Study of Properties and Performance of Biodiesel in C.I. Engine Produced from Waste Cooking Oil using Heterogeneous Catalyst

Thesis

Submitted to the Department of Mechanical Engineering

For the award of degree of

DOCTOR OF PHILOSOPHY

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DEDICATION

"This thesis is dedicated to my parents (Late Sh. Suraj Parkash Kataria) & Smt. Harsh Bala Kataria, my wife Rati, son Nikunj, sisters Ms. Preeti & Ms. Jyoti and my niece Pihu."

CERTIFICATE

This is to certify that the thesis entitled **'Study of Properties and Performance of Biodiesel in C.I. Engine Produced from Waste Cooking Oil Using Heterogeneous Catalyst'**, which is being submitted by **Mr. Jatinder Kataria** to Thapar Institute of Engineering & Technology (Deemed University), Patiala, India, is a record of bonafide research work carried out by him under our guidance and supervision. The matter presented in this thesis has not been submitted either partially or fully to any other University or Institution for the award of any degree to the best of our knowledge.

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DECLARATION

I hereby declare that the research work presented in this thesis entitled "Study of Properties and Performance of Biodiesel in C.I. Engine Produced from Waste Cooking Oil Using Heterogeneous Catalyst", submitted for the award of degree of Doctor of Philosophy in the Department of Mechanical Engineering, Thapar Institute of Engineering & Technology (Deemed to be University), Patiala, India, is original and my own account of research. This research work is independent and its main content work has not previously been submitted for degree at any university in India or Abroad.

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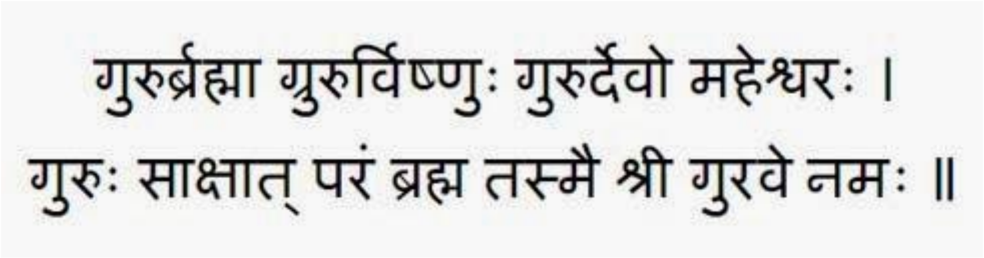

गुरुर्ब्रह्मा गुरुर्विष्णुः गुरुर्देवो महेश्वरः ।
गुरुः साक्षात् परं ब्रह्म तस्मै श्री गुरवे नमः ॥

First of all, I wish to thank Lord for giving me an opportunity to carryout present research work. Throughout my entire span of training as a Ph.D. student in the department of mechanical engineering, Thapar Institute of Engineering and technology (Deemed to be University) Patiala, I have been fortunate to work with several people who not only supported my endeavors in my research activity but also aided the progression of my scientific career. I am fortunate to have been surrounded by individuals with competitive spirit and who push things forward with attitude. I owe my sincere thanks to the **Department of Mechanical Engineering, Thapar Institute of Engineering and technology (Deemed to be University), Patiala,** for taking me into its folds and allowing me to be a part of this legacy.

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Kataria
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ABSTRACT

The world is dependent on fossil fuels for more than a century. In recent years exponential growth in industrialization and world population has increased the demand for the energy. Approximately 80% energy need is fulfilled by the fossil fuels. A major part, nearly 57% from it is utilized by the transport sector. From present scenario there is a huge gap between world energy requirement and energy demand. Therefore, world is facing twin crises of depleting fossil fuel reserves and environmental degradation. This fast diminishing of fossil fuel reserves has adversely affected the world oil supply which increased the oil price. This fluctuation in increasing petroleum prices, limited fossil fuel reserves and environmental degradation escalated the search for substitute for fossil fuels especially in transport sectors. Due to these reasons liquid fuels such as biodiesel is in lime light and become more attractive because of environmental benefits.

Chemically biodiesel is defined as the mixture of long chain fatty acids and is typically produced from non-toxic biological resources such as vegetable oils, animal fats or waste cooking oils. Compared to traditional diesel fuel, biodiesel is technically and economically more competitive due to its renewability, biodegradability, liquid nature-portability, low emission profiles, high flash point and lower sulfur and aromatic content. Biodiesel has properties very similar to conventional diesel and can be run on diesel engine without any major modification in it.

Generally the biodiesel production comprises of transesterification of vegetable oil (edible or non-edible oils) in presence of homogeneous base or acid catalysts. Sodium hydroxides (NaOH), potassium hydroxide (KOH) are homogeneous

base catalysts and are widely used for biodiesel production. The merits of homogeneous catalyst are that it possesses high conversion rate under mild reaction conditions and the reaction completes in one hour. However, transesterification in the presence of base catalysts associates several drawbacks viz. non-reusability, formation of the catalyst contaminated biodiesel and glycerol, deactivation by free fatty acid (FFA) and moisture content. These limiting factors of homogenous catalysts can be overcome by using heterogeneous catalysts instead of homogeneous catalysts.

Utilization of these catalysts offers some advantages such as easy catalyst separation from reaction mixture or final product, reusability and regenerability of the catalyst. In addition to this, these catalysts are less sensitive to water which makes them even more attractive for biodiesel production from a variety of feedstocks. There is large number of heterogeneous catalysts such as metal oxides, alkaline earth metal oxides, transition metal oxides, ion exchange resins, sulfated oxides, carbon based heterogeneous catalysts, enzyme supported catalysts that have been reported in literature for biodiesel production.

Among the reported literature of these catalysts, vast study has been done on different metal oxide for biodiesel production. Among the different metal oxides reported, the most popular metal oxide was found to be calcium oxide which was due to its easy availability, low price, low toxicity and high catalytic activity. Moreover, calcium oxide can be prepared from the waste matters consisting of calcium carbonate, such as mollusk shells, egg shells. The use of the waste matters is not only effective in enhancing the cost advantage of CaO catalyst but is also related to recycle of the naturally available mineral resources.

This study is focused on biodiesel production from waste cooking oil using zinc doped calcium oxide as heterogeneous catalyst and its operational characteristics on VCR compression ignition engine. The optimum experimental conditions were methanol/oil molar ratio 12:1 with 5wt.% zinc doped calcium oxide, temperature of 65°C and 140 min provided yield above 98% methyl esters.

The fuel properties of the produced biodiesel such as the calorific value, flash point and density were examined and compared to conventional diesel. The properties of produced biodiesel and their blend for different ratios (B20, B40, B60, B80 and B100) were comparable with properties of diesel oil and ASTM biodiesel standards. Tests had been conducted on CI engine which runs at a constant speed of 1500 rpm, injection pressure of 200bar, compression ratio 15:1 and 17.5, and varying engine load. The performance parameters include brake thermal efficiency, brake specific energy consumption and emissions parameters such as carbon monoxide (CO), hydrocarbon (HC), oxides of nitrogen (NO_x) and smoke opacity varying with engine load (BP). Diesel engine's thermal performance and emission parameters such as CO, HC, and NO_x on different biodiesel blends demonstrated that biodiesel produced from waste cooking oil using heterogeneous catalyst was suitable to be used as diesel oil blends and had lesser emissions as compared to conventional diesel.

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NOMENCLATURE

MToe	Million ton of oil equivalent
PAH	Polycyclic aromatic hydrocarbon
ASTM	American society for testing and materials
NSSD	National strategy for sustainable development
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
TG	Triglycerides
DG	Diglyceride
MG	Monoglyceride
FFA	Free fatty acid
WCO	Waste cooking oil
FAME	Fatty acid methyl ester
KOME	Karanja oil methyl ester
ME	Methyl ester
WCOME	Waste cooking oil methyl ester
OOME	Olive oil methyl ester
VCR	Variable compression ratio
BTE	Brake thermal efficiency
ITE	Indicated thermal efficiency
BSFC	Brake specific fuel consumption
BSEC	Brake specific energy consumption
BMEP	Brake mean effective pressure
EGT	Exhaust gas temperature
HRR	Heat release rate
CI	Compression ignition

DI	Direct injection
IDI	Indirect injection
EGR	Exhaust gas recirculation
CO	Carbon monoxide
UHC	Unburnt hydrocarbons
NO_X	Oxides of nitrogen
SO_x	Sulphur oxides
PM	Particulate matter
AV	Acid value
SD	Standard deviation
MW	Molecular weight
XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
TLC	Thin layer chromatography
^{1}HNMR	Proton nuclear magnetic resonance
CV	Calorific value
CP	Cloud point
PP	Pour point
FP	Flash point
FP	Fire point
CH_3O	Methoxide
$Ca(NO_3)_2$	Calcium nitrate
$Ca(OH)_2$	Calcium hydroxide
$CaCO_3$	Calcium carbonate
$Ca(OCH_3)_2$	Calcium methoxide
ZnO	Zinc oxide

$C_{19}H_{32}O_2$	Methyl oleate
$CDCl_3$	Deuterated chloroform
TMS	Tetramethylsilane
C_3H_8O	Metoxyethane (Ethyl methyl ether)
$C_{20}H_{14}O_4$	Phenolphthalein

Chapter-1

Introduction

CHAPTER 1

Introduction

Limited fossil fuel reserves, fluctuating crude oil prices and environmental degradation have focused the worldwide researcher's interest in the alternative fuels. The increasing energy demand is causing environmental concerns like greenhouse gas emissions, CO_2 and global warming (Kafuku and Mbarawa, 2010). World energy consumption was almost doubled in the era of 1971 to 2001 and it will increase rapidly, approximately 53% at the end of 2030 (Talebian-Kiakalaieh, Amin and Mazaheri, 2013). Moreover fossil fuels are non-renewable in nature and they will be completely drained in few years. Some research reports revealed that fossil fuel resources will be wiped out in nearly 50 years, if the usage pace does not change.

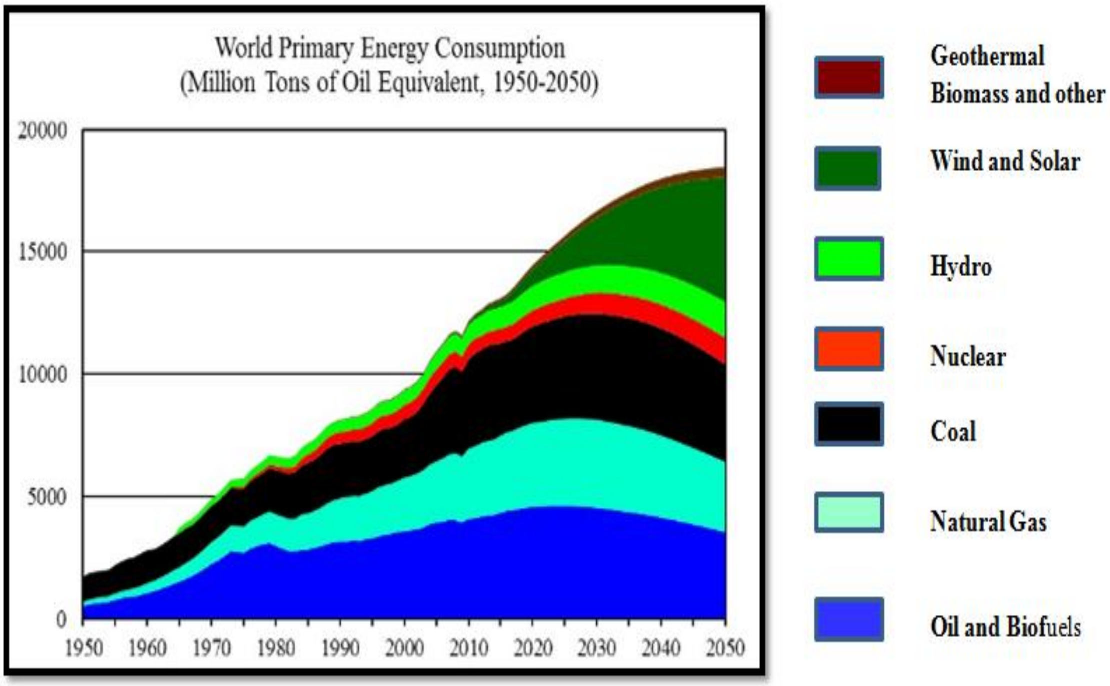


Figure 1.1 Worldwide primary energy consumption (MTOE, 1950 -2050)
(BP. 2017 Statistical review of world energy 2017)

The fluctuation in crude oil prices is a severe threat for the developing countries (Santori *et al.*, 2012). That is why there is an urgent need to develop some alternative fuel which is technically feasible, environment friendly, economically viable and ready to use. By virtue of its renewability, biodegradability and lesser harmful gas emissions, biodiesel has gained tremendous attention all over the world. It has been predicted that biodiesel could exchange nearly 10% usage of diesel fuel in Europe and 5% in Southeast Asia (Phan and Phan, 2008).

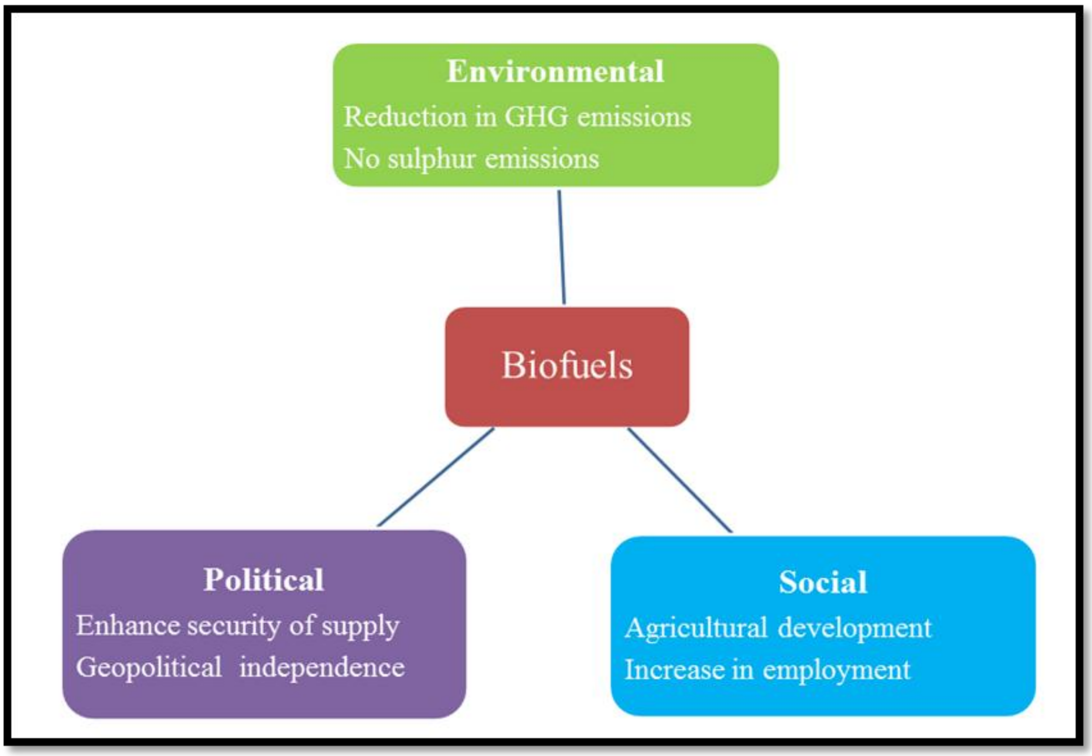
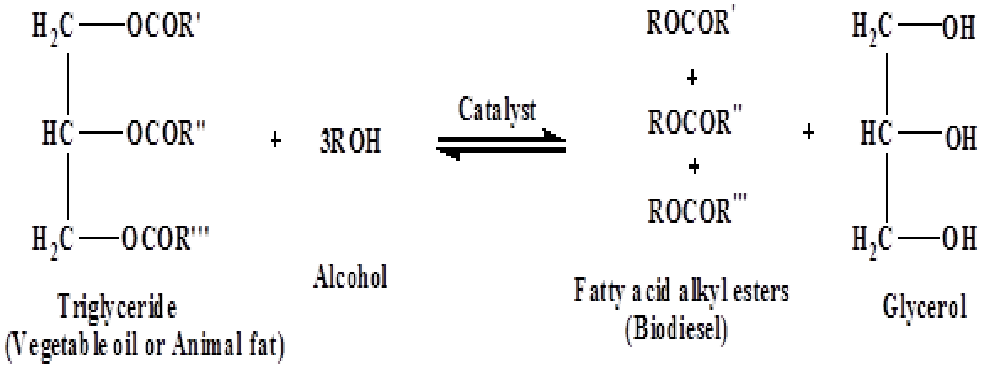


Figure1.2 Major drivers for the revival of biodiesel

This has resulted in increasing demand of alternative sources of petroleum based fuels. Biodiesel, which is an environment friendly fuel, can be considered as a good alternative to traditional fuel. Biodiesel has nearly identical physicochemical properties comparable to conventional diesel fuel. It can be used in any CI engine without any alteration (Hassan and Kalam, 2013) and it has a quality to decompose more easily on exposure to environment and can be easily produced as compared to petrol or diesel.

Biodiesel has an important benefit that its production is completely free of polycyclic aromatic hydrocarbons (PAH) and nitrated PAH which are known carcinogen in humans and emissions of carbon dioxide, hydrocarbons and particulate matters are reduced. Biodiesel itself acts as a lubricant which increases the engine life. On the other hand it has a limitation of releasing higher NO_x emissions. According to ASTM 6751 “biodiesel is comprised of mono alkali esters of long chain fatty acids (chain length C_{14}–C_{20}) derived from renewable vegetable oils, animal fats or even waste cooking oil through a chemical reaction called transesterification” as shown below:-



Generalized equation for transesterification process (R’ R’’ and R’’’ represents straight hydrocarbon chains of fatty acids.

1.1 Origin of Biodiesel

“Rudolf Christian Karl Diesel” (1858-1913) invented the diesel engine. He firstly tried peanut oil as fuel for his engine in August 1893. In the years 1930s and 1940s, in emergency situations the vegetable oils were frequently utilized as substitutes for diesel fuels. **The name biodiesel was introduced in the United States during 1992 by the National Soy diesel Development Board (presently national biodiesel board) which has pioneered the commercialization of biodiesel in the United States. Currently, biodiesel fuels have been commercialized in Austria, Czech Republic, Germany, France, Italy, Slovakia, Spain, and the USA.**

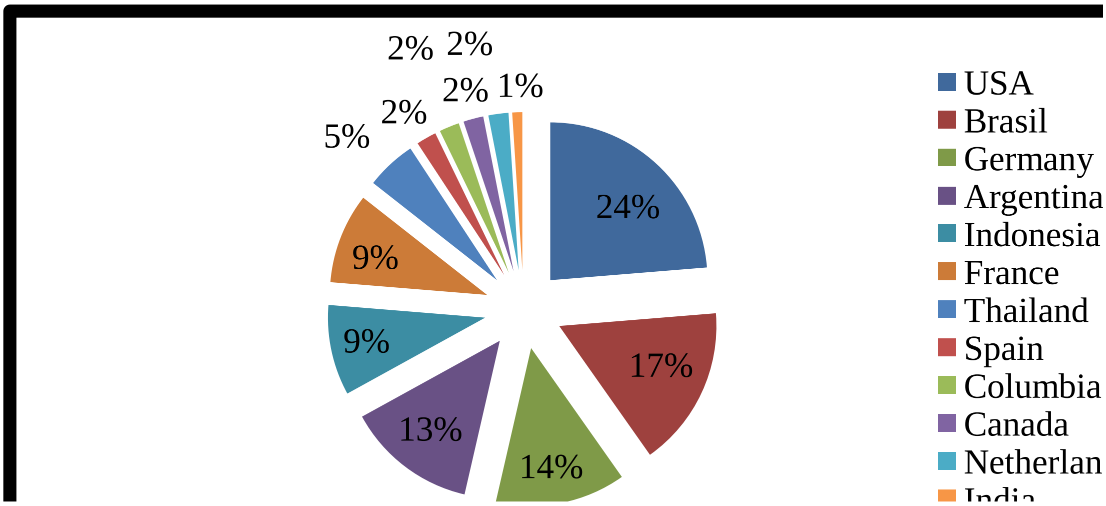


Figure 1.3 Top biodiesel producing countries worldwide in 2017 (Billion liters) (Source Statista 2018)

1.2 Respective Feed Stocks for Biodiesel Production

Biodiesel could be produced from any triglyceride (i.e. edible or non-edible oils) available in geographical vicinity. The feed stock can be categorized as edible oil, non-edible oils and other sources (Verma and Sharma, 2016). The cost and the availability are the two important criteria that determine the choice of raw material (feed stock). In general the feedstock's alone cost is 75% of biodiesel production cost. Figure 1.5 represents the percentage cost break-up for biodiesel production.

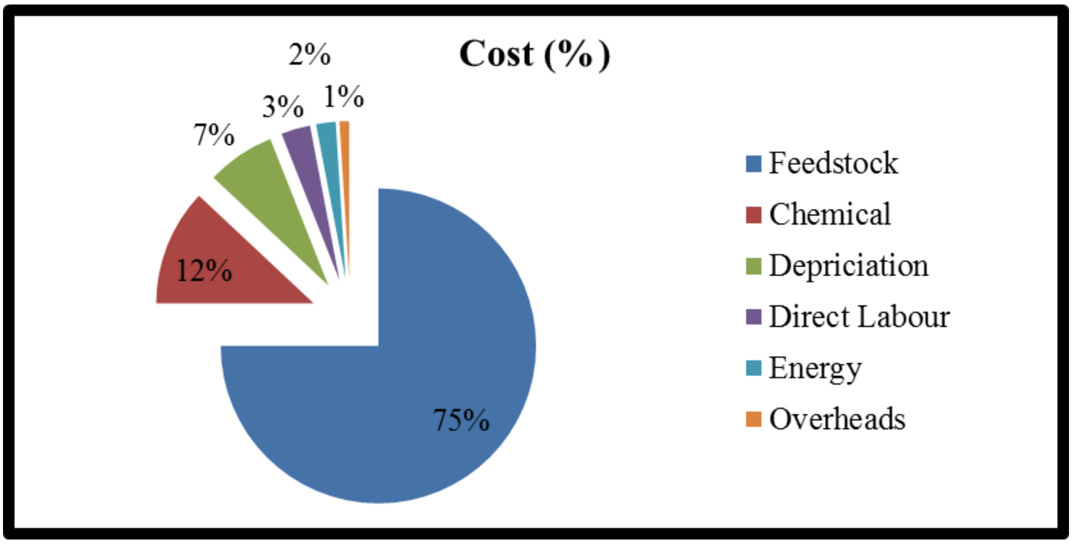


Figure 1.4 Percentage cost break-up for biodiesel production (Lin *et al.*, 2011)

1.2.1 Edible Oils

These are the vegetable oils incurred from food crops such as rice, wheat, potato wastes and sugarcane etc. (in the past) and edible oils such as rapeseed, mustard etc. are used now a day to produce alternative fuels. However, using these oils results in social, economic and environmental challenges since these oils are directly obtained from the food crop feedstocks. This also results in increase in food prices especially in countries like India where demand supply ratio is already high which causes food crisis in the market. Further, cultivating these food crops for biodiesel production requires increased use of fertile land which multiplies the problem of food shortage (Azad *et al.*, 2015).

1.2.2 Non Edible Oils

Considering the drawbacks of using edible oils for biodiesel production, inedible oils are the better choice without harming the environment and disturbing the food supply and demand balance (Gui, Lee and Bhatia, 2008). Examples of non-edible oil feedstock are Jatropha curcas, Pongamia pinnata (karanja), Madhuca Indica (Mahua), Nicotiana tabacum (tobacco), Salmon oil, Babassu, Coriander (Coriandrum sativum L.), Simmondsia chinensis (Jojoba), Cerbera odollam (Sea mango), Champaca, Scheleichera triguga (kusum), Garcinia indica, Desert date, Thevettia peruviana (yellow oleander), Shorea robusta (sal), Croton megalocarpus, M. azedarach (syringe), Sapindus mukorossi (Soapnut), Radish Ethiopian mustard, Terminalia belerica roxb, Tomato seed, Deccan hemp, Asclepias syriaca (Milkweed), Putranjiva roxburghii (Lucky bean tree), Zanthoxylum bungeanum etc. (Atabani, 2013)

1.2.3 Other Sources

Waste cooking oil, micro algal biomass, fish oil, chicken fat, pig fat oil etc. all these sources come under this category. Among all these resources of feed stock for biodiesel production, the used frying oil can be utilized as environmental-friendly feedstock, since they have originated from already existing oil sources and are cheaper than virgin oils (2-3 times) (Jindal, 2014). The transesterification of waste cooking oil into methyl/ethyl ester will result in two third reduction in molecular weight, six-seventh reduction in viscosity and slight reduction in flash point, whereas, there will be marked increase in pour point (Balat and Balat, 2010). The various sources of feedstock for biodiesel production are summarized in table 1.1.

Table 1.1 Various sources of feedstock for biodiesel production (Singh and Singh, 2010)

Edible oils	Non-edible oils	Animal fats	Other sources
Cotton seed	Jatropha	Fish oil	Tarpenes
Soybean	Karanja	Poulltry	Algal oil
Groundnut	Babasu	Tallow	Latexes
Rice bran	Tobacco seed	Lard	Waste cooking oil
Rapeseed	Pongamia pinnata		Fungi
Copra	Mahua		Bacteria
Wheat	Kusum		
Oat	Rubber plant		
Coconut	Salmon oil		
Safflower	Jojoba oil		
Sorghum	Andiroba		
Barley	Cumaru		
Copra			
Canola			

1.2.4 Significance of Non-Edible Oils for Biodiesel Production

The use of edible oils as feedstocks has been of severe concern in the recent past. For instance, expanding world population and mass consumption of these oils might result in food shortage particularly in the developing countries and other problems resulting from extensive use of fertile land (Banković-Ilić, Stamenković and Veljković, 2012). Therefore, to overcome these problems it is necessary to look out for a substitute of edible oils for biodiesel production.

The inedible oils are unfit for human use due to harmful substances in them. Some other significant reasons for the production of biodiesel from these feedstocks are listed here; (i) The land unfit for cultivation can easily be used for cultivating the non-edible oil plants and hence reducing the cost of cultivation (Gui, Lee and Bhatia, 2008); and (ii) growth of these plants minimizes CO_2 concentrations in the atmosphere. The diverse variety of available feedstocks of inedible oils makes them most sought after for biodiesel production. The figure 1.6 shows the some common non-edible oil species used for biodiesel production.

Figure1.5 Common non-edible oil feedstock for biodiesel production(a) Jatropha plant and seed, (b) Pongamia plant and seed, (c) Rubber plant and seed, (d) Mahua tree and seed, (e) Neem tree and seed and (f) Moringa plant and seed

1.3 Current Status of Biofuel Development in India

National biodiesel mission was started in 2003 for promoting the growth and development of alternative fuels in India. Planning commission decided for blending five percent of ethanol with petrol for eight major cities in country (phase 1). In phase 2 the blending was proposed to increase to ten percent and 20 percent by 2011-2012. To meet the increase in energy demand, National policy on biofuels was proposed and was first approved in the year 2009. The key highlights of the national biofuel policy proposed in 2018 are:

- A suggestive target of B20 of ethanol with petrol and B5 of biodiesel with diesel by the year 2030.
- Providing funding of 5000 crore in six years for 2nd generation ethanol bio-refineries along with more tax benefits, higher purchase price in comparison with 1st generation bioethanol.
- Classification of biofuels into
    1. Basic biofuels: 1st generation bioethanol
    2. Advanced biofuels: 2nd generation ethanol
    3. Algal based: 3rd generation biofuels
- Development of national biomass repository by conducting appraisal of biomass across the country.
- Promoting biodiesel production from in-edible oil seeds, used frying oil, short gestation crops and developing supply chain mechanisms.
- Thrust on research development and demonstration in the field of biodiesel feedstock production, advanced conversion technologies from identified feedstock.

- Formulating “National Biofuel Coordination Committee” (NBCC) under “Ministry of Petroleum and Natural gas”.

1.4 International Status of Biodiesel

Brazil

Government of Brazil introduced “PROBIODIESEL” in early 2000s whose sole purpose was to encourage small scale agricultural development throughout the pan Brazil and looking for diverse feedstock for biodiesel. Key features of biodiesel production policy in Brazil are:-

- Current blending requirement for ethanol is 27%.
- The benefits for flex-fuel vehicle as compared to gasoline fueled vehicle.
- National biofuel production program was launched in 2004 that mandated the procurement of vegetable oils from small producers and family farms.
- Tax benefits according to feedstock production, producer size and regions

China

Biofuel policy has been initiated in the early 2000s. The main key points of the policy are:-

- Targets of producing 15% biofuels (of total fuel) by 2020.
- 10% mandate for biodiesel blending for future target

Europe

- EU Energy and Climate Change Package (CCP, 2009) describes the regulations for using biofuels in transportation sector.
- CCP mandates that 20% of all energy requirement should be from renewable in nature by 2020.

- RED (Renewable energy directive) issues guidelines for liquid biofuels such as decreased GHG, judicial utilization of land and other social, environmental and financial aspects.
- Advanced (obtained from non-edible feedstock) biofuels to be produced at 5% of national target mandatory for member states.

United Sates

- Renewable fuel standard (RFS) policy was established with the energy policy act of 2005.
- Environmental Protection Agency (EPA) proposes to increase biofuel consumption volumes from 9 bn. gallons of renewable fuel in 2008 to 36 bn. by 2022.
- Tax exemption for using 100% biodiesel for transportation.
- Incentives for producing feedstock for production of advanced biodiesels.

1.5 Reactant for Biodiesel Production

Methanol, ethanol, propanol and butanol are widely recommended alcohols for biodiesel production. Out of these, methanol is the most frequently used alcohol due to virtue of its low cost and its physical and chemical advantages. Moreover, modest reaction conditions and easy phase separation are its positive attributes. However, having low boiling point and high volatility there are fair chances of explosion.

1.6 Catalysis in Transesterification

Generally there are two types of catalyst used in transesterification reaction one is chemical based and another is enzyme based. The chemical based catalysts are further divided into homogenous catalysts and heterogeneous catalysts. Homogeneous catalysts act with the reaction mixture in the same phase. On the other hand heterogeneous catalysts work in a different phase which eases their separation from reaction mixture for their reuse.

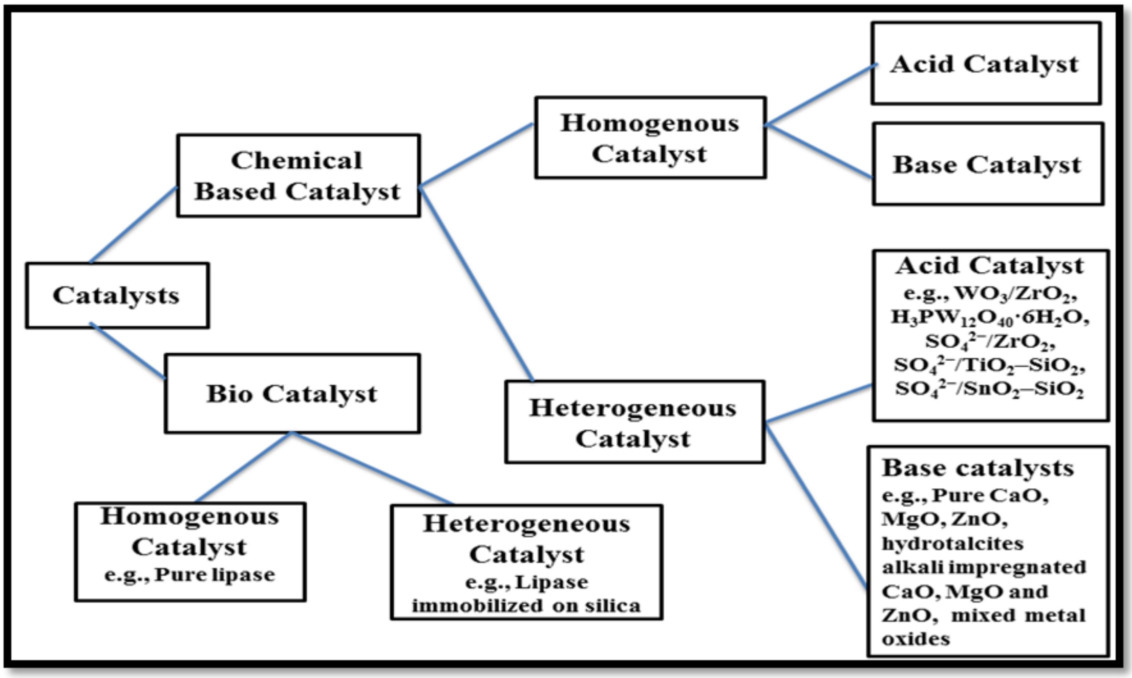
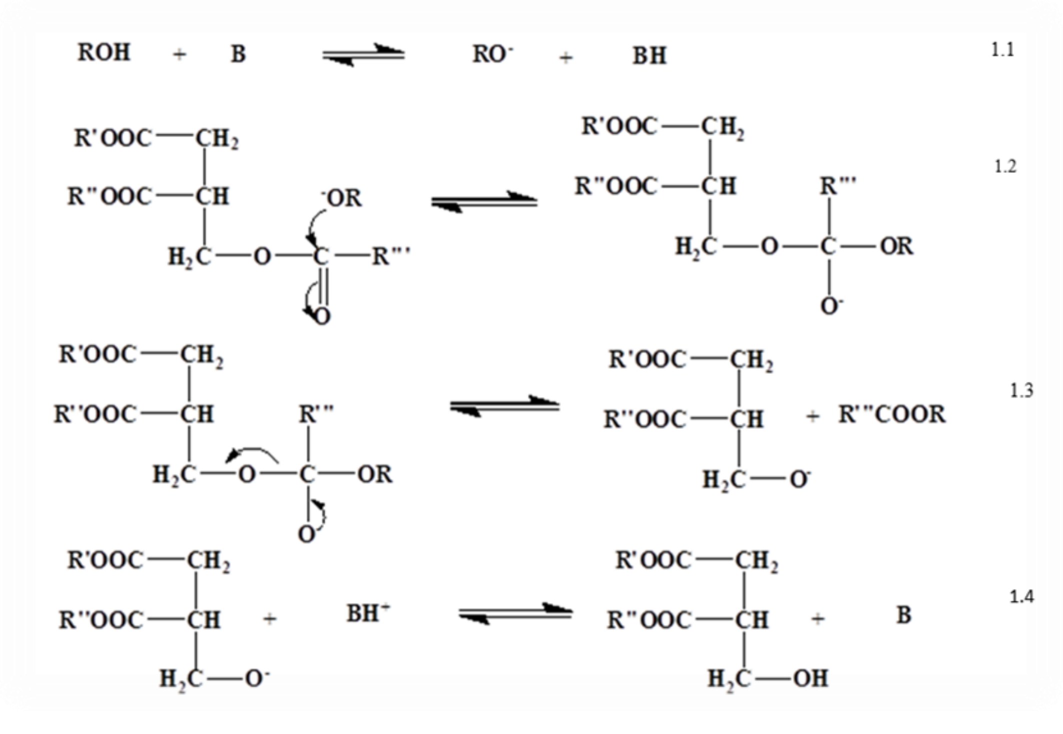


Figure 1.6 Classification of catalyst

1.6.1 Homogeneous Base Catalysts

FAME is generally produced on industrial scale using homogeneous catalysts (i.e. NaOH, KOH etc.). These catalysts are inexpensive and possess higher conversion rate under ambient reaction conditions and they take nearly an hour to complete (Kawashima, Matsubara and Honda, 2008). In spite of industrial application these catalysts have some limitation: as the mixture is in one phase therefore the catalyst is fully dissolved in it due to which product separation becomes difficult and requires a cumbersome purification process to remove excess catalyst. Moreover, the process effluent is environmentally toxic because of its high basicity. Contaminated glycerin has little value in today’s market and its disposal is another issue. Further if FFAs and moisture contents are >0.5 and 0.6 wt. % respectively in feedstock (Fangrui and Hanna, 1999), catalysis will result in soap formation rather than biodiesel. Non-reusability is another negative aspect of homogeneous catalysts. The process of the base-catalyzed transesterification of triglyceride is explained in figure 1.8. Equation 1.1 shows the reaction between the base and the alcohol resulting in formation of alkoxide and protonated catalyst. Equation 1.2 shows the production of a tetrahedral intermediate from reaction between the alkoxide and carbonyl group of the triglyceride. This reaction results in the formation of alkyl ester and the corresponding anion of di glyceride as described in equation 1.3. The diglyceride anion in turn deprotonates the catalyst resulting in the regeneration of the active catalyst as described in equation 1.4. This active catalyst can now be used for the next reaction. Diglycerides and mono glycerides are converted by the same process. The flow diagram for the production of biodiesel is depicted in figure 1.7.



Base-catalyzed transesterification mechanism

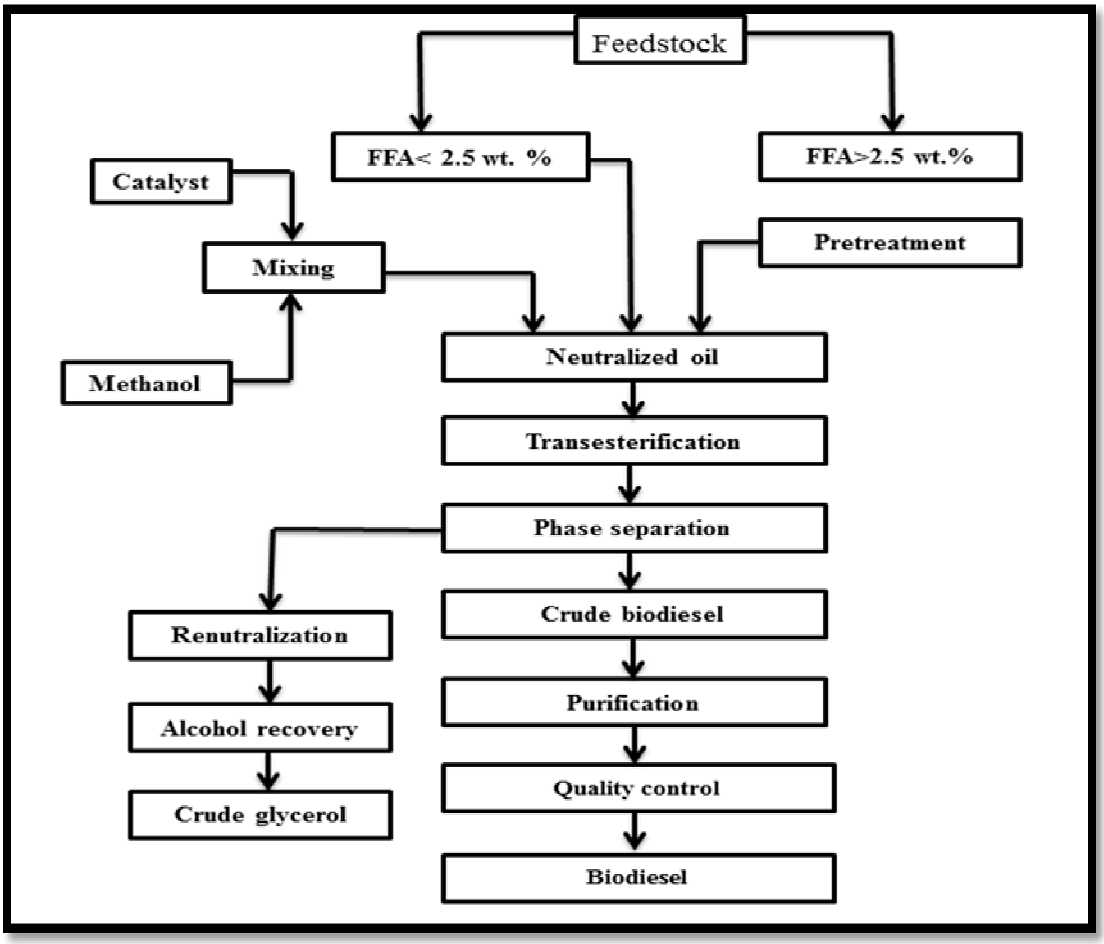


Figure 1.7 Process flow diagram for biodiesel production

1.6.2 Heterogeneous Catalysts

In order to overcome the difficulties related to the use of homogeneous catalysts, a lot of research is being done in the recent past to develop the heterogeneous catalysts for biodiesel production. This has resulted in experimenting with numerous heterogeneous catalysts viz. alkali earth oxides, alkali oxides, metal oxides, cation exchange resins etc.). The benefits of solid heterogeneous catalysts are given below:-

- Less quantity of catalyst is used in transesterification of triglyceride and easy recovery from the methyl ester,
- Heterogeneous catalysts are less corrosive in nature.

- These catalysts are environmentally benign, recyclable and have long life. (Gomes *et al.*, 2012; Choudhury, Chakma and Moholkar, 2014; Tan, Abdullah and Nolasco-Hipolito, 2015)
- **These are insensitive to FFA content (Islam *et al.*, 2013)**
- **Esterification and transesterification occurs simultaneously (Chopade *et al.*, 2013)**
- **Washing step is eliminated in heterogeneous catalysts (Jitputti *et al.*, 2006).**

On the other hand, they have a drawback of having less efficacy as compared to homogeneous catalysts. Variety of feedstock, operating parameters, catalyst activity, cost and availability are some of the significant criteria for the selection of catalyst. Frequently reported heterogeneous base catalysts are alkaline metal carbonates, alkaline earth metal oxides such as CO, MgO, BaO and SrO and other oxides as zinc oxide; alkaline earth metal carbonates such calcium carbonate etc.

The reaction mechanism for the heterogeneous base catalysts is comparable with the homogeneous base catalysts. In the first step, O^{2-} (Lewis base/B) of metal oxide surface extracts H^+ from methanol producing surface methoxide anion (CH_3O), that adheres with the surface metal ion (Lewis acid / M). Methoxide is intensely basic and hence depicts strong catalytic activity for transesterification.

Afterward methoxide anion is bombarded by carbonyl carbon of triglyceride molecule producing an alkoxycarbonyl intermediate on the catalyst surface. In the next step the intermediate reacts either with H+ from the catalyst surface or methanol to generate CH_3O. In the final step, the alkoxycarbonyl intermediate is broken into FAME and diglyceride molecule.

1.7 Lacunae

Currently the biodiesel is not commercially competitive with conventional diesel owing to high feedstock cost and energy consumption throughout transesterification and purification. In order to cut down the biodiesel production cost, inexpensive feedstock such as animal fats, in-edible vegetable oils, greases and used vegetable oil could be utilized for biodiesel production. These feedstock contain high FFA contents and moisture content therefore homogeneous catalysts are not a good choice for transesterification. After studying the extensive literature the following lacunae were identified.

- Production of biodiesel from low quality feedstock applying efficient and economical catalyst processes needs to be experimented.
- A heterogeneous catalyst that acts under ambient conditions for the transesterification is not commercially available.
- Fewer reports with regard to the preparation of biodiesel from WCO.
- Fewer reports regarding the evaluation of heterogeneous catalyst of waste material as catalytic support for the transesterification.

1.8 Motivation for the Present Work

The growth of any country is directly proportional to the adequate availability of energy sources and technology advancement. In the present scenario a significant part of the energy comes from fossil fuels globally. The inflating energy requirement, depleting fossil fuel reserves and deteriorating environment conditions are the primary motivation for exploring the alternative and environment friendly substitutes of energy production. It has been found that industrial sector consumed the highest quantum of energy followed by transportation and agriculture sectors. Diesel engines are highly efficient, due to high compression ratio and are a popular prime mover in transportation, agriculture and industrial sectors. However, they also emit a large quantity of particulate matters (PM), SO_X, soot, oxides of nitrogen (NO_X) and smoke emissions, which pose environmental challenges. So, there is a need for emerging cleaner combustion technologies and alternative fuels.

1. 9 Objectives

Keeping in view the above challenges, following objectives are defined for my Ph.D. dissertation

- **Catalyst preparation and characterization**

  The nano crystalline Zinc doped calcium oxide catalyst will be prepared by wet impregnation method. The prepared catalyst will be characterized by XRD, SEM and EDX at SAI lab Thapar.

- **Biodiesel production and characterization**

  The waste cooking oil will be used as feedstock for biodiesel production which will be procured from local caterer Patiala. By using waste cooking oil and prepared heterogeneous catalyst with proportionate methanol, biodiesel production has been accomplished. The characterized will be done by HNMR technique at SAI lab. The fuel properties of prepared biodiesel will be performed at biofuel lab CSIR-CMERI centre of excellence for farm and machinery Ludhiana.

- **Evaluation of thermal and emission performance of CI engine using biodiesel and its blend with diesel**

  The prepared biodiesel and its blends (B20, B40, B60, B80 and B100) will be utilized as fuel in variable compression ratio CI engine and check the thermal and emission performance. The experimental setup consist of VCR CI engine test rig equipped with engine-soft software for data

acquisition, DI gas 444 analyzer and smoke meter for emission performance.

1.10 Organization of Thesis

This thesis is comprised of five chapters. The organization of the chapters is listed below:-

Chapter1 Introduction

This chapter describes the significant reasons for searching of alternative and renewable energy sources. It fulfills the selection of alternative fuel for compression ignition engine. It includes origin, history and importance of biodiesel. It describes different catalysts for biodiesel production, merits of heterogeneous catalyst over homogeneous catalyst.

Chapter 2 Literature Review

This chapter gives an insight to literature review and problem identification. The chapter is divided into the three sections described below:

- Extensive literature on biodiesel production, its chemical structure and different methods used for biodiesel production.
- Literature regarding biodiesel production from homogeneous and heterogeneous catalyst
- Literature related to thermal and emission performance parameters of biodiesel on CI engine.

This chapter paved the path for problem formulation in the present work.

Chapter 3 Materials and Methods

This chapter deals with the procurement of feedstock such as waste cooking oil, different chemicals and different analytical instruments for characterization of heterogeneous catalyst. A detailed description of methods used for biodiesel production and its standardization using different parameters has also been described. The fuel characteristics of biodiesel and their test methods are also described in this chapter. The VCR compression ignition engine test rig and emission instrument used in the present study are also described.

Chapter 4 Results and Discussion

In this chapter, the impact of different variables i.e. molar ratio, catalyst concentration, reaction temperature and reaction time on production of biodiesel is being discussed. The effect of calcination temperature and doping of zinc on calcium oxide on biodiesel yield is being discussed. Further, the parameters of engine performance (i.e. BTE, BSEC), combustion characteristics such as combustion pressure and exhaust gas temperature and emission parameters such as CO, UHC, NO_x and SO are also discussed in this chapter. Furthermore the effect of compression ratio on different blends of waste cooking oil methyl ester on engine performance and emission parameters is also studied.

Chapter 5 Conclusions and Future Scope

Conclusions regarding using heterogeneous catalyst for biodiesel production, transesterification processes, fuel characterization and variable compression ratio CI engine testing for prepared biodiesel are described in this chapter. Future scopes of present work recommendations are included in this chapter.

Chapter-2

Literature review

CHAPTER 2

Literature Review

This chapter is divided into the three sections which are listed below:-

- Extensive literature on biodiesel production, its chemical structure and different methods used for biodiesel production.
- Literature reported biodiesel production from homogeneous catalyst and heterogeneous catalyst.
- This section deals with thermal and emission performance parameters of biodiesel on compression ignition engine.

2.1 Background and Chemistry behind Biodiesel

Vegetable oils used as substitute to conventional fuels have been 10 decade old. Rudolph Diesel had also given a statement that “**The use of vegetable oils for engine fuels may seem insignificant today. But such oils may in course of time be as important as petroleum and the coal tar products of the present time”**. Still owing to low price of petroleum products, non-conventional fuels could not make it into the main stream. Vegetable oils play a vital role in developing the alternative fuels. Still a lot of obstacles have come in the way for adopting it straightly in compression ignition engine (especially in direct injection). The demerits of vegetable oil are: higher viscosity (which is 11-17 times to that of conventional diesel fuel), lower volatilities and reactivity of unsaturated hydrocarbon chains which tends to cause incomplete combustion inside the engine. The common issues, possible causes and their remedies to use vegetable oils in CI engines are summarized in Table 2.1.

Table 2.1 Common problems, probable cause and potential solutions for using vegetable oil in engine

Problems	Probable cause	Potential solutions
Carbon deposits on piston and head of engine	High viscosity of vegetable oil, poor combustion of fuel	Chemically alter the vegetable oil to ester.
Excessive engine wear	High viscosity of vegetable oil, poor combustion of fuel. Presence of free fatty acids in vegetable oil	Preheat fuel before injection, chemically treatment of fuel in order to remove the phosphatides
Short term cold weather starting, plugging and gumming of filters, line and injectors	High viscosity, low cetane and low flash point of straight vegetable oils, phosphatides present in the vegetable oils	Preheat fuel before injection, chemically treatment of fuel in order to remove the phosphatides
Engine knocking	Improper injection timing	Adjust injection timing, use high compression engine, heat fuel prior to injection

In order to reduce its viscosity, thermal and chemical processes were examined for making vegetable oil suitable for diesel engine. Several efforts have been made in the past to overcome the problems related to use of vegetable oils. Some of the common processes which can be used for overcoming such problems are: heating, blending with conventional diesel, pyrolysis, micro-emulsification and transesterification. In transesterification process triglycerides present in the vegetable oils react with a lower alcohol to form fatty acid alkyl esters having properties identical to conventional diesel.

It is the most common and simple technique to produce biodiesel. It was first conducted in 1853 by two researchers "E. Duffy and J. Patrick", before the 1^{st} conventional diesel engine became operational. In 1937, "G. Chavanne" of the University of Brussels" patented the procedure to produce biodiesel from edible oils for the conversion of edible oils to be used as fuels. Despite this the adaptation of biodiesel as fuel was done much later and its significance grew many folds due to the energy crisis in the year 1973.

Later on in 1977, Brazilian scientist "Expedito Parente" became the first researcher to invent and patent the first industrial process for biodiesel production. From chemical perspective, oils from diverse origins have different fatty acid composition. Fatty acids (triglycerides) usually have un-branched carbon chain of different length and different degree of saturation. Chemical composition of the oil comprises of approximately 98% TGs and rest MGs and DGs (Giakoumis, 2013). Triglyceride consists of three FA esters and one glycerol and possesses significant proportions of oxygen in their chemical structure. If three FAs are similar, it is termed as simple TGs and if FAs are different the product is mixed TGs that are rich in hydrogen and with no double bonds. On the other hand mono glyceride fatty acids are those in which one hydrogen molecule is missing and which own one double bond between carbon atoms. If in triglyceride more than one hydrogen molecule is missing and if they are having more than one double bond they are known as polyunsaturated triglycerides. Fully saturated TGs result in exuberant carbon deposits in engine. The term biodiesel is used for "variety of ester based oxygenated fuel from renewable biological sources". It can be adopted in CI engines with minimal or no modifications.

2.2 Biodiesel Formulating Techniques

The biofuels must be technically, environmentally fit and acceptable and also economically feasible. By considering these pre-requisites, triglyceride (vegetable oils) and their derivatives may be regarded as feasible substitutes to conventional diesel fuel. As stated earlier, the main problem with substituting vegetable oils directly in engine is their high viscosity, low volatilities and poly-unsaturated nature. There are various techniques by which the viscosity of vegetable oils is reduced to make vegetable oil compatible to the hydrocarbon based diesel fuel.

2.2.1 Heating or Pyrolysis

Pyrolysis is a well-established technique that consists of "breakdown of high molecular weight compound into smaller compound using thermal energy with or without catalyst". The liquid portions of the pyrolyzed vegetable oils are likely to get transformed into liquid oils. Extensive work has been carried out on the pyrolysis of triglycerides for obtaining suitable fuels for diesel engines. The pyrolyzate oils have nearly similar properties as that of conventional diesel. The pyrolyzate oils have lower cetane number.

Pyrolyzate oils obtained from vegetable oils are found to contain sulfur water and sediment within admissible limits. They give copper corrosive values within admissible limits. Whereas ash and carbon residue are not within permissible limits.

The thermal cracking of biodiesel plant consists of a reactor having safety valve, drain pipe, temperature indicator, etc. The oil/animal fat that needs to be transformed to the biodiesel is placed inside the reactor, and then heated. Now the vaporization of the feedstock occurs that reaches the condenser through pipe. The vapor thus formed gets liquefied in the condenser. The liquid thus collected in the beaker is termed as biodiesel. (Van Gerpen *et al.*, 2004).

2.2.2 Dilution or Blending

Dilution or blending is a technique in which high viscosity vegetable oil is mixed with fuel having low viscosity (e.g. conventional diesel) fuel to lower down the viscosity as a whole, so that these can be successfully utilized in C.I. engine. Substitutes like solvents, methanol/ ethanol can be used for diluting the vegetable oils. A lot of researchers have worked on blending the vegetable oil with conventional diesel and then successfully operated the diesel engine. Example include testing of blends of sunflower oil and diesel in 1:3 ratio by volume on engine performance (Ziejewski *et al.*, 1984). The conclusion of the study suggested that a long term use of the blend could not be recommended in the direct injection diesel engines.

2.2.3 Micro-emulsion

This process helps in lowering the viscosity of vegetable oils and optimization properties of oil. The issue of high viscosity of vegetable oil can successfully be resolved by the process of micro-emulsion. The micro emulsion is elaborated as “thermodynamically stable, isotropic liquid mixture of oil, water and surfactant and often a small amphiphillic molecule called co-surfactant” (Avhad and Marchetti, 2015). The micro emulsion process possesses a good spray property when injected into the engine by nozzle. However a few major drawbacks of using micro emulsified fuel in diesel engine are incomplete combustion, carbon deposit and nozzle failure.

2.2.4 Transesterification

This is the most popular and suitable technique for producing biodiesel from vegetable oils which reduces the viscosity of biodiesel thus produced. In this process an alcohol (mostly methanol) reacts with the triglyceride present in the oil fats or recycled greases to produce biodiesel and glycerol. The reaction requires high temperature and a strong base catalyst, such as NaOH or KOH. The temperature required for the reaction is about 65°C. The methyl and ethyl esters of vegetable oil have been found to produce better biodiesel than neat vegetable oil. The table 2.2 shows the various merits and limitation for different biodiesel production techniques.

Table2.2 Merits and limitations of different biodiesel production techniques

S. No	Production techniques	Merits	Limitations
1.	Heating or Pyrolysis	Simple, pollution free	Requires high temperature, need costly apparatus, low purity because of carbon residue, clinkers
2.	Blending or Dilution	Simple process, less time consuming	Incomplete combustion, formation of carbon deposits
3.	Micro-emulsion	Simple process	High viscosity, poor volatility, and stability
4.	Transesterification	Suitable for industrial scale, fuel properties obtained are similar to conventional diesel.	Success depends upon the free fatty acid content in the feedstock and type of catalyst used

2.3 Parameters Affecting Biodiesel Yield

Parameters that affect the biodiesel yield through the transesterification process have been found to be reaction temperature, reaction time, molar ratio (alcohol to oil), catalyst concentration and lastly free fatty acids and water content in feedstock.

2.3.1 Reaction Temperature

The reaction temperature is directly proportional to the rate of reaction and biodiesel yield i.e. the reaction rate increases with increase in temperature and vice versa. This is because of lowering of oil viscosity at high temperature. However, further increasing the temperature beyond optimal level, decreases the yield due to the fact that very high temperature results in saponification of TGs. Generally reaction temperature should remain below the boiling point of the alcohol so as to prevent its evaporation. The spectrum of reaction temperature is dependent on the oils or fats used (Ma and Hanna, 1999; Leung, Wu and Leung, 2010).

2.3.2 Reaction Time

The effect of reaction time on fatty acid ester conversion was studied by (Freedman et al., 1986). They found that by increasing the reaction time there was increase in the fatty acid ester conversion. Initially the speed of the reaction is less due to mixing and dispersion of alcohol and oil. After that the reaction speed accelerates. Maximum conversion was obtained in 90 mins. Further increase in the reaction time results in reduction in biodiesel yield due to the reversible reaction of transesterification leading to saponification (Leung and Guo, 2006; Alamu et *al.*, 2007).

2.3.3 Molar Ratio

Molar ratio of alcohol has a significant impact on biodiesel yield. The alcohol-oil molar ratio to produce biodiesel stoichiometrically is 3 to 1. However, owing to the reversible nature of the transesterification reaction some extra alcohol is usually taken so as to ensure that there is complete conversion of the oil into ester. 6:1 molar ratio of alcohol to TGs has been found to cause complete conversion in many studies. The biodiesel yield is directly proportional to the concentration of methanol/ethanol up to some permissible concentration. On further increase of methanol/ethanol, the biodiesel yield is not affected but cost of methanol recovery is increased (Leung and Guo, 2006). Furthermore the ratio of methanol/ethanol content required also depends on the catalyst used. For example alkali catalyst uses 6:1 molar ratio of methanol to oil for catalyzing the alcoholysis of oils or fats (Zhang et al., 2003; Freedman et al., 1986). If oils have high FFA, the reaction does not take place in presence of alkali catalyst, whereas acid catalysts effectively accelerate the reaction in such scenario for catalyzing the reaction but the reaction will require more amount of alcohol than alkali catalysts. This is because of the acid catalysts which have more tolerance towards FFA and water content present in oil samples.

2.3.4 Catalyst Concentration

Catalyst concentration also affects the biodiesel yield. NaOH or KOH are most frequently used catalysts for biodiesel production. However the study performed by Freedman et al (1984) revealed that NaOH would be more efficient for the formation of biodiesel because the reaction of sodium hydroxide with methanol resulted in the production of small amount of water that inhibited the biodiesel production due to the hydrolysis reaction. This is why the catalyst is first mixed with methanol, and is then added to the oil or fats. Furthermore when there is increase in the catalyst concentration in oil sample, the conversion of triglyceride into biodiesel also increases and vice versa. (Leung and Guo, 2006; Guo, 2005). However, maximum biodiesel yield was obtained with 1.5 wt. % of NaOH concentration, beyond which there was decrease in the product yield with increase of catalyst concentration. This was because the excess amount of alkali catalyst resulted in more soap formation when it reacted with triglyceride (Leung and Guo, 2006).

2.3.5 Free Fatty Acid and Water Content

The FFA and water content are important factors for transesterification reaction. Transesterification reaction using base catalyst need zero water and minimal acid value feedstock for production of biodiesel. Thus with increase in the FFA content in the oil samples more alkali catalyst is required for neutralizing the FFA. Also higher water content in the oil samples results in more soap formation and frothing resulting in increased viscosity. This formation of foams and gels further hinders the separation of glycerol from biodiesel (Demirbas, 2009). To eliminate this problem, (Kusdiana and Saka, 2004) suggested a supercritical methanol method which was compared to alkaline and acid catalyzed method where water has less influence on the process of biodiesel production.

2.4 An Overview of Heterogeneous Catalysts used in Biodiesel Production

The heterogeneous catalysts are concerned with many merits as compared to homogeneous catalysts such as they are immiscible in the reaction mixture and their separation from end products is easier. Furthermore these catalysts could be recycled as well as regenerated and are environmental friendly because they don't require acid or washing in the separation step.

Generally alkali earth metal oxides and transition metal oxides are the most widely used heterogeneous catalysts for transesterification. The chemical composition of these catalysts is comprised of cations owning Lewis acid and anions owning Bronsted base. In the process of methanolysis of oils, the structure of these catalysts provides adequate adsorptive sites for methanol, where there is fast breakdown of O-H bonds. Methoxide anions and hydrogen are formed from this breakdown (Figure 2.1). Methoxide anion thus produced reacts with triglyceride producing corresponding fatty acid methyl esters.

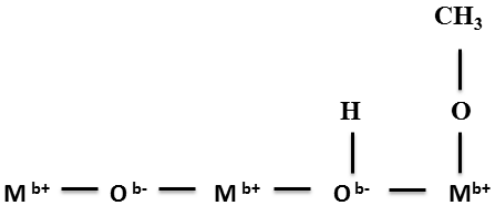


Figure 2.1 Surface morphology of metal oxides

Among different metal oxides which are suitable for transesterification of vegetable oil, calcium oxide is the most prominent and popular earth metal oxide owing to its lower cost, non-toxicity and abundance. $Ca(NO_3)_2$, $CaPO_4$, $Ca(OH)_2$ and $CaCO_3$ are the basic materials to produce CaO. CaO has relatively immense basic strength and more environment friendly owing to its less miscibility in alcohol. Moreover its production is very cheap because of cheaper raw materials (like limestone and calcium hydroxide) required for its synthesis. Based on their utilization in transesterification these catalysts can be divided into four types: (a) neat, (b) doped, (c) loaded and (d) mixed

CaO. Commercially available pure CaO is most often used catalyst after calcination. Various factors can increase the catalytic activity of neat CaO described as follows:

- By increasing the surface area.
- By enhancing the number of basic sites (i.e. by doping the particles of CaO with alkaline compounds) the catalyst thus formed is termed as doped CaO.
- By incorporating CaO into different carriers such as alumina, MgO, silica and others which are all termed as supported CaO.
- By mixing the CaO with metal oxides like Zn, La and CeO_2 (termed as mixed CaO).

Other CaO based catalysts that have been tested in transesterification reactions are calcium methoxide, diglyceroxide and glycerolate.

The activated calcium oxide had been employed as a catalyst by (Granados *et al.*, 2007) in the alcoholysis of sunflower oil to examine the correlation amongst H_2O and CO_2 with catalyst activity by exposure to air with respect to time. The study revealed that there was a rapid hydration and carbonation of CaO in air. The catalytic activity of CaO was reduced on air exposure more than 20 days. This was due to the fact that the active catalytic sites were blocked with carbon dioxide and water. This was nullified by the calcination of CaO at 700°C. This process of thermal activation of catalyst (CaO) chemically eliminates CO_2 before being used during the reaction. After performing the reaction for 100 mins more than 90% yield was achieved. The parameters used were: temperature at 60°C, alcohol/oil molar ratio 13:1 and catalyst of 3 wt.%. Activation of catalyst at elevated temperature caused leaching in the reaction media, although it did not negatively affect the catalytic activity which could be used for 8 cycles.

The transesterification of soybean oil was studied by (Liu *et al.*, 2008) using $Ca(OCH_3)_2$ as heterogeneous catalyst which resulted in obtaining a biodiesel yield of 98% within a reaction time of 2 hours. Further while checking its reusability it was observed that it was still active even after 20 cycles. The same authors examined the usability of CaO as catalyst for alcoholysis of soybean oil and revealed the effect of water in methanol. By mixing 2% water in methanol there was increase in the biodiesel yield (95%) in 3 hours reaction time with 8 wt. % catalyst and alcohol/oil molar ratio 12:1. A small amount of water could improve the catalytic activity of CaO thereby enhancing the methoxide anion generation. Methoxide anion is strongly basic in nature. It plays a significant role in transesterification of triglyceride. CaO had been reported by (Gryglewicz, 1999) as a potential catalyst in the formation of methyl esters from rapeseed oil. However, it was observed that it had 2-4 fold longer reaction times in comparison to homogeneous NaOH. Despite this, cost effectiveness and the less cumbersome process are the major advantages of using CaO as catalyst. A lot of research has been done to improve the catalytic activity of CaO by impregnating it with some active ingredient. (Kaur and Ali, 2015b) have worked on the loading of lithium on CaO. Wet impregnation method was used for the preparation of Li/CaO catalysts.

The Li/CaO catalysts thus produced in series were utilized as heterogeneous catalyst for the alcoholysis using WCO with ethanol. Under optimal reaction conditions the yield of FAEE obtained was 98% in 2.5 hours of reaction time. viz., molar ratio of 12:1, catalyst of 5 wt.% and 65°C reaction temperature.

Another study by (Watkins, Lee and Wilson, 2004) evaluated Li-loaded CaO in the transesterification of glyceryl tributyrate to form methyl butanoate. Maximum activity was demonstrated by loading amount of 1.23 wt. % of lithium on CaO and resulted in increase in its basicity. This Li/CaO was studied by (Alonso *et al.*, 2009) where transesterification of sunflower oil into methyl esters was performed. The conclusion of the study reported that the optimum parameters for obtaining highest catalytic activity are 4.5 wt. % of lithium loading onto CaO and activation of catalyst at 800°C. Percolation of the active catalyst was observed in the reaction mixture with activation of catalyst at a temperature more than 500°C.

(Ngamcharussrivichai, Totarat and Bunyakiat, 2008) used palm kernel oil with methanol for transesterification. They experimented the use of CaO-ZnO as catalyst at 60°C and 1 atm. The characterization of catalysts was performed with XRD, SEM and TGA techniques. The study concluded that CaO-ZnO catalyst had small particle size and large surface area to that of CaO or ZnO alone. The use of mixed oxide also decreased the calcination temperature for transforming them into active oxides. The methyl ester (ME) obtained was >94% under the condition of 60°C, catalyst amount of 10 wt. %, methanol: oil 30:1 for 1 hour reaction time. They also concluded that regeneration of catalyst can be achieved by washing with methanol. The respective catalyst can be reused for at least 3 times. The tables 2.3 and 2.4 show the work of different researchers on biodiesel production using different alkaline earth metal oxide heterogeneous catalysts.

Table 2.3 Different alkaline earth metal oxides heterogeneous catalysts for biodiesel production

Catalyst	Feedstock	Reaction conditions					Reference
		Catalyst amount (wt%)	Alcohol to oil molar ratio (m/m)	Reaction temp. (°C)	Reaction time (h)	Yield (%)	
CaO	Sunflower oil	3	13:1	60	1.66	94	Grandos et al., 2007
CaO	Sunflower oil	1.2	4:1	75	0.75	80	Vujicic et al., 2010
CaO	Soybean oil	8	12:1	65	3	95	Liu et al., 2008
CaO from waste mollusk shell	Palm	10	18:1	60	2	90	Empikul et al., 2010
CaO from natural calcites	Palm oil	7	15:1	60	0.75	95.7	Yoosuk et al., 2010
BaO	Palm	3	9:1	65	1	95.2	Mootabadi et al., 2010
SrO	Soybean oil	3	12:1	65	0.5	95	Liu et al., 2007
ZnO	Palm	3	6:1	200	1	86	Jitputti et al., 2006
CaO-Al_2O_3	Palm oil	3.5	12:1	65	5	94	Zebeti et al., 2009
$CaTiO_3$	Rapeseed oil	NR	6:1	60	10	90	Kawashima et al., 2008
$CaOLa_2O_3$	Waste cooking oil	5	20:1	58	1	94.3	Yen et al., 2009
CaMgO, CaZnO	Jatropha	4	15:1	65	6	83.81	Yap et al., 2011
CaO-CeO_2	Palm	5	20:1	85	6	>90	Thitsartarn and Kawi, 2011

Table2.4 Alkali metal doped catalyst for biodiesel production

Catalyst	Feedstock	**Reaction conditions**					Reference
		Catalyst amount (wt%)	Alcohol to oil molar ratio (m/m)	Reaction temp. (°C)	Reaction time (h)	Yield (%)	
Li/MgO	Soybean oil	5	12:1	65	0.66	>98	Kaur and Ali, 2013
Li/CaO	Used cotton seed oil	5	12:1	65	0.75	>98	Kaur and Ali, 2011
K/CaO	Waste cotton seed oil	7.5	12:1	65	1.25	98	Kaur and Ali, 2012
Li_4SiO_4	Soybean oil	6	18:1	65	2	98.1	Wang et al., 2012
$NaSiO_2$	Jatropha	6.5	15:1	65	0.75	99	Akbar et al., 2009
KF/Al_2O_3	Palm	4	12:1	65	3	90	Bo et al., 2007
Na_2SiO_3	Soybean oil	3	7.5:1	60	1	100	Guo et al., 2010
K/La-Mg	Used cotton seed oil	5	54:1	65	0.33	96	Mutreja et al., 2014
Li/CaO	Waste cotton seed oil	4	10:1	65	4	94	Boro et al., 2014

2.5 Waste CaO

Utilization of waste as raw material for developing heterogeneous catalyst not only eliminates the waste but also makes the biodiesel production process economical. There are several wastes like egg shell, mollusk shell, oyster shell, waste fish scale and animal bones which could be utilized as heterogeneous catalyst for synthesis of biodiesel. These wastes are inexpensive sources of CaO for utilization as heterogeneous base catalyst which are used in transesterification of triglyceride. Erstwhile, these materials were believed as fritter materials but these materials have very prominent influence in the trade market exclusively in biodiesel production industries. Since these catalysts were developed by the waste materials they cut down the biodiesel production cost and enable it to be highly competitive with commercial diesel. In addition to this there are other three aspects in support of these catalysts i.e. they are environmentally benign, biodegradable and easily available. These catalysts can also solve the problem of disposal. This utilization of waste materials as a heterogeneous catalyst means a value addition to these materials. These can be reused for multiple reaction cycles since these catalysts are being produced from renewable biomasses. These catalysts can be termed as green catalysts and hence consequent biodiesel production is also a promising green process. In the recent research various authors like (Hu, Wang and Han, 2011) examined a low cost environmentally benign heterogeneous catalyst from waste mussel shell. The catalyst was produced by wet impregnation method and used for biodiesel production using Chinese tallow oil as feedstock. The catalyst was calcined at 900°C. The reaction was carried out with catalyst (5wt.% of oil) at 70°C with 12:1 molar ratio and achieved 96% biodiesel yield in 1.5 hours. It was also reported by the author that the catalyst was active for 7 consecutive cycles with the yield more than 90%.

(Wei, Xu and Li, 2009) reported better prospects in waste egg shells as low cost solid heterogeneous catalyst for biodiesel production from soybean oil. The experiment revealed that methanolysis of soybean oil with calcined (1000°C) waste egg shell under the reaction conditions of 3wt.% catalyst, 9:1 molar ratio at 65°C in 3 hours reaction time achieved 95% biodiesel yield. The catalysts were also examined for their reusability in transesterification and it was observed that they could be reused for 13 cycles without any apparent loss in their activity.

The use of waste egg shell derived catalyst, which was environment friendly and highly efficient, made the biodiesel production more economic thereby increasing its competitiveness with petroleum diesel.

(Boey *et al.*, 2011) examined the catalytic activity of waste cockle shell as heterogeneous catalyst for converting extra space of palm oil to biodiesel. The author achieved 97 % yield in 3 hours under reaction conditions of 4.9wt.% calcined at 900°C for 2 hours and 0.54:1 methanol to oil mass ratio. The study shows that the catalyst from waste cockle shell was highly active for alcoholysis of palm oil. The reusability of catalyst had been investigated and found the catalyst active for at least 3 times with 96.5% yield under the same reaction conditions (Sharma, Singh and Korstad, 2010) developed a heterogeneous catalyst from chicken egg shell for the biodiesel production from P. pinnata oil. The catalyst was produced by calcined chicken egg shell at 900°C for 2 hours and confirmed CaO generation at this temperature. The experiment concluded that there was 95% biodiesel yield and 97.43% conversion was achieved by following the optimized reaction conditions of 8:1 methanol to oil molar ratio, 2.5wt.% catalyst (eggshell) and 2.5 hours reaction time at 65±5°C.

(Chakraborty, Bepari and Banerjee, 2011) prepared catalyst from fish scale (Labeorohita scale) and used it for biodiesel production from soybean oil as feed stock. The reaction parameters were methanol/oil molar ratio of 6.27:1, catalyst amount 1.01wt.% of oil, reaction temperature 65°C with 97.93% biodiesel yield in 5 hours.

2.6 Thermal Performance and Emissions

The fast diminution of fossil fuel reserves, increasing demands for diesel and uncertainty in their availability are considered to be important triggers for many initiatives to look for the alternative source of energy, which can replace or substitute for fossil fuels. Numerous researchers have done a great deal of work to find an alternative fuel from various sources like vegetable oil, animal fats, waste cooking oil, algae etc. This section trades with the thorough studies of the experimental work carried out by renowned researchers on the thermal performance and different emission parameters of CI engine using variety of feedstocks. The review revealed that in general, biodiesels and vegetable oils are used as blends with conventional diesel to run the compression ignition engine. The experiments are mostly carried out on the engine by varying load, speed, compression ratio, brake power, brake mean effective pressure in appropriate step and appropriate range. The performance of diesel engine is mostly inspected on the BTE, BSFC, BSEC and EGT. CO, NO_x, UHC and SO are generally inspected emissions by the most investigators.

(Demirbas, 2009) investigated the performance characteristics of CI engine (such as BTE, BSFC and different emission attributes) fuelled with biodiesel. The author stated that since the biodiesel is made of mono alkali esters of long chain fatty acids so does have approx.10wt.% oxygen. It was also revealed that although oxygen enhances the combustion efficiency, there is apparent increase in fuel consumption rate during the engine operation using biodiesel due to the fact that O_2 occupies space in the blend. BTE was observed to be higher in the dual fuel operations. BTE was observed to be 27.4%

with neat Jatropha oil, slightly higher in dual fuel operations with Jatropha oil methyl ester (28.7%) and maximum with methyl ester (29%).

(Kalam and Masjuki, 2008) investigated palm biodiesel on IDI compression ignition engine having 3.9 kW rated power and 21:1 compression ratio at 5000 rpm. They observed that increase in brake power is directly proportional to the proportion of palm biodiesel blend in the blend of conventional diesel. In addition to this, two fuels were also tested named A and B. One contained 50 ppm CIA, 7.5% palm biodiesel and 92.5% conventional diesel and the other contained 50 ppm CIA, 15% palm biodiesel and 85% conventional diesel respectively. The results showed that fuel B developed maximum BP (12.4 kW) at 1600 rpm in comparison to fuel A. The higher brake power was explained to be due to the addition of corrosion inhibitor in palm biodiesel which resulted in conversion of heat energy to work.

(Stalin and Prabhu, 2007) tested the performance of B20 – B80 of KOME with conventional diesel. 7.5 kW rated power four stroke DI water cooled CI engine coupled with electric dynamometer was used for the experimental work. The purpose of the study was to compare the torque, power, SFC and emissions. The experiment revealed that KOME and its blends (B20 to B80) had comparable engine performance and emission parameters with that of conventional diesel. Biodiesel blends B20 and B40 produced more torque and power than diesel while running the diesel engine under same conditions. This was because of its complete combustion. The inference could be made that up to B40 of KOME blends with diesel could be a good alternative to conventional diesel in operating diesel engine with producing same output. (Ghai, Das and Babu,

2008) accomplished engine performance test on a direct injection four stroke single cylinder air cooled diesel engine. The test was performed at different loads initially from zero load conditions to rated full load conditions using conventional diesel, biodiesel from fresh oil and biodiesel from waste cooking oil. The author reported that the performance of the WCOME was marginally lower at part loads compared to neat diesel performance. At higher loads there is approx. 1-1.5% reduction in the BTE. On the other hand the thermal performance of WCO biodiesel and fresh oil biodiesel are comparable.

(Li *et al.*, 2015) performed experiment on direct injection, mono cylinder four strokes, constant speed having 1500 rpm, air cooled compression ignition engine coupled with dynamometer. The engine was fueled with VO and its blends of B25, B50 and B75 with conventional diesel. Every test fuel was tested six times with same procedure for maintaining the accuracy of the experiments. The engine worked at 1500 rpm speed and load of 0%, 25%, 50%, 75% and 100%. They compared the emission characteristics of exhaust gases and engine performance. It was observed that the engine performance was comparable to biodiesel obtained and its blends. It was found that NO_x emissions with pure diesel fuel were higher than that of VO and its blends which suggested that use of vegetable oil could be considered as an alternative to conventional diesel fuel for diesel engine.

(Dorado *et al.*, 2003) investigated a three cylinder four strokes DI conventional CI engine with olive oil methyl ester. They revealed that the methyl ester of respective feedstock and conventional diesel had comparable combustion efficiency, marginal reduction in BSFC, and reduction in CO, CO_2 and NO_x emission (8.9%, 37.5% and 32% respectively) for OOME in comparison with conventional diesel.

(Altın, Çetinkaya and Yücesu, 2001) investigated the performance and emission tests in a diesel engine using biodiesel from various VO (such as sunflower oil, cotton seed oil etc.) and reported that use of vegetable oil resulted in little power loss, increased particulate matter emissions and decreased NO_x emission as compared to diesel.

(Raheman and Phadatare, 2004) studied the fuel characteristics of KOME and its blends (B20 – B80) with conventional diesel on a CI engine. Their results showed that KOME blends (B20 and B40) can be used as alternative fuel for diesel engine that decreases the exhaust emissions and BSFC and increase torque and BTE.

(Abedin *et al.*, 2014) conducted the experiment on four cylinders four stroke diesel engine coupled with eddy current dynamometer. The test engine was fuelled with blended palm biodiesel (PB5, PB10, and PB20) and Jatropha (JB10 and JB20) compared with conventional diesel at full load and in the speed range of 1000-4000 rpm. They concluded that there was decline in brake power with B10 and B20 of palm and Jatropha biodiesel and increase in BSFC for PB20 and JB 20 blends. There was considerable reduction in NO_x emission while running on PB10 and PB20 However it was increased by 30% with JB10 and JB20 blend.

(Gangil *et al.*, 2016) investigated the performance of CI engine using karanja oil methyl ester at variable load compared with conventional diesel to evaluate engine performance and emission parameters. It was inferred that at blend 40 there were better fuel properties and engine performance. There was increased brake thermal efficiency with increased load. It was observed that emission levels of CO and HC were inversely proportional to blend proportion in diesel fuel. There was increase in NO_x emission with increase in blend proportion.

(Dhar and Agarwal, 2014) carried out experiment on four stroke water cooled in-line compression ignition engine using karanja biodiesel and its blends (BD05, BD10, BD20 &BD50) with conventional diesel at variable speed and variable load. The author revealed that at lower blends torque was increased whereas at higher blends engine provided less torque as compared to conventional diesel. The value of BSFC increased at higher blend and vice versa. The value of CO emission decreased with high load and speed whereas, higher value of CO was observed at lower loads and higher blends. The value of unburnt hydrocarbons and smoke opacity of biodiesel and its blends were in the range of lower side as compared to conventional diesel. The value of NOx emission was reduced in case of higher engine loads with higher biodiesel blends as compared to pure diesel. The combustion analysis was also carried out and it was observed that there was low cylinder pressure at high speed with higher blends. The Combustion started in advance for lower blends but slightly delayed for higher blends.

(Agarwal, Sinha and Agarwal, 2006) studied the performance and emission analysis of CI engine using rice bran oil and its methyl esters with diesel. Experiment was performed on compression ignition engine for determining the NO_X reduction by various EGR rates. The experiments revealed that 15% exhaust gas recirculation rate gives maximum NO_X reduction. It is inferred from the results that 20% biodiesel blend with

15% EGR is found to be the optimum concentration for biodiesel, which improves thermal efficiency, reduces exhaust emissions and brake specific energy consumption

(Rao, Sampath and Rajagopal, 2008) worked on the performance, combustion and emissions of compression ignition engine using Jatropha methyl ester at various load conditions. The ignition delay was found to be lower for biodiesel and its blends as compared to conventional diesel because of enriched oxygen content in biodiesel. The pressure rise is found to be high for diesel and lower for biodiesel. The BTE of biodiesel and its blends are marginally lower than that of conventional diesel because of primitive start of the combustion of biodiesel and its blends. NO_X from biodiesel and its blends are customarily higher than diesel while the emission of HC, CO and SO were lower than that of diesel.

(Utlu and Koçak, 2008) studied the performance and emission analysis of a diesel engine using waste frying oil. Compared to diesel, waste frying oil methyl ester's SFC is increased to 14.34%, whereas emission values are decreased as 17.14% of CO and 1.45% of NO_X. Smoke intensity is increased at an average of 22.46% for the utilization of WCOME compared to diesel fuel. EGT of WCOME are decreased at an average of 6.5% than conventional diesel.

2.7 Reflections from literature review

After the extensive literature review the following conclusions are made:

- There is an urgent need to look for biodiesel production from WCO or in-edible oils such as Jatropha, Karanja, Pongamia pinnata, algae etc.

- As biodiesel production from edible oils is ruled out in a country like India keeping in view demand and supply situation, biodiesel production from WCO in place of virgin oils can effectively bring down the cost of raw material.
- Productions of biodiesel by using homogeneous catalysts have been extensively reported though it has its limitation such as biodiesel contamination and deactivation by FFA.
- Use of heterogeneous catalyst in biodiesel production is gaining momentum due to its reusability, less effluent and favorable glycerol purification.
- Since biodiesel is environment friendly and biodegradable, therefore its use in CI engines can minimize the emissions of greenhouse gases significantly.
- Limited literature has been reported on engine performance and emission using biodiesel produced from WCO using heterogeneous catalysts.

Various studies performed by some others eminent researchers on engine performance and emissions using different drive biodiesel from non edible oils have been critical reviewed in table 2.5.

Table 2.5: Critical review on engine performance and emissions using different derived biodiesel from non edible oils

S No	Investigators	Fuel used	Engine performance conclusions	Emission conclusions	Remarks
1.	De and Panua, 2014	Jatropha and its blend with diesel (B10,B30,B50 and B80)	➢ The value of BTE for Jatropha blended fuel was less as compared to pure diesel (0 to full load). ➢ There was increase in EGT throughout engine operation with respect to engine load and compression ratio both for base diesel and blended fuel. The value of EGT was higher for pure Jatropha oil and diminished gradually with decrease in Jatropha and lowest for base diesel.	➢ NO_X level increased with respect to engine load and compression ratio for both diesel and Jatropha blend. NO_X emissions are decreased with the increase of Jatropha oil percentage in the blends. ➢ CO emissions slightly increased at low engine load but considerably increase at high engine load. It increases with increase of Jatropha oil percentage in blends compared to that of diesel. It decreases with the increase in compression ratio.	Thermal efficiency, exhaust gas temperature and emission parameters such as NO_X and CO at CR of 18 for the blends containing up to 30% (by volume) Jatropha oil is close to that of diesel fuel. But with the increase of Jatropha oil concentration in the blends increasing the exhaust gas temperature and emission parameters like NO_X, CO and decreases the thermal efficiency of the engine.
2.	Liaquat et al., 2012	Jatropha and its blend with pure diesel and waste oil (DF, JB5, JB10 and J5W5)	➢ The peak torque values were noticed at 2200 rpm, for all fuel tested. The value of torque was higher for pure diesel as compared to blended fuels. ➢ The brake power increased with increase of engine speed up to 2200 rpm and after that its value diminished due to the effect of higher frictional force. ➢ The engine brake power for DF was found higher than those obtained for blends.	➢ The value of HC emissions decreased with increase in blend proportions for all fuel tested. The oxygen content present in the blended fuel improved the oxidation of fuel thus reducing HC emissions. ➢ The value of CO was lower for blended fuel as compared to pure diesel. J5W5 shows more reduction when compared to JB10. ➢ CO_2 emission was decreased for all blended fuels than pure diesel. J5W5 produced more reduction compared to JB10.	Engine torque and brake power for blend fuels were decreased when compared to diesel fuel. The BSFC values for blend fuels were found lower than that of pure diesel. It was concluded from exhaust emission analysis that there was reduction in HC, CO and CO_2 for JB5, JB10 and J5W5 when compared to pure diesel. Whereas, NOx emission for all blend fuels was increased as compared to pure diesel.

S No	Investigators	Fuel used	Engine performance conclusions	Emission conclusions	Remarks
			➢ The BSFC for the tested fuels was found slightly higher than that for pure diesel.	➢ The NO_x emissions with blend fuels were found little higher than that with pure diesel.	
3.	E. Buyukkya, 2010	Rapeseed and its blends (B5, B20, B70) and pure diesel)	➢ It was found that there was no significant change in measured engine power at full load for B5 and pure diesel. However, the output engine power for other blends was found lower as compared to pure diesel. Maximum reduction in engine power for B20, B70 and B100 fuels is 6, 8 and 10 kW, respectively. ➢ BSFCs of the B5, B20, B70 and B100 fuels were observed to be higher by 2.5%, 3%, 5.5% and 7.5% than that of the diesel fuel, respectively At full-load, brake thermal efficiency increased with increasing engine BTE of the engine was improved with increasing concentration of the biodiesel in the blend except for B70. ➢ The BTE obtained with B100 and their blends were close to that of one obtained with the diesel fuel.	➢ CO emission was decreased with the engine speed. At low speeds the CO emissions of the B5, B20, B70 and B100 are 12%, 25%, 31% and 35% lower than that of diesel fuel, respectively. ➢ NO_x emission was proportional to amount of biodiesel. At B100, the increase in NO_x emission was 12% compared to the diesel fuel. There were also 6% and 9% increase in NO_x emissions for B20 and B70, respectively. ➢ The HC emissions of B20, B70 and B100 fuels were lower than that of diesel fuel. ➢ The smoke opacity for pure biodiesel and their blends were lower than that of the diesel fuel. The smoke opacity reduction was 45% with B70 while it was 60% with pure biodiesel.	B20 gives the best brake thermal efficiency of engine. On the other hand, the use of rapeseed oil as a blend has not any positive effect on BSFC of the engine. At the same time, it should be noted that higher NOx formation occurred in biodiesel use. Therefore, research is needed to propose NO_x reduction strategies for biodiesel combustion.
4.	Gopal et al., 2014	Waste cooking oil methyl ester	The value of SFC was higher for all blends of WCOME than pure diesel under different loading conditions. The SEC of all blends was decreased at peak load conditions. It was found that	➢ It was observed that there was decrease in UBHC with increasing the percentage of WCOME in blend. It was also observed that ppm of UBHC increased as engine load increased.	1. The diesel engine can perform satisfactorily on biodiesel and its blends with the diesel fuel without any engine modifications.

S No	Investigators	Fuel used	Engine performance conclusions	Emission conclusions	Remarks
			BTE of WCOME and its blends was slightly lower than that of pure diesel.	➢ Experimental results reveal that CO concentration of biodiesel and its blends is 59%, 38%, 35% and 31% lesser for B20, B40, B80 and B100, respectively, when compared to diesel fuels. ➢ NO_x formation of all biodiesel and blends is slightly higher than that of diesel fuel and NO_x content of B100 was 18.33% higher than conventional diesel fuel under full load condition. It was also observed that as load increased, the NO_x formation increased and attained maximum value at maximum load smoke content of biodiesel and its blends were 24% higher than that of diesel fuel at low and middle engine loads.	2. The SEC increases with change in percentage of biodiesel in the blends due to the lower heating value of biodiesel. 3. It is also observed that there is significant reduction in CO, UBHC and smoke emissions for biodiesel and its blends compared to diesel fuel. However, NO_x emission of WOCME biodiesel is marginally higher than petroleum diesel.It can be concluded that WCO biodiesel could replace the diesel in order to help in controlling air pollution, encouraging the collection and recycling of waste cooking oil to produce biodiesel and reduce the dependency on fossil fuel resources to some extent without sacrificing engine performance.
5.	Amarnath and prabhakaran, 2012	Karanja and its blends with pure diesel	➢ BSFC decreases with increase in compression ratio, load and injection pressure for all fuel tested. BSFC was found higher for B100 (9%) as compare to conventional diesel. ➢ The BTE was found increased with increase in IP. BTE is found to increase from 31.34% to 32.7% for diesel and 29.85% to 31.25% for B100 at full load and 18CR when IP was increased from 150 bar to 250 bar.	➢ Smoke opacity was increased with increase of engine load and biodiesel proportions in blend. Its decreases with increasing CR. CO increases with increase in engine load. CO reduces with increase in biodiesel content. ➢ NO_x emission was higher at higher loads and higher biodiesel content. At higher CR its value also increases. The value of HC emissions were found lower at both higher CR and higher biodiesel blend.	BSFC for B100 is found to be higher by about 9% as compared to that of diesel. With the increase in CR from 14 to 18, BTHE increases up to 7% for all fuels. It is observed that carbon monoxide and unburnt hydrocarbon emissions are less in case of biodiesel, whereas formation of NO_X and smoke intensity is more with biodiesel.

S No	Investigators	Fuel used	Engine performance conclusions	Emission conclusions	Remarks
6.	Anandet al., 2012	Methyl ester of cotton seed oil with pure diesel(B5,B10, B15 and B20)	➢ The value of BSFC decreased with increase in load at all CR (15:1, 17:1 and 19:1) for all fuel tested. ➢ The BTE increases for all CR with respect to increase in load. The maximum BTE obtained about for B5 (27.37@CR15:1), B10 (27.98% @ CR17:1) and B20 (29.28% @CR 19:1) which was higher than pure diesel.	➢ It was found there was reduced CO emission at higher loads when running on biodiesel blends at increasing compression ratios from 15: 1 to 19:1.The CO emissions for blends B5, B15, and B20 were 0.27%, 0.18% and 0.37% by volume respectively. ➢ HC emissions for all fuels tested were reduced for all compression ratios compared to pure diesel. The value of HC found slightly increased with increase in load. ➢ The emission of nitric oxide increases with increase in load. The minimum value was obtained at B20 @ CR 15:1. The smoke opacity was lower for all biodiesel blends and lower compression ratio. At all compression ratios, B15 was found to emit maximum smoke at full load.	Brake specific fuel consumption was found to be minimum for neat diesel as compared to biodiesel blends at all loads. The brake thermal efficiency was found to increase with increase in compression ratio and there minimal difference in the brake thermal efficiency of bio diesel blends and neat diesel. The maximum NO emissions increased proportionally with the mass percent of oxygen in the biofuel and compression ratio. Smoke opacity emitted by biodiesel blends is lower than neat diesel at low load and lower compression ratios. A general practical conclusion is that, all tested biodiesel blends can be used safely without any modification in engine. So, blends of methyl ester of cotton seed could be successfully used.
7	Meng et al., 2008	Waste cooking oil methyl ester (B20 and B50) with pure diesel.	For all fuels tested, brake specific fuel consumption decreased with increasing in load.	For all fuel tested the value of CO and HC were reduced whereas the value of NO_x for all higher blends was higher as compared to pure diesel.	Engine testing results showed without any modification to diesel engine, under all conditions dynamical performance kept normal, and the B20, B50 blend fuels led to unsatisfactory emissions whilst the B 20 blend fuels reduced significantly particles, HC and CO emissions.

S No	Investigators	Fuel used	Engine performance conclusions	Emission conclusions	Remarks
8	Alirija Shirneshan, 2013	Waste cooking oil methyl ester (B20, B40, B60 and B80) with pure diesel	The author did not address the engine performance part.	➢ The HC emission decreased with increase of engine load. For biodiesel blended fuel, the HC emission decreased with increase of biodiesel in the fuel. ➢ For each fuel, there was a decrease of CO emission on increase of the engine load. With the addition of biodiesel, CO emission also decreased. ➢ The CO_2 emission increased with increase in load, as expected. The lower percentage of biodiesel blends emitted very low amount of CO_2 in comparison with diesel. B20 emitted very low level of CO_2 emissions. ➢ The NO_x concentration increased with increase of engine load for all the fuels. Compared with diesel, NO_x emission of the biodiesel blended fuel increased slightly at all tested engine loads and the increase was more obvious at higher engine loads.	Biodiesel used in the present study was manufactured from waste frying oil. Blended fuels containing 20%, 40%, 60% and 80% by volume of biodiesel, were used in the tests. The effect of engine load and fuel mix on emissions was investigated. The use of diesel blended with biodiesel, compared with diesel on the emissions; in general, HC and CO emissions are higher at low engine loads and lower at high engine loads while NO_x increase with engine loads.
9.	Yang et al., 2013	Waste cooking oil methyl ester (B10, B50 and B100) with pure diesel	➢ It was noted that the brakes power at full load was nearly the same for both B10 and pure diesel whereas for blend B50 and B100 there was drop in brake power at all engine speeds. ➢ The BSFC decreased with increase of engine load at same engine speed. The BSFC of B10 was almost	➢ The CO emission dropped to extremely low levels at 50% and 100% loads. The CO emission increased significantly as the biodiesel blend ratio increased especially at low engine speed. ➢ CO_2 emissions generally decrease with the increase of biodiesel blend ratio except for B10 which does not vary much	The experimental results showed that the low engine speed and partial load condition significantly affected the combustion and emission formation processes. The BSFC of B10 was almost the same as that of diesel, and an

S No	Investigators	Fuel used	Engine performance conclusions	Emission conclusions	Remarks
			the same as that of diesel fuel at 1200 rpm and 2400 rpm, lowered by 9.5% at3600 rpm. With further increase in the oxygen content for B50 and B100, the BSFC increased significantly. ➢ The use of biodiesel resulted in a higher thermal efficiency at full load condition, but a reduced thermal efficiency at 25% load. The largest BTE was found to be at 2400 rpm under full load conditions.	compared to diesel. It can be observed that the CO_2 emission of the diesel engine fueled by B100 is consistently lower compared to that with diesel at all engine operating conditions. ➢ The hydro-carbon emissions of all tested fuels are found to be very low at all engine operating conditions. The HC emission was lower for B100 as compared to those of diesel. ➢ The nitrogen oxides emissions are very sensitive to the combustion temperature which generally increases with the increase of engine speed and engine load.	improved performance was also observed under some engine operating conditions. However, as the biodiesel blend ratio increased to 50% and 100%, a tangible increase in BSFC was observed. With regard to the exhaust emissions, the experimental results showed that the use of biodiesel generally resulted in a lower CO_2 and HC emissions. Significant increase in the CO emission was observed at 25% load. For the NO_x emission, it was found that under most of the engine operating conditions, the NO_x emissions produced by B100 were lower compared to those of diesel. However, the opposite trend was seen at low engine speed and high load conditions.
10	Aldiah and Alqdah, 2012	Waste cooking oil (B5 and B20) with pure diesel	➢ The power initially increased with increasing of engine speed until it reached a maximum value and then decreased with further increasing engine speed. ➢ The power initially increased with the addition of biodiesel content in the blend, reached a maximum value and then decreased with more increase of the biodiesel content.	➢ The engine emits less CO using less percentage of biodiesel as compared to that of diesel fuel under all loading conditions. ➢ The HC emissions increase with increasing in load. HC emissions decrease with increasing biodiesel percentage in the blend. ➢ The NO_x emission for biodiesel is	The characteristics of Biodiesel are close to diesel fuels, and therefore Biodiesel becomes a strong source to replace the diesel fuels. Different blends with diesel fuel were used as fuel in a compression ignition engine and its performance and emission characteristics were analyzed. Lower percent of blends (B5, B20) give a good improvement

S No	Investigators	Fuel used	Engine performance conclusions	Emission conclusions	Remarks
			➢ The BSEC initially decreased with increasing of engine load until it reached a maximum value and then increased slightly with further increasing engine load for all kind of fuels. ➢ The increased biodiesel blend result in decreased BSEC until it reached maximum value at B20 and further increase in blend will increase in BSEC.	higher than that of the diesel oil. The NO_x emission increases with increasing of biodiesel include in the blends and reaches	in the engine power. Lower percent of blends also reduced BSEC. B20 produced significant reductions in the CO, HC, and smoke emissions compared with standard diesel and B5. Regarding NO_x emissions the results obtained in this study1 show that the higher the biodiesel content, the higher the NO_x emissions

Chapter-3

Materials and methods

CHAPTER-3

Materials and Methods

3.1 Materials

Waste cotton seed (once used) was procured from reputed caterers in Patiala. ZnO, CaO, silica gel and other chemicals such as methanol, ethyl acetate, hexane etc. were provided by the SCBC, TIET Patiala.

3.2 Physicochemical Properties of WCO

The physicochemical characteristics of waste cooking oil such as free fatty acid, moisture percentage, saponification value and iodine value were determined and reported in table 3.1.

Feedstock	**FFA content (wt.%)**	**Moisture content (wt. %)**	**Saponification value (mg of KOH/g of sample)**	**Iodine value (mg of I_2/g of sample)**
WCO	4-5	0.27	192.3	94.3

Table 3.1 Physicochemical properties of waste cooking oil

3.3 Conversion of FFA

The conversion of esterification reaction is determined by the following formula.

$$\text{Conversion of FFA (\%)} = \left(\frac{A.V_{initial} - A.V_{final}}{A.V_{initial}}\right) \times 100 \qquad (3.1)$$

Where

A.V. = Acid Value (mg of KOH/g of sample).

Mean of three experiments having SD ± 2% are taken.

AV was calculated by the equation 3.2.

$$A.V. = (V \times 1000 \times MW \times C)/ W \qquad (3.2)$$

Where

V = Vol. of solution used for titration (ml),
MW = Molecular weight of KOH
C = Molar concentration of the KOH solution employed for titration

W = Weight (in mg) of the reaction mixture

3.4 Instruments Used for Characterization of Heterogeneous Catalyst

3.4.1 XRD Analysis

“PANalytical’s X’Pert Pro diffractometer” maintaining at 40 kV having nickel-filtered monochromatic Cu Kα radiation (λ = 1.54060 Å) was used for X-ray diffraction pattern analysis. The examination of the catalyst was done over a 2θ span of 5–80° at the scanning rate of 2º/min.

3.4.2 Scanning Electron Microscopy (SEM) Analysis

JEOL JSM 6510LV series model was used for taking the SEM images of catalyst. For sample preparation, small amount of powdered sample was ultrasonicated in diethyl ether and small amount of the sample was kept in sample holder with the aid of carbon tape. Further a minute layer of gold was coated on it.

3.4.3 EDX Analysis

Energy dispersive X-ray spectrometry was also performed on the same instrument (JEOL JSM 6510LV). EDX studies were performed to analyze the presence of various elements present in the catalyst qualitatively.

3.5 Methods and Equipment Used for Monitoring the Transesterification Progress as follows:-

3.5.1 Thin Layer Chromatography

Thin layer chromatography technique was used. Thin layer chromatography is one of the simplest, fastest, easiest and least expensive of several chromatography techniques used in qualitative and quantitative analysis to separate organic compounds and to test the purity of compounds. The progress of the reaction was observed by withdrawing the sample from reaction mixture after every 15 mins with the help of dropper and centrifuged to separate the catalyst from supernatant. The liquid thus obtained was diluted with hexane/ethyl acetate in 90:10 v/v as mobile phase and silica gel used as stationary phase. Production of biodiesel was identified by comparing its Retention factor with methyl oleate ($C_{19}H_{32}O_2$), standard.

3.5.2 Proton Nuclear Magnetic Resonance (HNMR)

After the preliminary investigation by thin layer chromatography the FAME obtained from transesterification reaction was characterized by JEOL ECS-400 (400 MHz) spectrophotometer in $CDCl_3$ solvent using tetramethylsilane (TMS) as internal reference and chemical shifts were evaluated in ppm. FAME yield was enumerated by HNMR analysis according to method reported in literature (Li *et al.*, 2005) and (Gelbard *et al.*, 1995; Knothe, 2001)**.** The fatty acid methyl ester conversion was given by the following equation. An inaccuracy of ± 2% was detected when the FAME yield was computed.

$$\text{FAME Conversion } (\%) = 100 \left(\frac{2\, I_{OCH_3}}{3\, I_{\alpha CH_2}} \right) \tag{3.3}$$

Here

I_{oCH3} = Integrated value of the proton of the methyl esters (the strong single peak)

$I_{\alpha CH2}$ = Integrated value of the methylene protons

The derived factors 2 and 3 for the methylene carbon which possesses two protons and alcohol (methanol derived) carbon possesses three protons.

3.6 Methods and Equipment used for Determination of Fuel Properties

3.6.1 Kinematic Viscosity

“Viscosity can be defined as resistance to flow of fluid because of internal friction caused by one layer of fluid moving over another”. The performance of fuel system of an engine is dependent on it. Kinematic viscosity has impact on injection system. Low value of fuel viscosities pave the way to greater pump and injector leakage, which adversely affect the fuel economy and power output (Li *et al.*, 2005). Whereas high viscosity causes exaggerated pump friction, filter choking, high pressure and coarse atomization rate and low fuel distribution rate

Limits and Methods

Limits: Kinematic viscosity was measured according to EN-ISO 3104 and its range was 3.5 – 5.0 mm^2/s according to ASTM D-445 its range was 1.9 – 6.0 mm^2/s.

Methods: Redwood Viscometer (WISWO make) was used for measuring kinematic viscosity. It works on the principle of gravity flow of fluid with respect to time. The apparatus was comprised of cylindrical cup (vertical) having an aperture in the centre of its underneath. A silver coated ball was used for opening and closing the orifice. The cylindrical cup was surrounded by the water bath having immersed electric heater which maintains the inside temperature of cup in which biodiesel is tested. A standard

50ml beaker was placed underneath the metallic orifice jet so that fuel sample from cup could be collected in it. In order to check the accuracy every sample was tested thrice. Kinematic viscosity of fuel sample was then determined by the equations 3.4 and 3.5 given below by (Guthrie, 1960).

$vk = 0.26\,t - \frac{179}{t}$	(For 34 < t < 100)	(3.4)
$vk = 0.26\,t - \frac{179}{t}$	(For 34 < t < 100)	(3.5)

3.6.2 Calorific Value

Calorific value may be defined as the thermal energy discharged from a specified quantity of fuel during complete combustion and its product of combustion returned to its initial temperature of the combustible mixture. It is an important parameter for measuring the energy content in a fuel. Thus, the CV is the main power characteristic of a fuel quality.

Limits and Methods

Limits: Calorific value was measured according to **IS: 1448 [P: 6]: 1984**

Methods : Widson Scientific Works made Isothermal Bomb Calorimeter was used to measure out the CV. The procedure was conducted with 1ml of tested fuel which was electrically ignited in the bomb of apparatus in the oxygen atmosphere. As the heat was liberated, the climb in temperature was checked and documented. Each sample was tested for three times for maintaining the accuracy. The gross heat of combustion was calculated by the following equation.

$$Hc = \frac{WcX\,\Delta T}{\mathrm{Mc}} \tag{3.6}$$

Where,

H_c = Heat of combustion of the fuel sample. Cal / g

W_c = Water equivalent of the calorimeter, Cal / °C

ΔT = Rise in temperature, °C

3.6.3 Cloud Point and Pour Point

CP and PP are very crucial attributes of any fuel especially liquid. “Cloud point concerns to temperature below which wax in fuel (biodiesel) develops a cloudy appearance”. The cloud point of any liquid fuel depicts the fuel performance in cold weather circumstances. Whereas pour point indicates the minimum temperature of fuel at which it turns into semi solid and loses its ability to flow. Cloud and pour points are low temperature properties and tell the response of fuel at low temperatures.

Methods: CP and PP were measured as per **IS: 1448 [P: 10]: 1970.** The instrument was filled up with ice. The sample was filled in the test tube and kept in apparatus, in ice bath. The thermometer was placed concentric vertical in it. The temperature at which the paraffin in the tested fuel started converting into solid state and the biodiesel was remarked as CP. The cooling of test tube was continued in the same aspect until the temperature reached a point at which the sample in test tube did not show any movement for at least 5 sec. This was noted as the PP of the sample.

3.6.4 Flash point and fire point

“Flash point is the minimal temperature of the fuel/oil at which a fuel emits adequate vapours which will ignite spontaneously as it comes in contact with ignition source”. FP varies contrarily to fuel’s volatility. Its lowest temperature signifies the safety and handling feature of the fuel. “The fire point of a fuel is the minimal temperature at which the fuel produced vapours and continues to burn for notably 5 seconds after ignition by an open flame”.

Limits: Minimum 120°C

Methods: Pensky-martens closed cup instrument was employed for testing the flash point and fire point. The sample of fuel (biodiesel) was heated first and then ignited in the cup. When the fuel ablaze note down the temperature was noted down. The apparatus recorded the minimal temperature when vapour formed at which the sample was ignited. The biodiesel was kept inside the apparatus cup in specified quantity up to the standard mark. After closing the cup, heat 5°C per minute was supplied to the fuel using Bunsen burner. During entire span of heating the fuel was constantly stirred. As soon as fuel exhibited flashes the injector burner was enlightened and injected into the cup every twelve seconds gaps and observed a distinct flash within the container. As the flash appeared the temperature was noted down. The above said procedure was repeated thrice and its mean was taken.

3.6.5 Ash Content

Ash content may be termed as left over residue after the decomposition of organic substance at high temperature generally 500-600°C. It is comprised of metal salts and ion such as sodium, potassium and calcium. Electric muffle furnace was employed for determining the ash content present in the fuel. Initially 5 gm. of fuel sample in a pre-weighted crucible was taken and placed in muffle furnace. The muffle furnace was switch on for 2 hours at a temperature of 500°C. The remaining residue left in the crucible was weighed. The ash content was calculated by applying the equation given below:-

$$As = \frac{Wa}{Ws} X\ 100 \qquad (3.7)$$

Where

A_s = the ash content (%)

W_a = the weight of ash (g)

W_s = the weight of the sample

3.6.6 Carbon Residue Test

Carbon residue apparatus was used for determination of carbon residue. The measurement was performed by following the procedure as per ASTM D169 IP 13 (Institute of Petroleum, London). This test would help to provide some indication about relative coke forming characteristics. A weighed sample underwent destructive distillation process in a crucible. The residue experienced reaction such as cracking and coking during a specific interval of extreme heating. After the assigned heating span, the carbonaceous residue left in the crucible was cooled in a desiccator and weighed. The residue remaining was termed as Conradson carbon residue.

The percentage of carbon residue can be calculated by the equation which is given below:-

$$Cr = \frac{Wc}{Ws} X\ 100 \qquad (3.8)$$

Where,

Cr = Carbon residue, %

W_c = Weight of carbon residue, g

W_s = Weight of sample, g

3.6.7 Acid Value

It is also known as neutralization number or acid number which is the mass of KOH weighed in mg, that is needed to neutralize the acidic constituents in one gm. of sample. The AV of oil predicts the traces of acid in fuel. The existence of free fatty acids in vegetable oil may harm some engine parts because of corrosive nature. At higher temperature free fatty acids involve in chemical reaction with different metal parts and its secretion in the form of acid metal salts results in wear. Therefore acid value is significant characteristic. Titration method was used for finding the acid number of biodiesel. A prescribed sample (0.1 – 0.5 ml) of biodiesel was taken in the conical flask. A 50 ml of reaction mixture (95% ethanol and diethyl ether in 1:1 ratio) was added to it and mixed vigorously. The respective mixture was titrated with 0.1 N potassium hydroxide using phenolphthalein indicator. The formula for determining acid number is given below:-

$$\text{Acid Value} = \frac{\text{56.1 X Normality of KOH solutionX volume of KOH used}}{Weight\ of\ sample\ taken} \qquad (3.9)$$

3.6.8 Free Fatty Acid (FFA content)

High free fatty acids may cause saponification which affects biodiesel production. Therefore it is very necessary to find out FFA content in an oil batch so that necessary steps may be taken to reduce the content of FFA in order to achieve better success during transesterification. The procedure for FFA determination is given below:

- 5 g of oil was placed in conical flask.
- Approx. 50 ml of C_3H_8O (N) was then mixed in the respective oil.
- 1% $C_{20}H_{14}O_4$ (Hln indicator) was then added to the mixture.

- The respective mixture was heated on gas stove and heated until first bubbling occurs (approximately 70 °C)
- The mixture was then titrated with KOH solution (0.1 N) till a pink color appeared for at least 30 seconds.

The FFAs% was calculated by the equation given below:

$$\text{FFA}\ (\%) = \frac{(\text{ml of titrant}) \times (\text{Neutrality of titrant}) \times 25.6}{\text{Weight of sample in gm.}} \qquad (3.10)$$

3.7 Experimental Test Setup for Performance and Emission Analysis

3.7.1 Variable Compression Ratio Engine Concept

3.7.1 VCR Engine Theory

The theory of VCR assures best engine performance, efficiency and reduces emissions. The peak cylinder pressure and temperature throughout the initial stage of combustion and small exhaust gas fraction due to higher CR provides faster laminar flame speed consequently shorter ignition delay period. Therefore, at low loads, higher the compression ratio, shorter the combustion time result in lower fuel consumption rate at part load. In fact variable compression ratio can make a substantial improvement to thermodynamic efficiency. The primary characteristic of this type of engine is to function at varied compression ratios reckon on the vehicle performance demands. In variable compression ratio engine thermodynamic benefits are seen through the entire range. At low power steps, it works at higher CR in order to achieve high fuel efficiency advantage. Whereas at high power steps the engine performs at low CR in order to avoid knock.

3.7.2 Merits of VCR

This type of engine provides a principal remedy for homogeneous lean-burn combustion because it allows a rise in compression pressure and temperature to revive favorable circumstances for the combustion process even under high air/fuel ratio circumstances. Thus this type of engine furnishes better control over its emission attributes than a fixed compression ratio diesel engine. Volumetric ratio of the engine is kept within the limit because of its geometry therefore engine works under the lower limit of knock irrespective to engine load. There should be a trade- off between engine CR and ignition advance to get the best ITE. Variable compression ratio diminishes the exhaust gas temperature at peak power. Lower exhaust temperature decrease the engine thermal stresses and circumvent charge embellishment at high power. Henceforth the essential merits of variable compression ratio engine are outlined as follows:-

- Highest combustion efficiency throughout the engine load (i.e. zero to maximum) hamper complete burning thereby increasing speed range.
- Lesser fuel consumption and minimum exhaust pollutants.
- Better fuel adaptability with optimum combustion efficiency.
- Extremely smooth idling and peak load are accomplished.
- Improves ITE as compared to fixed compression ratio engine.
- Allows for a dominant idle speed reduction caused by reduced improper firing and cyclic deviation which reduces the vibration levels.
- Reduced engine noise owing to stable peak pressures.
- Smoother combustion due to constant HRR for both at low and high CR.
- Low CO_2 emissions.
- Better idling performance at low ambient temperatures.

3.7.3 Methodology of Experimentation

The experimental test rig for the experiment was comprised of four strokes, water cooled single cylinder, variable compression ratio (VCR) direct injection diesel engine which was vertically oriented. Performance analysis was done with the aid of performance analysis software package “Engine Soft”. The engine was running at rated speed of 1500 rpm. Before conducting the experiment the engine oil sump was drained out and fresh lubricating oil was filled for the smooth operations. Eddy current type dynamometer was connected to engine for loading. A specially designed tilting cylinder block mechanism was fitted for changing of compression ratio which could vary the compression ratio without any modification in combustion chamber geometry. The compression ratio can be changed without stopping the engine. The variable compression ratio compression ignition engine test rig setup is shown in figure 3.1.

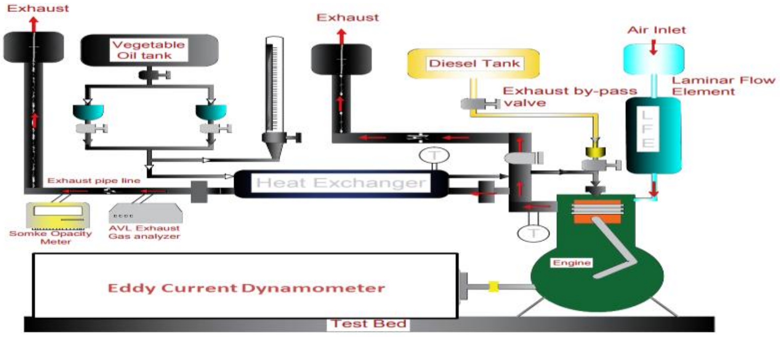


Figure 3.1 Symbolic representation of VCR engine Setup

The setup has stand-alone panel box consisting of air box for volumetric efficiency, two fuel tanks for duel fuel test (diesel oil and biodiesel), manometer, fuel measuring unit, transmitters for air and fuel flow measurements, process indicator and engine indicator. Before starting the engine all electrical and mechanical connections were checked. The engine was started initially with diesel oil and when the engine warmed-up, it was switched to biodiesel made from waste cooking oil. A two way valve was incorporated at control panel for switching purpose from diesel oil to biodiesel. Rotameters were provided for cooling water and calorimeter water flow measurement. The setup enabled the VCR engine operating parameters such as brake power (BP), brake mean effective pressure (BMEP), indicated mean effective pressure, brake thermal efficiency, indicated thermal efficiency and mechanical efficiency, etc. to be studied.

The engine was used to run on pure diesel mode as well as WCOME (waste cooking oil methyl ester) diesel blends. The blends were prepared in laboratory itself by mixing appropriate volume of diesel and WCOME. The blends are designated as B20, B40, B60, B80 and B100. For example B20 referred as 20% of WCOME and 80% diesel and so on.

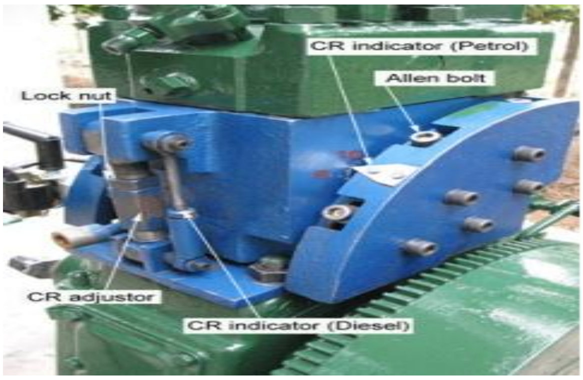


Fig.3.2 Compression ratio adjustment mechanism

3.8 Instruments used for Emission Measurement

3.8.1 Exhaust Gas Analyzer

AVL Di gas 444 was employed to measure UHC, CO, and NO_x emissions. Probe of the instrument was inserted for taking the reading of emissions. It works on NDIR principle. According to this principle exhaust gas species are measured by selective absorption theory. Each elemental gas during the test will absorb some infra-red energy at a peculiar wave length because IR energy of a specific wavelength is designated to a specific gas in which the gas will assimilate the IR of designated wavelength and transmit the infrared energy of different wavelengths. The absorption band for CO goes somewhere in the ranges of 4.5 and 5 microns. Thus the energy assimilated at this wavelength is a sign of CO concentration in the exhaust gas. The NDIR analyzer is made up of two IR sources, interrupted concurrently by an optical chopper. Radiations coming out from IR sources travel in parallel pathway through a reference cell and a sample cell. Exhaust gas from the tailpipe of the engine/vehicle is passed through the sample cell during the measurement of exhaust emissions. There is nitrogen in the reference cell, which does not assimilate the IR energy for the wavelength akin to the measured compound.

An enclosed container having the compound to be measured worked as detector which split up into two uniform volumes by fine metallic diaphragm. Radiation coming out from infrared source was blocked by the chopper. At that moment there was constant pressure in both parts of detector. During this operation the diaphragm is at neutral position. As the chopper either allowed or stopped the radiations, the radiant energy passed unchanged from one source through the reference cell. On the other hand the sample cell absorbed the IR energy at the wavelength of the compound in the cell. The assimilation is directly proportional to the concentration of the compound being measured. Hence variable amounts of energy were transferred to the two volumes of the detector and the pressure differential so induced caused movement of the diaphragm of the detector. This changed the capacitance between the diaphragm and a fixed probe generates D. C. signal which was amplified and, after rectification to D.C. displayed on a meter. The NDIR can precisely measure CO, CO_2 and UHC.

Flame Ionization Detector (FID)

The operation of the flame ionization detector is based on the detection of ion formed during combustion of organic compounds in a hydrogen flame. Formation of these ions is directly proportional to the concentration of organic species in the exhaust gas sample stream. Basically there is no ion present in the pure hydrogen flame but initiation of a small quantity of hydrogen results in formation of large number of ions and becomes electrically conducting. The ionization current depends upon the number of carbon atoms present in the hydrocarbon molecules. Therefore Flame ionization detector effectively counts the carbon atom e.g., one molecule of propane generates three times the response generated by one molecule of methane. The measurement of HC by FID is expressed in ppm (parts per million) of methane. All classes of hydrocarbons i.e., paraffin, olefins, aromatics, etc. show practically the same response to FID. Oxygenates, e.g. aldehydes and alcohols however, have a somewhat lower response. Hydrogen air burner and ion collector assembly are the essential parts of flame ionization detector.

Exhaust gas sample was initiated with hydrogen in the burner assembly which was burned in a diffusion flame. Electric pulses were applied in the middle of collector plates which caused the ionization current to flow and produce signal proportional to HC concentration in the exhaust gas sample. This current was amplified and the output signal was recorded.

3.8.2 Smoke Meter

Basically two types of smoke meters are used to measure smoke density- Filter darkening types and Light extinction type. The light extinction type of meters can measure both white and black smoke whereas the filter paper darkening type meters can give only black smoke. The light extinction meter can be used for continuous measurements while the filter type can be used only under steady state conditions.

Bosch Smoke Meter

Bosch smoke meter is filter darkening type. A measured volume of exhaust gas is drawn through a filter paper which is blackened to various degrees depending upon the amount of carbon present in the exhaust. The density of soot is measured by determining the amount of light reflected from the sooted paper. The diameter of the filter paper, the sample volume etc., all are well defined.

Hartridge Smoke Meter

The smoke meter is based on the light extinction principle. A stream of exhaust gas sample is flown through a tube approximately 46cm in length having light source at one end and photovoletic cell on the other end. The intensity of light passed from smoke column is an indicator of smoke level.

This smoke density is termed as the ratio of electric output from the photovoletic cell to the electric output when clean air is passed through it. The fraction of the light passed through the smoke (T) and the length of the light path (L) are relatedby the Beer-Lambert law.

$$T = e^{-KL}$$

$$K = n A \theta$$

Where,

K = the optional absorption coefficient of the obscuring matter per unit length

n = the number of soot particles per unit volume

A = the average projected area of each particle

θ = specific absorbance per particle.

Chapter-4

Results and discussions

CHAPTER-4

RESULTS AND DISCUSSION

Results obtained from experimental work are discussed in this chapter. The first section describes the results from catalyst preparation and its characterization, biodiesel production from WCO using respective catalyst, WCOME (biodiesel) quantification using TLC and ^{1}HNMR techniques, effect of catalyst on different operating parameters with its reusability. Further the second section describes the results from the experimental work on VCR compression ignition engine and divided into following sub section.

- Effect of WCOME blends with conventional diesel on thermal performance parameters and emission parameters.
- Combustion characteristics such as combustion pressure and exhaust gas temperature results
- Effect of different compression ratios on biodiesel and diesel blends

4.1 Experimental Section

4.1.1 Catalyst Preparation

The nano crystalline Zn/Cao was prepared by wet impregnation method. In this process suspension of CaO was prepared with CaO 40 ml of deionized water to which 10 ml of an aqueous solution of zinc sulphate was added in desired concentration to achieve 1.5 – 5 wt. % concentration in CaO. Then the calcination of dried mixture was carried out in the muffle furnace at 700°C for 4 hours. The prepared catalyst was designated as x-Zn/Cao-T where x and T represent the Zn concentration (wt. %) and calcination temperature respectively. The graphical representation is shown in figure 4.1.

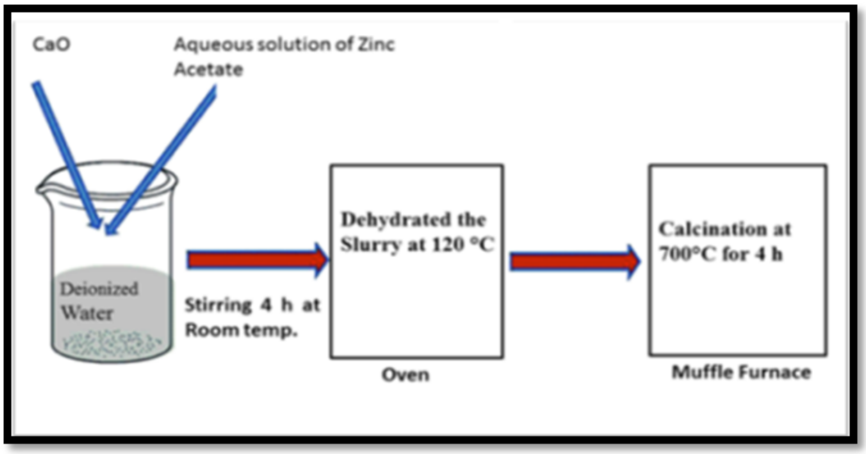


Figure 4.1 Pictorial representation of catalyst preparation

4.2 Catalyst Characterization

4.2.1 X-Ray Diffraction Analysis (XRD)

Powder XRD study was performed to establish the effect of doping of zinc on calcium oxide. It is evident from the figure 4.4, that the intensity of peaks conforms the doping of zinc on calcium oxide. The appearance of sharp peaks in diffraction pattern indicated the formation of highly crystalline materials. The XRD of Zn/CaO showed the typical diffraction pattern of CaO in cubic phase and ZnO in hexagonal phase. The 2θ values 32.33°, 36.38°, 54°, 68° conformed peak of calcium oxide and 34°, 36°, 47°, 57°, and 63° conformed presence of zinc in the catalyst.

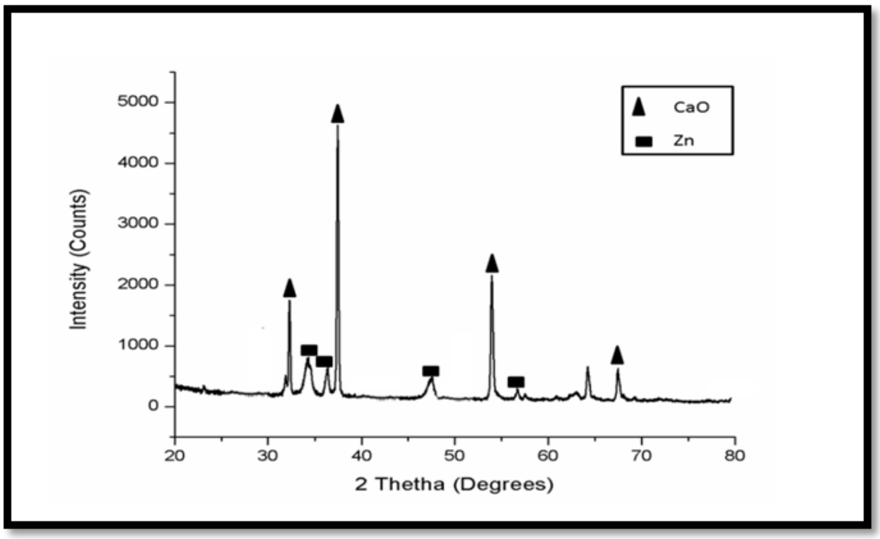


Figure 4.2 XRD pattern of 5Zn/CaO-700

4.2.2 SEM and EDX Analysis

The size, shape, and morphology of the Zn/CaO particles were observed by SEM, and the study depicts that 5Zn/CaO-700 exists as a hexagonal, cubic, and irregular-shaped particle of 2-5µm size, as shown in Figure 4.5. The irregularities in geometry of particles are due to the significant clustering of the Zn/CaO nano particles during their preparation and calcination. To investigate the elemental composition of the catalyst, EDX analyses were also carried out. The different elements present in the catalyst are shown in table 4.1.

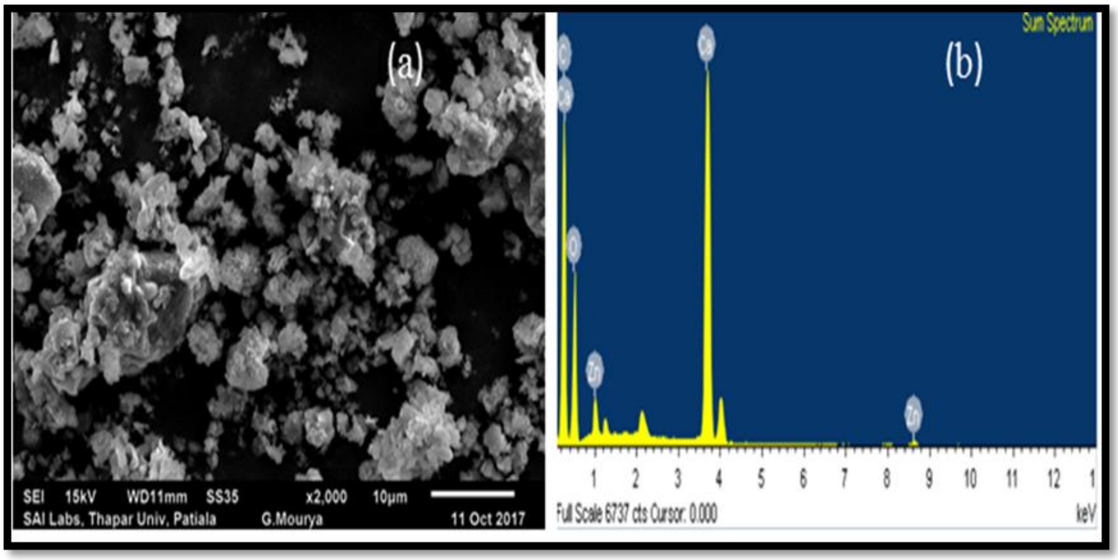


Figure 4.3 (a) SEM and (b) EDX analysis of 5Zn/Cao- 700

Table 4.1 EDX analysis of 5Zn/CaO-700

S.No.	Elements	Weight	Atomic (%)	Composition (%)
1	C (CO_2)	19.93	28.09	73.04
2	Ca (CaO)	17.17	7.25	24.02
3	Zn (ZnO)	2.39	0.60	2.94
4	O	60.54	64.05	-

4.3 Biodiesel Production from Waste Cooking Oil

4.3.1 Transesterification of Waste Cooking Oil

Transesterification was carried out in a 50 ml two necks, round bottom flask fitted with a water-cooled reflux condenser, oil bath and magnetic stirrer. A schematic diagram for biodiesel production is shown in figure 4.4.

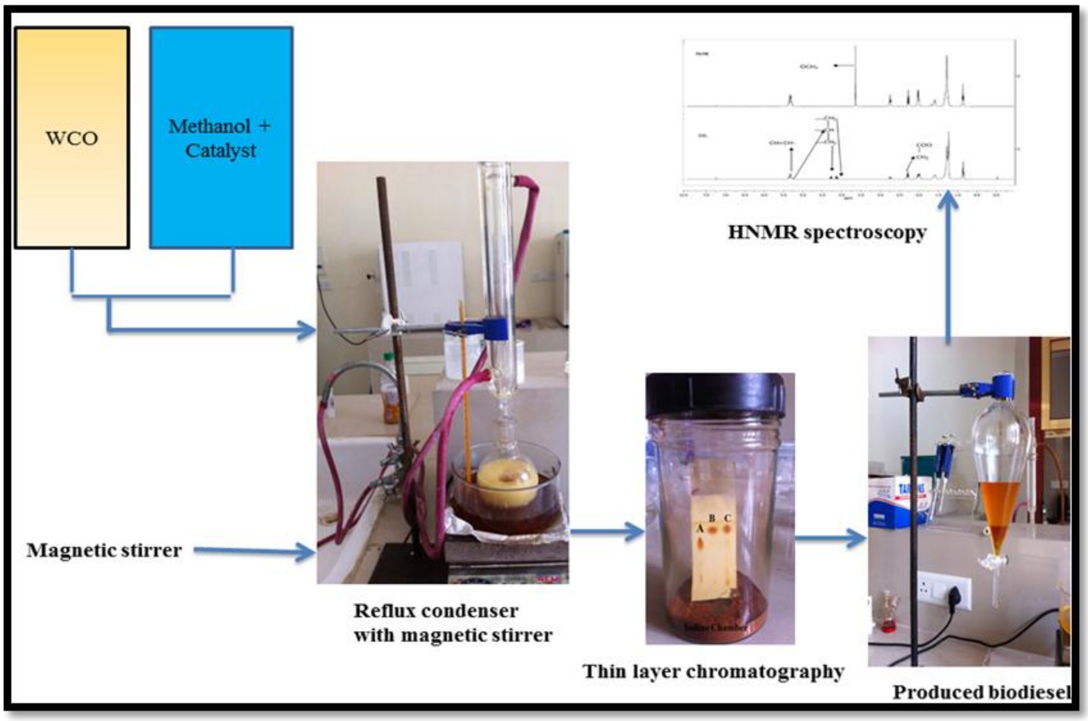


Figure 4.4 Schematic diagram for biodiesel production setup

In a typical transesterification reaction, 50 g of waste cottonseed oil was mixed with a desired molar concentration of methanol and catalyst, and stirred at a constant speed at a desired temperature (Kumar and Ali, 2013). To observe the progress of reaction, thin layer chromatography technique was employed. Thin layer chromatography is one of the simplest, fastest, easiest and least expensive of several chromatography techniques used in qualitative and quantitative analysis to separate organic compounds and to test the purity of compounds. The progress of the reaction was observed by withdrawing the sample from reaction mixture after every 15 min with the help of dropper and centrifuged to separate the catalyst from supernatant. The liquid thus obtained was diluted with hexane/ethyl acetate in 90:10 v/v as mobile phase and silica gel used as stationary phase. Production of biodiesel was identified by comparing its retention factor with methyl oleate ($C_{19}H_{32}O_2$), standard as shown in figure 4.5. The characterization of free fatty acid methyl ester thus produced was done by^{1}H-NMR.

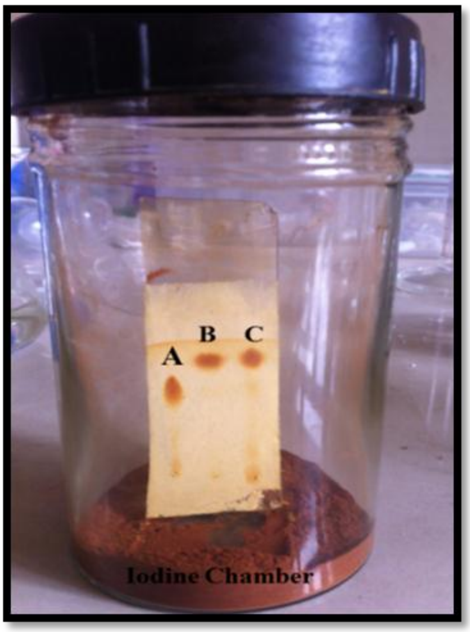


Figure 4.5 TLC analysis of (A) waste cooking oil, (B) waste cooking oil derived methyl ester and (C) methyl oleate standard

4.3.2 Fatty Acid Methyl Ester Characterization

Fatty acid methyl ester characterization was done by NMR spectroscopy. In ^{1}H-NMR spectrum of methyl oleate (MO), appearance of a singlet at 3.75 ppm due to methoxy protons supported the formation of methyl ester of OA. The fatty acid methyl ester conversion was given by the following equation. An inaccuracy of ± 2% was detected when the FAME yield was computed.

$$\text{FAME Conversin (\%)} = 100\left(\frac{2\,I_{OCH_3}}{3\,I_{\alpha CH_2}}\right) \quad = \quad (4.1)$$

Here

$IOCH_3$ = Integrated value of the proton of the methyl esters (the strong single peak)

$I\alpha CH_2$ = Integrated value of the methylene protons

They derived the factors 2 and 3 from the fact that the methylene carbon possesses two protons and alcohol (methanol derived) carbon has three attached protons. ^{1}H-NMR spectrum of waste cooking methyl ester is shown in figure 4.6.

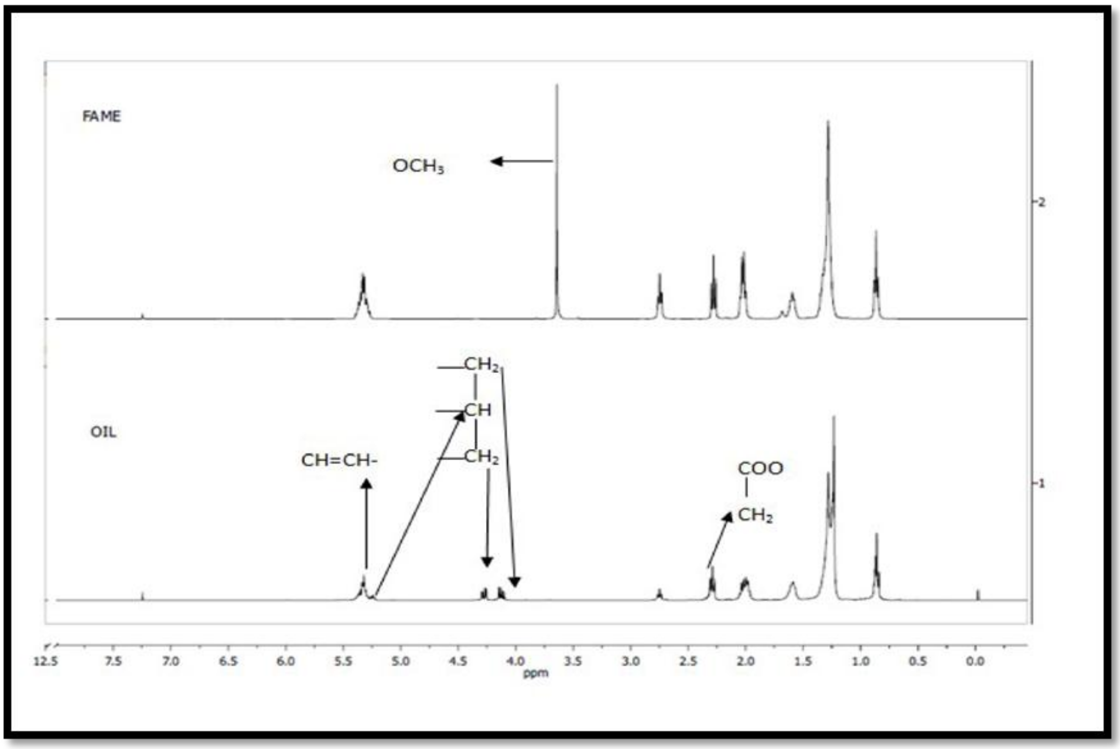


Figure 4.6 Comparison of the H NMR spectra of waste cooking oil and biodiesel

4.4 Catalytic Activity

4.4.1 Effect of Different Doping on the Catalytic Activity

The activity of heterogeneous base catalysts is more than that of acid catalysts in transesterification process (Kaur and Ali, 2015a). In order to optimize the concentration of catalyst the transesterification reaction was carried out with methanol/oil molar ratio (12:1), at 1.5-5 wt. % (with respect to oil) of 5-Zn/CaO-700. During experiment it was observed that the yield was almost same but the reaction time was varying. When we took calcium oxide alone it took three hours to complete the reaction and when we doped it with zinc calcium the reaction was completed in two and half hours for 1.5-Zn/CaO-700 which is economical as compared to previous. The best results were achieved in one hour forty minutes for 5-Zn/CaO-700 which was 98.5% yield. However, as the concentration of the catalyst was further increased (≥ 5 wt. %) there was reduction in conversion because with increase in catalyst concentration there was difficulty in stirring the mixture and mass transfer due to increased viscosity.

4.4.2 Effect of Calcination Temperature on Catalytic Activity

The result of our study showed that the calcination temperature greatly influences the activity of catalyst. When the CaO and Zn were thermally treated at 500°C and 600°C lesser conversions were achieved. As the calcination temperature was increased from 600°C to 700°C, the conversion of waste cooking oil was gradually increased. The highest conversion of 98.5% was achieved at 700°C. However, further increasing the temperature beyond 700°C there was slight decrease in conversion due to sintering of fine crystals and cluster agglomeration, reducing activity of the catalyst. The possible reason for increase in conversion efficiency from 600°C–700°C could be increase in the catalytic activity due to calcination at higher temperature that may result in decreased leaching of calcium based catalysts. This was also explained and supported by (Ali, Hanna and Leviticus, 1995; Liu *et al.*, 2008; Yu *et al.*, 2011), (Yan *et al.*, 2009; Thitsartarn and Kawi, 2011).

4.4.3 Effect of Methanol to Oil Molar Ratio

The molar ratio of methanol to oil is the most significant factor that affects the transesterification reaction as well as the biodiesel production cost.

Stoichiometrically, the transesterification of triglyceride (vegetable oil) requires three mol of methanol for each mole of oil (3:1), and excess part of methanol tilts the equilibrium towards the methyl ester yield because excessive alcohol not only promotes the transesterification rate but also takes out product molecules from the catalyst surface and, thus, regenerates the catalytic sites. The excess part of methanol might increase the biodiesel production cost, therefore it was very necessary to find out an optimal molar ratio to cut down the process expense. The most commonly used molar ratio for biodiesel production for heterogeneous catalysts were 6:1, 9:1, 12:1 and 15:1. The yield of biodiesel was increased with an increase in the molar ratio up to a value of 12:1. Consequently molar ratios between 9:1 and 12:1 gave the best results. 98.5% biodiesel yield was obtained at 12:1 molar ratios. The experiment revealed that at both molar ratios there was negligible percentage change in the yield as shown in figure 4.7. In addition, incomplete reaction was observed for molar ratios above 12:1 because the separation of glycerol was complicated and the apparent yield of biodiesel was reduced because a fraction of the glycerol remained in the biodiesel phase. For that reason, molar ratio 12:1 appears to be the most suitable.

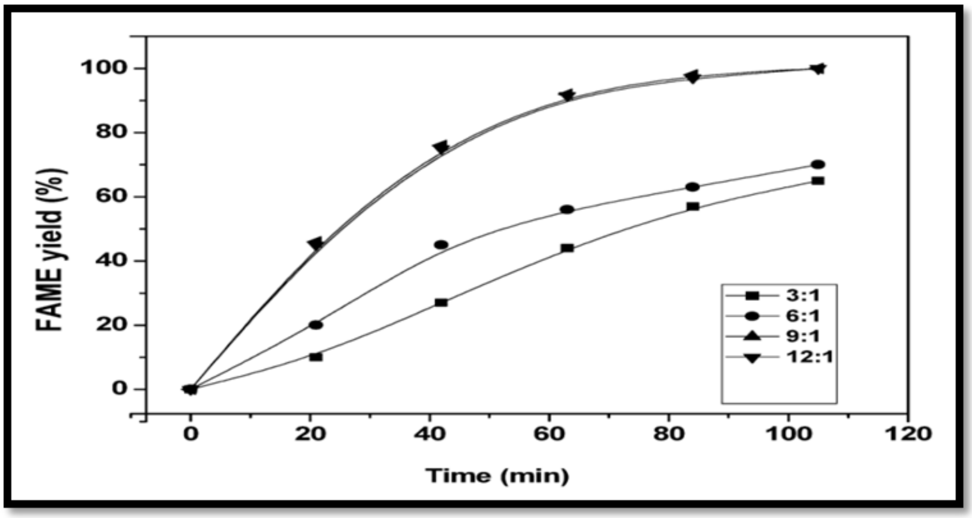


Figure 4.7 Effect of molar ratio on 5Zn/CaO-700 catalysed transesterification of WCO

4.4.4 Effect of Reaction Temperature

In order to determine the optimum reaction temperature, transesterification reaction was performed by varying the reaction temperature from 50 to 70°C in a step increment of 5°C. At low temperature (50-55°C) low yield was obtained, because of mass transfer and solubility limitation. As we increased the temperature the viscosity of the heterogeneous mixture decreased resulting in high mass transfer rate. Secondly it was expected that the reactant may gain sufficient kinetic energy which boosts the mass transfer rate between oil and methanol phases, resulting in better conversion. The complete conversion was obtained at 65°C and beyond it, there was loss of methanol and lower catalytic activity probably due to the reason that methanol has a boiling point nearly 65°C. The relationship between reaction temperature and FAMEs yield is depicted in figure 4.8.

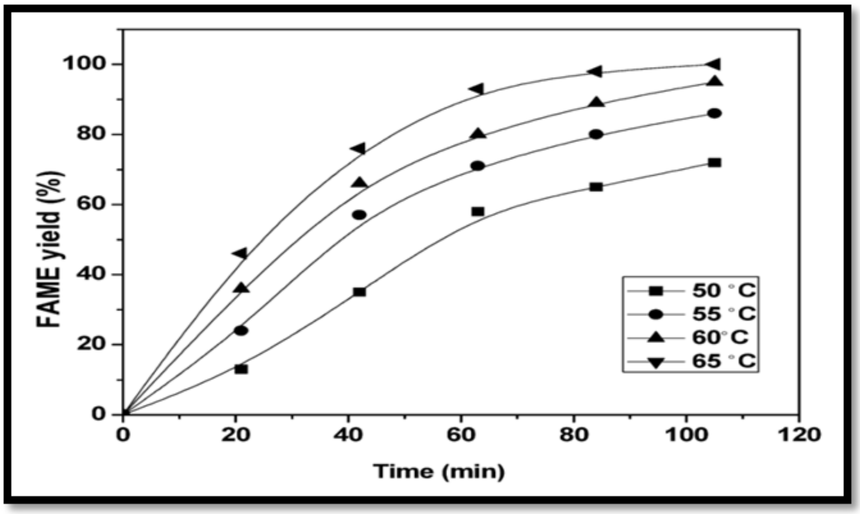


Figure 4.8 Effect of reaction temperature on 5-ZN/CaO-700 catalyzed transesterification of waste cooking oil. Reaction conditions: methanol to oil molar ratio of 12:1

4.4.5 Effect of Catalyst Loading

The effect of catalyst loading on conversion to methyl esters was examined. The catalyst amount was varied in the range of 1.5 -7 wt.% with respect to oil weight.

From table 4.2 it is evident that the conversion increased gradually from 60.45% to 98.5% with increasing the catalyst amount from 1.5wt.% to 5wt.%. On further increasing the catalyst amount it adversely affected the conversion because of mass transfer limitations of the reactants in heterogeneous reaction mixture. The excess amount of catalyst also resulted in increased viscosity of the mixture which produced resistance to mass transfer resulting in decrease in yield. Therefore the appropriate amount of catalyst would be used for transesterification. In our work the 5wt.% of Zn-Cao gave the maximum results in terms of biodiesel yield.

4.4.6 Effect of Reaction Time

The dependence of reaction time on the methyl ester conversion is also shown in table 4.2. In the first 30 mins the conversion of 40% was achieved and it was increased to 55% after one hour. The complete conversion was done in one hour 40 mins. With further prolongation of the reaction beyond this, no remarkable increase in the conversion was observed. Hence, the time required to approach reaction equilibrium for the transesterification is essentially 1h and 40 mins.

Table 4.2 Comparison of different loading of Zn catalytic activity for transesterification reaction.

Catalyst	Catalyst Amt. (wt %)	Reaction temperature (°C)	Methanol: oil molar ratio	Reaction Time (h)	FAME Yield (%)
CaO	5	60-65	12:1	3	95
1.5-Zn/CaO-700	5	60-65	12:1	2.5	95
3-Zn/CaO-700	5	60-65	12:1	2.5	96
5-ZnCaO-700	5	60-65	12:1	1.40	98.5
7-ZnCaO-700	5	60-65	12:1	2	86

4.5 Reusability of Catalyst

The success of biodiesel production technology depends on its production cost. Catalyst reusability could minimise the biodiesel production cost up to some extent. To check the reusability of the 5Zn/Cao-700 catalyst, it was recovered after the transesterification and then filtered and washed with the hexane and calcined again at a temperature of 700°C. The regenerated catalyst was utilized for four successive catalytic cycles under the same experimental and regeneration methods. As could be seen from Figure 4.9, no significant loss in catalytic activity was observed during first three runs, however, a partial decrease in activity was observed in fourth cycle. The gradual loss of the catalytic activity could be due to the blockage of active sites because of the absorbed organic molecules and another reason was partial leaching of the active species from the catalyst.

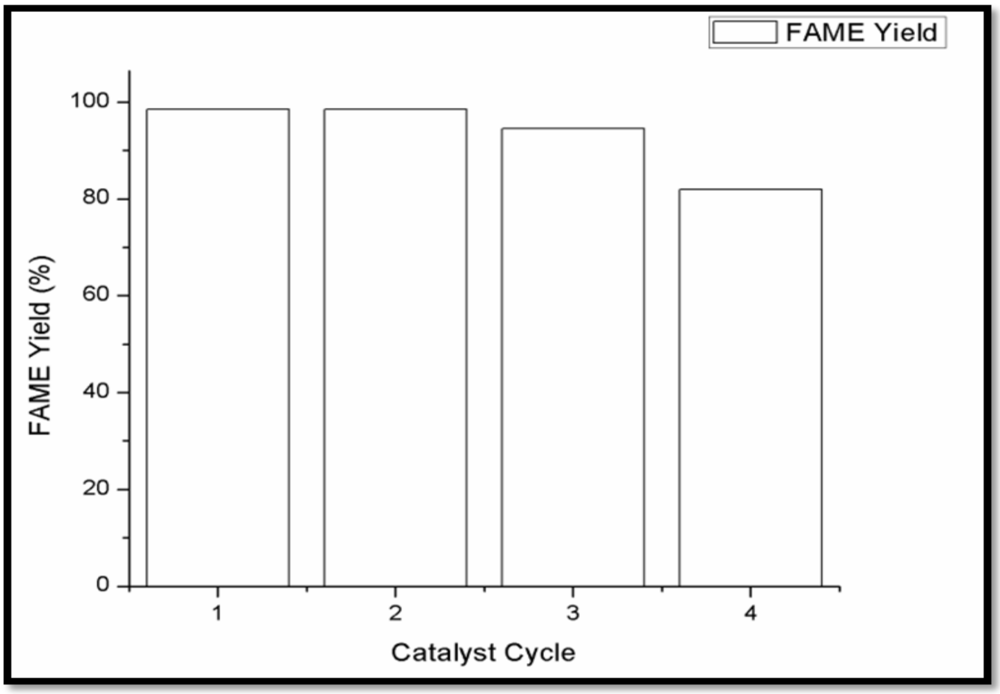


Figure 4.9 Reusability study of the 5Zn/Cao-700 catalyst

4.6 Properties of Biodiesel and their Significance

The physical and chemical fuel properties of biodiesel basically depend on the type of feedstock and their fatty acids composition. Biodiesel derived from waste cooking oil was examined for physical and chemical properties at CSIR-CMERI Ludhiana. The results are shown in the table 4.3. The sample met the ASTM D6751 and EN14214 standards. This section gives some general properties of biodiesel and their significance. Kinematic viscosity is concerned directly with the resistance of liquids to flow. Therefore, it is very important property to determine the efficiency of a biodiesel as a fuel. High viscosity would deteriorate the quality of the liquid fuel due to poor fuel atomization, tubing blockage and possible deposits formation in the engine causing incomplete combustion and severe fouling (Agarwal, 2005).

As viscosity varies inversely with temperature, all these drawbacks increase at low temperature, so fuels with high viscosities are not suitable for cold regions (Cataluña and Da Silva, 2012). Kinematic viscosity for waste cooking methyl ester, for this study was found 4.05 centistokes at 40°C. This value falls in the range (1.9-6.0 cSt) specified by ASTM standards. The density of waste cooking methyl ester was found to be 876.2kg/m^3. The density of fuel is important because it gives an indication of the delay between the injection and combustion of the fuel in a diesel engine (ignition quality) and the energy per unit mass (specific energy). Higher density of biodiesel compared to diesel oil fuel will increase the fuel consumption and consequently NO_x emissions. ISI448 P: 32 test methods were used to measure the density of the biodiesel.

According to these standards, density should be tested at the temperature reference of 31°C. High flash point of biodiesel fuel is another advantage of biodiesel over petroleum-based diesel oil fuel. Flash point is a measure of the flammability of the fuel, higher the flash point more safe the fuel in handling and storage (ISMAIL *et al.*, 2014). The flash point of the produced biodiesel in this work was 110°C which was higher than the diesel oil (52-96°C). However, high flash point indicates low volatility properties, leading to negative effect on diesel engine performance (Sarojray, 2013). The behaviour of biodiesel in cold climatic conditions or at low temperature is an important quality criterion. This is because partial or full solidification of the fuel may cause blockage of the fuel lines and filters, leading to fuel starvation, problems of starting, driving and engine damage due to inadequate lubrication.

The cloud point (CP) and pour point (PP) are important for low-temperature application for fuel. The cloud point is the temperature at which wax crystals first become visible when the fuel is cooled under controlled conditions during a standard test. Pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. In general, biodiesel has higher cloud point and pour point than diesel oil fuel (Verma, Sharma and Dwivedi, 2016), (Isaac JoshuaRamesh Lalvani *et al.*, 2016). Acid value is expressed as mg KOH required for neutralizing 1 gm. of FAME. Higher acid content can cause severe corrosion in fuel supply system of an engine. The acid value is determined using the ASTM D664. For this study it was 0.7 mg of KOH per gram sample.

The iodine number is an index of the number of double bonds in biodiesel which determines the unsaturation degree of the biodiesel. This property can greatly influence the oxidation stability and polymerization of glycerides. This can lead to the formation of deposits in diesel engine injectors. Iodine value is directly correlated to biodiesel viscosity, cetane number and cold flow characteristics (cold filter plugging point). Saponification value of oil, fat or of an ester is defined as the number of milligrams of potassium hydroxide (KOH) required to completely neutralize the free fatty acids to saponify the ester present in 1gm of the substance. The magnitude of saponification value gives an idea about the average molecular weight of fat or oil. Saponification value also indicates the length of carbon chain of the acid present in that particular oil or fat. Higher the saponification value, greater is the percentage of the short chain acids present in the glycerides of the oil or fat. ASTM D5558 method was used for determination of saponification value of waste cooking oil methyl ester.

The cetane number (54.5) was higher than diesel oil resulting in a smoother running of the engine with less noise. Biodiesel sample is an oxygenated fuel naturally with oxygen content about 10% of which contributes to the favourable emission (Raheman and Ghadge, 2008), (Hwang, Bae and Gupta, 2016), but leads to a little bit low calorific value (32.9 MJ/kg) compared with petro-diesel. Biodiesel nearly meets all the properties of normal diesel oil fuel according to ASTM D6751 and EN 14214 standards, which indicates that Biodiesel derived from WCO has permissible values compared to diesel oil fuel.

Table 4.3 Physicochemical properties of the FAME

S.No.	Parameters	Units	FAME	Test method
1	Ester content	%	98.5 %	H-NMR
2	Flash point	ºC	110	ASTM D93
3	Pour point	ºC	1	ASTM D2500
4	Kinematic viscosity at 40 ºC	cSt	4.50	ASTM D445

5	Density at 31 ºC	kg/mm^3	870	ISI448 P:32
6	Ash	%	NIL	ASTM D874

S.No.	Parameters	Units	FAME	Test method
7	Iodine value	mg of I_2/g of sample	75.9	^{1}H-NMR*
8	Acid value	mg of KOH/g of sample	0.7	ASTM D664
9	Saponification value	mg of KOH/g of sample	180	ASTM D5558

4.7 Experimental Section on VCR Engine Filled with WCOME (Biodiesel)

In this section the results from the experiments of a variable compression ratio engine fuelled with waste cooking oil methyl ester (WCOME), diesel blends for various load conditions at different compression ratios (15:1 to 17.5) have been discussed. The results got from the experiments are compared with diesel for all fuels tested. The performance characteristics such as brake thermal efficiency, brake specific energy consumption with respect to brake power are discussed. Emission characteristics such as carbon monoxide, hydro carbon, nitric oxide and smoke opacity are also discussed. The fuel used in this experimental study includes conventional and different biodiesel blends. The biodiesel blends B20, B40, B60, B80 and B100 are taken respectively for experiment. The compression ratios 15:1 and 17.5:1 are considered.

4.8 Engine Performance Characteristics

4.8.1 Brake Thermal Efficiency

The variation of brake thermal efficiency (BTE) for compression ratios (15:1, 16.5:1 and 17.5:1) and for different blends is depicted in figures **4.10, 4.11 and 4.12 respectively.** It has been noticed that the brake thermal efficiency of the blend B40 is higher than that of the diesel at compression ratio 17.5. The brake thermal efficiency of the diesel and blend B40 for compression ratio 17.5 was 28.34% and 31.40% respectively. The higher thermal efficiency may be due to better atomization, spray characteristics and air fuel mixing with air, which results in an improved combustion. However at compression ratios 16.5:1 and 15:1 the brake thermal efficiency deteriorated respectively at same parameters (i.e. B40 with full load). Brake thermal efficiency is directly proportionate to the compression ratio (Pushparaj and Ramabalan, 2013).

The mixing of bio-diesel in diesel oil yielded good thermal efficiency curves. Initially the thermal efficiency of the engine was improved by increasing concentration of the bio-diesel in the blend. The possible reason for this is the additional lubricity provided by bio-diesel. The molecules of bio-diesel (i.e. methyl ester of the oil) contain some amount of oxygen, which takes part in the combustion process. It was noticed that after a certain limit with respect to diesel ester blend, the thermal efficiency trend was reversed and it started decreasing as a function of the concentration of blend. These results agree with the previous works reported by other researchers (Buyukkaya, 2010; Kumar Maurya and Kumar Agarwal, 2014).

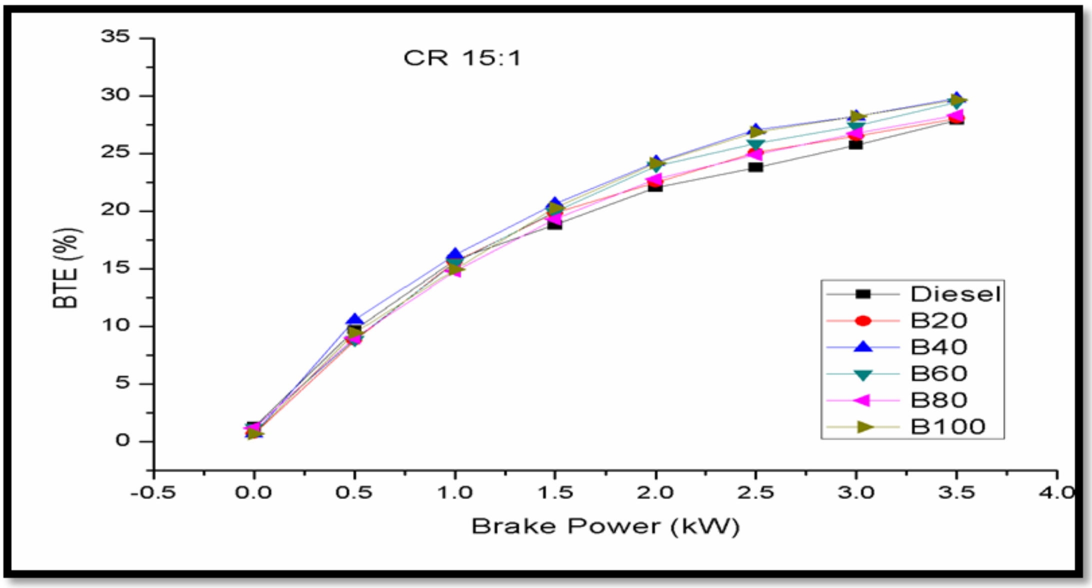


Figure 4.10 Brake thermal efficiency Vs brake power CR 15:1

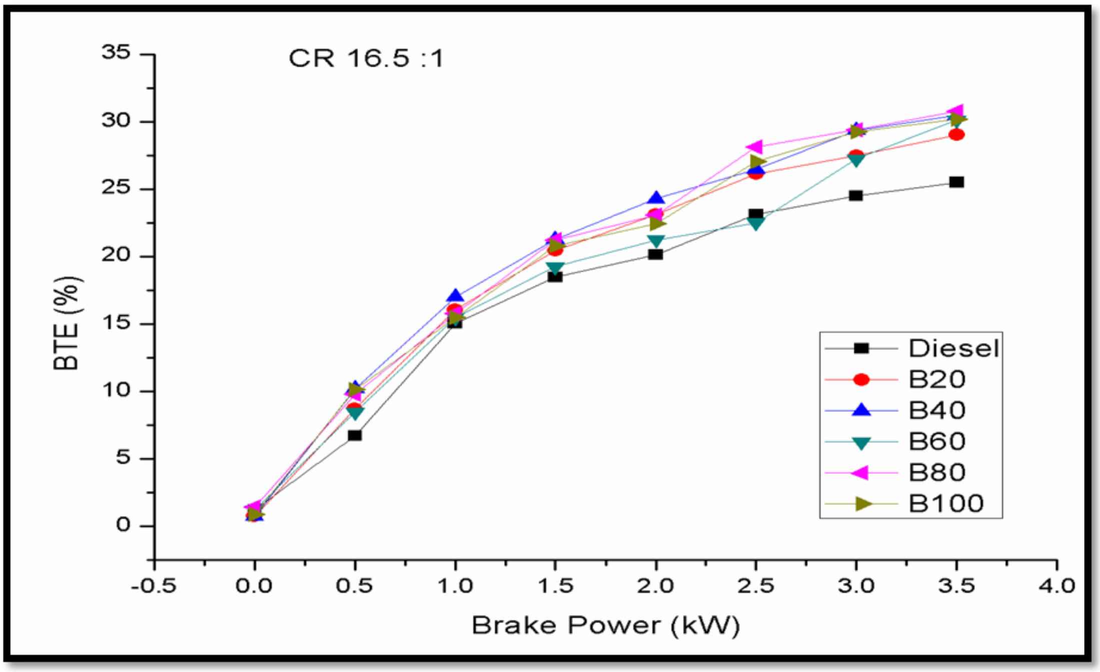


Figure 4.11 Brake thermal efficiency Vs brake power CR 16.5:1

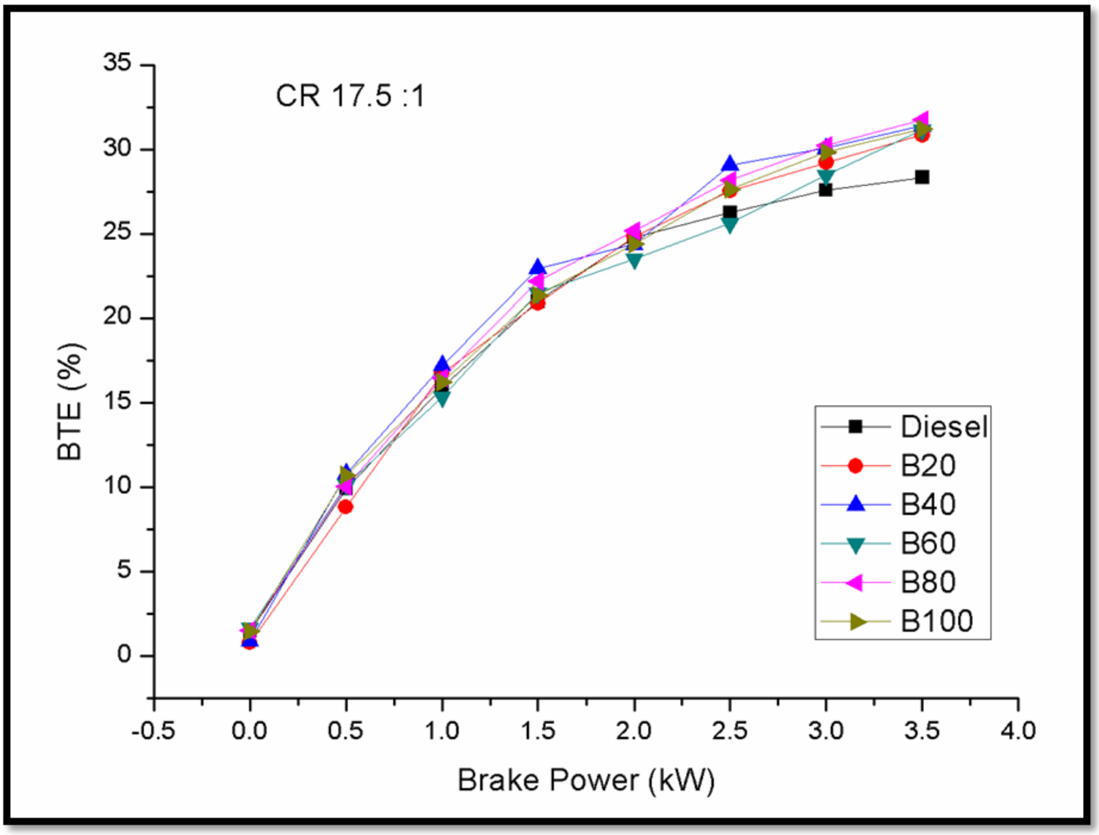


Figure 4.12 Brake thermal efficiency Vs brake power CR 17.5:1

4.8.2 Brake Specific Energy Consumption

Figures 4.13, 4.14 and 4.15 shows the variation of the brake specific energy consumption with brake power at CR 15:1, 16.5:1 and 17.5:1 respectively. When two different fuels were blended in some proportions simultaneously, then fuel consumption might not be authentic because the heating value and density were different. Therefore, in such cases the brake specific energy consumption would give more accurate values. The brake specific energy consumption was determined for waste cooking methyl ester diesel oil fuel blends as the product of the specific fuel consumption and the calorific value. It was observed that, as the load increased, SEC of all fuels decreased. At full load condition, the difference in SEC of all biodiesels (B20, B40, B60, B80 and B100) and diesel oil was found to be marginal. This may be attributed to the combined effect of lower heating value, higher density and viscosity of WCOME.

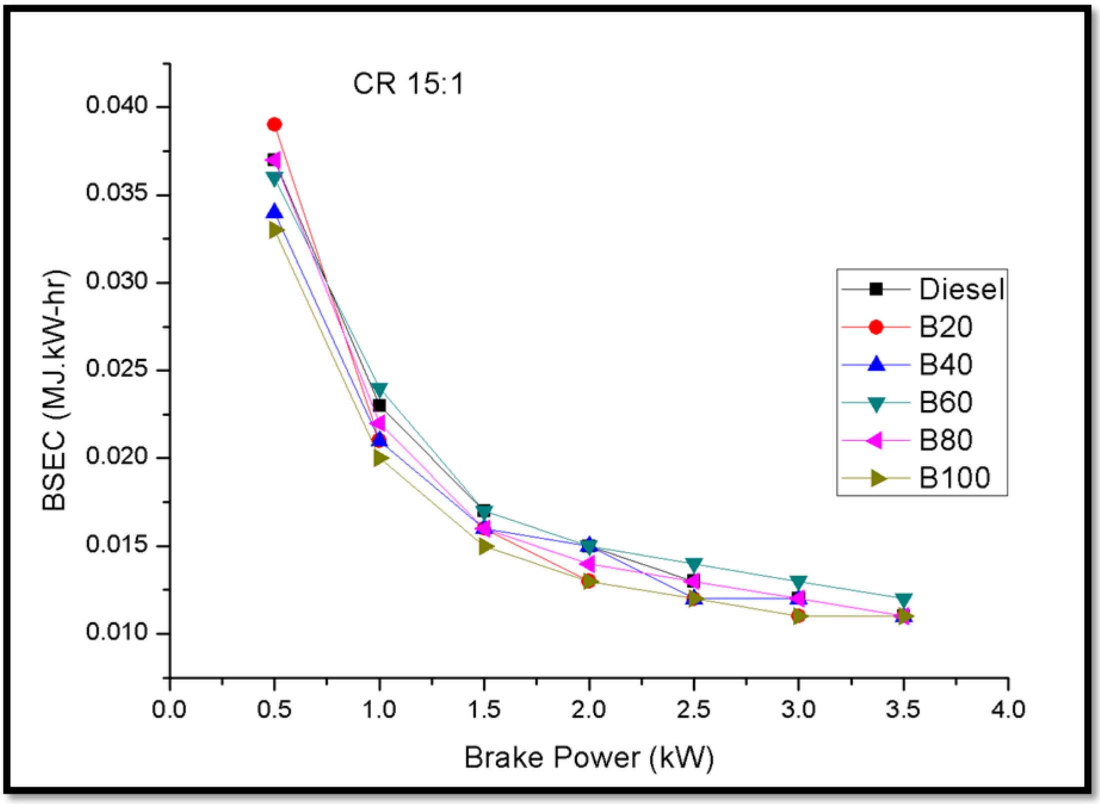


Figure 4.13 Brake specific energy consumption Vs brake power CR 15:1

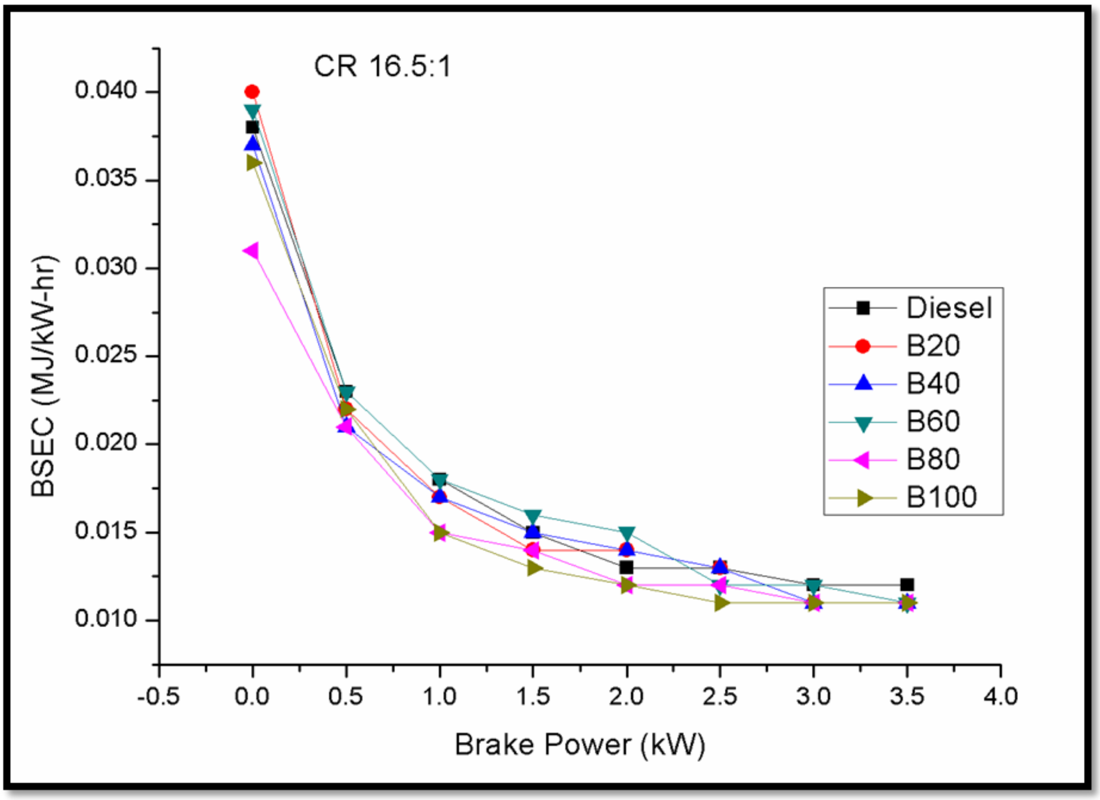


Figure 4.14 Brake specific energy consumption Vs brake power CR 16.5:1

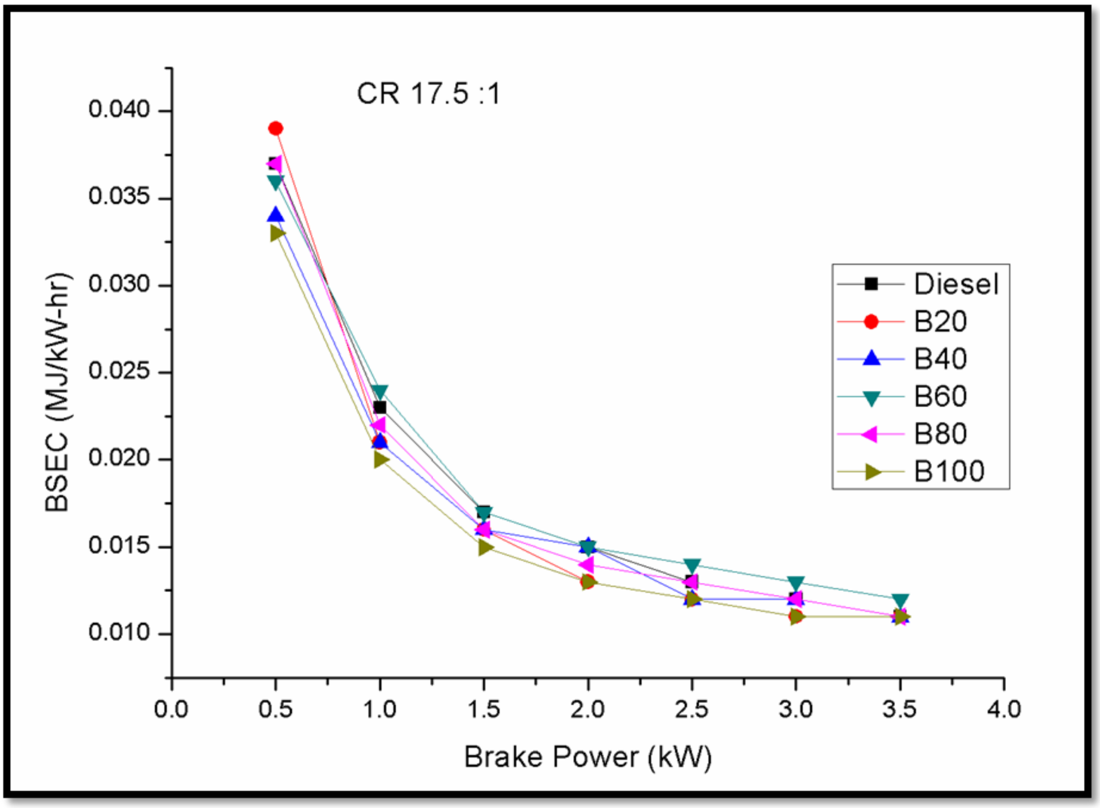


Figure 4.15 Brake specific energy consumption Vs brake power CR 17.5:1

4.9 Emission Parameters

4.9.1 Carbon Monoxide Emissions

Carbon monoxide is one of the arbitrate compound formed during the intermediate combustion stage of hydrocarbon fuels. CO formation depends on air fuel equivalence ratio, fuel type, combustion chamber design, atomization rate, starting of injection timing, injection pressure, engine load and speed (Sayin and Gumus, 2011). CO emissions were reduced when compression ratio was increased from 15 to 17.5 which can be seen from the **figures 4.16, 4.17 and 4.18**. This inverse relationship was noticed for all blends. The possible explanation for this trend could be that as the compression ratio increases the inside cylinder temperature consequently reduces the delay period causing better combustion of the fuel and so lower CO formation.

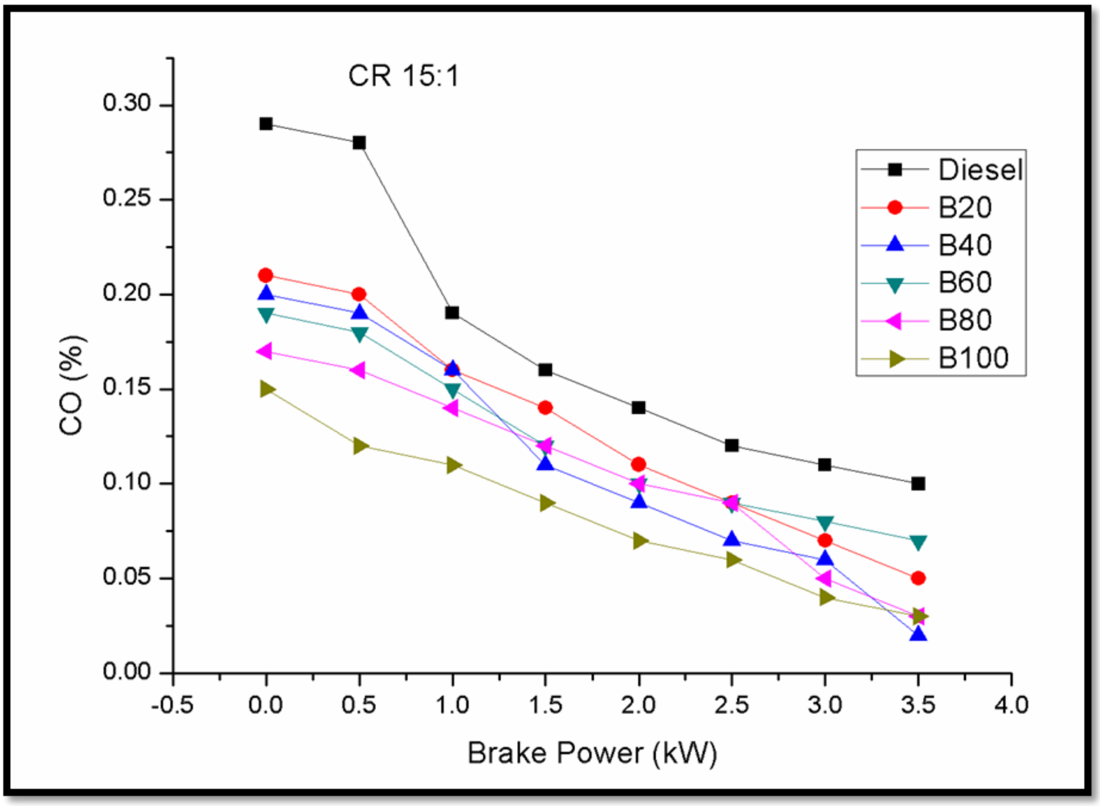


Figure 4.16 CO Vs brake power CR 15:1

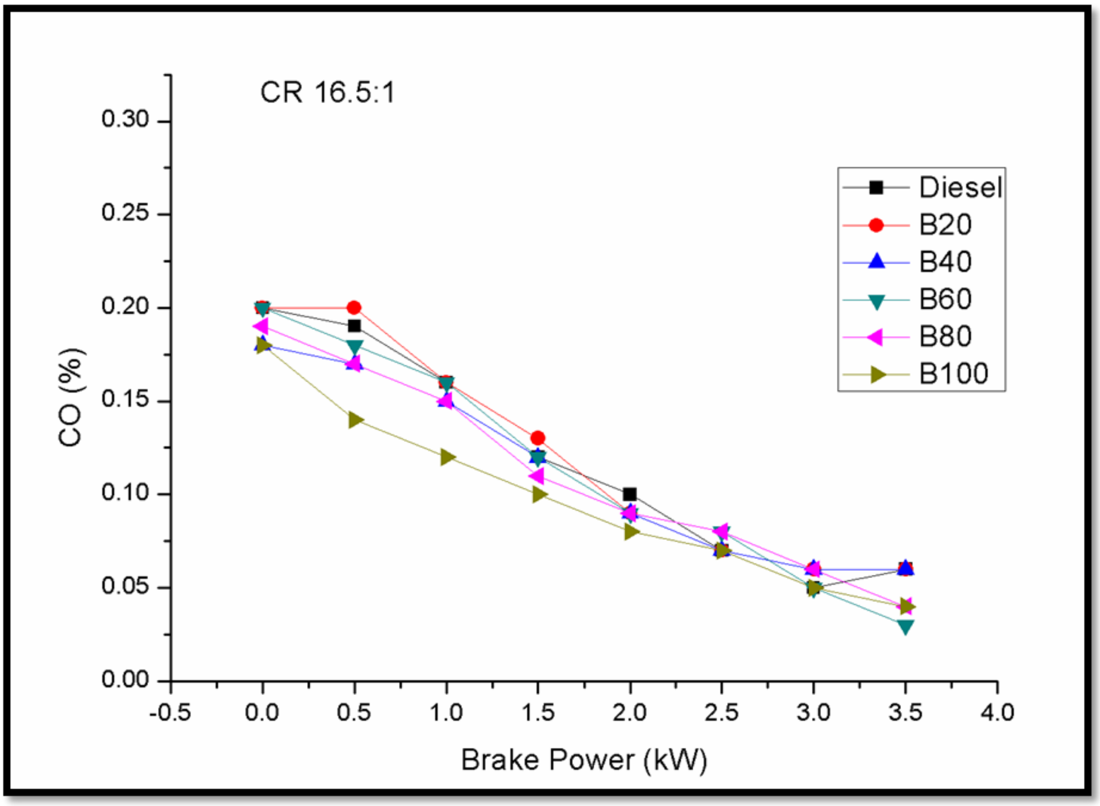


Figure 4.17 CO Vs brake power CR 16.5:1

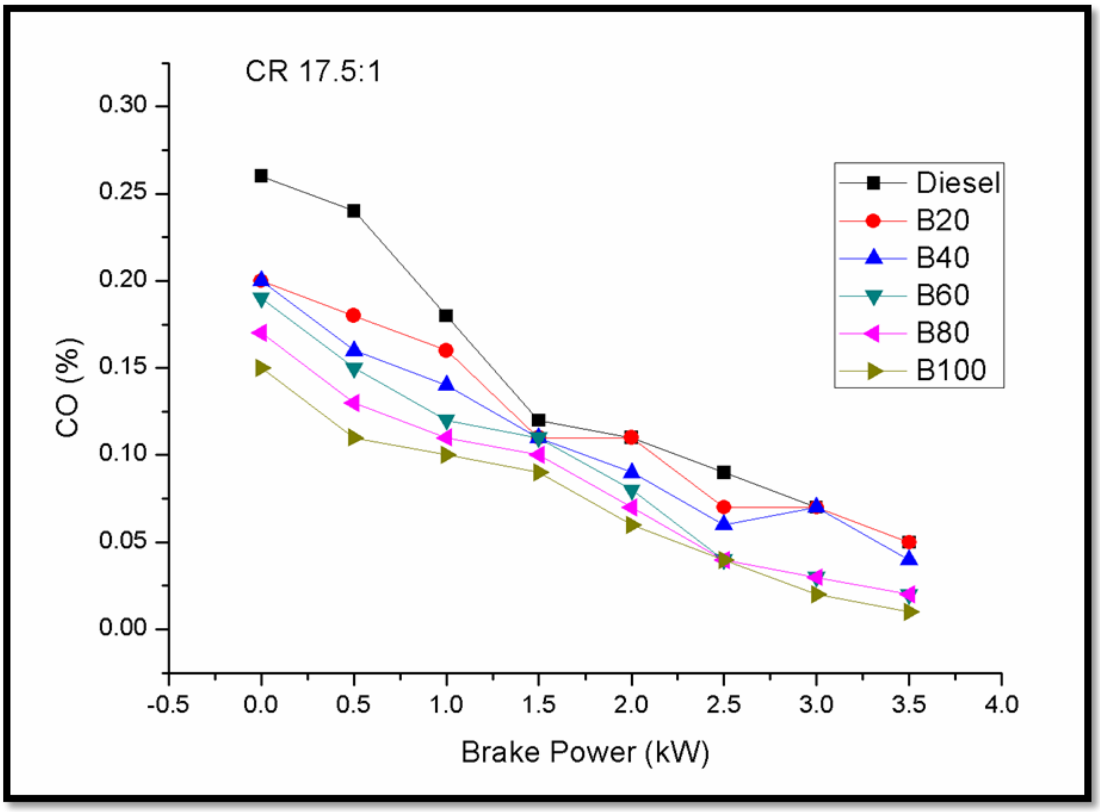


Figure 4.18 CO Vs brake power CR 17.5:1

4.9.2 Hydrocarbon Emissions

Unburnt hydrocarbons are formed when the fuel is not burnt properly inside the combustion chamber. It is one of the significant parameters for finding out the emission behavior of compression ignition engine. The structure of the fuel, the engine construction and operating conditions are effective on HC emissions. In the combustion chamber of a diesel engine, there are fuel rich zones decreasing the regional temperature, slowing the chemical reaction down and even quenching the flame. In addition the longer ignition delay period makes the HC emission increase but the biodiesel blend in diesel makes the hydrocarbon emission decrease as we increase the biodiesel blend as shown in figures 4.19, 4.20 and 4.21 respectively. The reduction in the HC was linear with the addition of biodiesel for the blends tested. These reductions indicate a cleaner and complete combustion of the fuel.

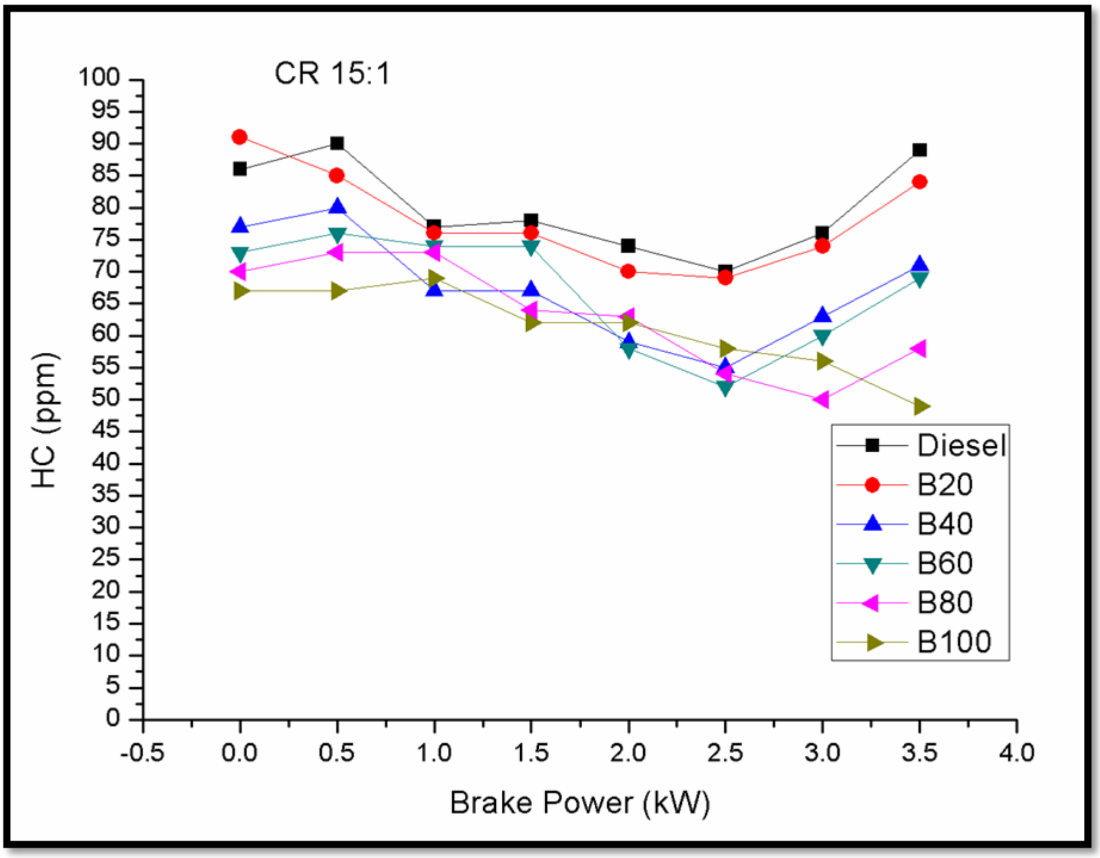


Figure 4.19 HC Vs brake power CR 15:1

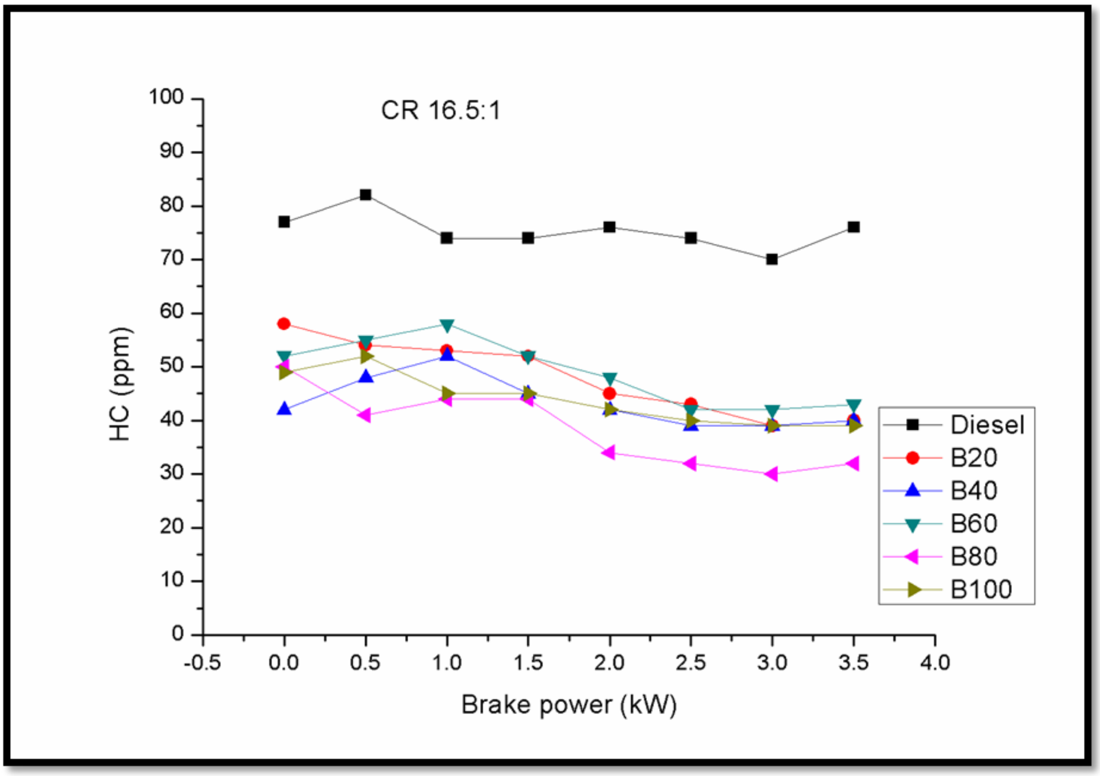


Figure 4.20 HC Vs brake power CR 16.5:1

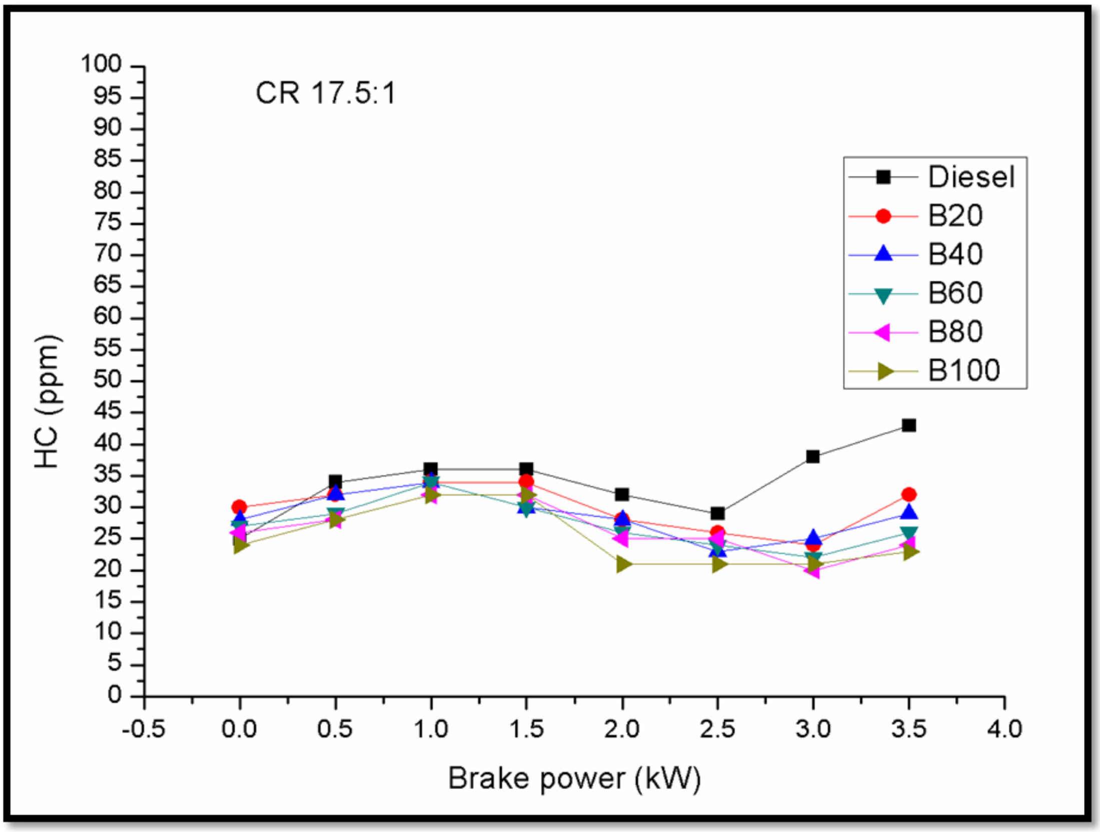


Figure 4.21 HC Vs brake power CR 17.5:1

4.9.3 Oxide of Nitrogen Emissions

NO_x emission is a combination of nitric oxide (NO) and nitrogen dioxide (NO_2) which is formed from the reaction of nitrogen and oxygen gases in the air during combustion. The combustion flame temperature, oxygen concentration and combustion duration are three important parameters on which NO_x formation depends. The variation in NO_x concentration with brake power for B20, B40, B60, B80, B100 and diesel are plotted **in figures 4.22, 4.23 and 4.24 respectively**. NO_x emissions of all biodiesel blends were higher than that of conventional diesel oil. Here the lowest value of NOx was obtained at B40 (i.e. 1129 ppm at CR16.5, 1168 ppm at CR 17.5 and 1212 ppm at CR 15) for full load which was below the base line diesel. The NO_x obtained in this experiment follows the trends as described by Shirneshan and Nabi (Nabi, Rahman and Akhter, 2009; Shirneshan, 2013).

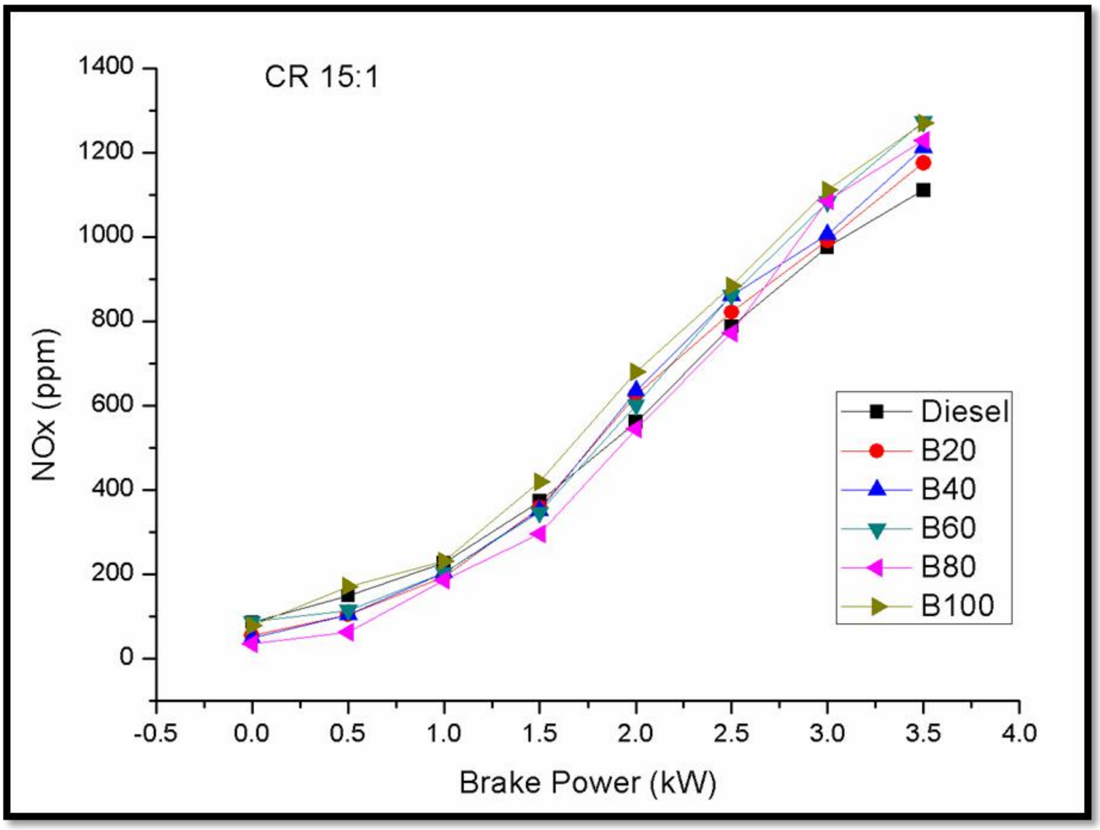


Figure 4.22 NO_X Vs brake power CR 15:1

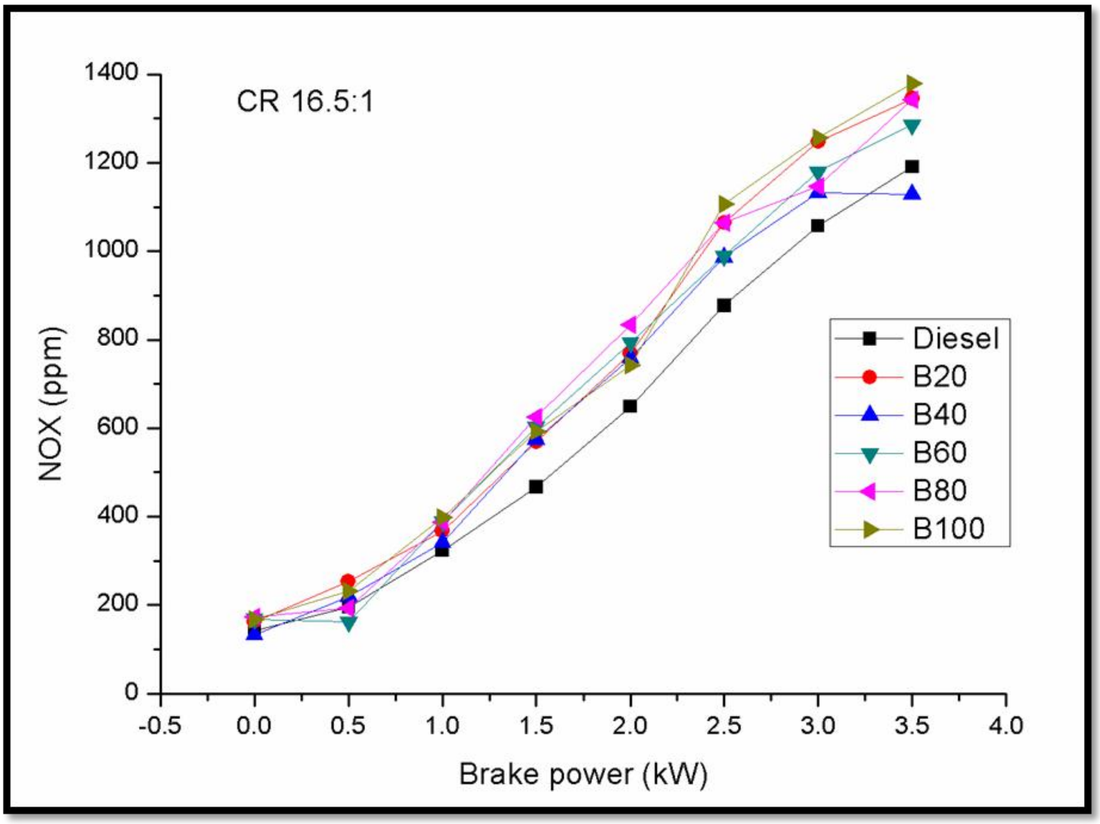


Figure 4.23 NO$_X$ Vs brake power CR 16.5:1

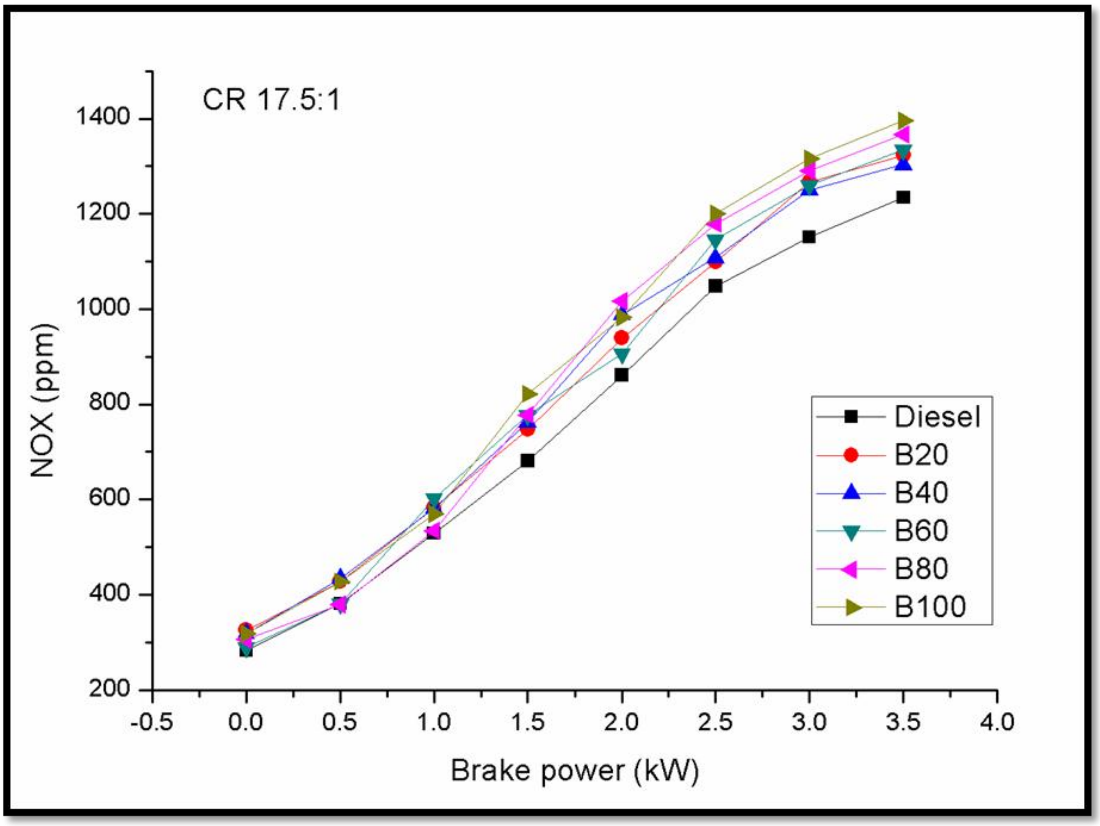


Figure 4.24 NO$_X$ Vs brake power CR 17.5:1

4.9.4 Smoke Opacity

Smoke is the visible product of the diesel engine emissions. The figures 4.25, 4.26 and 4.27 respectively depicts the comparison of smoke opacity of B20, B40, B60, B80, B100 and diesel with respect to brake power at all compression ratios (i.e. 15, 16.5 and 17.5). From the graphs it is observed that smoke opacity of diesel, biodiesel and its blends were significantly higher at zero and part load conditions but as the load increased to maximum level, smoke opacity was reduced effectively. The formation of local rich mixtures in the combustion chamber due to high viscosity of biodiesel resulted in poor atomization at part load conditions. At full load the smoke formation diminished because of oxygenated nature of biodiesel that leads to complete combustion. **The smoke opacity for biodiesel diesel blends decreased due to the enrichment of oxygen content in the fuel. On the other hand the high smoke opacity of diesel was due to higher sulfur content present in it. It was agreed with (Pushparaj and Ramabalan, 2013).**

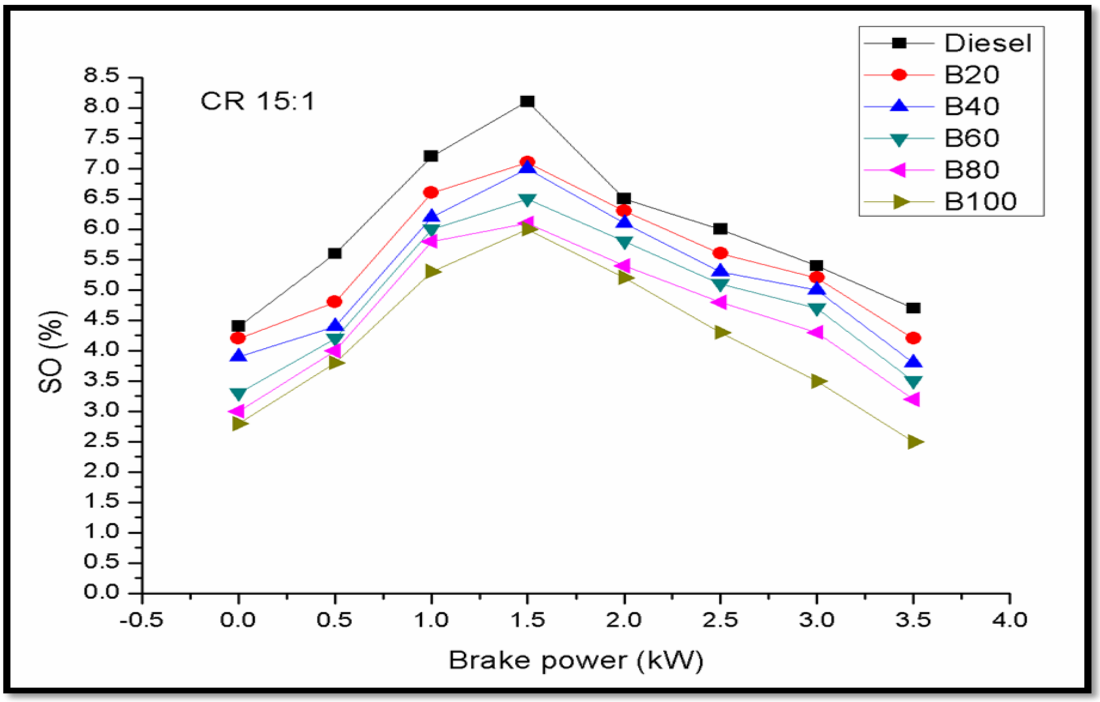


Figure 4.25 SO Vs brake power CR 15:1

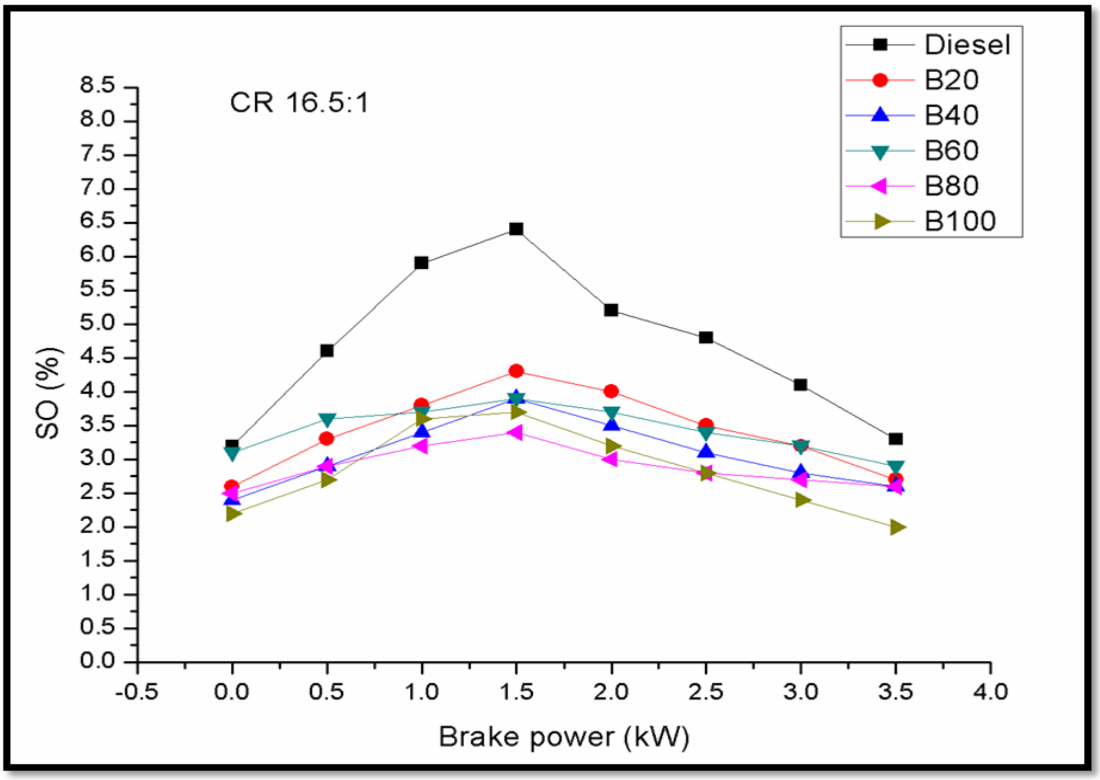


Figure 4.26 SO Vs brake power CR 16.5:1

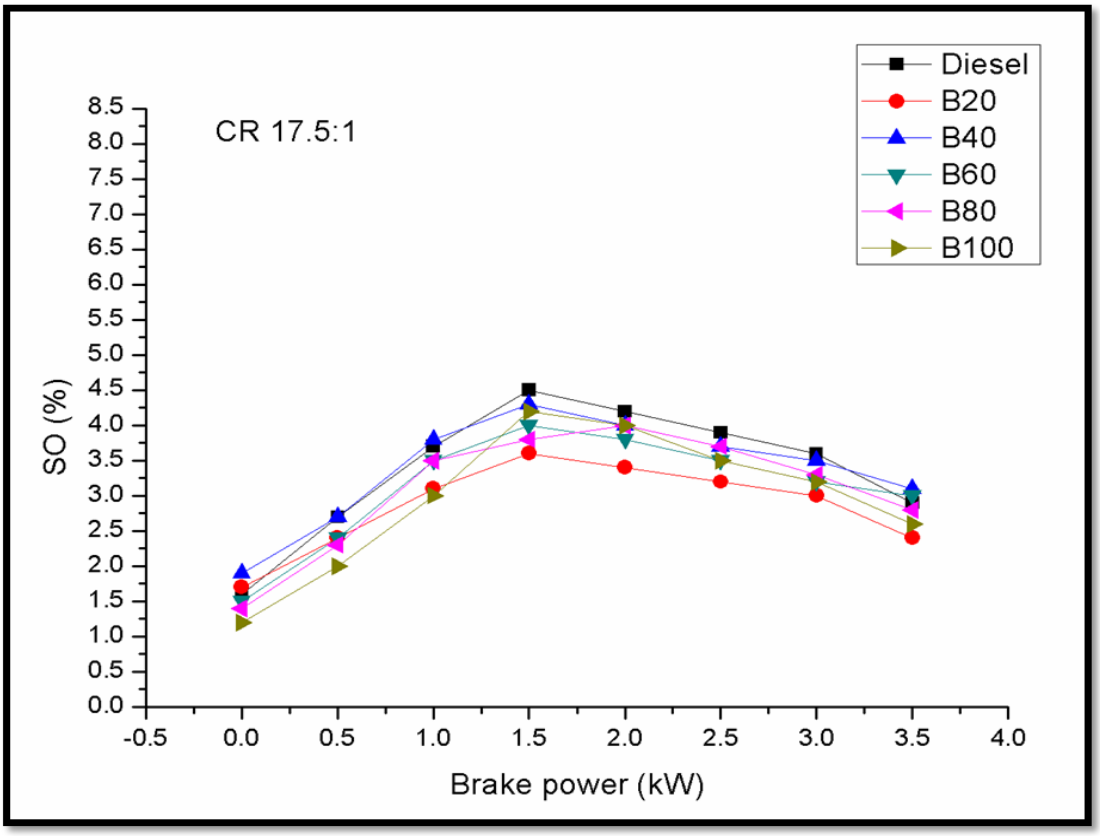


Figure 4.27 SO Vs brake power CR 17.5:1

4.10 Combustion Characteristics

Here we have discussed the effect of CR on engine combustion characteristics such as combustion pressure and EGT for different blends.

4.10.1. Combustion Pressure

The effect of various WCOME proportions of blends and conventional diesel on peak combustion pressure and crank angle at CR 15, CR 16.5 and CR 17.5 are shown in **figure 4.28**. It is revealed from the figure that the combustion pressure from WCOME for various blends and conventional diesel was nearly equal. The maximum combustion pressure for B100 was 56.88 bar at CR 15:1 which is 1.04 % higher than conventional diesel. The peak combustion pressure at CR 15:1 for pure diesel, B20, B40, B60, B80 and B100 were 54.56, 51.61, 54.15, 54.64, 53.56 and 56.88 bar respectively.

The figure 4.29 shows the variation of combustion pressure with crank angle at CR 16.5. The values of peak compression pressure for pure diesel, B20, B40, B60, B80 and B100 were 58.43, 54.60, 57.34, 57.40, 56.67 and 58.30 respectively. Figure 4.30 shows the comparison of combustion pressure with crank angle at CR 17.5. The values of peak compression pressure for diesel, B20, B40, B60, B80 and B100 were 67.40, 67.25, 66.40, 67.40, 69.00 and 68.30 respectively. It is noted from the results that the highest value of peak combustion pressure was obtained at CR 17.5 at B80. These results also suggest that by increasing the CR from 15 to 17.5, the peak combustion pressure also increased for all the blends. The possible cause of this increase in combustion pressure is longer ignition delay that permits more fuel admitted into the cylinder (Puhan *et al.*, 2009). For conventional diesel, the pre-combustion stage is very dominant compared to waste cooking oil lower blends that results in combustion pressure rise because of accumulation of rich fuel during delay period. The high combustion pressure increases the inside cylinder temperature which reduces the viscosity of the oil and will increase the probability of ignition and thus reduce the ignition delay period. The lower combustion pressure values were obtained for B20 because of decreased ignition delay and LCV of biodiesel. The rise in combustion pressure attained for B60 and B100 were 1.00 and 1.04% respectively as compared to conventional diesel.

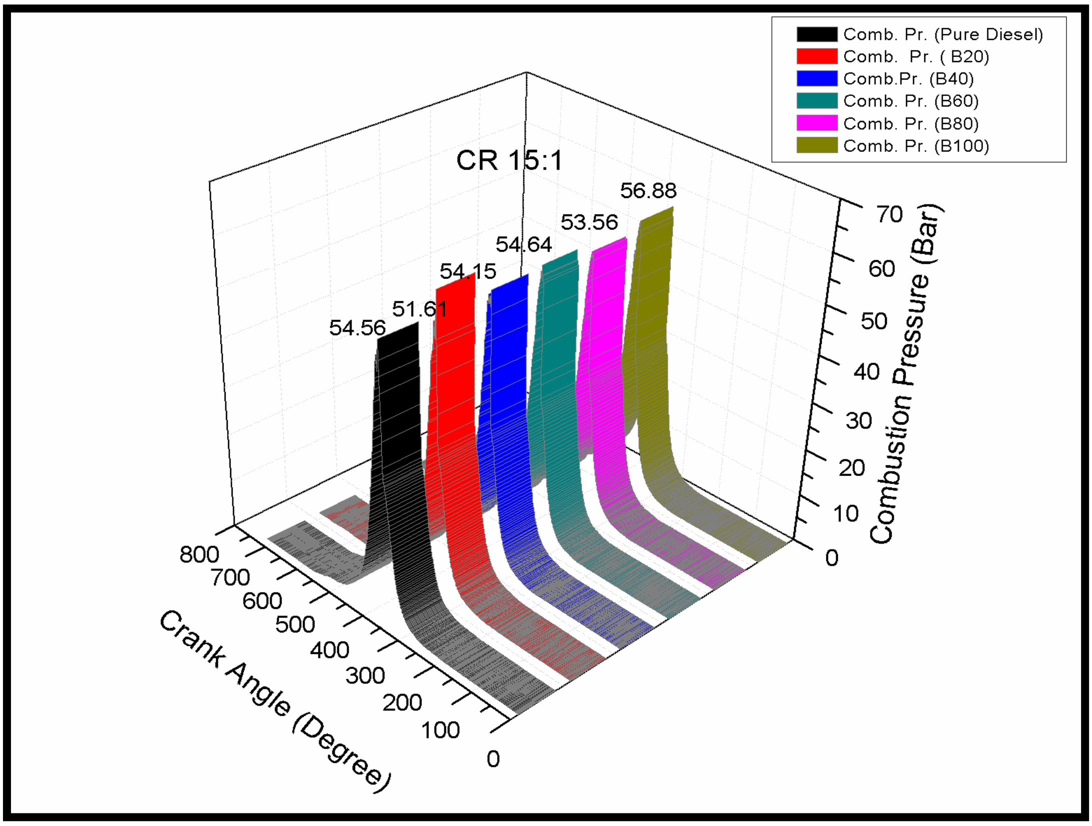


Figure 4.28 Combustion pressure Vs crank angle CR 15:1

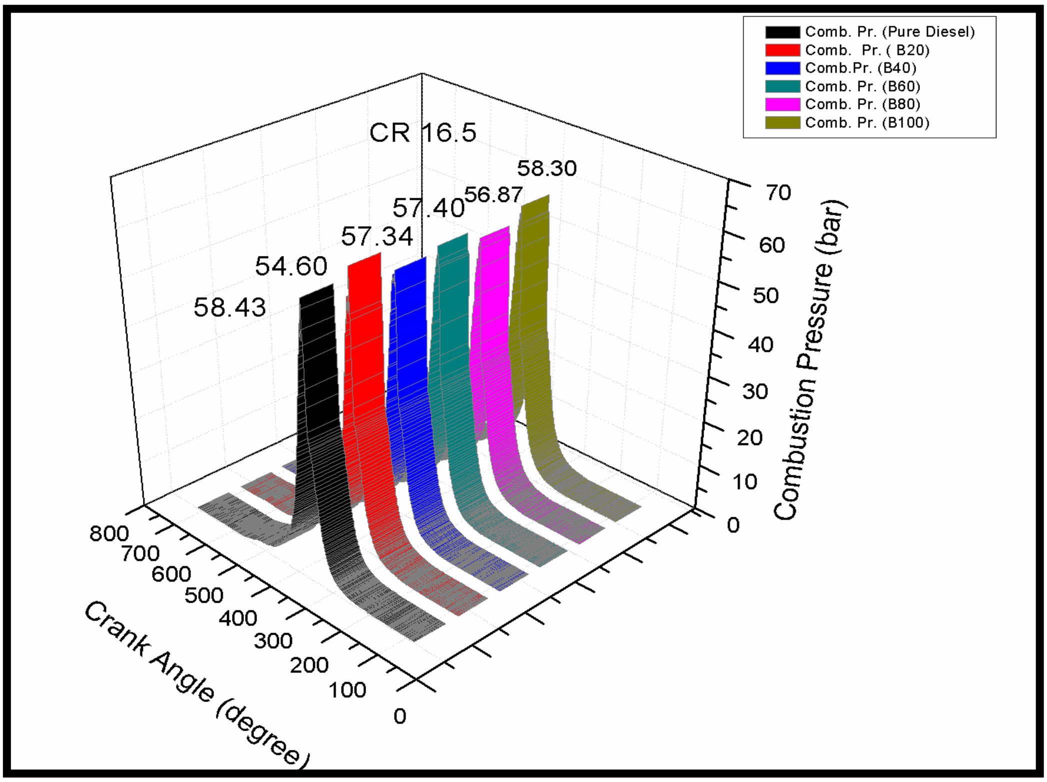


Figure 4.29 Combustion pressure Vs crank angle CR 16.5:1

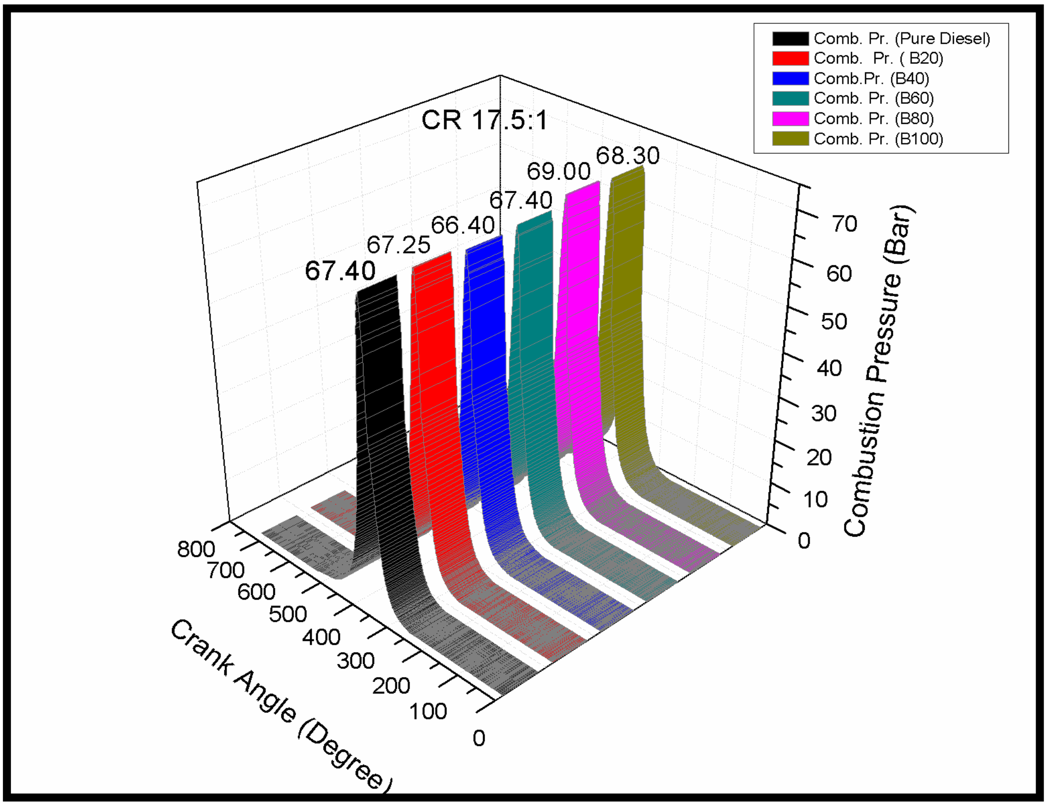


Figure 4.30 Combustion pressure Vs crank angle CR 17.5:1

4.10.2 Exhaust Gas Temperature

EGT describes the state of combustion and amount of heat carried out by the exhaust gases. **Figures 4.31, 4.32 & 4.33 respectively** depicts the deviation of EGT with respect to BP for diesel, different blends of WCOME with diesel at compression ratio 15:1, 16.5:1 and 17.5:1. The results reveal that the EGT decreases for biodiesel and its blends in comparison with diesel. The results reveal that the EGT decreases for biodiesel and its blends in comparison with diesel. Moreover, the EGT decreases with increase in CR and this trend is mirrored in both the biodiesel blends and diesel. The increased CR provides higher temperature before the start of combustion which induces better vaporization of fuel facilitating better mixing with air. This phenomenon leads to sudden and complete combustion resulting in reduced EGT. This trend is consistent with all blends resulting in reduced EGT at higher CRs. The higher oxygen content and the lower calorific value are the possible reasons for the reduction in EGT.

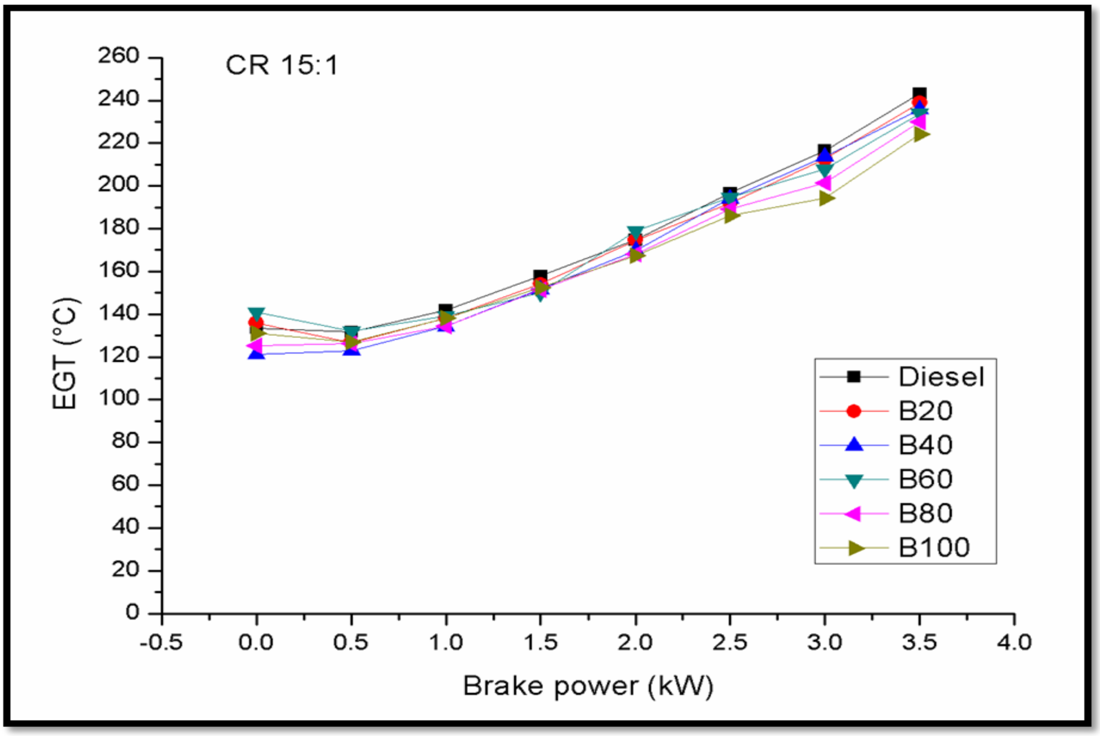


Figure 4.31 Exhaust gas temperature Vs brake power CR 15:1

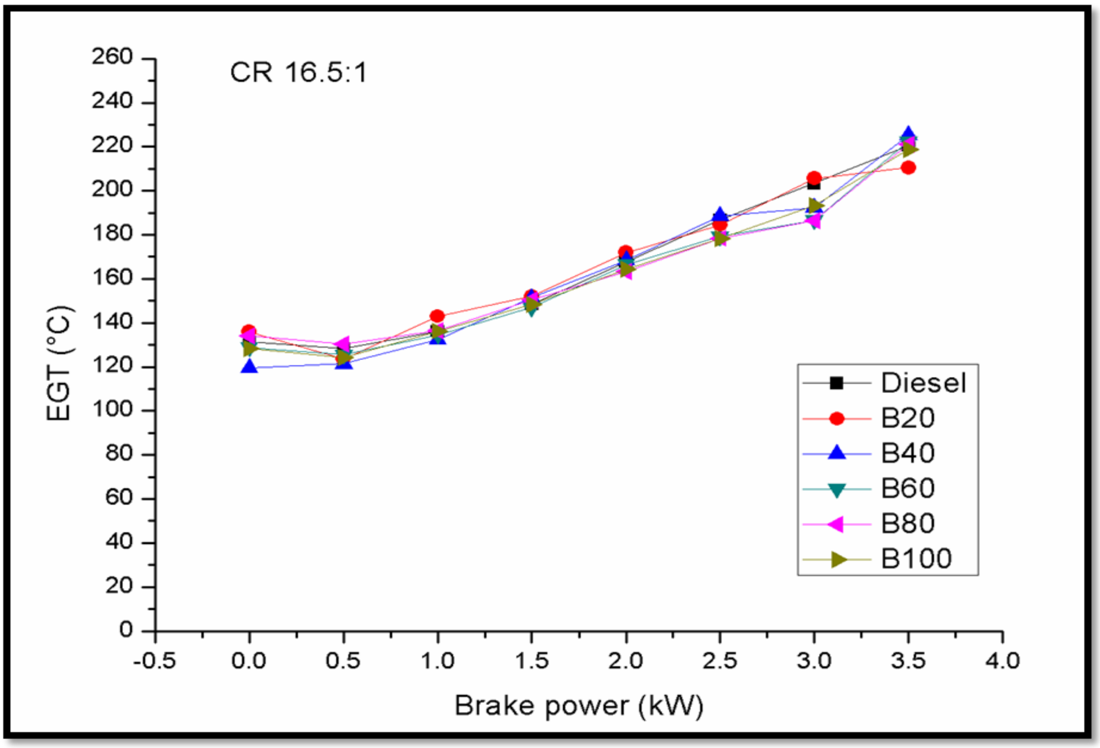


Figure 4.32 Exhaust gas temperature Vs brake power CR 16.5:1

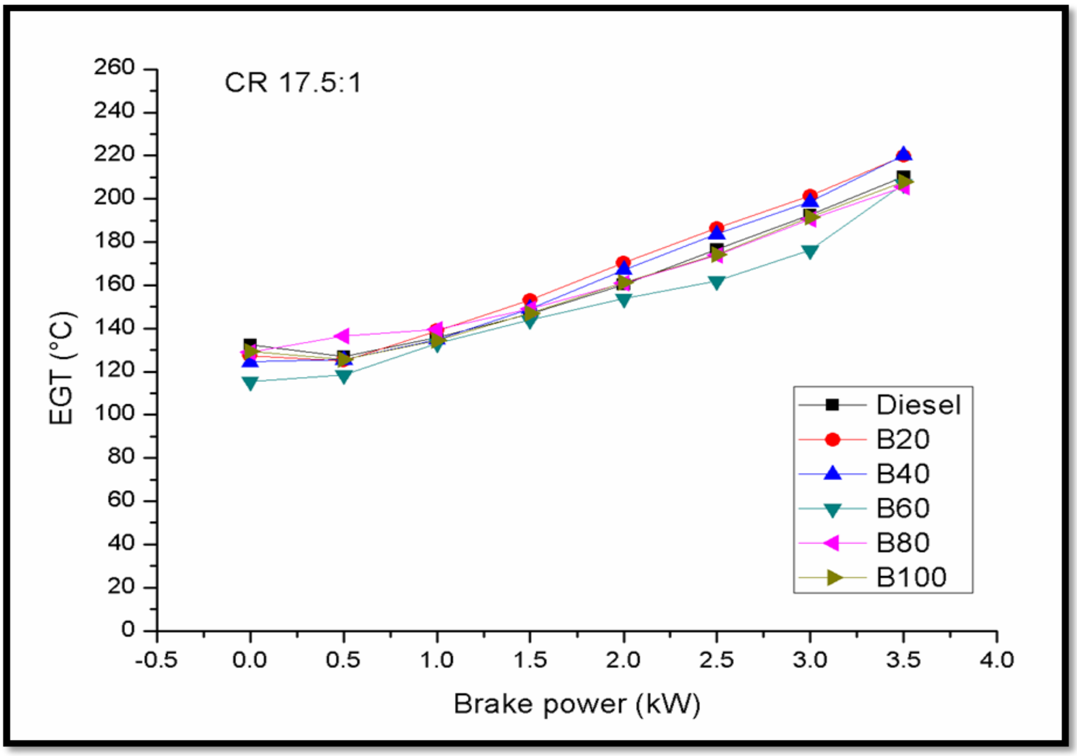


Figure 4.33 Exhaust gas temperature Vs brake power CR 17.5:1

4.11 Effect of CR on performance of biodiesel and diesel blends

This section describes the results obtained from the experiments of a VCR diesel engine fuelled with the WCOME, and its blend with conventional diesel for various load conditions at different compression ratios such as 15:1, 16:1, 17.5:1. The results obtained from the experiment are compared with the conventional diesel for all fuels tested. The performance parameters such as BTE and BSEC are discussed. Emission parameters like CO, UHC, NO_x, and SO are taken up for the discussion. The biodiesel blends of 20%, 40% 60% 80% and 100% by volume are taken and designated as B20, B40, B60, B80 and B100. The compression ratio varied from 15:1 to 17.5:1 at fixed speed (i.e. 1500 rpm). The experimental procedure was repeated for different blend proportions of biodiesel and results are discussed below:-

4.11.1 Brake thermal efficiency

Figures (4.34 to 4.39) depict the changes of BTE with different blends of WCOME with diesel. The mean BTE of B20, B40, B60, B80 and B100 were 18.37, 19.47, 19.01, 18.25, and 18.03 respectively for CR 15:1. The mean BTE for CR 16.5 was found to be 18.37, 20.21, 20.10, 19.93 and 19.52% respectively whereas the mean BTE for CR 17.5 found for all the blends were 19.95, 20.83, 20.45, 20.34, 20.03, and 19.89 respectively. The maximum mean BTE obtained was 20.83 for B40 at CR 17.5. The effect of change in CR on BTE shows that higher CR leads to improvement in the engine efficiency. This could be due to the lower volatility of the biodiesel blends as compared to diesel resulting in improvement in their combustion characteristics due to higher compression ratio.

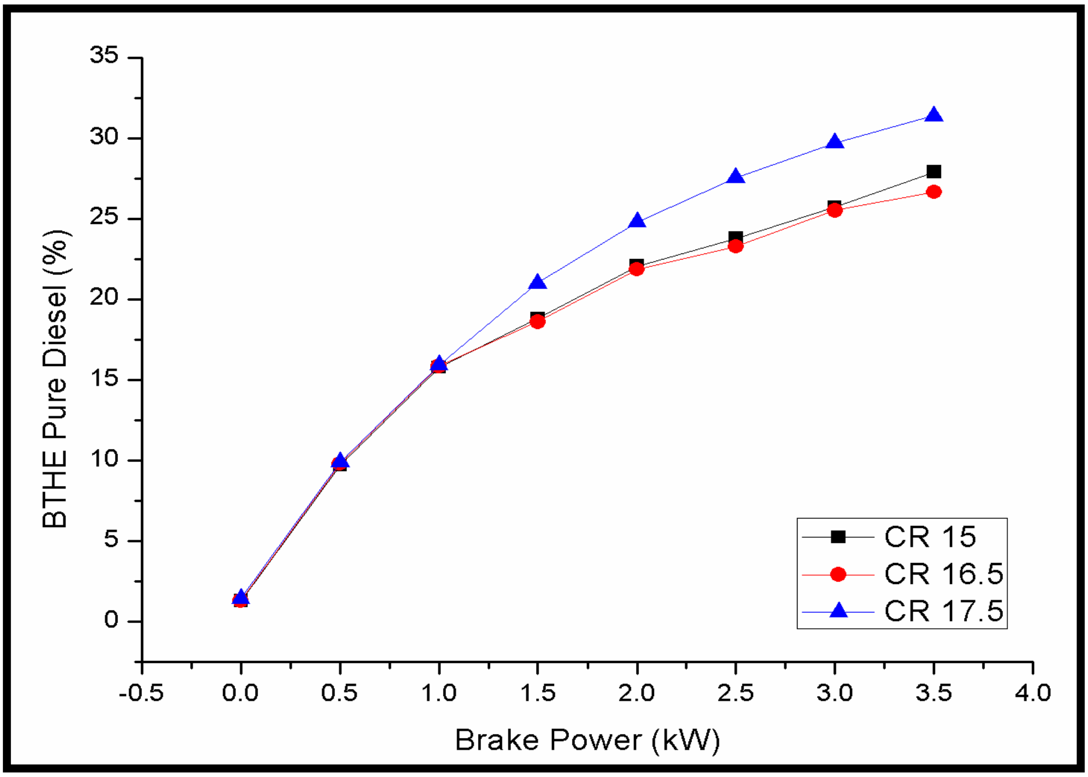


Figure 4.34 Trends of brake thermal efficiency Vs brake power (diesel) at CR 15, 16.5 and 17.5

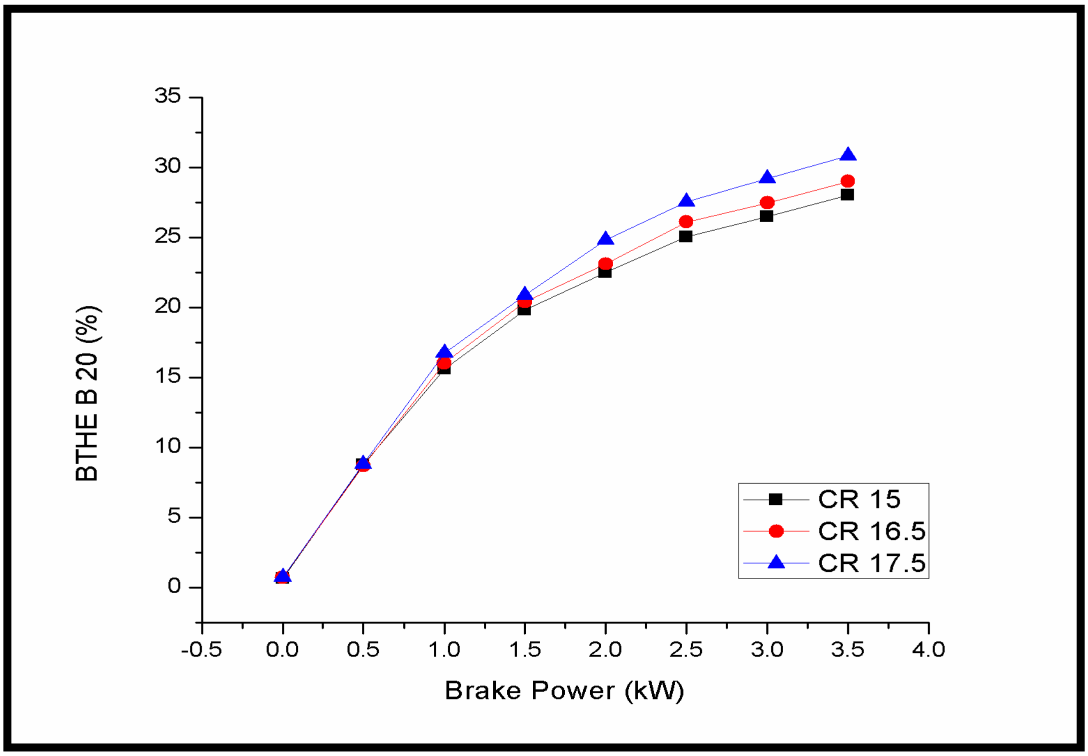


Figure 4.35 Trends of brake thermal efficiency Vs brake power (B20) at CR 15, 16.5 and 17.5

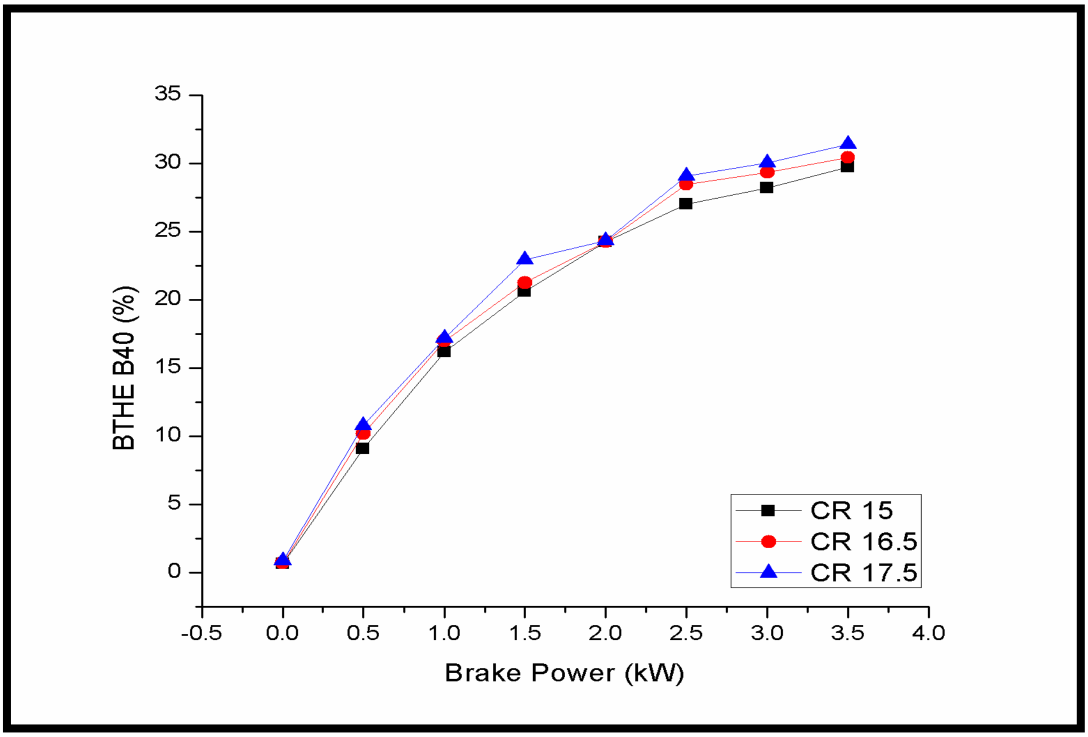


Figure 4.36 Trends of brake thermal efficiency Vs brake power (B40) at CR 15, 16.5 and 17.5

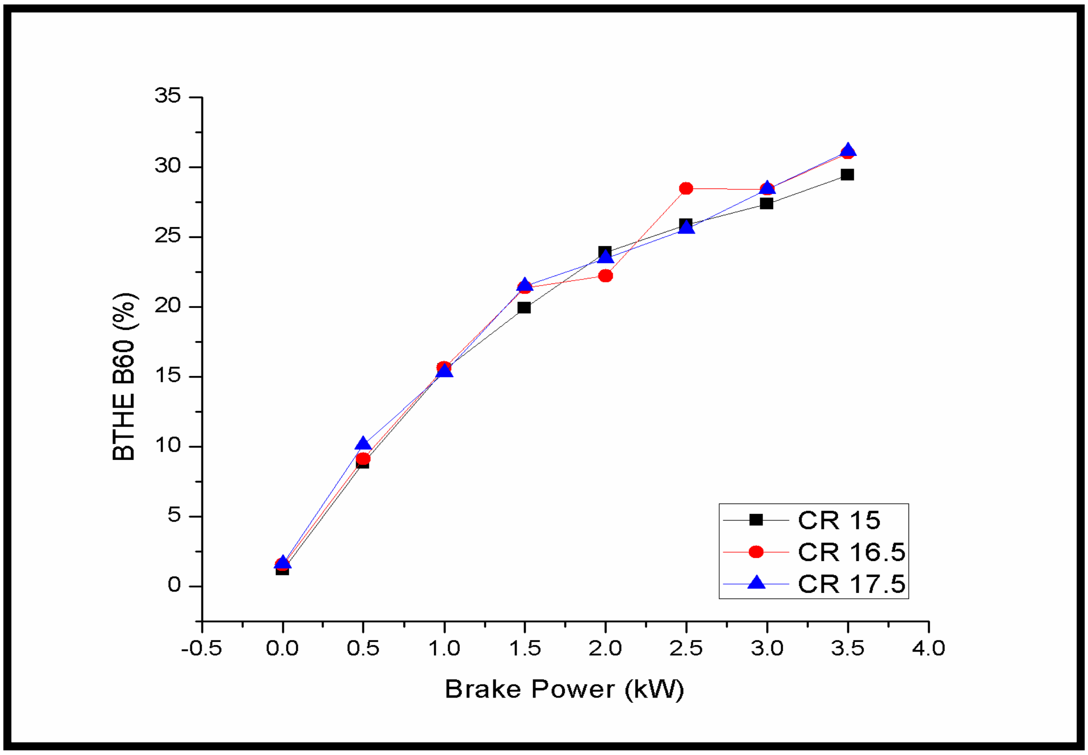


Figure 4.37 Trends of brake thermal efficiency Vs brake power (B60) at CR 15, 16.5 and 17.5

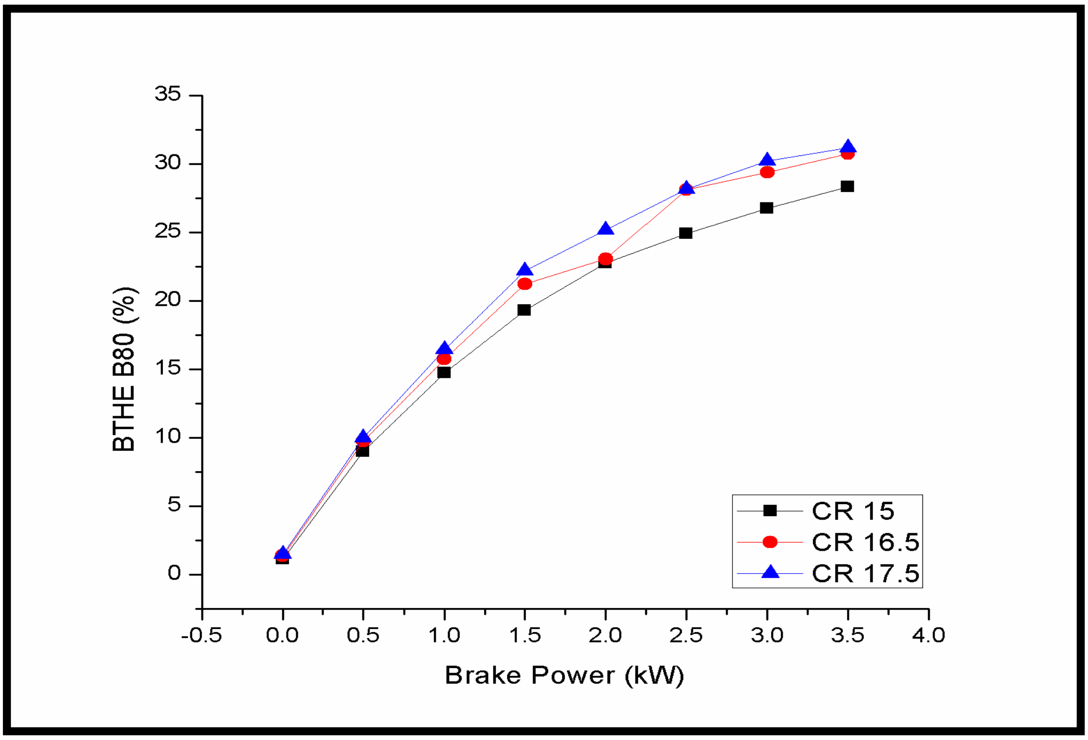


Figure 4.38 Trends of brake thermal efficiency Vs brake power (B80) at CR 15, 16.5 and 17.5

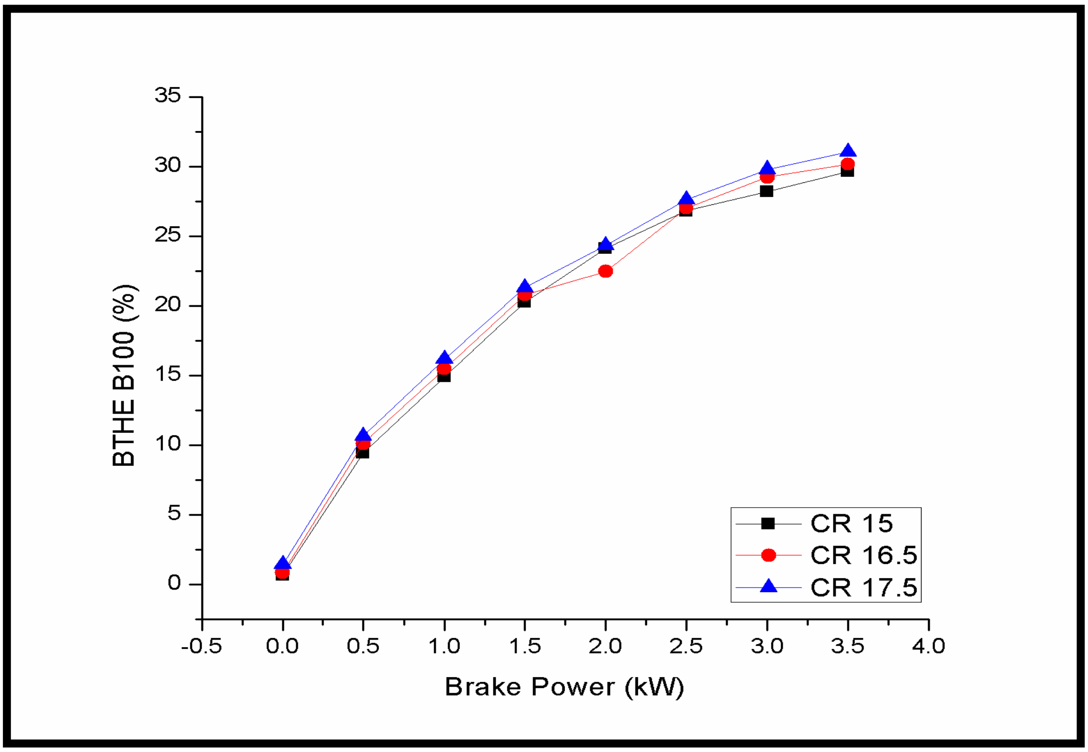


Figure 4.39 Trends of brake thermal efficiency Vs brake power (B100) at CR 15, 16.5 and 17.5

4.11.1.2 Brake Specific Energy Consumption

The BSEC is a significant characteristic for measuring the engine efficiency. It is the product of BSFC and LHV of the fuel. The variation of BSEC of various blends of waste cooking methyl ester (WCOME) with respect to BP at different compression ratios are depicted in **figures (4.40 to 4.45).** BSEC increased with increase in biodiesel proportions in the blend. The probable cause of this trend is LHV of biodiesel. The LHV of biodiesel-diesel content caused some reduction in the engine power. Due to this there was reduction in the effective power with the increase in biodiesel proportions in the fuel mixture. This resulted in more fuel consumption for maintaining the same amount of output power. The CR 17.5:1 exhibited lowest BSEC for all blends (B20, B40, B60, B80 and B100). BSEC decreased with increase in CR from 15:1 to 17.5:1. It is also noticed that BSEC decreased with increase of load among all compression ratios. At part loads the increase in BSEC was higher but as the load increased this value decreased and reached to lowest at full load condition.

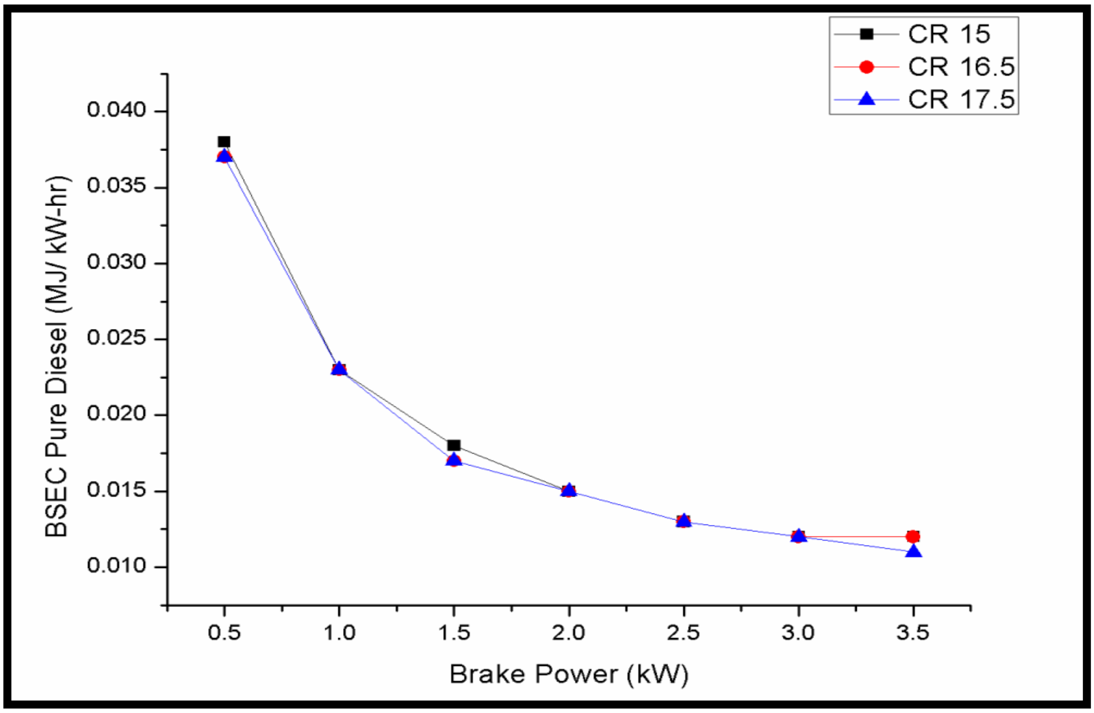


Figure 4.40 Trends of brake specific energy consumption Vs brake power (diesel) at CR 15, 16.5 and 17.5

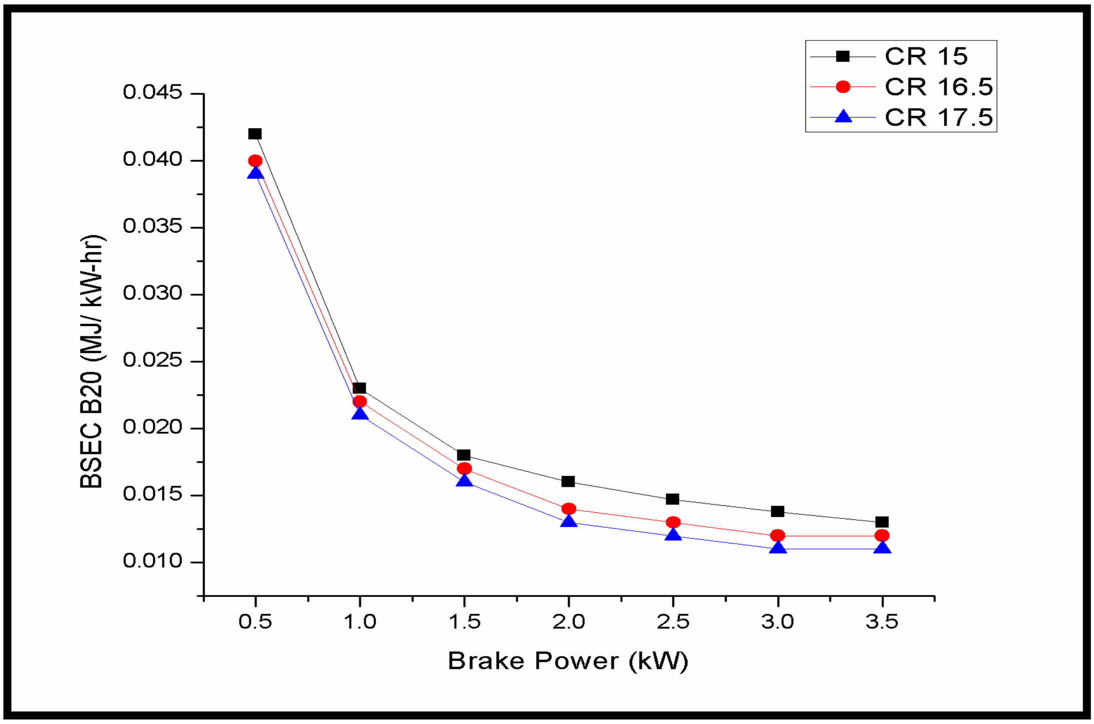


Figure 4.41 Trends of brake specific energy consumption Vs brake power (B20) at CR 15, 16.5 and 17.5

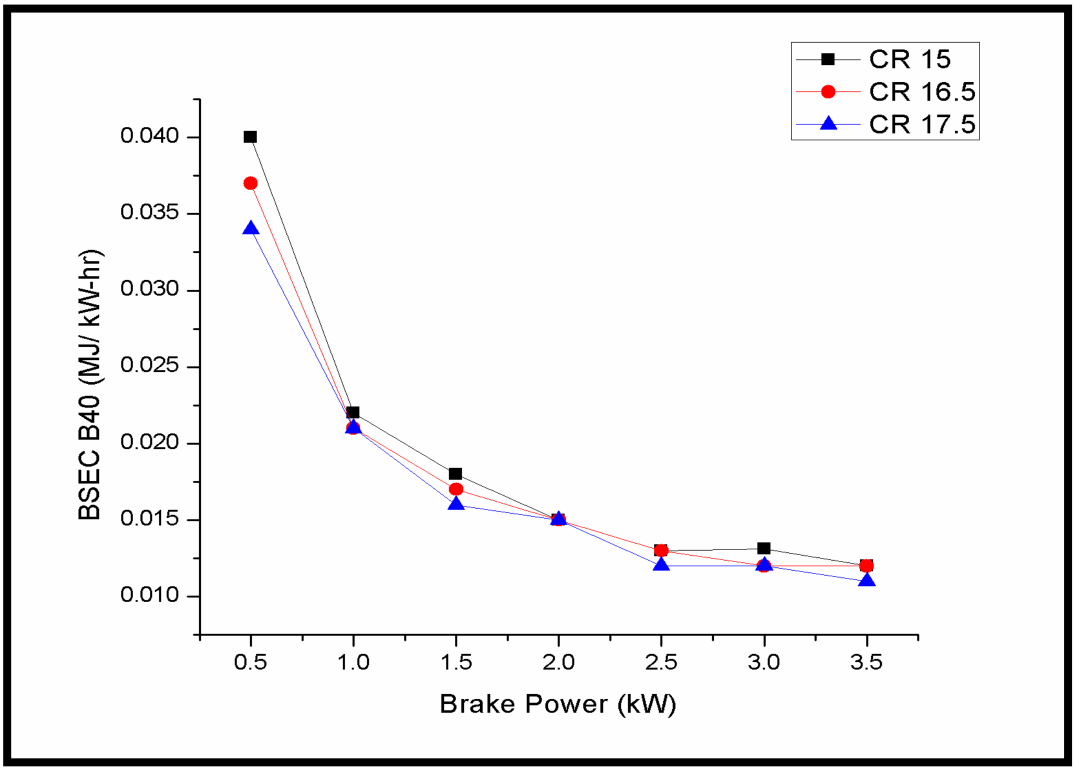


Figure 4.42 Trends of brake specific energy consumption Vs brake power (B40) at CR 15, 16.5 and 17.5

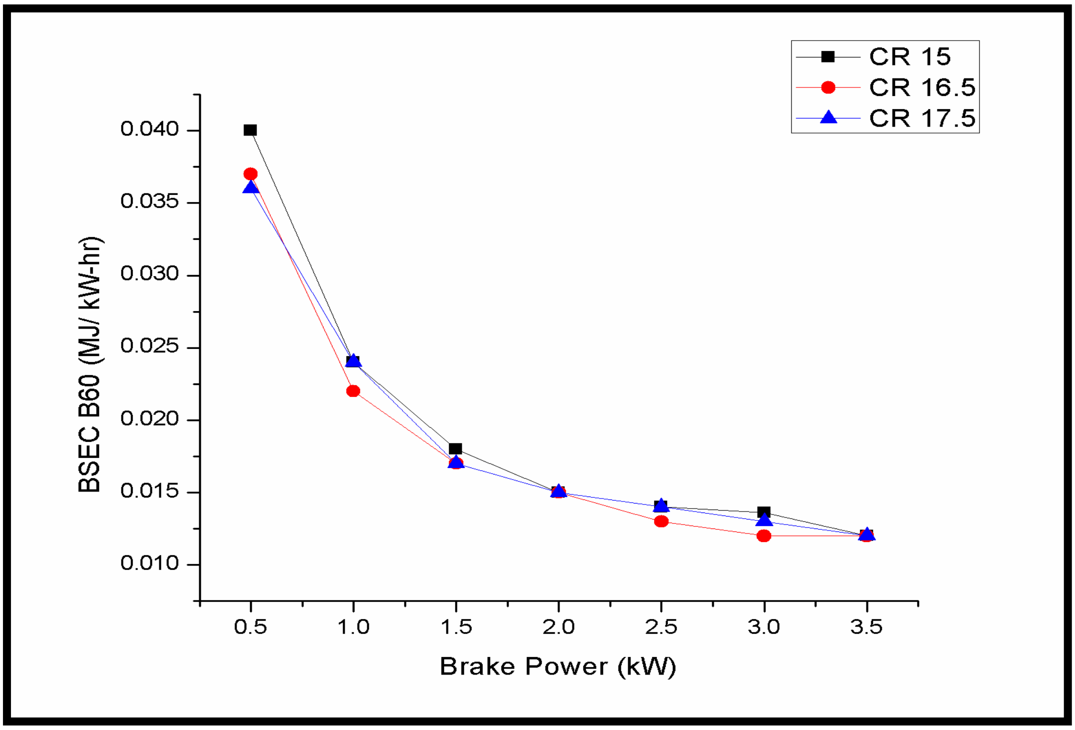


Figure 4.43 Trends of brake specific energy consumption Vs brake power (B60) at CR 15, 16.5 and 17.5

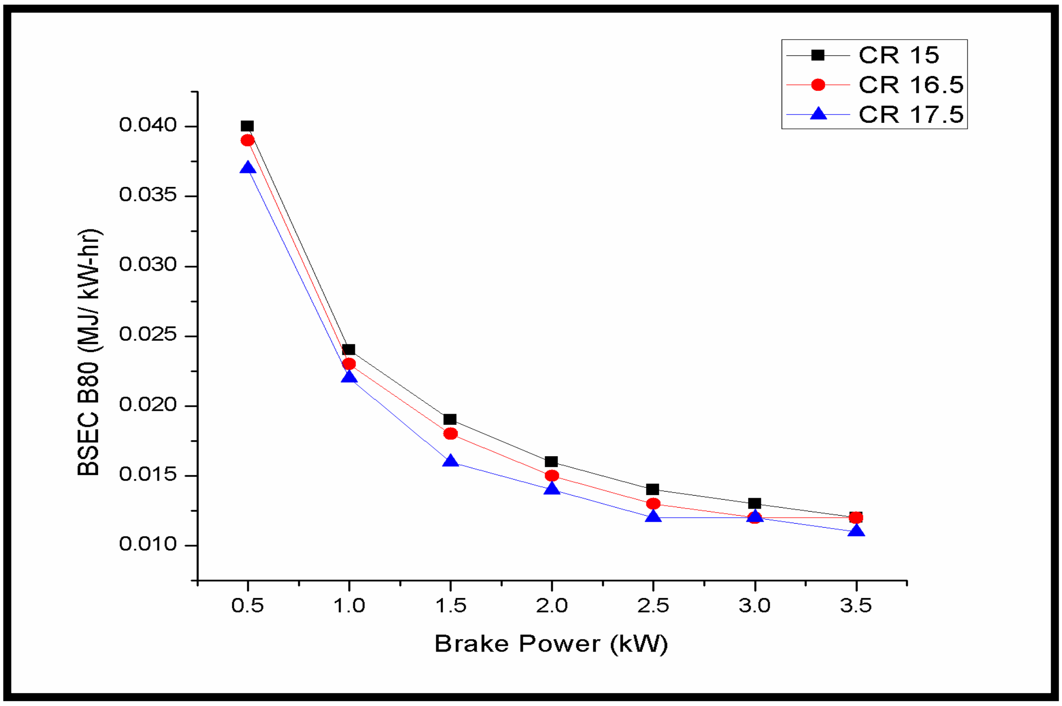


Figure 4.44 Trends of brake specific energy consumption Vs brake power (B80) at CR 15, 16.5 and 17.5

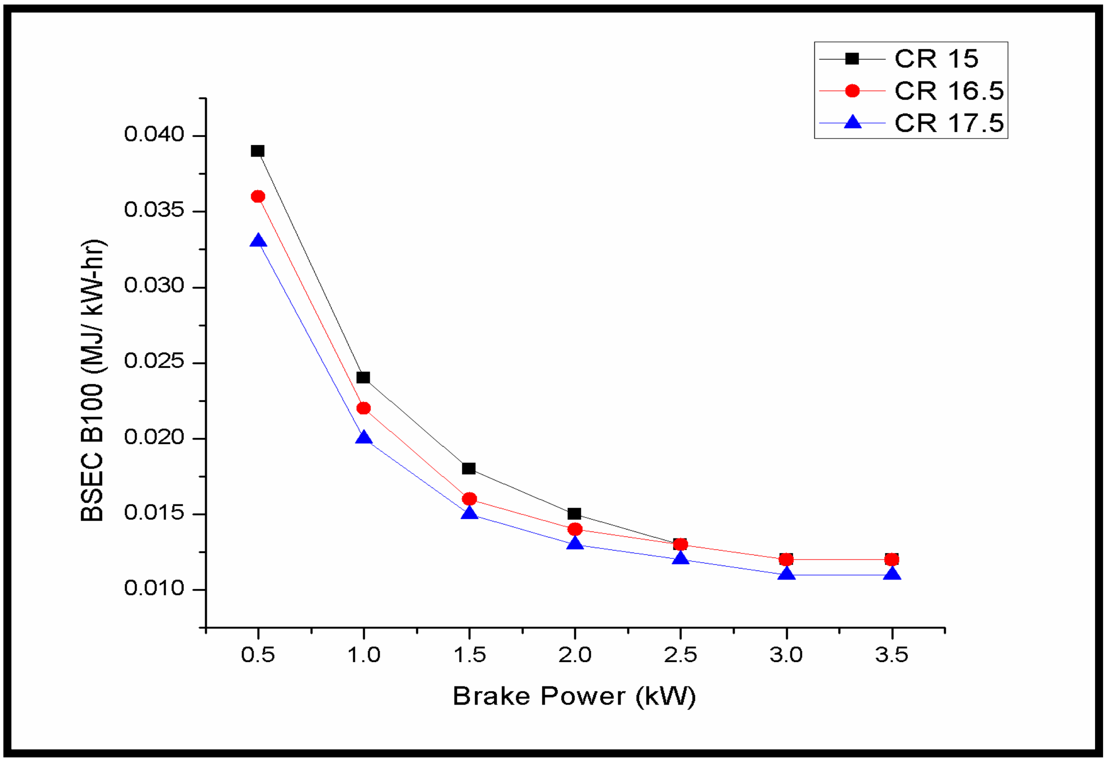


Figure 4.45 Trends of brake specific energy consumption Vs brake power (B100) at CR 15, 16.5 and 17.5

4.12 Emission Characteristics

The effects of compression ratio on engine emission parameters like CO, UHC, NOx and SO for different proportion of blends are discussed.

4.12.1 Carbon Monoxide Emissions

The CO emissions for different compression ratios, different proportions of blends and for diesel are described in the **figures (4.46 to 4.51).** It is observed that the CO emission decreased with an increase in CR. This could be due to the reason that the air temperature inside the cylinder increases with increase in compression ratio resulting in decreased delay period and better burning of the fuel.

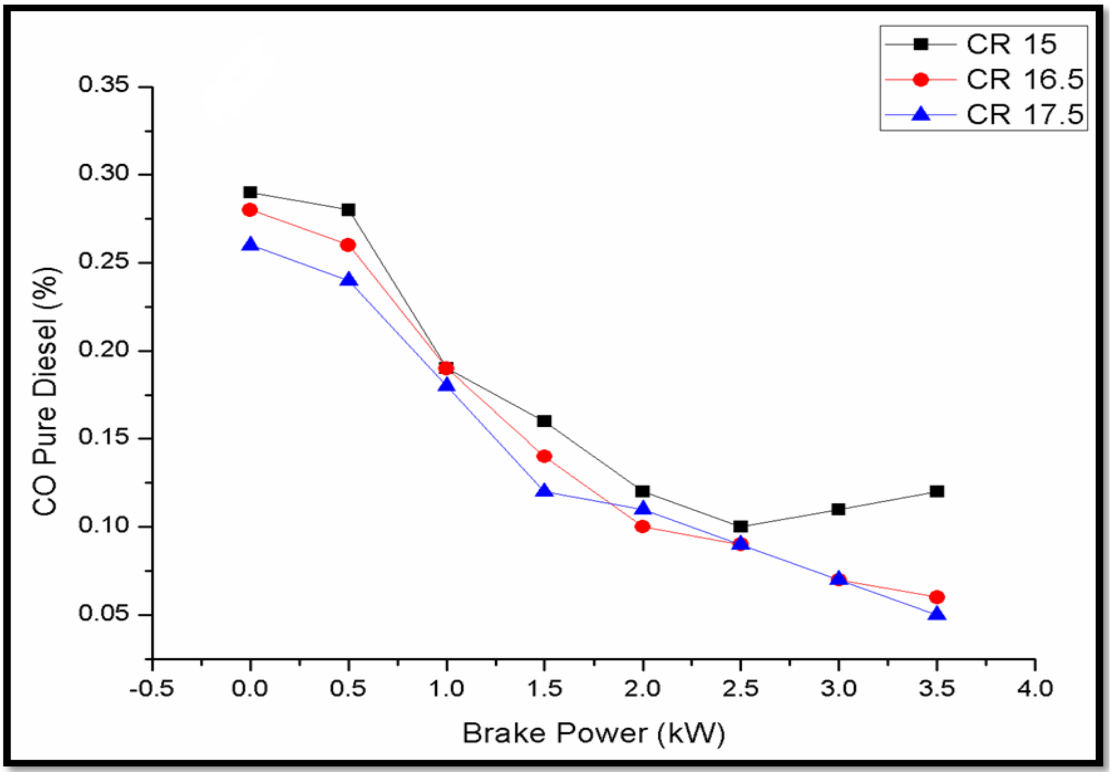


Figure 4.46 Trends of CO Vs brake power (diesel) at CR 15, 16.5 and 17.5

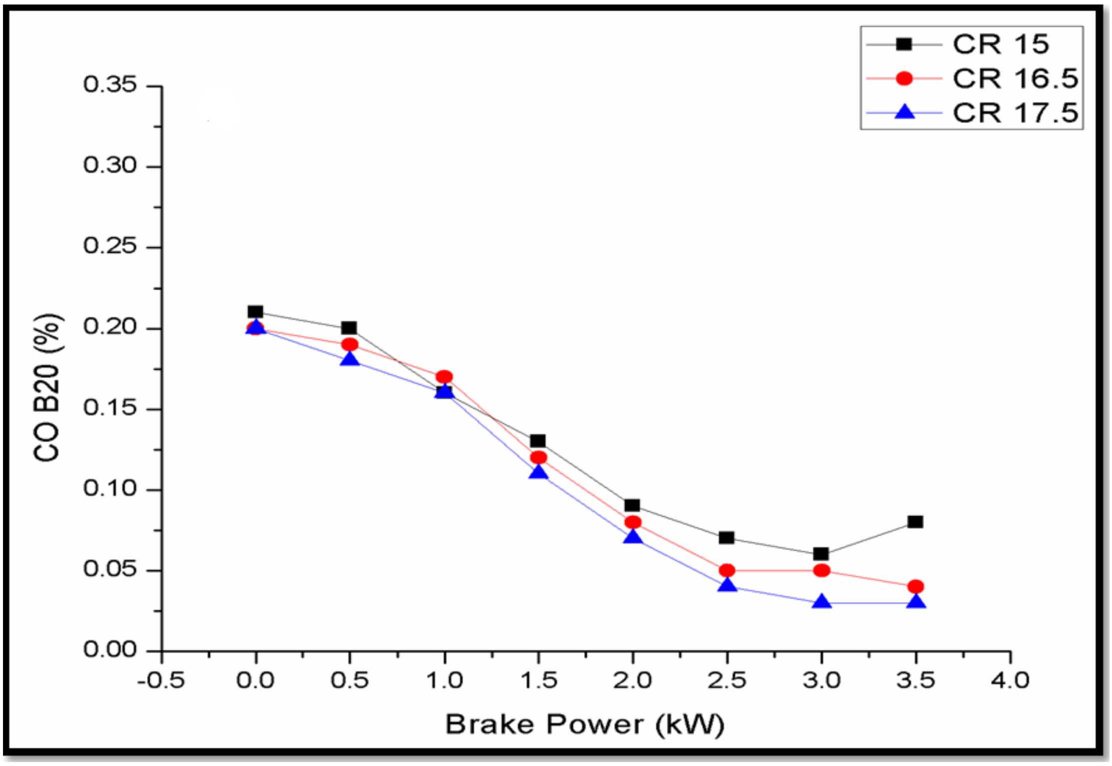


Figure 4.47 Trends of CO Vs brake power (B20) at CR 15, 16.5 and 17.5

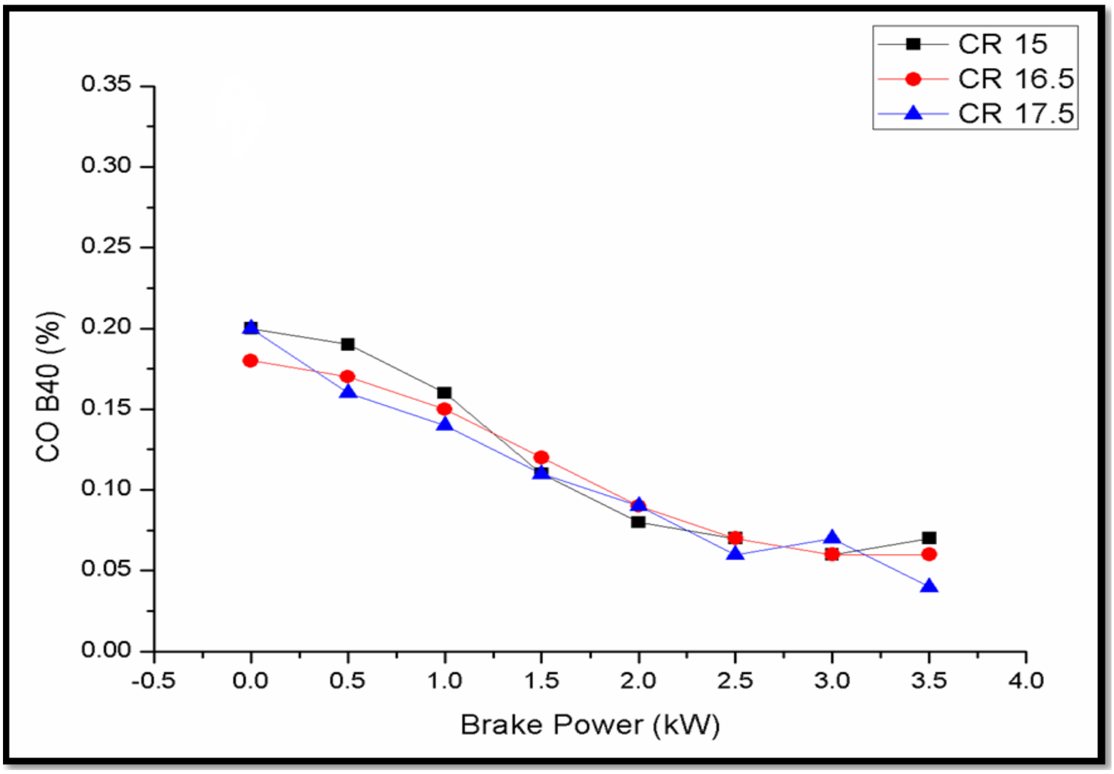


Figure 4.48 Trends of CO Vs brake power (B40) at CR 15, 16.5 and 17.5

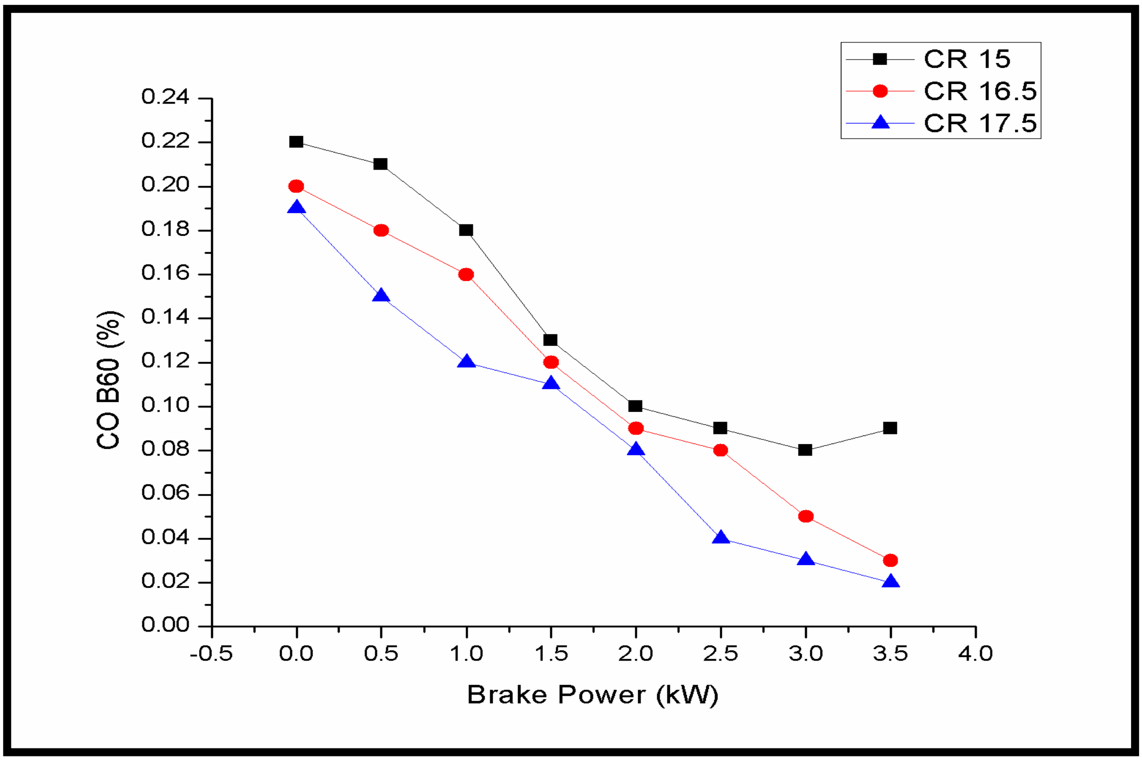


Figure 4.49 Trends of CO Vs brake ower (B60) at CR 15, 16.5 and 17.5

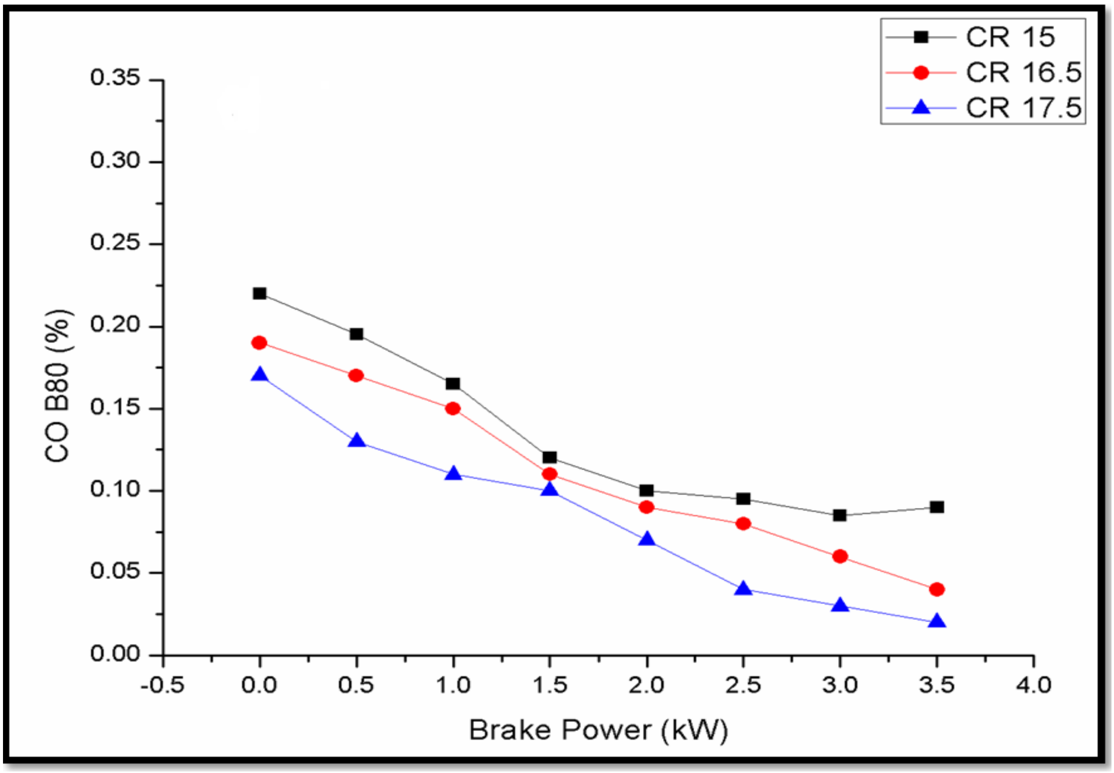


Figure 4.50 Trends of CO Vs brake power (B80) at CR 15, 16.5 and 17.5

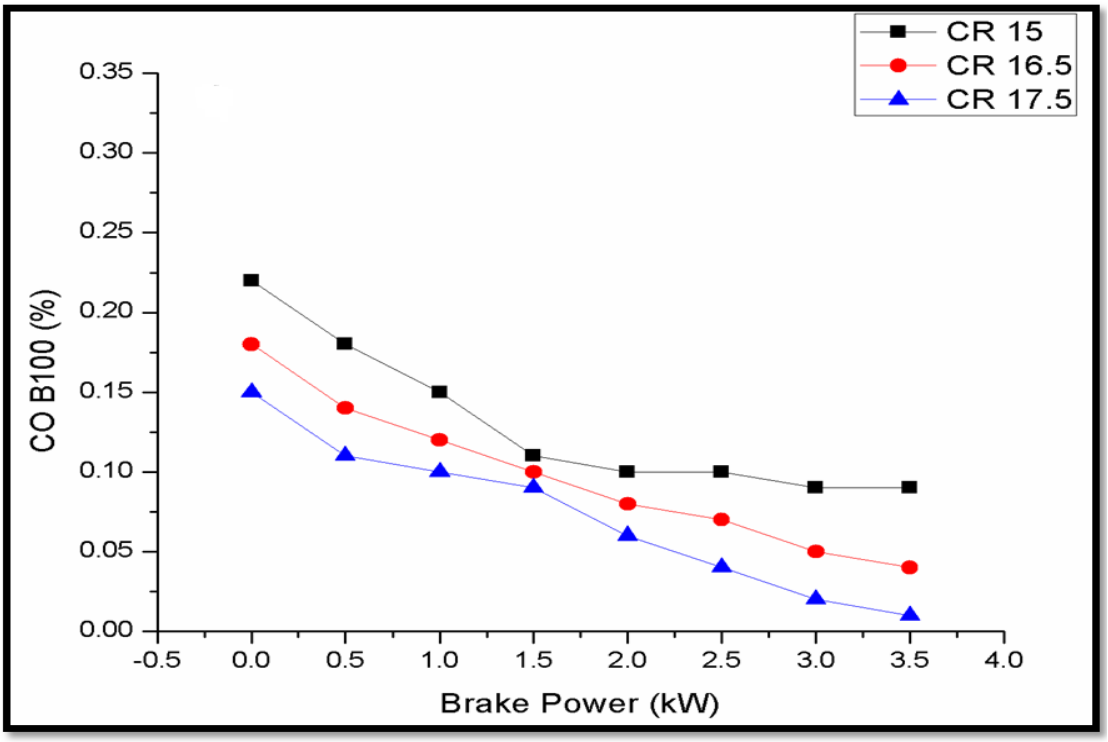


Figure 4.51 Trends of CO Vs brake power (B100) at CR 15, 16.5 and 17.5

By increasing the CR, the volumetric efficiency of engine was also increased whereas residual gas fraction decreased which permits more fresh air inside the chamber. Since CO is primarily dependent on the air/fuel ratio, the increase in the air/fuel ratio results in low CO emission. Similar results were also found for the blend B100 at all compression ratios (15:1, 16.5:1 and 17.5:1). This is because of higher temperature which decreases the ignition lag and in turn achieves complete combustion in cylinder. When compared to conventional diesel, the emission of CO decreased with an increase in blend proportions at all CR.

4.12.2 Hydrocarbon Emissions

The unburnt hydrocarbons are generally formed due to incomplete combustion of fuel. These unburnt hydrocarbons cause eye irritation and choking sensation which adversely affects the human health. The characteristic diesel exhaust odour is primarily because of these unburnt hydrocarbons. Furthermore they also put a negative impact on the environment. The main source of hydrocarbons in diesel engine is the little amount of combustible mixture in combustion chamber gets entrapped in its crevice volume which is inaccessible to flame. This results in incomplete combustion of gases. Bulk quenching of flame is another cause of incomplete combustion. Bulk quenching happens when flame extinguishes before reaching cylinder wall, a quench layer of the fuel is formed due to the unburnt mixture which is left on the wall. This occurs due to incomplete oxidation of the fuel.

The hydrocarbon emission for different CR and different proportions of blends and for diesel is explained in **figures (4.52 to 4.57)**. It is observed that the HC emission is inversely proportional to blend proportions and compression ratios (Lapuerta, Rodríguez-Fernández and Agudelo, 2008). At lower CR, the viscosity of the fuel is higher so there is under mixing of the fuel with air whereas, at higher CR the viscosity decreases and the mixing of the fuel with air increases resulting in complete combustion of the fuel and decreased HC emissions.

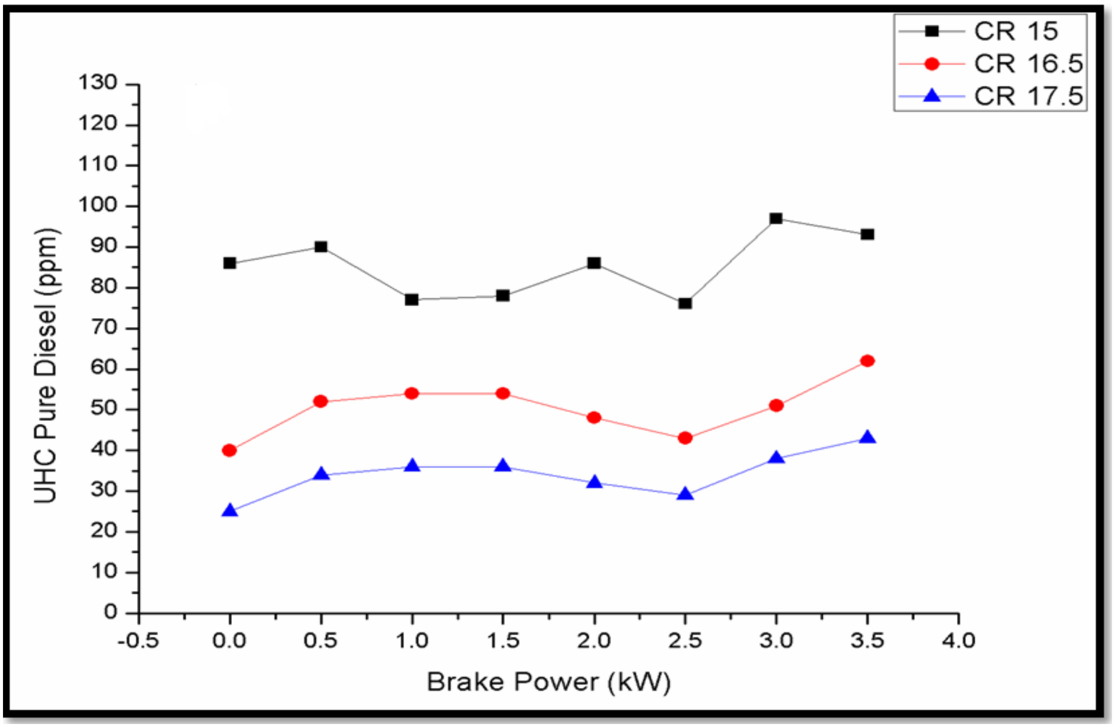


Figure 4.52 Trends of HC Vs brake power (diesel) at CR 15, 16.5 and 17.5

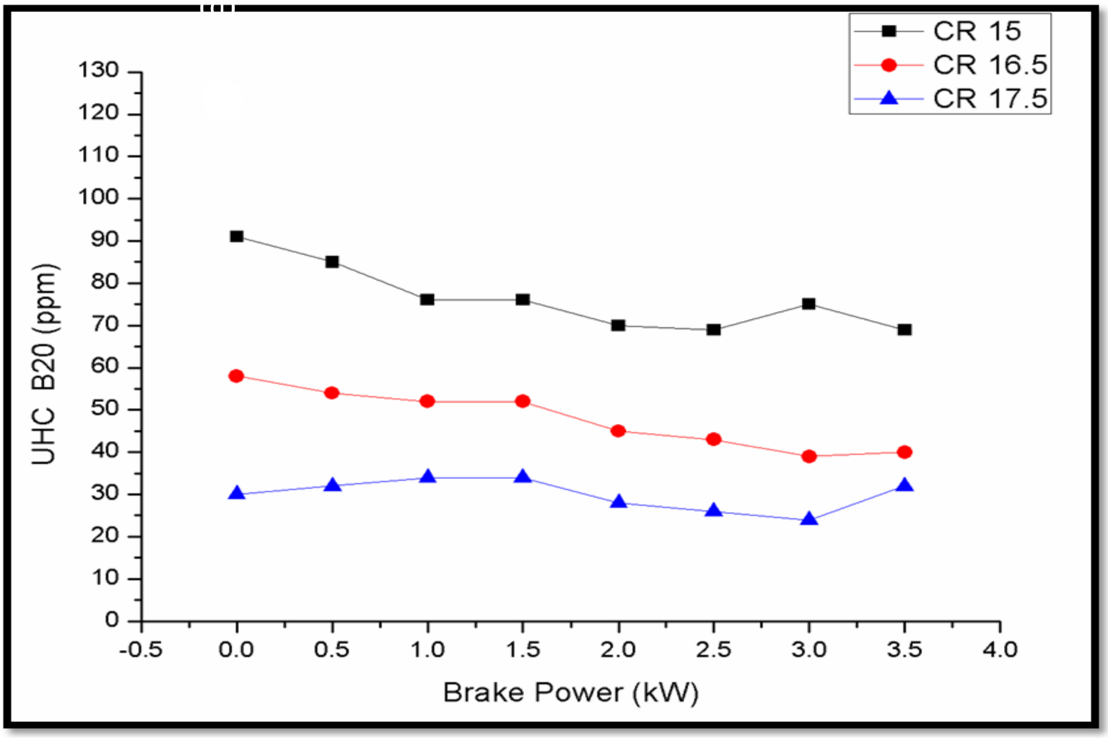


Figure 4.53 Trends of HC Vs brake power (B20) at CR 15, 16.5 and 17.5

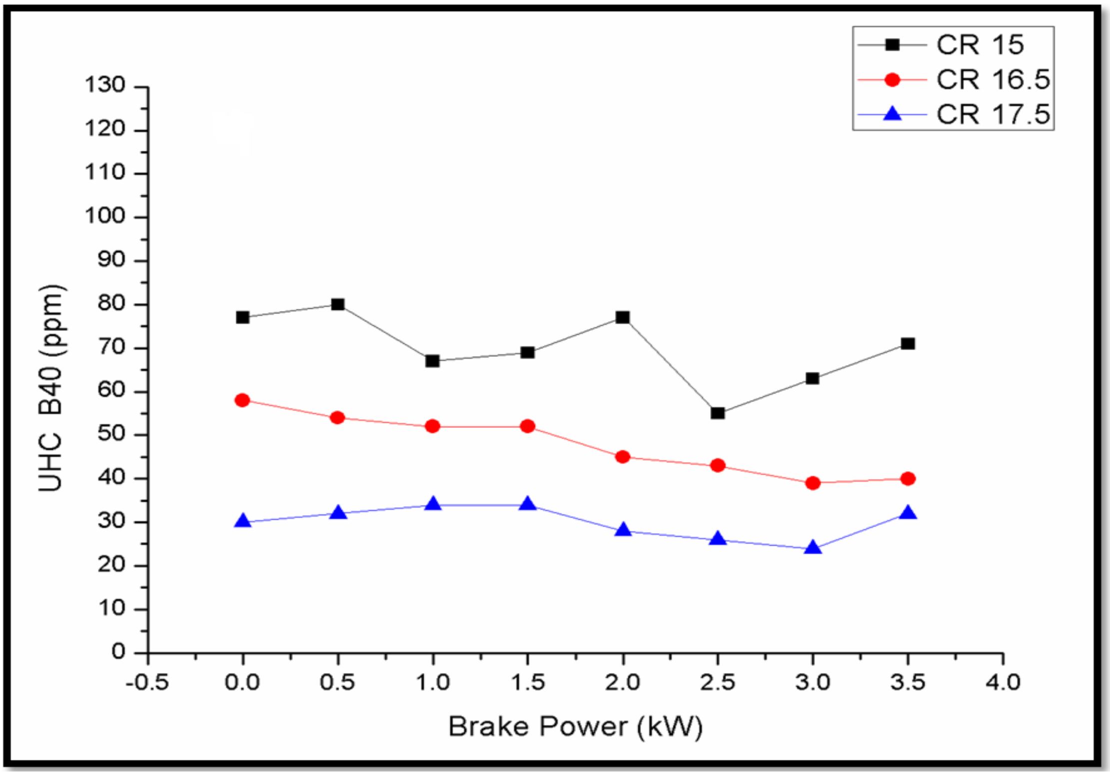


Figure 4.54 Trends of HC Vs brake power (B40) at CR 15, 16.5 and 17.5

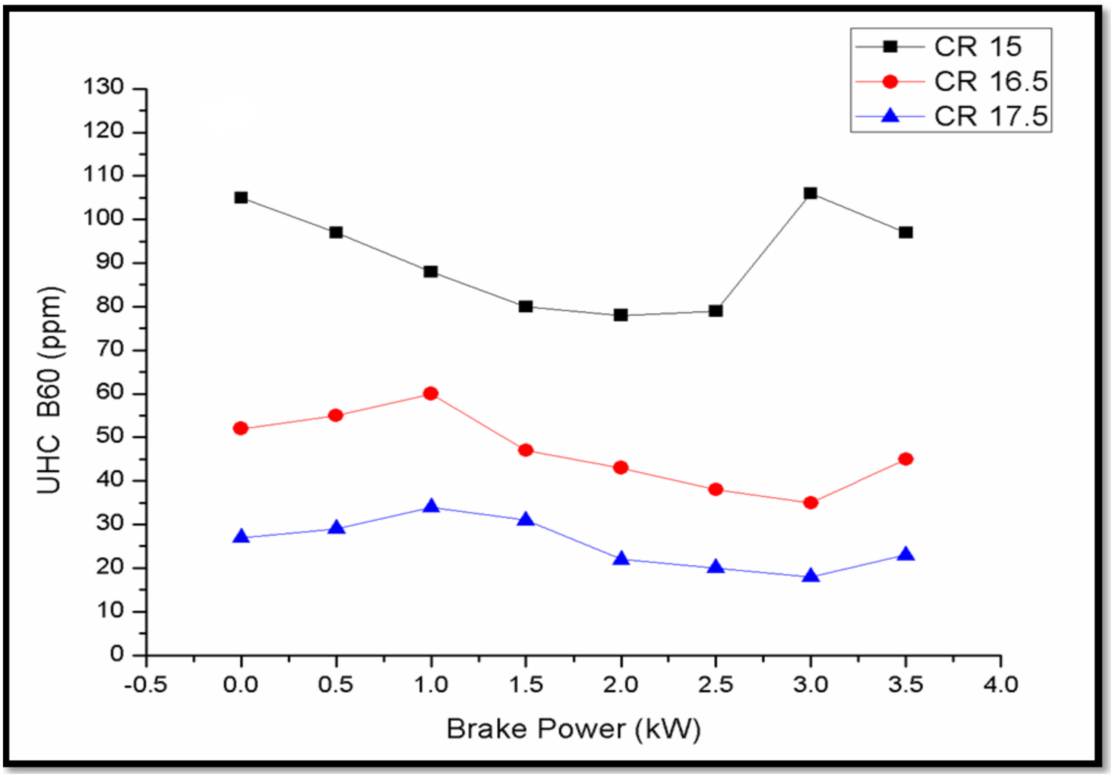


Figure 4.55 Trends of HC Vs brake power (B60) at CR 15, 16.5 and 17.5

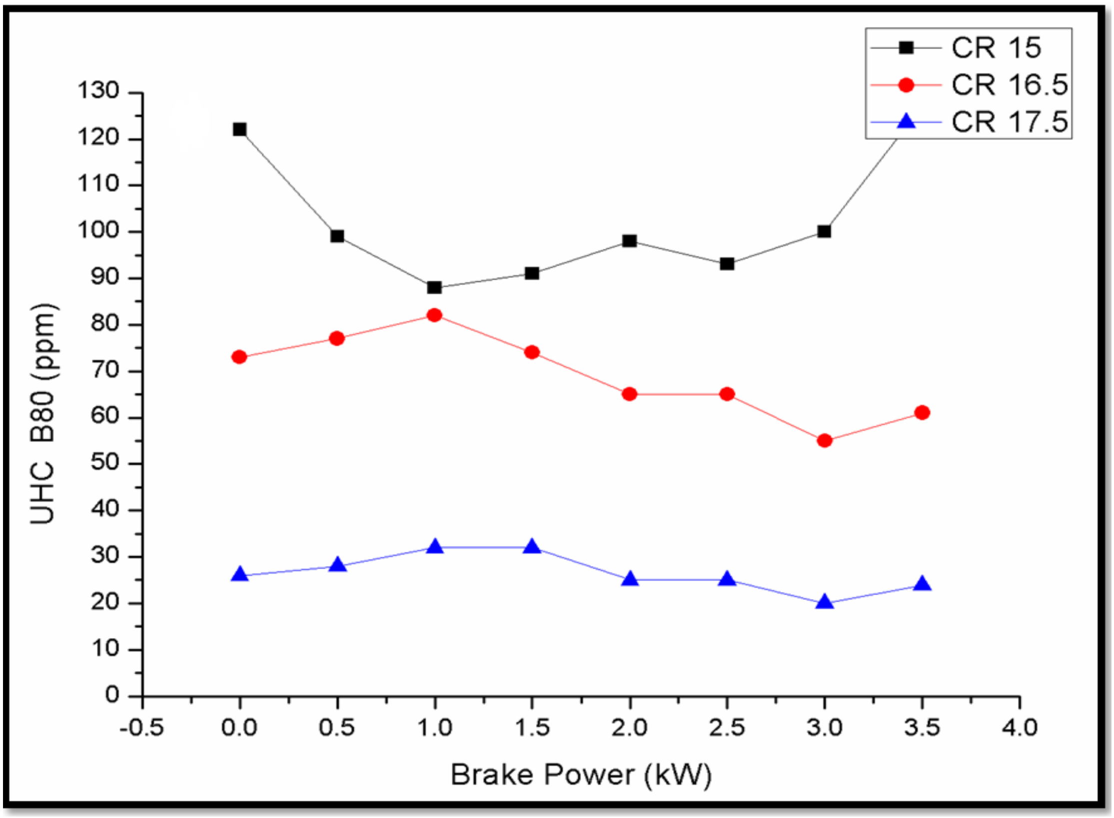


Figure 4.56 Trends of HC Vs brake power (B80) at CR 15, 16.5 and 17.5

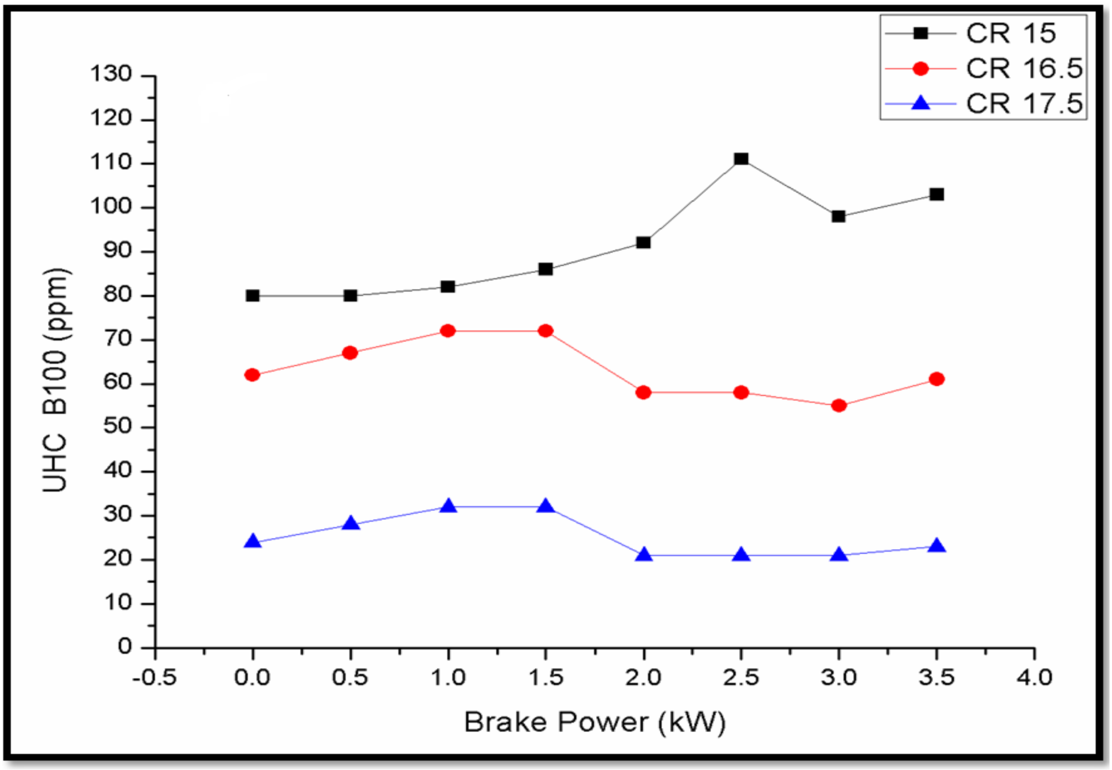


Figure 4.57 Trends of HC Vs brake power (B100) at CR 15, 16.5 and 17.5

4.12.3 Nitrogen oxide emissions

Nitrogen oxide is formed throughout the combustion chamber during the combustion process due to a chemical reaction between the atomic oxygen and nitrogen. Reaction forming NO_x are mainly temperature dependent. Due to this reason there is less NO_x emission from engine at lesser loads. Nitrogen oxide basically consists of nitrogen oxide (NO_2) and nitric oxide (NO). The nitrogen oxide emissions for different CR, different proportions of blends with diesel are examined and shown in the **figures (4.58 to 4.63).** It is found that the nitrogen oxide emission increased with an increase in CR for all WCOME blend proportions. This was due to the high temperature resulting in high burning rate with increasing CR at higher loads. Whereas, at lower CR less O_2 is available to form NO_x due to decreased temperature of compressed air. On the other hand at higher compression ratio sufficient amount of oxygen is available and higher heat of compressed air initiates early combustion ensuring complete oxidation of fuel. The figure also implies that the emission of nitrogen oxide with increase in blend proportion was higher than diesel.

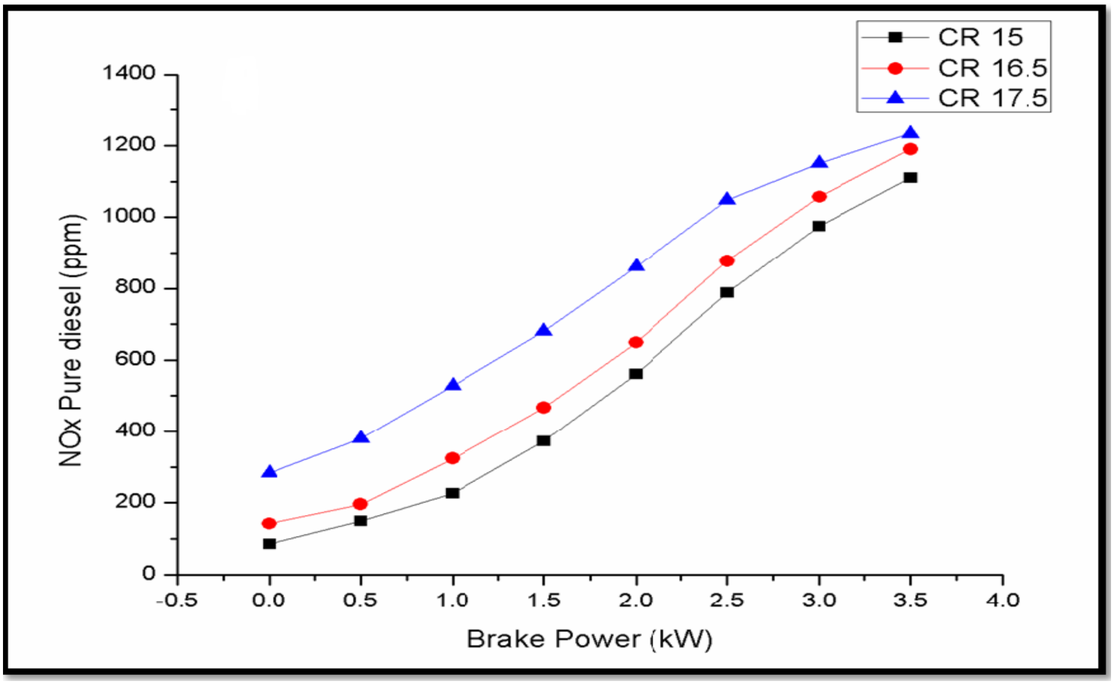


Figure 4.58 Trends of NO_x Vs brake power (diesel) at CR 15, 16.5 and 17.5

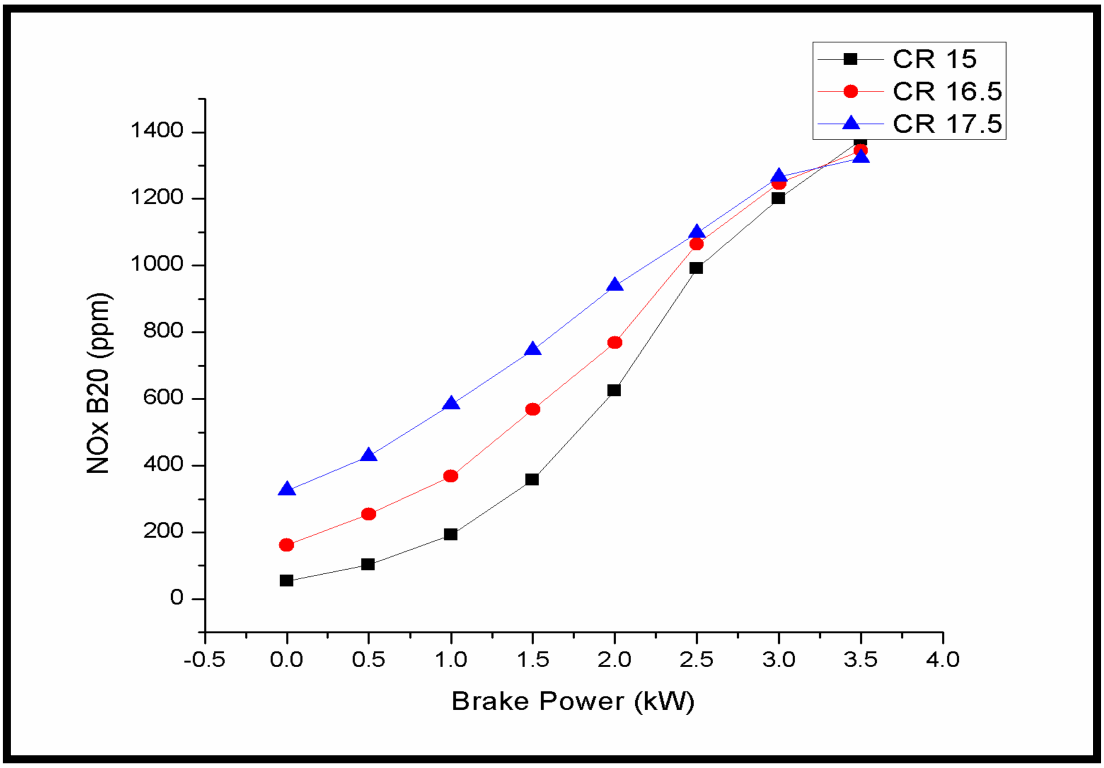


Figure 4.59 Trends of NO_x Vs brake power (B20) at CR 15, 16.5 and 17.5

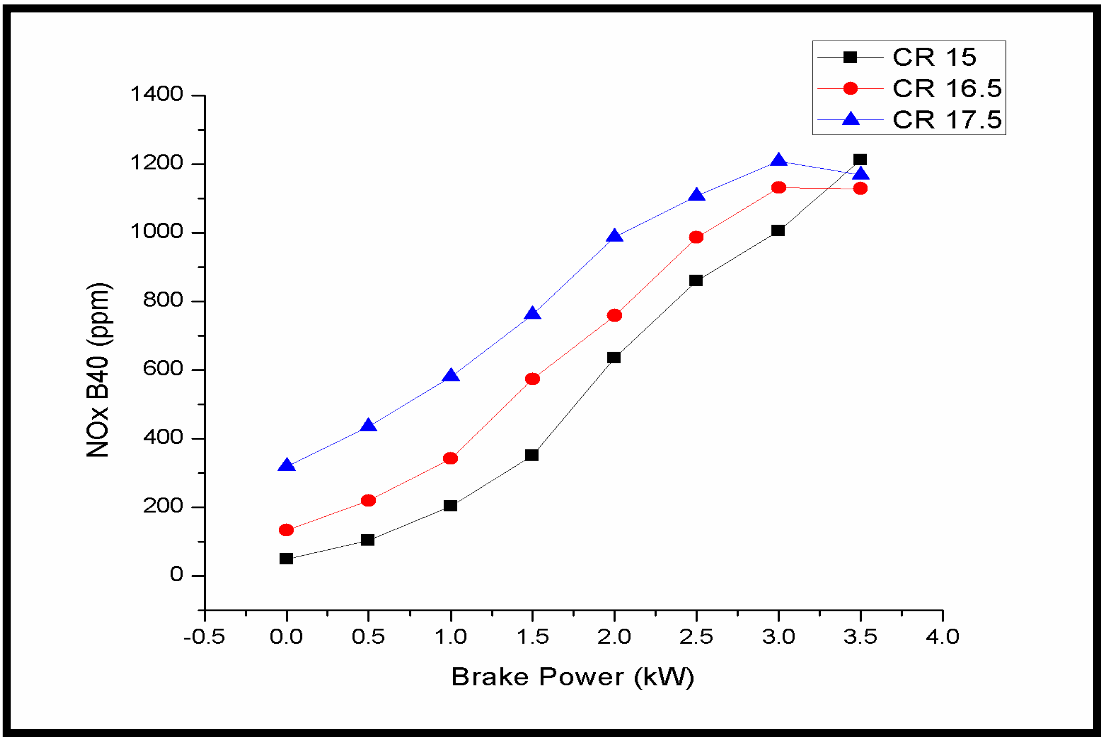


Figure 4.60 Trends of NO_x Vs brake power (B40) at CR 15, 16.5 and 17.5

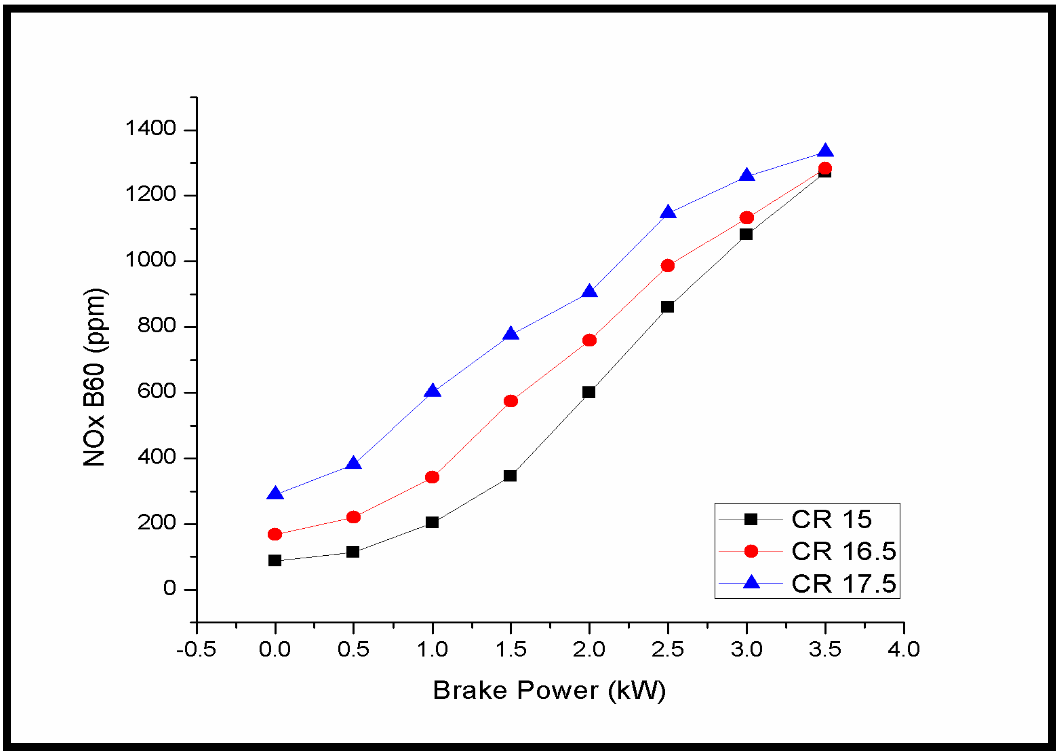


Figure 4.61 Trends of NO$_x$ Vs brake power (B60) at CR 15, 16.5 and 17.5

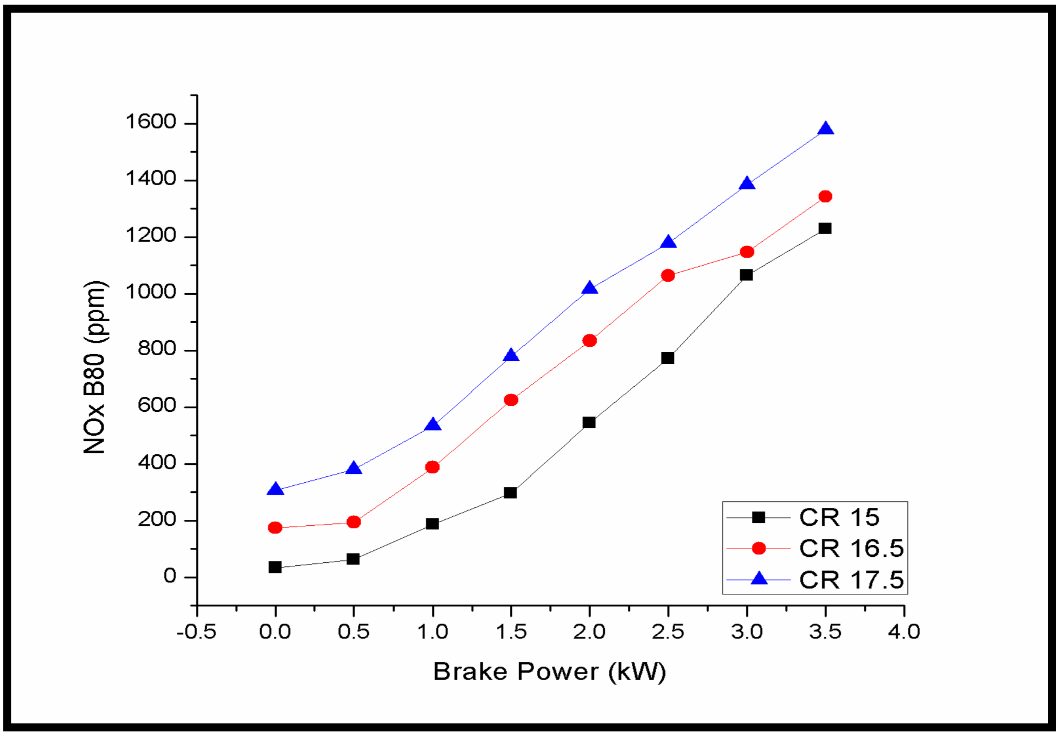


Figure 4.62 Trends of NO$_x$ Vs brake power (B80) at CR 15, 16.5 and 17.5

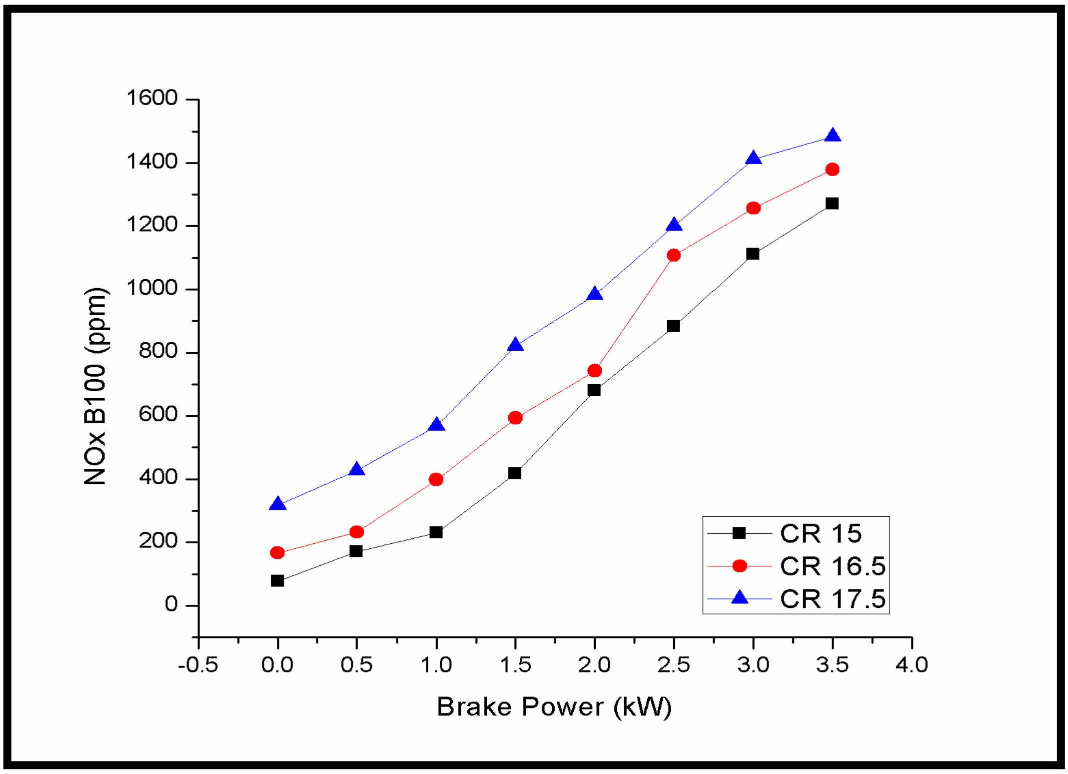


Figure 4.63 Trends of NO_x Vs brake power (B100) at CR 15, 16.5 and 17.5

4.12.4 Smoke opacity

The smoke opacity or smoke intensity is in the form of solid carbon, UHC in the exhaust gases. These emissions are a primary problem with diesel engine's heterogeneous combustion. Even partial oxidation products are considered under this category. Smoke emission is measured in HSU and represented in '%'. Higher HSU means that more fuel is burnt or the fuel burning process is interfered by some unfavorable conditions. It is revealed from the experiment that less smoke was formed at higher compression ratio for all fuel tested. The probable cause of these trends is because at higher compression ratio the heat of compressed air is high enough to cause complete combustion of fuel. On the other hand at lower compression ratio smoke was high because of incomplete combustion.

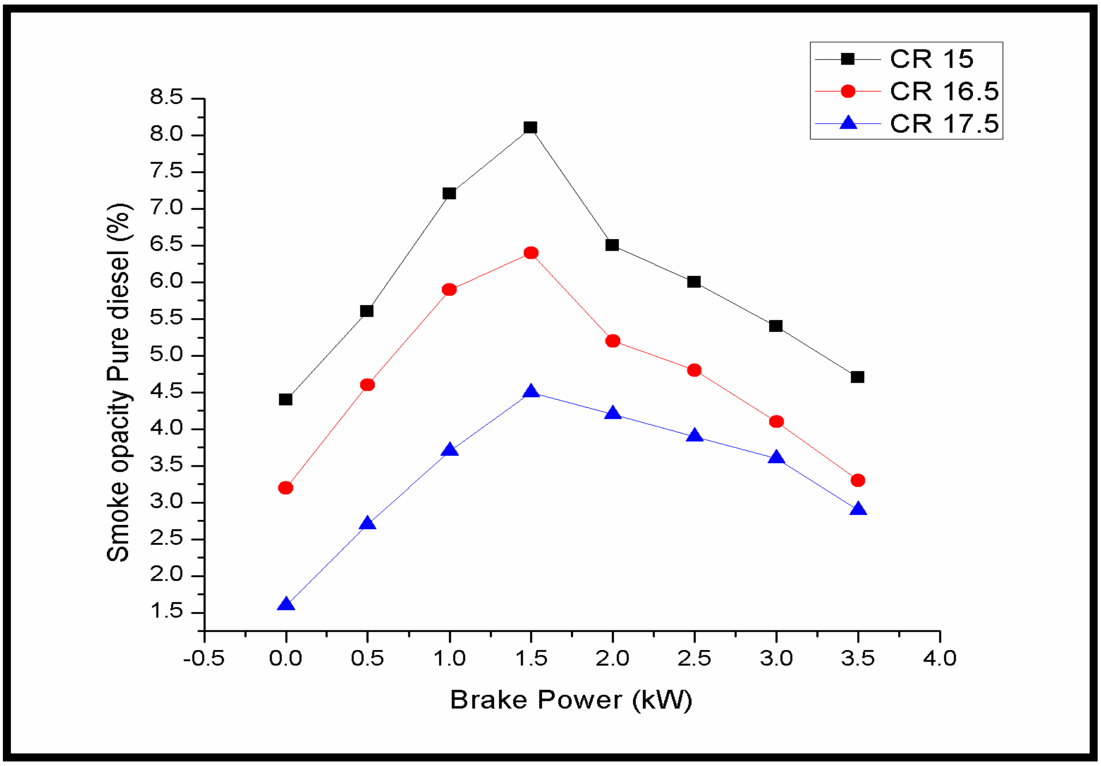


Figure 4.64 Trends of SO Vs brake power (diesel) at CR 15, 16.5 and 17.5

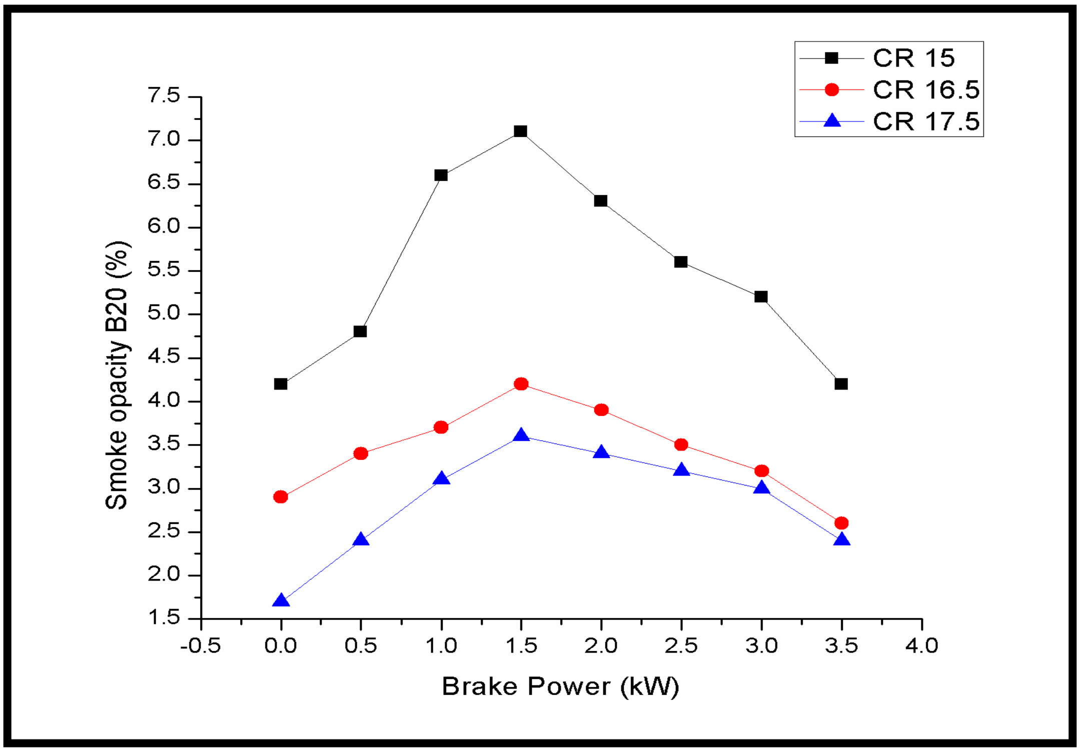


Figure 4.65 Trends of SO Vs brake power (B20) at CR 15, 16.5 and 17.5

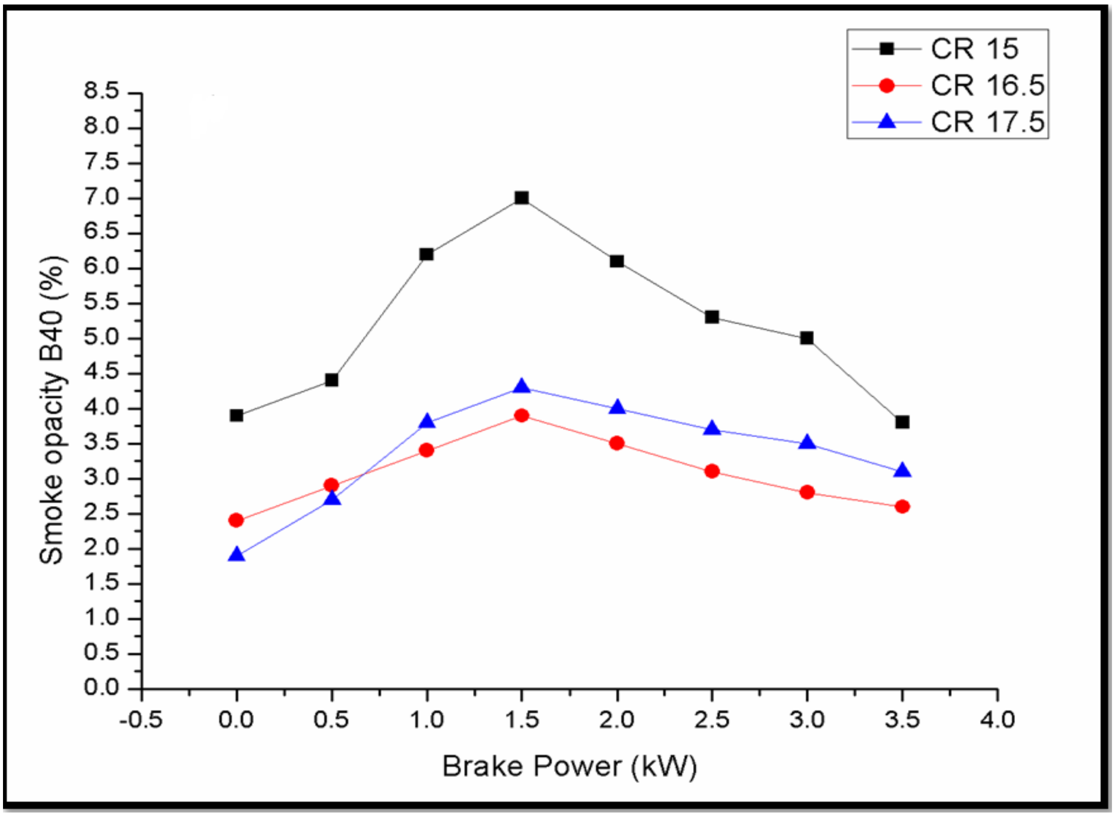


Figure 4.66 Trends of SO Vs brake power (B40) at CR 15, 16.5 and 17.5

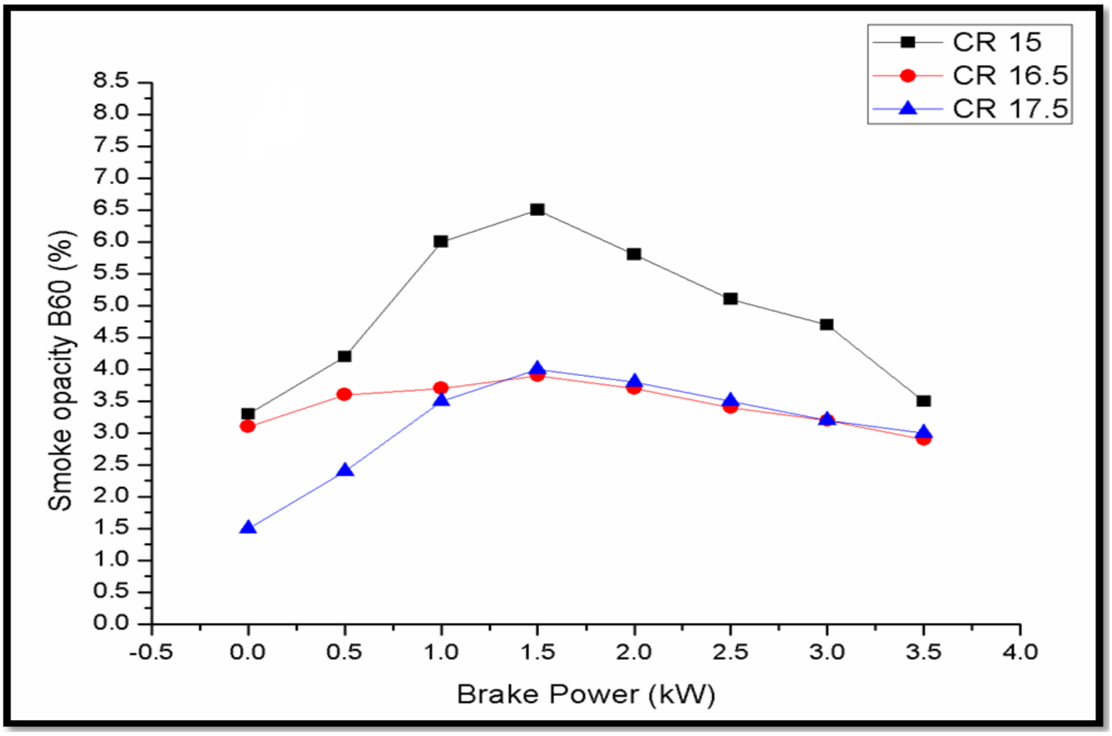


Figure 4.67 Trends of SO Vs brake power (B60) at CR 15, 16.5 and 17.5

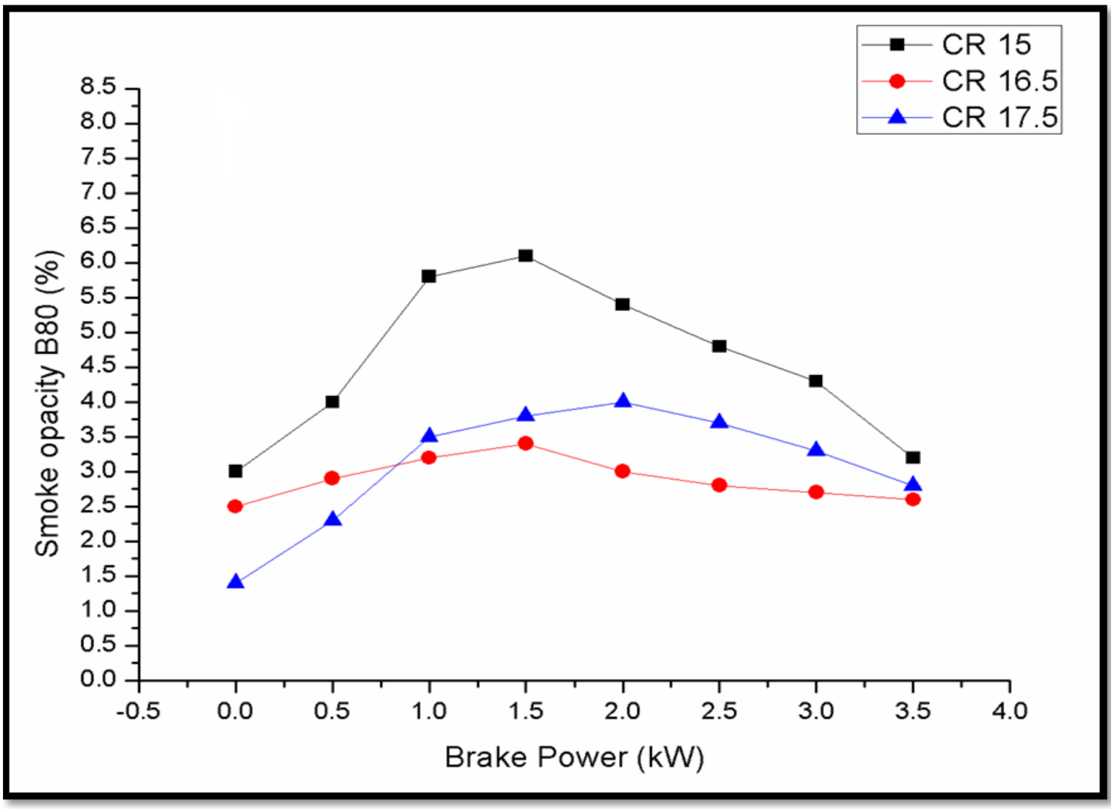


Figure 4.68 Trends of SO Vs brake power (B80) at CR 15, 16.5 and 17.5

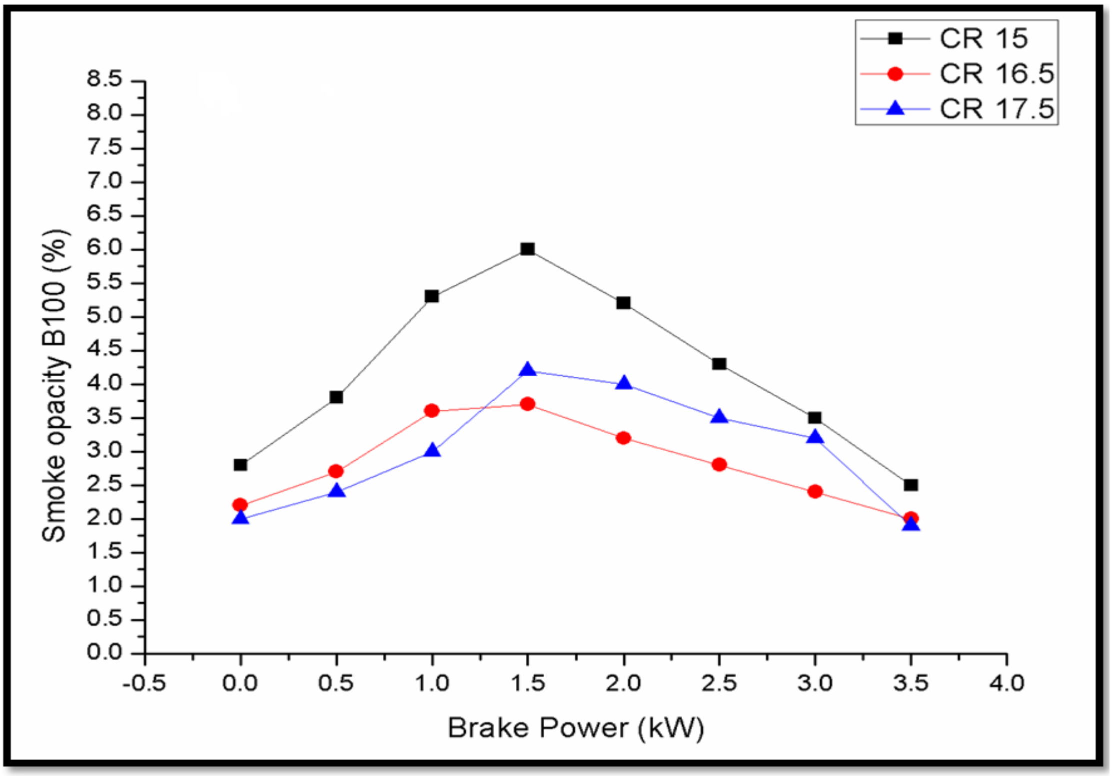


Figure 4.69 Trends of SO Vs brake power (B100) at CR 15, 16.5 and 17.5

Chapter-5

Conclusion
and
future scope

CHAPTER-5

5.1 Introduction

Biodiesel has attracted attention as a viable renewable energy source due to its lower greenhouse gas emission and its potential to reduce dependence on imported fossil fuels as well as meet the global energy demand. In the present thesis, work was carried out for the preparation and characterization of calcium and zinc doped calcium oxide heterogeneous catalysts. The respective catalyst was further utilized for production of biodiesel from waste cooking oil. The physical and chemical properties of produced biodiesel were determined and compared with the existing literature.

Moreover, this respective biodiesel in the form of blends such as B20, B40, B60, B80 and B100 with base line diesel were fuelled in single cylinder four stroke water cooled variable compression ratio direct injection compression ignition engine and checked its thermal performance and exhaust emissions at different compression ratios. The effects of different compression ratios (15, 16.5 and 17.5) on different blends such as B20, B40, B60, B80 and B100 on engine performance characteristics were also determined. On the basis of experimental study the major findings are enlisted below:-

5.2 Conclusion from Heterogeneous Catalyst Preparation and Biodiesel Production from WCO

- The heterogeneous catalyst prepared with 5 wt. % Zn in CaO at 700°C calcination temperature (5-Zn/CaO-700) by wet impregnation method has demonstrated better catalytic activity towards the methanolysis of waste cooking oil.

- Optimum values of the parameters, to achieve >98% fatty acid methyl ester yield, were: catalyst concentration of 5wt.%, methanol/oil molar ratio of 12:1 and reaction temperature 65°C.
- On using Cao as catalyst the yield obtained was 97.5% in 3 hours, whereas, doping of zinc on calcium oxide further enhanced the yield (more than 98%) in lesser reaction time i.e. 1hour 40 minutes.
- There was gradual increase in the conversion efficiency of waste cooking oil into its methyl ester with increase in calcination temperature of catalyst. The highest conversion was achieved at 700°C. Further increase in temperature beyond 700°C, the conversion efficiency deteriorated due to sintering of fine crystals and cluster agglomeration, reducing the activity of catalyst.
- The yield of biodiesel was increased with an increase in the molar ratio up to a value of 12:1. Consequently molar ratio between 9:1 and 12:1 gave the best results. Beyond 12:1, incomplete reaction was observed as the separation of glycerol was complicated and the apparent yield of biodiesel was reduced because a fraction of the glycerol remained in the biodiesel phase. For that reason, molar ratio 12:1 appears to be the most suitable.
- The complete conversion was achieved at 65°C and with further increase there was loss of methanol and lower catalytic activity probably due to the fact that methanol has a boiling point of nearly 65°C.
- The 5wt.% of Zn-Cao gave the maximum results in terms of biodiesel yield.

- The complete conversion was done in 1 hour 40 minutes. With further prolongation of reaction beyond this, no remarkable increase in the conversion was observed.
- Reusability of the 5Zn/Cao-700 catalyst was checked. The regenerated catalyst was utilized for four successive catalytic cycles under the same experimental and regeneration methods.

5.3 Conclusions from Experimental Work on Variable Compression Ratio CI Engine

5.3.1 Thermal Performance and Exhaust Emission

- The brake thermal efficiency increased with increase in compression ratios because brake thermal efficiency is directly proportionate to the compression ratio. Blend 40 among all fuel tested having CR 17.5 exhibited the maximum thermal efficiency at full load which was higher than the base line diesel.
- Brake specific energy consumption is a significant parameter which reflects the engine performance. For all fuels tested, brake specific energy consumption decreased with increase in load at both 15:1 and 17.5:1 compression ratios.
- Biodiesel provided significant reduction in CO at higher compression ratios. It may be expected due to complete oxidation. However, at CR of 15, the biodiesel showed slightly higher trends for CO emission than pure diesel mode.
- The emission of hydrocarbons (HC) tended to decrease with increasing the concentration of biodiesel in the blends which represents cleaner and complete combustion of the fuel.

- Constituents of NO_x for all fuels tested (Biodiesel and blends of biodiesel) is slightly higher than that of base line diesel fuel except B40. At B40 the lowest value of NO_x was obtained (i.e. 1129ppm at CR 16.5, 1168ppm at CR17.5 and 1212ppm at CR 15) for full load which is below the base line diesel.
- Smoke opacity of diesel, biodiesel and its blends was significantly higher at zero and part load conditions but as the load increased to maximum level, smoke opacity reduced effectively.
- The peak combustion pressure increased for all the blends. Highest value of peak combustion pressure was obtained at CR 17.5 at B80. The possible cause of this increase in combustion pressure is longer ignition delay that permits more fuel admitted into the cylinder. The lower combustion pressure values were obtained for B20 at CR 15, because of decreased ignition delay and lower calorific value of biodiesel.
- Exhaust gas temperature decreases with increased CR. This trend was consistent with all blends tested.

5.3.2 Compression Ratio Variation on Biodiesel - Diesel Blends

- Higher compression ratio led to improvement in the engine efficiency. This could be due to the lower volatility of the biodiesel blends as compared to conventional diesel resulting in improvement in their combustion characteristics due to higher compression ratio.
- Brake specific energy consumption decreased with increase of load among all compression ratios. At part loads the increase in specific energy consumption was higher but as the load increased, this value

decreased and reached to lower at full load condition. The compression ratio 17.5:1 exhibit lowest BSEC for all blends.

- CO emission decreased with an increase in compression ratio. This could be due to the reason that the air temperature inside the cylinder increased with increase in compression ratio resulting in decreased delay period and better burning of the fuel.
- The higher hydrocarbon emissions were observed at lower compression ratio because of ignition delay and flame quenching inside the cylinder leading to poor combustion.
- It is found that the nitrogen oxide emission increased with an increase in compression ratio for all waste cooking oil methyl ester blend proportions.
- Less smoke is formed at higher compression ratio for all fuels tested.

5.4 Summary of work

In this work, a series of the Zn/CaO was prepared by wet impregnation method, keeping the calcination temperature constant at 700°C. The catalyst prepared with 5 wt.% Zn in CaO at 700°C calcination temperature (5-Zn/CaO-700) has demonstrated better catalytic activity towards the methanolysis of waste cooking oil. Optimum values of the parameters, to achieve > 98 % fatty acid methyl ester yield, were: catalyst concentration of 5 wt.%, methanol/oil molar ratio of 12:1 at 65°C. Physicochemical properties of the FAME prepared from waste cooking oil were studied, and observed values were found within the limits of ASTM D 6751 and EN 14214 specifications.

Further tests have been conducted on CI engine which runs at a constant speed of 1500 rpm, injection pressure of 200 bar, variable compression ratio

(15:1, 16.5:1 and 17.5) and variable engine load. The performance parameters include brake thermal efficiency, brake specific energy consumption and emission parameters such as carbon monoxide (CO), hydrocarbons (HC), oxides of nitrogen (NO_x) and smoke opacity varying with engine load (BP). The core findings from the engine experimental work on variable compression ratio CI engine in terms of thermal performance and emission are given below:-

- **B40 among all fuel tested having CR 17.5 exhibited the maximum thermal efficiency (31.40%) at full load which was higher than diesel.**
- **The brake specific energy consumption decreased with increase in load at all CRs (15:1, 16.5:1 and 17.5:1).**
- **Biodiesel provided significant reduction in CO at CR 17.5:1 as compared to diesel.**
- **Hydrocarbons emission decreased with increasing the concentration of biodiesel in the blends which represents cleaner and complete combustion of the fuel. The lowest value 23 ppm for B40 was obtained at 2.5 kW brake power for CR 17.5.**
- **Constituents of NO_x for all fuels tested (biodiesel and blends of biodiesel) were slightly higher than that of diesel fuel except B40. At B40 the lowest value of NO_x was obtained (i.e. 1129 ppm at CR 16.5, 1168 ppm at CR17.5 and 1212 ppm at CR 15) for full load which is below the base line diesel.**
- **The smoke opacity for pure biodiesel (B 100) and their blends are lower than that of diesel fuel. Smoke opacity for biodiesel diesel blends decreased due to enrichment oxygen content in the fuel (Yadav and Singh, 2010)**

- **The peak combustion pressure increased for all the blends. Highest value of peak combustion pressure of 69 bar was obtained at CR 17.5 for B80. The possible cause of this increase in combustion pressure is longer ignition delay that permits more fuel admitted into the cylinder. The lowest combustion pressure value of 51.61 bar was obtained for B20 at CR 15.**
- **Exhaust gas temperature decreases with increase in CR. This trend was consistent with all blends tested.**
- **The results stated above indicate that biodiesel can be used without any modification in the engine and is an alternative environmental friendly fuel. Using waste cooking oil as feedstock and zinc doped calcium oxide as heterogeneous catalyst for biodiesel production, makes the process economical and environmental benign. Moreover it will also solve the problem of air pollution as well as help in proper utilization of waste cooking oil.**

5.5 Future Scope

- In future, other transition metals such as tungsten, nickel and iron based mixed oxide may be prepared and used as catalyst for simultaneous transesterification and esterification to produce biodiesel.
- In present work the catalyst was prepared by wet impregnation method. There are some other methods such as sol-gel, template assisted, solvothermal, and hydrothermal could also be explored for heterogeneous catalyst preparation in order to improve the stability.

- Non-conventional heating method such as microwave, may be used for catalyst preparation and biodiesel trans-esterification in order to reduce the reaction time and production cost.
- The common byproducts produced while processing the biodiesel are glycerol which is the byproduct of trans-esterification. The production of value-added chemicals such as propanediol, acrolein, polyglycerol, tartonic acid, hydrogen, synthesis gas and liquid chemicals etc. from glycerol may lead to decrease in biodiesel prices.
- In order to solve the problem of glycerol management, research can be further extended to search a biodiesel production method in which no glycerol is produced. A method has been developed by the Saka and Isayama termed as Saka-Isayama process. In this process, there is interesterification of triglycerides with methyl acetate in presence of prepared catalysts. In this process glycerol is not produced and mixture of FAME and triacetin can be used directly as biodiesel.

Furthermore, the experimental work on the variable compression ratio engine brings out the possibilities for future research.

- Thermal performance, emission and combustion of variable compression ratio engine may be experimentally studied using different biodiesels, their blends with conventional diesel and their blends with ethanol concentration for various compression ratios.
- Fuel injection pressure and injection timing may be varied and the experimental study may be carried out in variable compression ratio engine.

- The higher NO_x noticed during the experimental work may be reduced by the use of exhaust gas recirculation in the variable compression ratio engine.
- The effect of biodiesel on the engine wear and tear can also be tested in further researchers.
- Thermal performance, emission and combustion tests for biodiesel made from different feedstocks on multi cylinder compression ignition and surface transportation engine such as tractor, bus, trucks etc. can be studied.

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PUBLICATIONS FROM PRESENT RESEARCH WORK

1. **Kataria, J., Mohapatra, S.K. and Kundu, K.,** 2017. Biodiesel production from frying oil using zinc-doped calcium oxide as heterogeneous catalysts. ***Energy Sources, Part A: Recovery, Utilization, and Environmental Effects***, *39*(9), pp.861-866. DOI : 10.1080/15567036.2016.1270376.

   Publisher: Taylor and Francis, **Category:** SCI, **Impact Factor:** 0555.

2. **Kataria, J., Mohapatra, S.K. and Kundu, K.,** 2018. Biodiesel production from waste cooking oil using heterogeneous catalysts and its operational characteristics on variable compression ratio CI engine. ***Journal of the Energy Institute*****,** **https://doi.org/10.1016/j.joei.2018.01.008**.

   Publisher: Elsevier, **Category:** SCI, **Impact Factor:** 4.217.

APPENDIX – I

VCR ENGINE SETUP SPECIFICATION

S.No	Components	Details
1.	Engine	Make Kirloskar, Type 1 cylinder, 4 stroke Diesel, water cooled, power 3.5 kW at 1500 rpm, stroke 110 mm, bore 87.5 mm, 661 cc, CR 18, Modified to VCR engine CR range 12 to 18
2	Dynamometer	Make Saj test plant pvt ltd, Model AG10, Type Eddy current
3.	Dynamometer loading unit	Make Apex, Model AX-155, Type constant speed, supply 230V AC
4.	Manometer	Make Apex, Model MX-104, Range 100-0-100 mm, Type U tube, Conn. ¼’’ BSP hose back side
5.	Fuel measuring unit	Make Apex, Glass, Model FF0.012
6.	Piezo sensor	Make PCB Piezotronics, Model HSM111-A22, Range 5000 psi, Diaphragm stainless steel type and hermetic sealed
7.	Crank angle sensor	Make Kubler-Germany Model 8.3700. 1321.0360 Dia37 mm shaft Size: 6 mm x Length 12.5 mm, supply voltage 5-30V DC, output push pull (AA, BB, OO), PPR: 360
8.	Data acquisition Device	NI USB- 6210 Bus powered M series
9	Temperature sensor	Make Radix type K, Ungrounded Sheath, Dia 6mm x 110mm length, SS 316,

		Connection ¼’’ BSP (M)
10	Temperature sensor	Make Radix type K, Ungrounded SheathDia 6mm x 1110mm length, SS 316, Connection ¼’’ BSP (M) adjustable compression fitting
11.	Temperature Transmitter	Make Wika, Model T19.10.3 K0-4NK-Z, Input thermocouple (type K), Output 4-20mA, supply 24 VDC, calibration 0-1200°C
12.	Temperature Transmitter	Make Wika, Model T 19.10.1PO-1 Input RTD (Pt 100), ouput 4-20mA, supply 24 VDC, calibration 0-100° C
13.	Load sensor	Make SensotronicsSanmar Pvt Ltd., Model 60001, Type S Beam, Universal capacity 0–50 kg
14.	Load indicator	Make Selectron, Model PIC 152- B2, 85 to 270V AC, retransmission output 4-20mA
15.	Fuel flow transmitter	Make Yokogawa, Model EJA110-EMS-5A-92NN, Calibration range 0-500 mm H_2O, Output linear
16.	Air flow transmitter	Range (-) 250 mm WC
17.	Rotameter	Make Eureka Model PG 5, Range 25-250 lph, 40-400 lph Connection ¾’’ BSP vertical

APPENDIX – II

TECHNICAL SPECIFICATION OF AVL 437 SMOKE METER

Accuracy and Reproducibility : ± 1% full scale reading.

Measuring range : 0 - 100% capacity in %

0 - ∞ absorption m^{-1}.

Measurement chamber : effective length 0.430 m ± 0.005 m

Heating Time : 220 V …… approx. 20 min

Light source : Halogen bulb 12 V / 5W

Colour temperature : 3000 K ± 150 K

Detector : Selenium photocell dia. 45 mm

Max. sensitivity in light,

In Frequency range: 550 to 570 nm.

Below 430 nm and above 680 nm

sensitivity is less than 4% related to the

maximum sensitivity.

Maximum Smoke : 250ºC

Temperature at entrance

TECHNICAL SPECIFICATION OF AVL Di-GAS ANALYZER

Measurement principle	CO, HC, CO_2	Infrared measurement
Measurement principle	O_2	Electrochemical measurement
	NO (option)	
Operating temperature	+5 ……. +45º C	Keeping measurement accuracy
	+1 ……. +50ºC	Ready for measurement
	+5 ……. +35º C	with integral NO sensor (Peaks of : +40ºC)
Storage temperature	-20 ….. +60º C	
	-20 ….. +50º C	With integrated O_2 sensor
	-10 ….. +45º C	With integrated NO sensor
	0 ….. +50º C	With water in filter and / or pump
Air humidity	90% max., non-condensing	
Power drawn	150 VA	
Dimensions	432 x 230 x 470 mm (w x h x l)	
Weight	16 Kg	

APPENDIX – IV

Instrument conditions, calibrations, observation, reading and test planning are responsible for errors and uncertainties. Uncertainty analysis is needed to prove the accuracy of the experiments. In any experiment, the final result is calculated from the primary measurements. The error in the final result is equal to the maxi-mum error in any parameter used to calculate the result. Percentage uncertainties of various parameters like total fuel consumption, brake power, brake specific fuel consumption and brake thermal efficiency was calculated using the percentage uncertain-ties of various instruments used in the experiment. The total percentage of uncertainty of an experiment can be calculated as given below.

The total percentage uncertainty = Square root of [(uncertainty of BP)^2 + (uncertainty of BSEC)^2 + (uncertainty of TFC)^2 + (uncertainty of BTE)^2 + (uncertainty of HC)^2 + (uncertainty of CO)^2 + (uncertainty of NOx)^2 + (uncertainty of EGT)^2 + (uncertainty of SO)^2 + (uncertainty of pressure pick up)^2 + (uncertainty of crank angle encoder)^2]

The total percentage uncertainty = Square root of $[(0.2)^2 + (1.5)^2 + (1.5)^2 + (1.5)^2 + (1)^2 + (0.2)^2 + (0.1)^2 + (0.2)^2 + (1)^2 + (0.3)^2 + (1)^2]$

= 2.7%

The total percentage uncertainty = 2.7%

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Jatinder Kataria started his professional education with diploma in automobile engineering from Govt. Polytechnic, Ambala City, (Haryana) in 2000. The he worked in different Automobile Industries from 2000 to 2003. He completed his Bachelor Degree (Mechanical Engineering) from NC College of Engineering, Israna, Panipat, (Haryana) in year 2006. From 2006 to 2008 he worked in different Mechanical Industries. He joined the Master in Mechanical Engineering in 2008 at DCRUST, Murthal, Sonipat, (Haryana) and completed in 2011. Further he had joined has Assistant Professor in Mechanical Engineering at E-Max Institute of Engineering and Technology, Ambala, (Haryana) from January 2012 to December 2013. Presently he has doing Ph.D. (Thermal Engineering) from Thapar Institute of Engineering and Technology (Deemed to be University), Patiala, (Punjab).

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