.025%-m level of p-phenylenediamine with biodiesel presented best emission results and a mean NO_x reduction of 24.58% was observed with this additive. At this level, the minimum and maximum NO_x produced were 1.57 and 2.05 g/kW hr respectively, and also meets III B Euro emission standards

[14] (<3.3 g/kW hr) for non-road engines. Stage III standards are phased-in from the year 2006 to 2013. P phenylenediamine is the most widely used primary antioxidant in polymer and rubber industries and its antioxidative activity is implemented by the donation of an electron or hydrogen atom to a radical derivative. The kinetics involved in the mechanism of NO_x reduction by p-phenylenediamine is highly complex and there is limited understanding of the chemistry involved in these processes. Benzoquinonediimine, a reaction product of p-phenylenediamine has potent antioxidant properties that trap the free radicals effectively. Ethylenediamine is a most common lubricating oil additive that control deposits in the fuel system and also effectively reduces the friction between engine cylinder and piston rings. Ethylenediamine is a powerful chelating agent that reduces the free radical concentrations by chelating the metal catalysts.

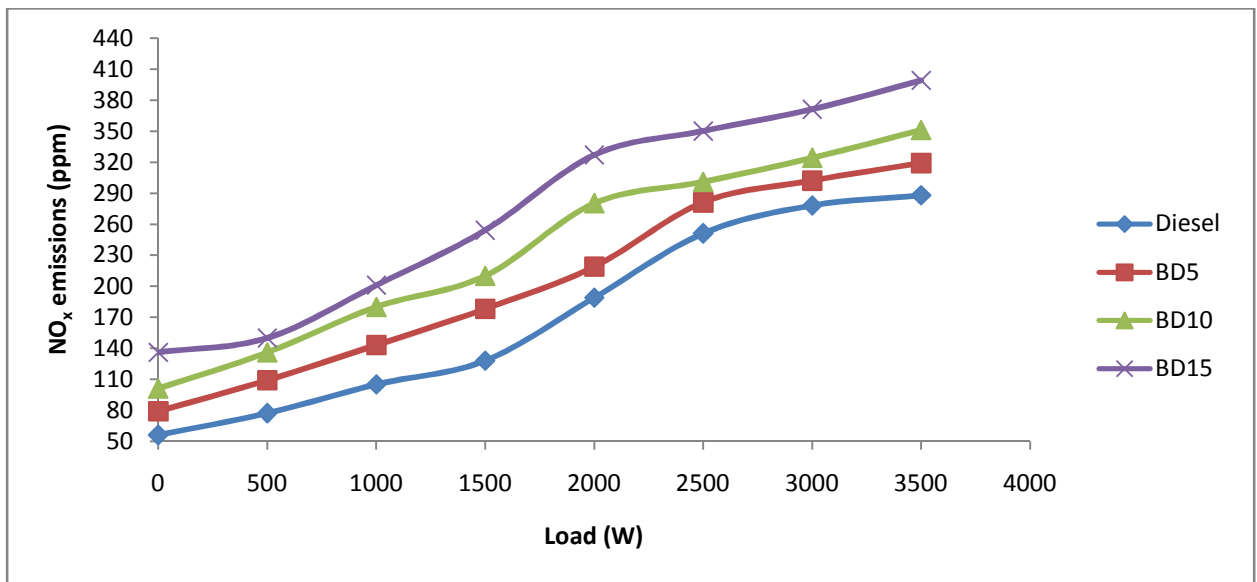


Figure 4.5 NO_x emissions for Diesel, BD5, BD10 and BD15

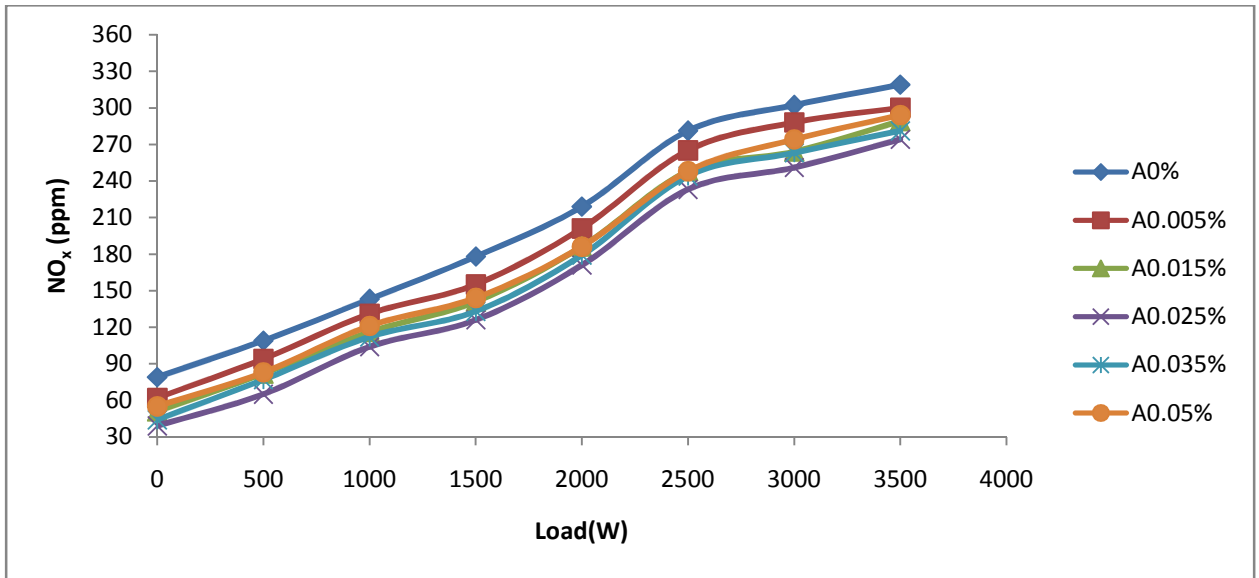


Figure 4.6 NO_x emissions for BD5 using different percentage of p-phenylenediamine

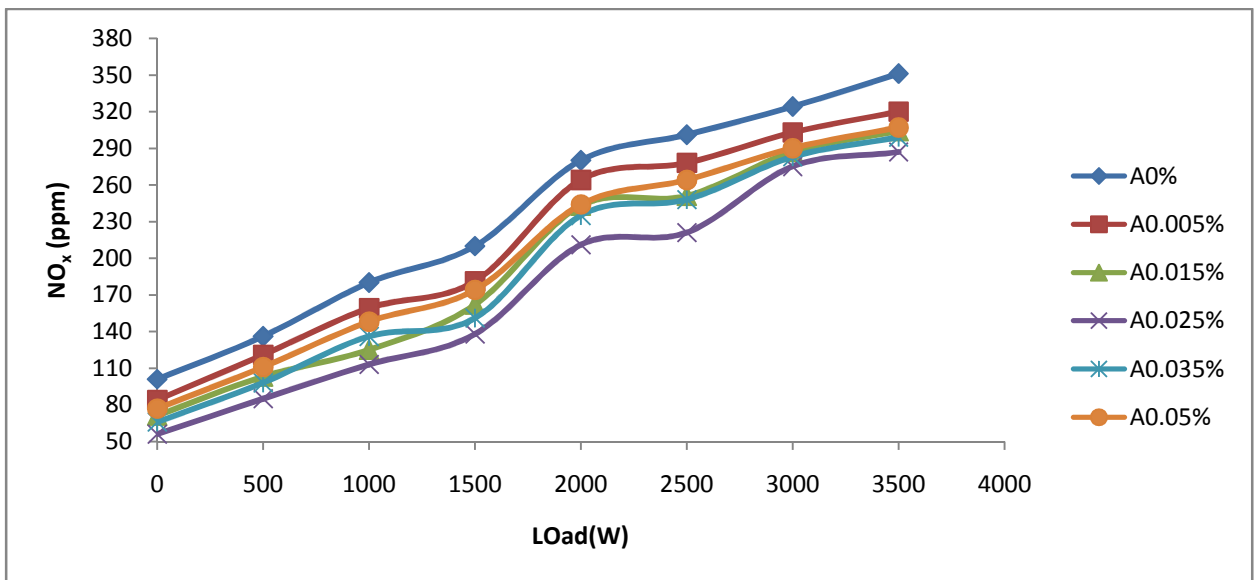


Figure 4.7 NO_x emissions for BD10 using different percentage of p-phenylenediamine

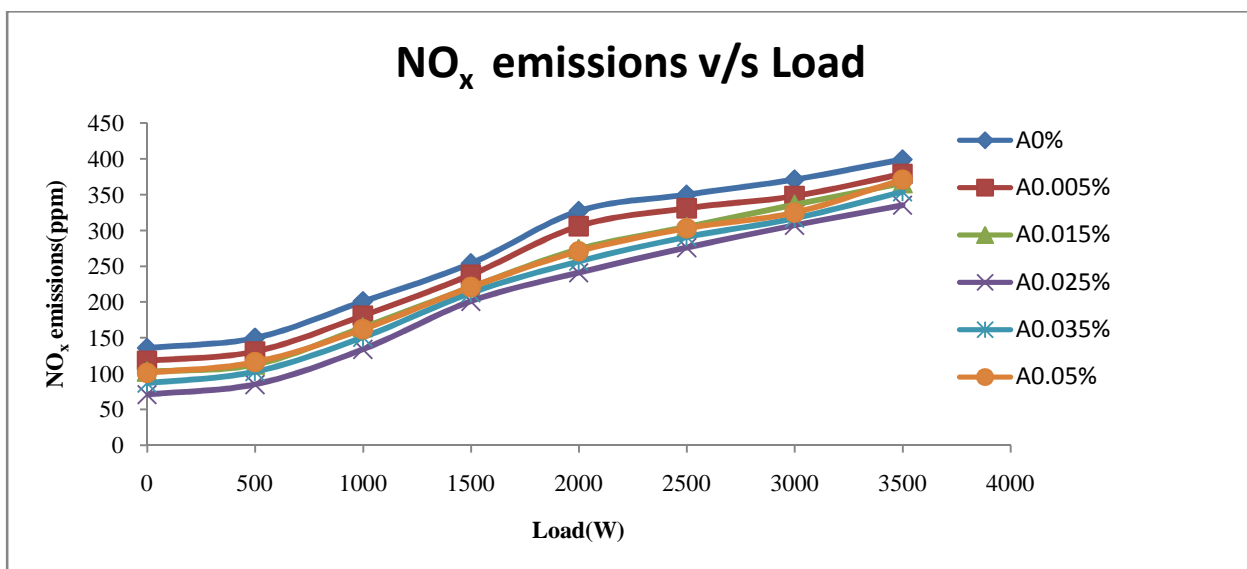


Figure 4.8 NO_x emissions for BD15 using different percentage of p-phenylenediamine

4.2.1 Hydrocarbon (HC) Emissions

Un-burnt hydrocarbons (UBHC) are the direct consequence of incomplete combustion [32]. UBHC variation with respect to load for all fuels is represented in the figure 4.8. By the experiments it was found that hydrocarbon emission was higher at low load conditions and then at the moderate load condition it was decreased and again rose slightly at higher load conditions. This might be due to the improper mixing of fuel which resulted in incomplete combustion of fuel giving high hydrocarbon emissions.

Unburned hydrocarbons come under different forms such as vapour, drops of fuel, or products of fuel after thermal degradation. HC emissions contribute to the formation of smog and may include photo chemically reactive species as well as carcinogens. The specific HC emissions for antioxidant Jatropa (SVO) mixture and load at different concentrations of p-phenylenediamine are shown in figures 4.9, 4.10 and 4.11. It is clear that addition of antioxidants led to some increase in HC emissions at all the loads. This increase in HC emissions could be due to reduction of oxidative free radical formation by antioxidants. It is quite clear that test antioxidant mixtures could not meet the stage III B Euro standards (<19 g/kW hr) in the whole load range.

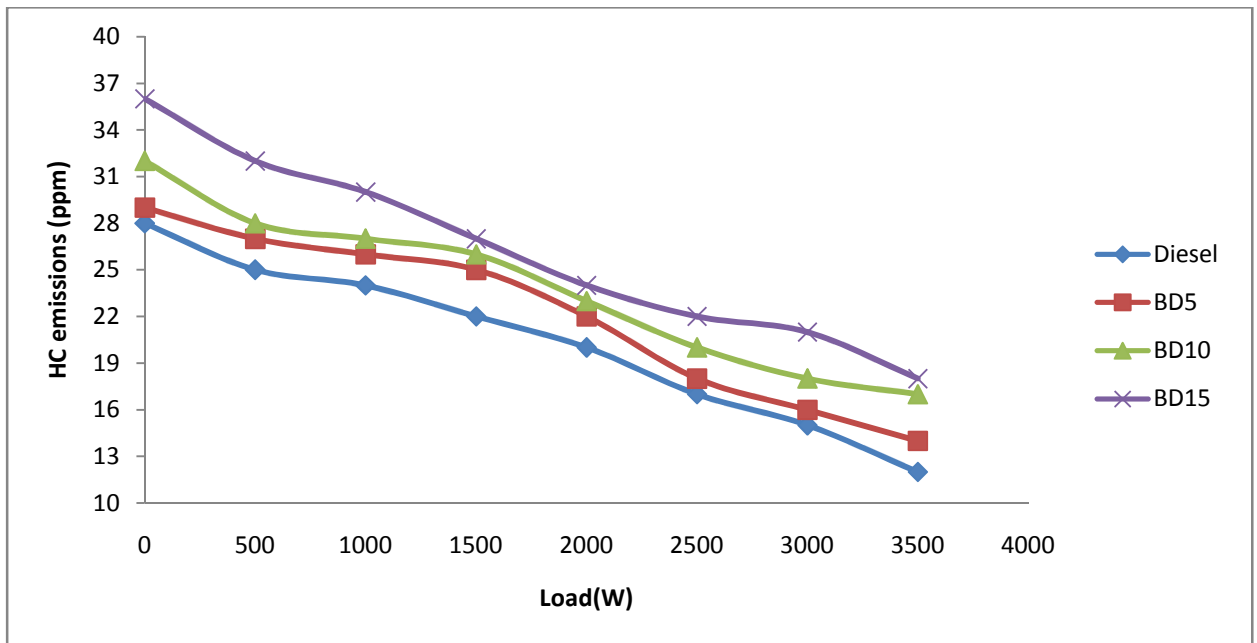


Figure 4.9 HC emissions for Diesel, BD5, BD10 and BD15

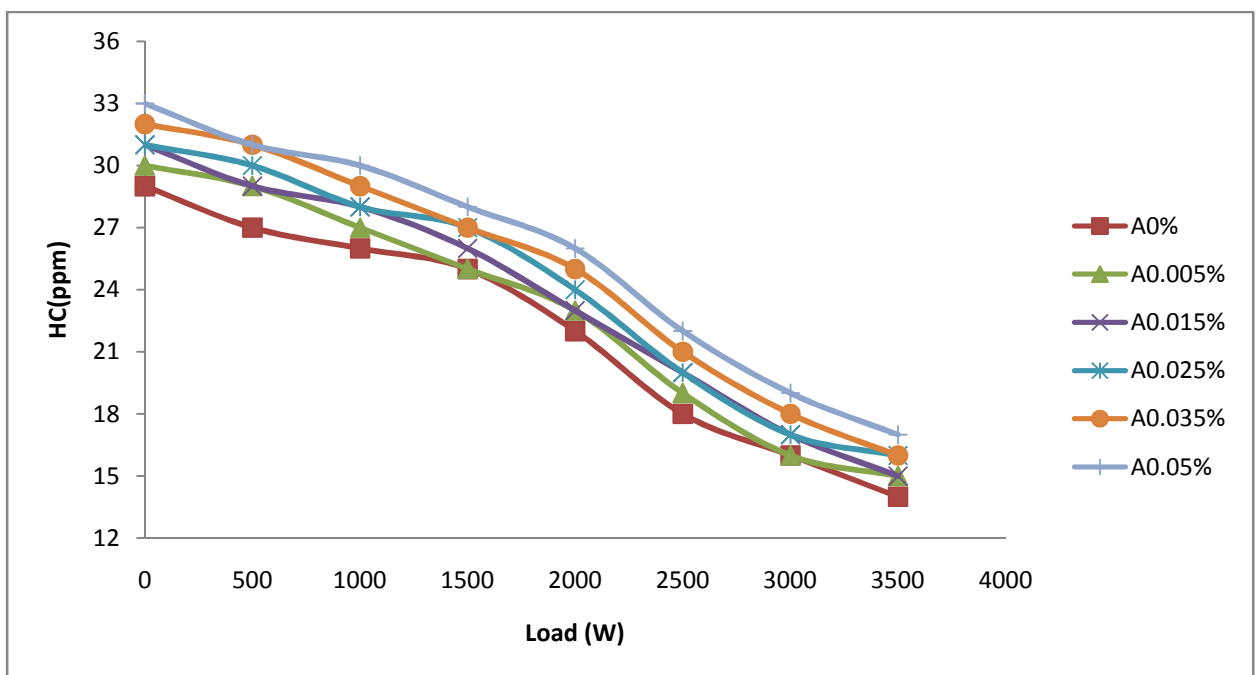


Figure 4.10 HC emissions for BD5 using different percentage of p-phenylenediamine

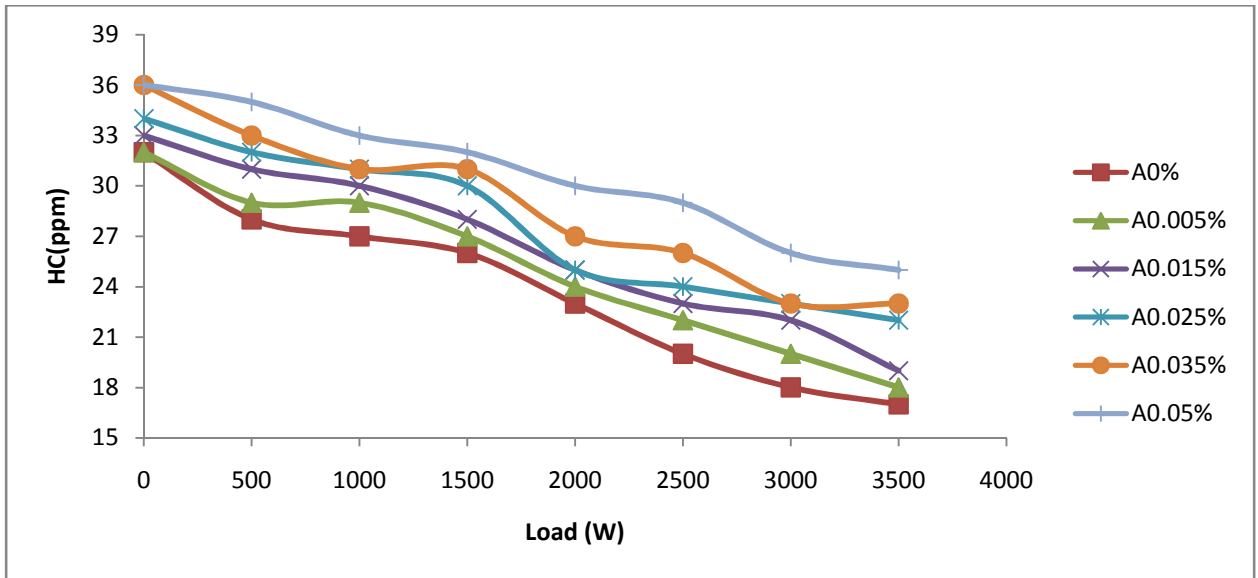


Figure 4.11 HC emissions for BD10 using different percentage of p-phenylenediamine

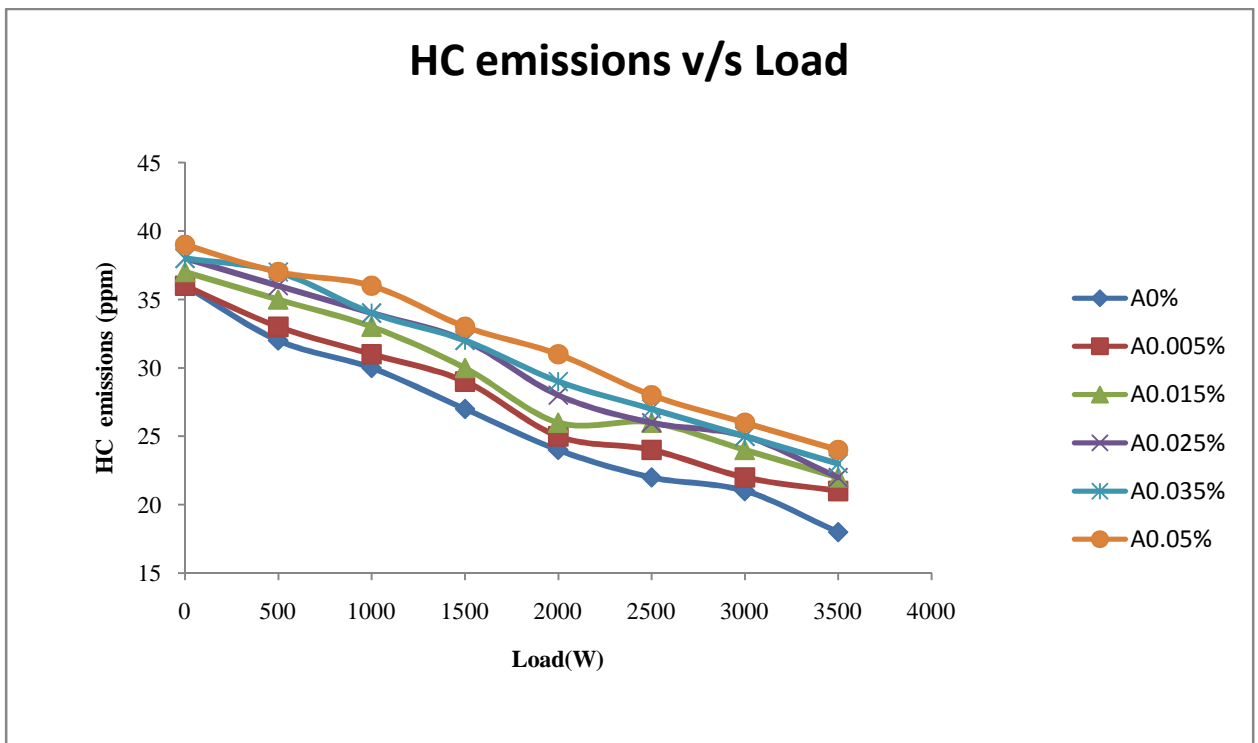


Figure 4.12 HC emissions for BD15 using different percentage of p-phenylenediamine

4.2.2 Carbon Monoxide (CO) Emissions

Carbon monoxide (CO) occurs only in the exhaust of engine. It is a product of incomplete combustion because of inadequate amount of air in fuel-air mixture or inadequate time in the cycle for complete combustion of fuel. Carbon content of fuel oxidized with Oxygen available in the air to CO and then to CO₂. Carbon which is not converted to CO₂ will come out as CO in exhaust.

Low flame temperature and too rich fuel air ratio are the major causes of CO emissions from engine. Higher CO emissions results in loss of power in engine. Different factors can be at the origin of its formation, insufficient residence time, too low or too high equivalence ratios are part of those reasons. The variation of specific CO emissions with power output at 0.025%-m concentration of antioxidants is presented. It is obvious that the CO emissions increase as the antioxidant content in the biodiesel increases. The increase is primarily due to incomplete combustion resulting from antioxidants addition. The oxidation of CO is directly related to the amount of OH radicals present in the reaction. Antioxidants slightly reduce carbon oxidation by scavenging the OH radicals. At full load, highest CO emissions were observed with p phenylenediamine (11.12 g/kW-hr) had the lowest. It is quite clear that test antioxidant mixtures could not meet the stage III B Euro standards (<5 g/kW hr) in the whole load range.

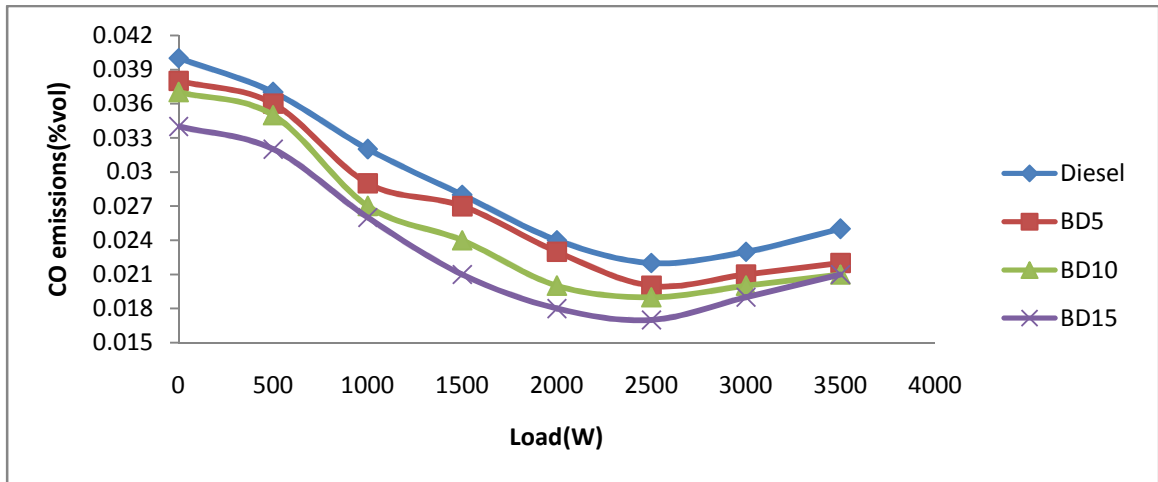


Figure 4.13 CO emissions for Diesel, BD5, BD10 and BD15

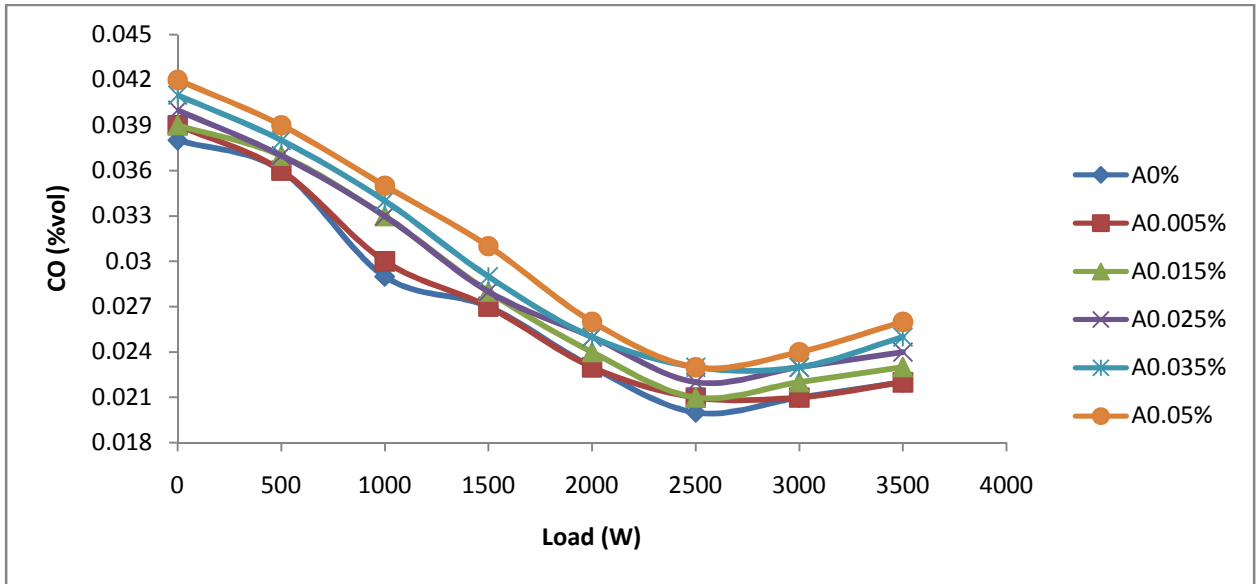


Figure 4.14 CO emissions for BD5 using different percentage of p-phenylenediamine

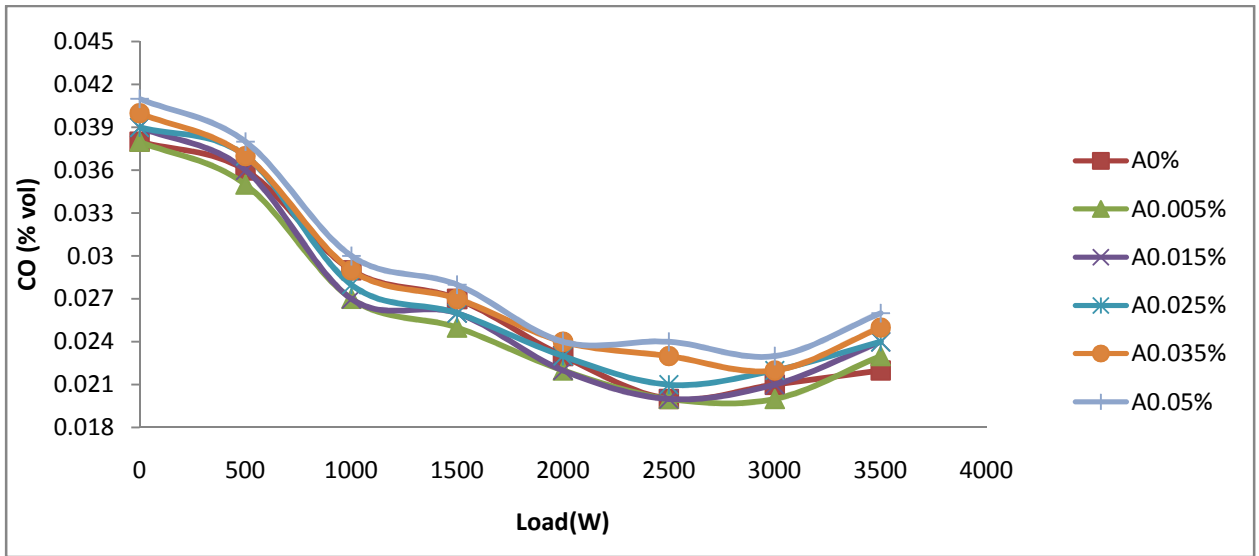


Figure 4.15 CO emissions for BD10 using different percentage of p-phenylenediamine

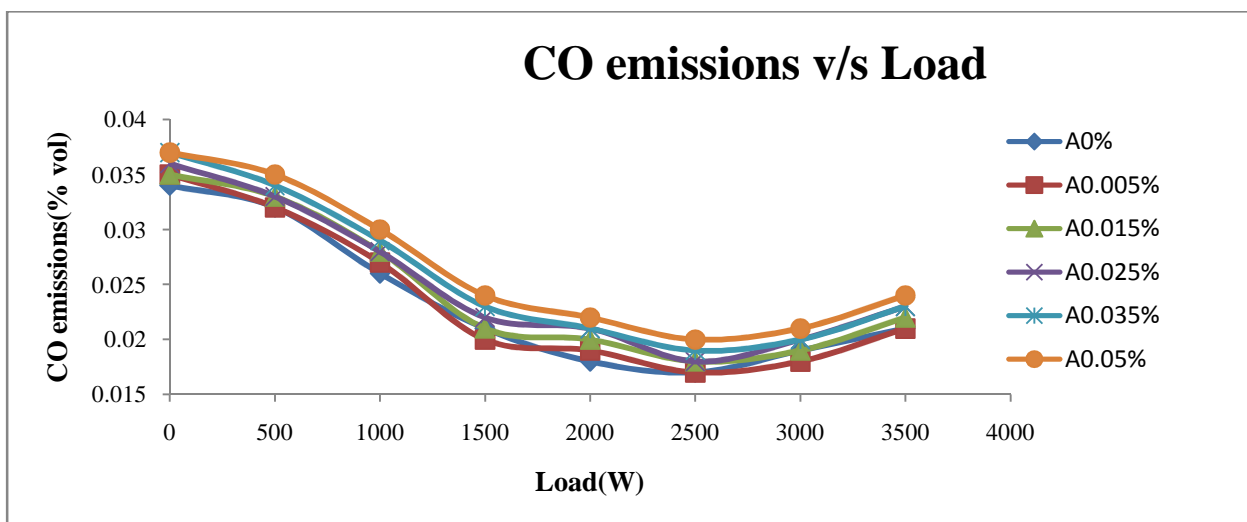


Figure 4.16 CO emissions for BD15 using different percentage of p-phenylenediamine

Antioxidant addition has been shown to percentage reduction in NO_x exhaust emissions. Figure 4.16 shows the NO_x reduction percent of different antioxidants relative to neat Diesel, BD5, BD10 and BD 15 at full load based on observed data in ppm. Results indicate that significant reductions in NO_x were observed while using antioxidants and this reduction is not linearly correlated with the amount of antioxidants present in the biodiesel. Optimum reductions were found at 0.025%-m concentration of additives. The decrease in NO_x emissions is assumed to results from a reduction in the formation of free radicals by antioxidants.

The effect of antioxidants on NO_x emissions for Jatropha (SVO) fuel with 0.025%- m of antioxidant. It is important to note that the 0.025%-m level of p-phenylenediamine with biodiesel presented best emission results and a mean NO_x reduction of 19.49% was observed with this additive. At this level, the minimum and maximum NO_x produced were 1.57 and 2.05 g/kW hr respectively, and also meets III B Euro emission standards [14] (<3.3 g/kW hr) for non-road engines. Stage III standards are phased-in from the year 2006 to 2013. P phenylenediamine is the most widely used primary antioxidant in polymer and rubber industries and its antioxidative activity is implemented by the donation of an electron or hydrogen atom to a radical derivative. The kinetics involved in

the mechanism of NO_x reduction by p-phenylenediamine is highly complex and there is limited understanding of the chemistry involved in these processes. Benzoquinonediimine, a reaction product of p-phenylenediamine has potent antioxidant properties that trap the free radicals effectively. Ethylenediamine is a most common lubricating oil additive that controls deposits in the fuel system and also effectively reduces the friction between engine cylinder and piston rings. Ethylenediamine is a powerful chelating agent that reduces the free radical concentrations by chelating the metal catalysts.

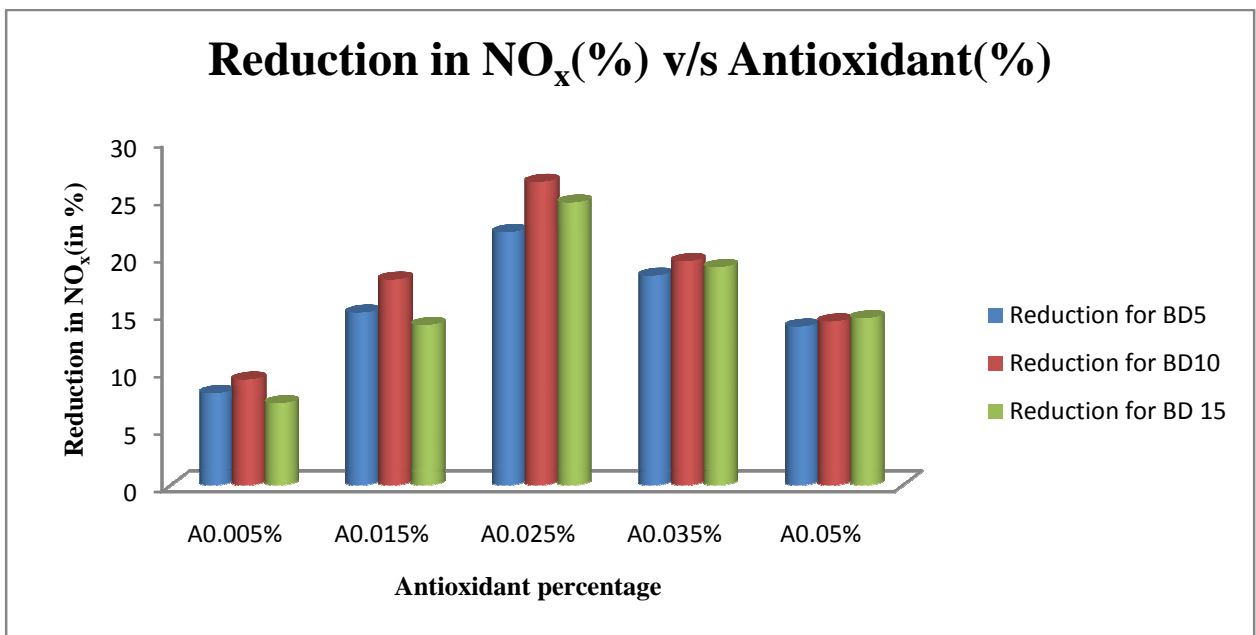


Figure 4.17 percentage reductions in NO_x with different percentage of p-phenylenediamine

Conclusion

The effects of antioxidants addition on NO_x, CO and HC emissions in a Jatropha (SVO) and Diesel fuelled CI diesel engine at different loads have been studied in this work. Results show the potential benefit of antioxidant additives for NO_x reduction in biodiesel fuelled diesel engines. The main conclusions of this study can be summarized as follows.

1. The presently studied antioxidant is quite effective in controlling NO_x formations. They do, however; have significantly more CO and HC emissions.
2. Antioxidant p-phenylenediamine showed the best emission performance compared to Jatropha (SVO) Diesel blends. It has shown optimum NO_x reduction at a level of 0.025%-m. The NO_x reduction efficiency of antioxidants was observed for p-phenylenediamine mean NO_x reduction percent relative to neat blends are 22%, 23.69 and 24.58% respectively at 0.025%-m concentration by mass.
3. There is no major change in thermal efficiency is observed with the use of different percentage of antioxidant.
4. The slight decrease in BSFC was observed with p-phenylenediamine signifies a slight reduction in specific fuel consumption compared to neat Jatropha (SVO) blend.

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Appendix C: India's Crude Oil Production Data

Sr. No.	Year	Production (Thousand Barrels per Day)	Change
1.	1980	182	-
2.	1981	325	78.57%
3.	1982	390	20.00%
4.	1983	480	23.08%
5.	1984	519	8.13%
6.	1985	620	19.46%
7.	1986	630	1.61%
8.	1987	609	-3.33%
9.	1988	635	4.27%
10.	1989	700	10.24%
11.	1990	660	-5.71%
12.	1991	615	-6.82%
13.	1992	561.15	-8.76%
14.	1993	534	-4.84%
15.	1994	589.9	10.47%
16.	1995	703.45	19.25%
17.	1996	651.02	-7.45%
18.	1997	674.62	3.63%
19.	1998	661.42	-1.96%
20.	1999	652.66	-1.32%
21.	2000	646.34	-0.97%
22.	2001	642.4	-0.61%
23.	2002	664.75	3.48%
24.	2003	660.03	-0.71%

25.	2004	683.11	3.50%
26.	2005	664.66	-2.70%
27.	2006	688.61	3.60%
28.	2007	697.53	1.30%
29.	2008	693.71	-0.55%
30.	2009	680.43	-1.91%
31.	2010	751.3	10.42%
32.	2011	782.34	4.13%
33.	2012	776.97	-0.69%
34.	2013	772.08	-0.63%

Appendix D: India's Crude Oil Consumption Data

Sr. No.	Year	Production (Thousand Barrels per Day)	Change
1.	1980	643	-
2.	1981	729	13.37%
3.	1982	737	1.10%
4.	1983	773	4.88%
5.	1984	824	6.60%
6.	1985	894.9	8.60%
7.	1986	947.44	5.87%
8.	1987	987.85	4.27%
9.	1988	1,083.78	9.71%
10.	1989	1,149.78	6.09%
11.	1990	1,168.33	1.61%
12.	1991	1,190.32	1.88%
13.	1992	1,274.91	7.11%
14.	1993	1,311.07	2.84%
15.	1994	1,413.27	7.80%
16.	1995	1,654.67	17.08%
17.	1996	1,740.92	5.21%
18.	1997	1,835.49	5.43%
19.	1998	1,924.37	4.84%
20.	1999	2,031.25	5.55%
21.	2000	2,147.44	5.72%
22.	2001	2,263.73	5.42%
23.	2002	2,333.44	3.08%
24.	2003	2,426.33	3.98%
25.	2004	2,571.55	5.99%

26.	2005	2,550.25	-0.83%
27.	2006	2,701.63	5.94%
28.	2007	2,888.06	6.90%
29.	2008	2,957.30	2.40%
30.	2009	3,067.78	3.74%
31.	2010	3,115.45	1.55%
32.	2011	3,280.98	5.31%
33.	2012	3,450.00	5.15%
34.	2013	3,509.00	1.71%

Table 1 brake thermal efficiency with respect to load for diesel, BD5, BD10 and BD15 without use of antioxidant

Load(W)	Efficiency (%) Diesel	Efficiency (%) BD5	Efficiency (%) BD10	Efficiency (%) BD15
0	0	0	0	0
500	5.34	4.97	4.89	4.67
1000	10.26	9.86	9.54	8.74
1500	13.23	12.49	12.03	11.54
2000	16.39	15.51	14.86	14.02
2500	19.25	18.86	18.03	17.54
3000	19.21	18.81	17.96	17.51
3500	19.15	18.76	17.94	17.46

Table 2 brake thermal efficiency with different load for BD5 and different percentage of p-phenylenediamine

Load(W)	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	0	0	0	0	0	0
500	4.97	4.88	4.75	4.73	4.7	4.68
1000	9.86	9.82	9.62	9.55	9.46	9.33
1500	12.49	12.43	12.39	12.31	12.25	12.11
2000	15.51	15.35	15.21	15.06	15.01	14.82
2500	18.86	18.75	18.65	18.62	18.45	18.34
3000	18.83	18.71	18.59	18.6	18.42	18.33
3500	18.81	18.65	18.55	18.56	18.37	18.28

Table 3 brake thermal efficiency with different load for BD10 and different percentage of p-phenylenediamine

Load(W)	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	0	0	0	0	0	0
500	4.89	4.83	4.65	4.62	4.55	4.41
1000	9.54	9.41	9.3	9.25	9.11	9.03
1500	12.03	11.95	11.87	11.82	11.75	11.67
2000	14.86	14.74	14.59	14.51	14.44	14.32
2500	18.03	17.94	17.78	17.69	17.45	17.41
3000	18.01	17.91	17.72	17.62	17.41	17.35
3500	17.95	17.88	17.69	17.57	17.36	17.3

Table 4 brake thermal efficiency with different load for BD15 and different percentage of p-phenylenediamine

Load(W)	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	0	0	0	0	0	0
500	4.67	4.6	4.56	4.48	4.39	4.32
1000	8.74	9.15	9.05	8.89	8.8	8.73
1500	11.54	11.03	10.94	10.85	10.81	10.74
2000	14.02	13.88	13.74	13.68	13.65	13.61
2500	17.01	16.55	16.42	16.38	16.29	16.21
3000	16.59	16.49	16.38	16.32	16.25	16.17
3500	16.5	16.46	16.35	16.27	16.19	16.12

Table 5 NOx emissions with respect to load for diesel, BD5, BD10 and BD15 without use of antioxidant

Load (W)	Diesel	BD5	BD10	BD15
0	56	79	101	136
500	77	109	136	150
1000	105	143	180	201
1500	128	178	210	254
2000	189	219	280	327
2500	251	281	301	350
3000	278	302	324	371
3500	288	319	351	399

Table 6 NOx emissions with different load for BD5 and different percentage of p-phenylenediamine

Load	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	79	62	51	39	44	55
500	109	94	82	65	77	83
1000	143	131	116	104	112	121
1500	178	155	141	126	133	144
2000	219	201	186	171	179	186
2500	281	265	248	233	244	248
3000	302	288	264	251	263	274
3500	319	300	289	274	281	294

Table 7 NOx emissions with different load for BD10 and different percentage of p-phenylenediamine

Load	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	101	84	71	56	66	77
500	136	121	103	85	98	111
1000	180	159	125	113	136	148
1500	210	181	162	138	151	174
2000	280	264	243	211	235	244
2500	301	278	251	221	248	264
3000	324	303	287	275	283	290
3500	351	320	304	287	299	307

Table 8 NOx emissions with different load for BD15 and different percentage of p-phenylenediamine

Load	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	136	118	103	71	87	101
500	150	131	113	85	103	116
1000	201	181	165	134	151	162
1500	254	238	221	201	213	221
2000	327	306	274	241	257	271
2500	350	331	305	276	291	303
3000	371	348	336	307	317	325
3500	399	379	366	335	354	371

Table 9 HC emissions with respect to load for diesel, BD5, BD10 and BD15 without use of antioxidant

Load (W)	Diesel	BD5	BD10	BD15
0	28	29	32	36
500	25	27	28	32
1000	24	26	27	30
1500	22	25	26	27
2000	20	22	23	24
2500	17	18	20	22
3000	15	16	18	21
3500	12	14	17	18

Table 10 HC emissions with different load for BD5 and different percentage of p-phenylenediamine

Load(W)	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	29	30	31	31	32	33
500	27	29	29	30	31	31
1000	26	27	28	28	29	30
1500	25	25	26	27	27	28
2000	22	23	23	24	25	26
2500	18	19	20	20	21	22
3000	16	16	17	17	18	19
3500	14	15	15	16	16	17

Table 11 HC emissions with different load for BD10 and different percentage of p-phenylenediamine

Load	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	32	32	33	34	36	36
500	28	29	31	32	33	35
1000	27	29	30	31	31	33
1500	26	27	28	30	31	32
2000	23	24	25	25	27	30
2500	20	22	23	24	26	29
3000	18	20	22	23	23	26
3500	17	18	19	22	23	25

Table 12 HC emissions with different load for BD15 and different percentage of p-phenylenediamine

Load(W)	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	36	36	37	38	38	39
500	32	33	35	36	37	37
1000	30	31	33	34	34	36
1500	27	29	30	32	32	33
2000	24	25	26	28	29	31
2500	22	24	26	26	27	28
3000	21	22	24	25	25	26
3500	18	21	22	22	23	24

Table 13 CO emissions with respect to load for diesel, BD5, BD10 and BD15 without use of antioxidant

Load (W)	Diesel	BD5	BD10	BD15
0	0.04	0.038	0.037	0.034
500	0.037	0.036	0.035	0.032
1000	0.032	0.029	0.027	0.026
1500	0.028	0.027	0.024	0.021
2000	0.024	0.023	0.02	0.018
2500	0.022	0.02	0.019	0.017
3000	0.023	0.021	0.02	0.019
3500	0.025	0.022	0.021	0.021

Table 14 CO emissions with different load for BD5 and different percentage of p-phenylenediamine

Load	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	0.038	0.039	0.039	0.04	0.041	0.042
500	0.036	0.036	0.037	0.037	0.038	0.039
1000	0.029	0.03	0.033	0.033	0.034	0.035
1500	0.027	0.027	0.028	0.028	0.029	0.031
2000	0.023	0.023	0.024	0.025	0.025	0.026
2500	0.02	0.021	0.021	0.022	0.023	0.023
3000	0.021	0.021	0.022	0.023	0.023	0.024
3500	0.022	0.022	0.023	0.024	0.025	0.026

Table 15 CO emissions with different load for BD10 and different percentage of p-phenylenediamine

Load	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	0.038	0.038	0.039	0.039	0.04	0.041
500	0.036	0.035	0.036	0.037	0.037	0.038
1000	0.029	0.027	0.027	0.028	0.029	0.03
1500	0.027	0.025	0.026	0.026	0.027	0.028
2000	0.023	0.022	0.022	0.023	0.024	0.024
2500	0.02	0.02	0.02	0.021	0.023	0.024
3000	0.021	0.02	0.021	0.022	0.022	0.023
3500	0.022	0.023	0.024	0.024	0.025	0.026

Table 16 CO emissions with different load for BD15 and different percentage of p-phenylenediamine

Load	A0%	A0.005%	A0.015%	A0.025%	A0.035%	A0.05%
0	0.034	0.035	0.035	0.036	0.037	0.037
500	0.032	0.032	0.033	0.033	0.034	0.035
1000	0.026	0.027	0.028	0.028	0.029	0.03
1500	0.021	0.02	0.021	0.022	0.023	0.024
2000	0.018	0.019	0.02	0.021	0.021	0.022
2500	0.017	0.017	0.018	0.018	0.019	0.02
3000	0.019	0.018	0.019	0.02	0.02	0.021
3500	0.021	0.021	0.022	0.023	0.023	0.024