

Optimization of Process Parameters for Production of Linseed Bio-fuel and Performance Investigation of Diesel Engine Fuelled with Linseed Biodiesel

A thesis submitted in the partial fulfillment of the requirements for the award of degree of

**Master of Engineering
In
Thermal Engineering
By
Chamandeep Singh
Roll No. 801283005**

Under the guidance of

Dr. Madhup K. Mittal
Assistant Professor
Mechanical Engg. Deptt.
Thapar University
Patiala


Dr. Krishnendu Kundu
Scientist and Head
Department of biofuels
CSIR-CMERI
Ludhiana



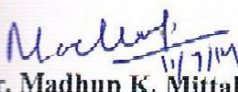
**DEPARTMENT OF MECHANICAL ENGINEERING,
THAPAR UNIVERSITY, PATIALA-147004, PUNJAB, INDIA
JULY 2014**

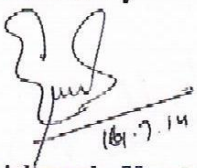
DECLARATION

I have declared that the thesis entitled "Optimization of Process Parameters for Production of Linseed Bio-fuel and Performance Investigation of Diesel Engine Fuelled with Linseed Biodiesel" is an authentic record of my study carried out as requirement for the award of degree of Master of Engineering (Thermal) at Thapar University, Patiala under the guidance of Dr. MADHUP KUMAR MITTAL, Assistant Professor, Department of Mechanical Engineering Thapar University, Patiala and Dr. KRISHNENDU KUNDU, Head of Department of Bio-fuels, CSIR-CMERI, Ludhiana. The matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any other degree.



(Chamandeep Singh)
Reg.No.801283005

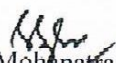
This is to certify that above declaration made by student concerned is correct to best of my knowledge & belief.


Dr. Madhup K. Mittal
Assistant Professor
Mechanical Engg. Deptt.
Thapar University
Patiala


Dr. Krishnendu Kundu
Scientist & Head
Department of Bio-fuels
CSIR-CMERI, Ludhiana

Countersigned by


Prof. Ajay Batish
Professor and Head,
Mechanical Engg. Deptt.,
Thapar University,
Patiala


Prof. S.K. Mohapatra
Dean of Academic Affairs,
Thapar University,
Patiala

ACKNOWLEDGEMENTS

With deep sense of gratitude I express my sincere thanks to my guide, Dr. MADHUP KUMAR MITTAL, for their valuable guidance, proper advice and constant encouragement during my work on this seminar. Working under their guidance is of immense pleasure and very worth full in the context of knowledge.

I would also like to thank Dr. KRISHNENDU KUNDU, Scientist E-1, MERADO, Ludhiana, for providing necessary facilities during my work at MERADO Lab, Ludhiana.

I also wish to thank the staff at MERADO who supervised me during the production of Biodiesel and staff of Internal Combustion engine laboratory, Thapar University who supervised me during the estimation of performance and emission characteristics of the C.I. engine.

I also wish to thank Dr. Ajay Batish, Head of department, Mechanical Engineering Department, Thapar University, Patiala.

I am very thankful to my friends and colleagues for their encouragement and support in building up this thesis report.



Chandandeep Singh

Roll No. 801283005

Thermal Engineering

Mechanical Engineering Department

Thapar University, Patiala

ABSTRACT

Biodiesel is receiving increased attention as an alternative, biodegradable, non-toxic and renewable diesel fuel. It is produced from vegetable oils and animal fats by using transesterification reaction. Due to continuous depletion of fossil fuels the global prices of crude petroleum are hiked considerably which is bound to affect the economy of many countries. In country like India, where edible oils are imported it would be worthwhile to explore the possibility of using non edible oils for biodiesel production. It will also help to avoid the fuel versus food conflict. Therefore in the present study, linseed oil has been chosen for biodiesel production. In this work optimization of parameters, such as molar ratio, catalyst concentration, catalyst type, reaction temperature and reaction time, controlling the production yield of linseed oil methyl ester was achieved. A large number of experiments were required to optimize the process parameters of linseed biodiesel production by full factorial design. So, Taguchi approach of orthogonal arrays (L18) was used to design the experiments and perform optimization by considering fewest experiments. Only 18 experiments were performed which were equivalent to 243 experimental situations. The optimal combination of controlling parameters was found to be 1.5% catalyst concentration by weight, 60°C reaction temperature, 60 minutes reaction time and by the use of KOH as catalyst. Theoretically 93.13% production yield of biodiesel was expected by using optimum conditions. By producing linseed oil methyl ester by optimal combination of experimental conditions obtained from Taguchi method 98.4% yield was achieved which was more than the expected yield. Statistical technique ANOVA (analysis of variance) was used to study the influence of different parameters on biodiesel production yield. Among all the parameters catalyst concentration was found to be most dominating with 31.86% contribution, followed by catalyst type with 24.95% contribution. Molar ratio and reaction time were found to be least significant parameters with only 1.99% and 20.32% contributions respectively for transesterification of linseed oil. The fuel properties of optimally produced linseed biodiesel were observed to be comparable to that of pure diesel and were also conforming to latest biodiesel standards. The various performance and emission parameters like brake mean effective pressure (BMEP), brake power (BP), brake specific fuel consumption (BSFC), mechanical efficiency (Mech. Eff.), brake thermal efficiency (BthEff), CO emissions, CO₂ emissions, HC emissions, NO_x emissions were evaluated at different loads and compression ratios in a 4 stroke, single

cylinder variable compression ratio engine. These performance and emission parameters of diesel fuel were compared with that of B10, B20, and B30. The performance parameters of B10 blend were observed to be nearly similar to that of pure diesel fuel at all load conditions. B10 blend showed better performance parameters than all other blends of biodiesel. At higher compression ratios the performance of engine was observed to be better. The brake specific fuel consumption of engine was lowest for B10 blend among all the blends. The different emissions parameters of engine such as CO, CO₂, and HC were observed to be nearly similar to the diesel fuel for B10 blend. With increase in amount of blend these emissions were decreased. Among all the blends, these emissions were found to be lowest for B30 blend while the NO_x emissions were found to be lowest for B10 blend among all three blends. The CO and HC emissions were observed to be decreased at higher compression ratios while NO_x and CO₂ emissions were increased for higher compression ratios.

TABLE OF CONTENTS

TITLE	PAGE NO.
DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iii-iv
TABLE OF CONTENTS	v-vii
LIST OF FIGURES	viii-ix
NOMECLATURE	x-xi
LIST OF TABLES	xii
Chapter 1 INTRODUCTION	1-11
1.1 Concept of biodiesel	1
1.2 History	2
1.3 Production of biodiesel	2
1.3.1 Methods of production of Biodiesel	3
1.3.2 Factors affecting production of biodiesel	5
1.4 Properties of biodiesel	5
1.5 Advantages of biodiesel	7
1.6 Disadvantages of biodiesel	7
1.7 Linseed oil as biodiesel	8
Chapter 2 LITERATURE REVIEW	9-25
Chapter 3 TAGUCHI APPROACH	26-30
3.1 Design of experiments	26
3.2 Selection of orthogonal arrays	27
3.3 Analysis of results	28
Chapter 4 EXPERIMENTAL SET UP AND METHODOLOGY	31-39
4.1 Design of experiments	31
4.2 Production of linseed biodiesel	33

4.3	Determination of properties of linseed biodiesel	34
4.4	Apparatus used for estimation of properties.	35
4.4.1	The redwood viscometer	35
4.4.2	Bomb calorimeter	36
4.4.3	Pensky Martin (closed) apparatus	37
4.4.4	Cloud and Pour point apparatus	38
4.4.5	Ash content apparatus	39
4.4.6	Rams bottom apparatus	40
4.4.7	Acid value	41
4.5	Equipments used for evaluation of the engine performance	42
4.5.1	The variable compression ratio ignition engine	42
4.5.2	Eddy current dynamometer	44
4.5.3	Horiba analyzer	45
4.5.4	Flue gas analyzer	45
4.6	Procedure of experiment	46
4.7	Precautions taken during the experiment	47
4.8	Exhaust emission evaluation	47
Chapter 5 RESULTS AND DISCUSSIONS		49 -72
5.1	Experimental Results	49
5.2	Determination of optimum conditions by design of experiments	49
5.3	Expected yield from optimum values of parameters	51
5.4	Validation studies by ANOVA (analysis of variance)	53
5.5	The effects of various parameters on ester yield	55
5.5.1	Effect of molar ratio on methyl ester formation	56
5.5.2	Effect of reaction time on methyl ester formation	56
5.5.3	Effect of reaction temperature on methyl ester formation	57
5.5.4	Effect of catalyst type and concentration on methyl ester formation	58
5.6	Engine performance and emission parameters of linseed oil and its blends.	60
5.6.1	Performance parameters	61
5.6.1.1	Brake power (BP)	61
5.6.1.2	Brake specific fuel consumption (BSFC)	63

5.6.1.3 Brake thermal efficiency (BthEff)	67
5.6.1.4 Mechanical efficiency	70
5.6.1.5 Brake mean effective pressure (BMEP)	73
5.6.1.6 Variation of cylinder pressure	75
5.7 Emission parameters	77
5.7.1 Hydrocarbon (HC) emissions	77
5.7.2 Carbon monoxide (CO) emissions	78
5.7.3 NO _x Emissions	80
5.7.4 Carbon dioxide (CO ₂) Emission	81
Chapter 6 CONCLUSION AND FUTURE SCOPE	84-85
6.1 Conclusion	84
6.2 Future scope	85
REFERENCES	86-89

LIST OF FIGURES

Figure No.	Figure Caption	Page No.
1.1	Tranesterification reaction	4
4.1	Linseed biodiesel at different KOH concentrations	34
4.2	The redwood viscometer	35
4.3	The bomb calorimeter	37
4.4	Pensky Martin apparatus	37
4.5	Cloud and pour point apparatus.	39
4.6	Carbon residue (rams bottom) apparatus	41
4.7	Variable compression ratio engine	43
4.8	Eddy current dynamometer	44
4.9	Horiba gas analyzer	45
4.10	Flue gas analyzer	46
5.1	Variation of S/N ratio with molar ratio	56
5.2	Variation of S/N ratio with reaction time	57
5.3	Variation of S/N ratio with reaction temperature	58
5.4	Variation of S/N ratio with catalyst type	59
5.5	Variation of S/N ratio with catalyst concentration	59
5.6	Contribution of different parameters on biodiesel production yield	60
5.7	Variation of brake power with load at CR12	61
5.8	Variation of brake power with load at CR14	62
5.9	Variation of brake power with load at CR16	62
5.10	Variation of brake power with compression ratio.	63
5.11	Variation of BSFC with load at CR16	64
5.12	Variation of BSFC with load at CR14	65
5.13	Variation of BSFC with load at CR12	66
5.14	Variation of BSFC with load and compression ratio	66
5.15	Variation of BthEff with load at CR16	67

5.16	Variation of BthEff with load at CR14	68
5.17	Variation of BthEff with load at CR12	69
5.18	Variation of BthEff with load and compression ratio	69
5.19	Variation of MechEff with load at CR16	70
5.20	Variation of MechEff with load at CR 14	71
5.21	Variation of MechEff with load at CR12	72
5.22	Variations in mechanical efficiency with compression ratio of B20 blend.	72
5.23	Variation of BMEP with load at CR16	73
5.24	Variation of BMEP with load at CR14	74
5.25	Variation of BMEP with load at CR12	74
5.26	Variation of cylinder pressure with crank angle at CR16	75
5.27	Variation of cylinder pressure with crank angle at CR14	76
5.28	Variation of cylinder pressure with crank angle at CR12	76
5.29	Variation of hydrocarbon emissions with CR 16	77
5.30	Variation of hydrocarbon emissions with load at CR14	78
5.31	Variation of carbon monoxide emissions with load at CR16	79
5.32	Variation of CO emissions with load at CR14	79
5.33	Variation of NOx emissions with load at CR16	80
5.34	Variation of NOx emissions with load at CR14	81
5.35	Variation of CO ₂ emissions with load at CR16	82
5.36	Variation of CO ₂ emissions with load at CR14	83

NOMENCLATURE

MT	Million Tonnes
HHV	Higher Heating Values
CN	Cetane Number
CO	Carbon Monoxide
HC	Hydrocarbon
CO ₂	Carbon Dioxide
NO, NO _x	Nitrogen Oxides
CP	Cloud Point
PP	Pour Point
ASTM	American Society of Testing and Petroleum
CFPP	Cold Filter Plugging Point
KOH	Potassium Hydroxide
FFA	Free Fatty Acid
H ₂ SO ₄	Sulphuric Acid
°C	Degree Celcius
mg	Milligram
g	Gram
BSFC	Brake Specific Fuel Consumption
BthEff	Brake Thermal Efficiency
DI	Direct Injection
VCR	Variable Compression Ratio Engine
SFC	Specific fuel Consumption
BMEP	Brake Mean Effective Pressure
SO ₂	Sulphur Dioxide
EGR	Exhaust Gas Recirculation
UHC	Unburnt Hydrocarbons
KME	Karanja Methyl Ester
MechEff	Mechanical Efficiency
C.I	Compression Ignition
ISO	Indian Standard Organization

N	Normality
ppm	Parts per million
MR	Molar Ratio
EU	European Union
IC`	Internal Combustion
B10	10% biodiesel by Volume and 90% diesel
B20	20% biodiesel by Volume and 80% diesel
B30	30% biodiesel by volume and 70% diesel
B100	100% linseed Methyl Ester by Volume

LIST OF TABLES

Table No.	Description	Page No.
1.1	Vegetable oils production in India	3
4.1	Parameters and their levels to design the experiments	32
4.2	Design of experiments using L18 (3^5) orthogonal array	32
4.3	Specifications of engine	43
4.4	Emission parameter test methods	47
5.1	Ester yields from linseed oil and S/N ratios of 18 experiments	50
5.2	Contribution of each parameter on methyl ester production.	51
5.3	Expected S/N ratio under optimum conditions.	52
5.4	Properties of diesel and linseed biodiesel according to ASTM standards.	52
5.5	ANOVA Table to determine influence of parameters.	54
5.6	ANOVA Table to determine influence of parameters (pooled).	55

CHAPTER 1

INTRODUCTION

1.1 CONCEPT OF BIODIESEL

In present times the petroleum fuels extracted from crude oil are widely used as energy resources but these resources are non-renewable and depletion of these fuels enforced the industry to focus on alternative renewable fuels [1]. Today biodiesel is seen as renewable substitute for petroleum and diesel fuels as these fuels are environment friendly and burn with better combustion efficiency. The previous researches has shown significant reduction in CO, CO₂, unburnt hydrocarbons and sulfur oxide emissions with little difference in engine performance by the use of biodiesel [2]. Compared to conventional diesel, biodiesel have similar viscosity, slighter less calorific value, higher flash point and better lubrication properties [3].

The main trouble in using vegetable oils directly in engine is high viscosity of these oils [4]. So to transform vegetable oils into combustible fuel mainly four processes transesterification, emulsification, thermal cracking (pyrolysis) and direct blending are developed in last twenty years among which transesterification reaction of triglycerides with basic catalyst has attracted industrial focus because of its faster reaction rate and lower cost [5]. Transesterification is a chemical reaction in which triglycerides of vegetable oil react with an alcohol in presence of alkali or acidic catalyst to produce alkyl esters. Reactants are mixed by mechanical stirring. Glycerol is produced in transesterification reaction as a byproduct and is later removed. Several parameters affect the production yield of biodiesel such as reaction temperature, reaction time, molar ratio (oil/alcohol) and concentration of catalyst used. Acidic, basic and enzymatic catalysts can be used for transesterification. Reaction is much quicker with alkali catalysts [6]. Catalyst concentration plays an important role in transesterification because soap formation occurs during reaction by excessive use of catalyst [7]. Reaction temperature also has an effect on transesterification. Conversion reaction is extremely slow at room temperature. Better results are seen at higher temperatures. Molar ratio above 1:4 can be used in conversion reaction because three moles of alcohol can transform one mole of triglyceride into alkyl ester but as transesterification is a reversible reaction so higher molar ratio is required to shift the equilibrium to product side [8].

1.2 HISTORY

Because of resource depletion in case of petroleum fuels work has been started on the production and implementation of vegetable oils as suitable alternative for petroleum fuels. The conversion of animal fats or vegetable oils into mono alkyl esters is known as transesterification. Transesterification of triglycerides in vegetable oils and animal fats is not a whole new process. In 1893 first diesel engine was designed, when the famous German inventor Dr. Rudolph Diesel operated the original diesel engine by using vegetable oil. In 1900 at Paris Exposition one of the engines designed by Dr. Rudolph was run by using peanut oil which showed that the diesel engine can also be run with vegetable oils and it will help in developing the agriculture of the countries using it. Until the 1920s vegetable oils were the fuels used in the diesel engines but after that engine manufacturers modified the engines which utilize lower viscosity of petroleum diesel. Again in early 1980s vegetable oils and animal fats were seen as an alternative fuel competing with the petroleum fuels. The main advantages of these vegetable oils as fuel are portability, renewability, higher heat content, lower aromatic content, lower sulfur content and most important biodegradability of these fuels. In 1980 biodiesel plants were opened in several European countries and some cities in these countries have run local transport buses on biodiesel or blends of petroleum diesel and biodiesels. The commercial production of biodiesel was started in 1990. Environmental and domestic economic issues have enhanced the use of biodiesel and its blends with petro diesel throughout the world. In 1991, the European Community (EC) offered a 90% tax rebate for the use of biodiesel. Peugeot and Renault have approved the use of biodiesel as a fuel in some of truck engines manufactured by them. In Europe, biodiesel production plants are now being set up by many companies.

1.3 PRODUCTION OF BIODIESEL

In present times bio-diesel is mainly produced from crops like rapeseed, sunflower etc., in Europe. In US biodiesel is produced from soybean oil and in Malaysia palm oil is used for biodiesel production. Total production of different types of vegetable oils in India in 2012-2013 was around 7.45 MT [9].

Table1.1 List of different vegetable oils production in India (2012-2013) [9]

Vegetable Oil MT	MT
Groundnut	0.12
Soya	1.76
Rape / Mustard	2.01
Sunflower	0.21
Palm oil	0.08
Cotton seed oil	1.13
Other oil & fats	2.14
TOTAL	7.45

1.3.1 METHODS OF PRODUCTION OF BIODIESEL

- **DIRECT BLENDING:** Direct use of the vegetable oils or their blends with petroleum diesel has not been considered to be satisfactory for diesel engines. The main problems noticed in engines by the direct use of vegetable oils or their blends are high viscosity, high free fatty acids, high acid composition. Moreover gum formation occurs due to oxidation, polymerization of oil during storage and combustion, carbon deposits on engine parts and lubricating oil thickening are some other problems associated with the direct use of vegetable oils or their blends in direct and indirect diesel engines.
- **EMULSIFICATION:** A micro emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1±150 nm range formed spontaneously from two normally immiscible liquids [10]. By this process the higher viscosity and free fatty acid contents of vegetable oils is reduced significantly. Micro emulsions of the vegetable oils can be produced by using the solvents such as

ethanol, methanol, 1-butanol etc. Spray and combustion characteristics of oils are improved by this process.

- PYROLYSIS (THERMAL CRACKING):** It is a process defined as the conversion of one material into another material by using heat or by using heat with the addition of a catalyst. This conversion is achieved in the absence of air [11]. The characterization of chemistry of pyrolysis is a difficult task because of different reaction rates and different products obtained after the completion of reaction. Thermal cracking is an expensive process because of high cost equipments used in it. The products obtained in pyrolysis reaction are chemically similar to the petroleum-derived fuels. In this process viscosity, cetane number, pour point and flash point of vegetable oils is lowered. The main disadvantage thermal cracking is that all the oxygen molecules are removed at the end of reaction which removes the main environmental benefits with the use of oxygenated fuels.
- TRANSESTERIFICATION:** Transesterification (also called alcoholysis) is the reaction of a animal fat or vegetable oils with an alcohol in the presence of a catalyst to form esters and glycerol. A catalyst is used to increase the reaction rate and production yield. Three moles of alcohol can convert the triglycerides into esters but because the reaction reversible so some excess alcohol is required to shift the equilibrium of the reaction to the products side. Fig 1.1 shows the conversion of triglycerides into esters by transesterification reaction with alcohol.

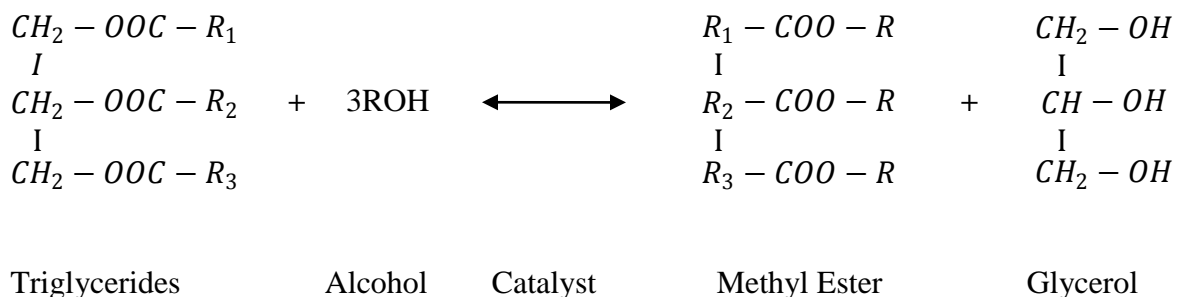


Figure 1.1 Methyl ester conversion of triglyceride by transesterification reaction.

The alcohols which are mainly used in transesterification process are methanol, ethanol, butanol, propanol and amyl alcohol but among these methanol and ethanol are most frequently used, especially methanol. This is because of its low cost and some other physical and chemical advantages. Methanol reacts rapidly with the triglycerides and the catalysts like KOH, NaOH are easily dissolved in methanol. Generally three moles of alcohol are stoichiometrically sufficient to complete transesterification reaction. But practically, the ratio of alcohol to oil needs to be higher to produce the maximum ester yield. The reaction can be catalyzed by any one of the acidic, alkalis or enzyme catalysts. The alkali catalysts like NaOH, KOH, carbonates are used most frequently because of their faster reaction rates. Cloud point and pour point are raised by this process. Alkali catalysts are not suitable for vegetable oils having higher free fatty acid contents so acidic catalysts are used in these vegetable oils. Sulfuric acid, hydrochloric acid and sulfonic acid are the mostly used acidic catalysts in transesterification.

1.3.2 FACTORS AFFECTING PRODUCTION OF BIODIESEL

- Increase in the molar ratio of alcohol to vegetable oil increases the yield of methyl ester from vegetable oil up to a particular limit. After a higher molar ratio than a particular limit the glycerol becomes difficult to separate.
- Amount and type of catalyst also affects the conversion rate from vegetable oil to methyl ester. For oils having less fatty acid content alkaline transesterification is used and for oils having higher fatty acid content acid transesterification is used.
- Stirring helps in higher conversion rate of methyl ester from vegetable oil.
- Impurities present in vegetable decreases the conversion rate into methyl ester.

1.4 PROPERTIES OF BIODIESEL

Biodiesels are characterized by some properties like viscosity, cetane number, flash point, cloud and pour points, density, distillation range, acid value, ash content, carbon residue sulfur content, higher heating value (HHV) and copper corrosion. The most important parameters affecting the production yield of methyl ester in transesterification reaction are the reaction temperature, reaction time, molar ratio (oil/alcohol), catalyst type and catalyst concentration. Below are the different properties of the biodiesel.

- **VISCOSITY:** One of the most important property of the biodiesel is their viscosity because of its effect on operation of fuel injection equipment, particularly at lower temperatures when increase in viscosity considerably affects the fluidity. High viscosity causes less accurate timings of the fuel injectors and improper atomization of fuel spray. The triglycerides conversion into methyl esters through the transesterification reaction reduces the viscosity and reduces the molecular weight. Biodiesels produced by transesterification have a lower viscosity close to the petroleum diesel. With increase in temperature viscosity of oil decreases. High viscosity of pure vegetable oils is a primary problem associated with direct use of these oils as fuel. So transesterification reaction is used to covert vegetable oils into methyl esters.
- **DENSITY:** Density of pure diesel is less than the biodiesel therefore when using the blends of biodiesel with petroleum diesel in compression ignition engine the biodiesel must be put at the top to ensure its proper mixing.
- **CETANE NUMBER (CN):** Higher the cetane number of a fuel betters the ignition properties it has so cetane number of any fuel should be higher. The cetane number of a fuel is a measure of its ignition quality, and a higher cetane number implies shorter ignition delay. When compared with petroleum diesel the cetane number is generally higher for biodiesel. This is because of long fatty acid chains and more saturation content in it. Cetane number affects the performance parameters like combustion, white smoke, stability, noise and emissions of HC and CO. Fuel with higher cetane number burns with better combustion efficiency.
- **CLOUD POINT:** Cloud point is defined as the temperature at which wax becomes visible when the temperature of the fuel is lowered. Conventional diesel fuel has lower CP than the biodiesel. There are no specifications for the CP provided by ASTM D 6751 but while using the engine in cold climates one should take care about the CP.
- **POUR POINT:** It is the minimum temperature at which the flow of a fuel starts. Conventional diesel has lower PP than the biodiesel.
- **COLD FILTER PLUGGING POINT (CFPP):** In areas where temperature is low the fuel may become thick which causes lower performance of fuel lines, injectors and fuel pumps. Various additives can be used to improve the CFPP.

- **FLASH POINT:** The value of temperature at which the fuel starts to ignite when exposed to spark or flame. Biodiesel has higher flash point than the petroleum diesel fuel. Combustion quality of a fuel is considerably affected by value of flash point. Low flash point may cause harm to seals and fuel pumps. According to ASTM D 6751 standards specified value of flash point is 130° C.
- **WATER CONTENT:** water content reduces the production yield of methyl esters. But in case of using supercritical methanol method it positively effects the formation of methyl ester.

1.5 ADVANTAGES OF BIODIESEL

The advantages of using biodiesel over conventional diesel fuel are as following -

- It is a renewable and biodegradable substitute for the conventional petroleum fuels.
- It has lower sulphur and aromatic contents.
- It is a readily available fuel.
- Flash point for biodiesel is higher than the petroleum diesel.
- Combustion efficiency of biodiesel is high.
- It has superior lubricity than the petroleum diesel.
- It has lower CO, HC, CO₂ and particulate emissions than petroleum fuels.

1.6 DISADVANTAGES OF BIODIESEL

Along with the advantages biodiesel has some disadvantages as following:

- It has low energy content and higher viscosity than diesel.
- It has higher pour point and higher cloud point.
- NO_x emissions are high for biodiesel as compared to the diesel.
- It has less engine power and speed.
- At present biodiesel is costly and causes more engine wear than the diesel.
- It causes more fuel consumption than the petroleum diesel.

1.7 LINSEED OIL AS BIODIESEL

Linseed is an oil and fiber crop which is also used to manufacture linen. Total worldwide output of linseed is recorded around 2.60 million ton per year with Canada being on the top of the list. India is having third position among all largest producers of linseed. In India, linseed is cultivated as rabi crop. Linseed is sown during October and harvested in April. About 600,000 to 700,000 ton of linseed oil is produced per year globally. Areas having the annual rainfall in the range of 45–75 cm are considered to be best for its cultivation. Biodiesel is produced by transesterification reaction of linseed oil with methanol or ethanol in the presence of one of alkaline catalysts. Transesterification is used to lower its viscosity and free fatty acid contents and convert linseed oil to its methyl esters. Because of food versus fuel conflicts use of edible oils for biodiesel production is avoided in these days. India can be a leading biodiesel producer, as biodiesel can be produced by using non-edible oils like *Jatropha*, *Pongamia Pinnata*, *Curcus*, *Neem*, *Linseed Mahua*, *Castor*, etc as feed stocks. Out of these non edible oil producing plants, *Linseed* and *Mahua* can grow in waste and arid lands. So, in India production of biodiesel will lead to many other advantages like support to agriculture, green cover to wasteland, reduction in dependence on crude oil and support to rural economy [12].

1.8 OBJECTIVES OF PRESENT WORK

The proposed research has been completed with biodiesel produced from linseed oil with following objectives.

1. Optimization of parameters affecting the production yield of linseed oil biodiesel using Taguchi's approach.
2. Determination of various properties of biodiesel produced by optimized conditions.
3. Evaluation of performance characteristics (brake specific fuel consumption, brake power, brake thermal efficiency, brake mean effective pressure, mechanical efficiency) of linseed oil biodiesel and its comparison with pure diesel fuel.
4. Evaluation of emission characteristics (carbon dioxide emissions, hydrocarbon emissions, nitrogen oxide emissions and carbon monoxide emissions) of linseed biodiesel and its comparison with pure diesel fuel.

CHAPTER 2

LITERATURE REVIEW

Alcantara *et al.* [13] – In their study fatty acids of three materials, tallow, used frying oil (mixture of 50% sunflower and 50 % olive oil) and soy-bean oil, were used as raw materials to produce biodiesel by using transesterification with methanol. These fatty acid materials, used frying oil, soy-bean oil and tallow, were converted into biodiesel by two different processes, by amidation and transesterification reactions with amidation and methanol respectively. The ignition characteristics of these two types of biodiesels were studied by calculating the blending cetane index of amide biodiesel blends with petroleum diesel and cetane index of biodiesels obtained by transesterification. The operating characteristics for this chemical conversion were evaluated and the analysis of ignition characteristics of these biodiesels was obtained. These three biodiesels showed the cetane indices which was nearly similar to petroleum diesel fuel. By amidation with diethylamine these three fatty acid oils were transformed into fatty acid diethylamides which is a amide biodiesel. The cetane index of amide biodiesel blends (in 5% blend with petroleum diesel) has been evaluated, and it was found that cetane number for ethyl fatty esters or methyl ester was lower than the amide biodiesel blends. So, amide biodiesel was considered as a better candidate to blend it to the conventional diesel fuels. It was shown that amide biodiesel improves the ignition characteristics of the petroleum diesel fuel.

Antolin *et al.* [14] - In their work the conversion of sunflower oil into its methyl ester by using the transesterification reaction was studied. Taguchi's approach was used for the optimization of the most effecting variables (reactants proportion, temperature conditions and methods of purification of oil). The primary purpose of this study was to obtain the maximum production yield of methyl ester and to produce a good quality bio-fuel that also fulfils the requirements of European pre-legislation. Finally, as fuels for diesel engines various characteristics such as viscosity, cold filter plugging point, flash point and acid value of methylveter were tested. Results of their study showed that the sunflower biodiesel produced under the optimal set of conditions is a good alternate for fossil fuels.

Behcet [15] - studied the transesterification of fish oils to produce the biodiesel to use it as a alternative fuel for single cylinder compression ignition engine. This engine was operated on pure anchovy fish oil biodiesel, different blends of fish oil biodiesel with petroleum diesel (B25 means 25% biodiesel blend with 75% pure diesel, B50 means 50% biodiesel blend in 50% pure diesel and B75 means 75% biodiesel blend in 25% pure diesel) and pure diesel fuel to evaluate the variation in performance and emission characteristics of engine with different fuels.. Different fuel properties of these fuels were analyzed. Performance and exhaust tests were performed by running the engine at full load conditions at different (1000, 1500, 2000 and 2500 rpm) engine speeds. From the investigations of these tests, 4.96% increase in bsfc and 5.16% decrease in engine power was found with the use of fish oil biodiesel. On the other hand there has been 4.576% reduction in CO₂, 21.3% reduction in CO and 33.425 reductions in HC emissions but there was 9.63% increase in O₂ and 29.37% increase in NO_x emissions. It was found out that bio-fuel obtained from fish oil has 37.93 wt.% saturated fatty acids because of which cetane number is improved and NO_x emissions are lowered.. It was concluded that anchovy fish oil biodiesel can be successfully used as a alternative fuel for conventional diesel in CI engines.

Chongkhong *et al.* [16] - produced fatty acid methyl ester (FAME) by using the palm fatty acid distillate (PFAD) as a raw material which has high amount of free fatty acids (FFA) and esterification process used in this study was investigated. Batch esterifications of palm fatty acid distillate were performed to evaluate and analyze the effect of: including molar ratios of methanol to palm fatty acid distillate 4:1 to 12:1, reaction temperatures of 70°C to 100°C, catalyst concentrations of 0.5 to 2.0 (% wt of sulfuric acid/wt of palm fatty acid distillate) and reaction times of 15 minutes to 240 minutes. The optimal combination of operating conditions for continuous esterification process was observed to be 8:1 molar ratio (methanol to palm fatty acid distillate) with 1.834 wt% concentration of sulfuric acid at 70°C reaction temperature with a reaction time of 60 minutes. By esterification the amount of free fatty acid content was reduced from value 93 wt% to even less than 2wt% at the completion of reaction. The methyl ester was purified by 3M sodium hydroxide neutralization and washing with water solution at a temperature of 80°C for 15 minutes followed by the transesterification reaction with 0.396M sodium hydroxide dissolved in methanol solution having a reaction temperature of 65°C again for 15

minutes. The specifications of finally produced methyl ester product were found out and it was observed that it meets the Thai biodiesels quality standards as well as ASTM D6751-02.

Demirbas [17] – produced ethyl and methyl esters of linseed oil as biodiesel fuels by non-catalytic transesterification in super critical conditions. Biodiesel is a renewable fuel which is considered as a potential substitute for petroleum fuels. Some positive properties of biodiesel such as non-toxicity, renewable, free from sulfur and aromatics and biodegradable, proves it a better fuel than the conventional diesel. The primary purpose of transesterification reaction is to reduce the viscosity of oil. Transesterification significantly reduces the viscosity of methyl and ethyl esters of linseed oil. Methyl and ethyl ester of all the linseed oil samples were lightly viscous. The value of flash point was raised significantly after transesterification reaction. The non-catalytic transesterification under supercritical conditions with fluids such as ethanol and methanol was observed to be a suitable conversion process to transform linseed oil into its biodiesel. Because of low cost of methanol it was used as reacting alcohol in this process. Reaction temperature and molar ratio (oil to alcohol) were seen to be most important parameters affecting the production yield of linseed oil methyl ester by transesterification reaction. Emissions from linseed oil biodiesel were seen to be far less polluting than petroleum diesel. So it was concluded that linseed oil methyl ester can be used as a fuel in diesel engines without much modification.

Dhar *et al.* [18] – told that quality and yield of any bio-fuel depends on quality of feedstock especially FFA content and moisture content. In their study, neem oil having high free fatty acids was transformed into biodiesel by two step conversion process i.e. esterification and transesterification. The physical, thermal and chemical properties of neem oil biodiesel were analyzed. Direct injection diesel engine was operated by using neem oil biodiesel and various performance, combustion and emission characteristics of the engine were evaluated by running it on neem oil biodiesel and its different blends with diesel and these characteristics were compared with pure diesel. The bsfc for neem biodiesel and its different blends was seen to be higher than pure diesel and BTE of all blends of neem biodiesel was found to be little higher than pure diesel. HC and CO emissions were reduced in case of biodiesel and its blends but NO emissions were little higher for all biodiesel blends. Detailed combustion characteristics evaluation showed that the combustion starts earlier in case of higher blends of biodiesel but combustion start was

delayed slightly for lower biodiesel blends in comparison of pure diesel. Combustion duration in case of all the blends of biodiesel was shorter than the pure diesel. Biodiesel produced from two step transesterification of high free fatty acid neem oil was found to be inferior compared to mineral diesel. The effects of molar ratio (oil to alcohol), reaction temperature, reaction time and catalyst amount on the production yield were evaluated. The optimum values of controlling parameters were obtained by the experiments: molar ratio (oil to alcohol)1:5, reaction time 2.0 h reaction temperature 55 °C and catalyst loading 0.8 wt.% . Using these optimum values of parameters 94% methyl ester production yield was reached. The properties of the neem oil biodiesel were found to be close to conventional diesel fuel and it was considered as a realistic fuel to use in diesel engines.

Ghadge and Raheman [19] – used central composite rotatable technique to analyze the effect of reaction time, methanol quantity and acid concentration on the reduction of fatty acids contents of mahua (*madhuca indica*) oil for its pretreatment for its conversion into biodiesel. All these three parameters significantly affect the acid value from which methanol was found to be most effecting followed by the reaction time and catalyst concentration of acidic catalyst. Using the response surface method, quadratic polynomial equation was prepared for the acid value by using multiple regressions. Performed experiments also confirmed the results of predicted model. The optimal combination to reduce the acid value of mahua oil and to bring it to less than 1% by pretreatment was molar ratio (methanol-to-oil) 0.32 v/v, catalyst loading (H_2SO_4)1.24% v/v and reaction time of 1.26 hour at 60°C reaction temperature. After performing pretreatment of the mahua oil, transesterification was performed with 1:6 molar ratio(oil to alcohol) and 0.7% w/v catalyst loading (KOH used as alkaline catalyst) to prepare biodiesel. The fuel characteristics of biodiesel obtained from mahua oil fulfilled the requirements of European and American standards for biodiesel.

Godiganur *et al.* [20] – told that neat mahua oil causes some problems when used for a prolonged time in CI engine. So, they transformed the mahua oil into methyl ester by transesterification reaction. A Cummins, turbocharged, 158 HP rated power, direct injection, and water cooled compression ignition engine was operated on pure diesel, biodiesel produced from mahua oil and different blends of mahua oil biodiesel with petroleum diesel at 1500 rpm engine

speed and variable load conditions. Engine was operated by fuelling it with three different blends of mahua oil biodiesel with petroleum diesel (B20- 20% biodiesel in 80% diesel, B40- 40% biodiesel in 60% diesel and B60- 60% biodiesel in 40% diesel), pure mahua oil biodiesel and pure diesel. Performance characteristics (brake specific fuel consumption, thermal efficiency exhaust gas temperature and brake specific energy consumption) and emissions characteristics (CO, NOx and HC) of engine were evaluated. The results showed significant reduction in CO and HC emissions with the increase in biodiesel blend, whereas NOx emission and fuel consumption increases slightly for biodiesel and its blends as compared to pure diesel. There was slight decrease in brake specific energy consumption and a slight increase in thermal efficiency of the engine was observed in case of B20 blend of mahua oil biodiesel. In their study it was concluded that B20 blend of mahua oil biodiesel can be successfully used as an alternative fuel in diesel engines without any major modification.

Guzatto *et al.* [21] - modified the transesterification Double Step Process (TDSP) to improve the quality of biodiesel and to yield a shorter reaction time for the production of biodiesel from vegetable oil. This process consist two steps of transesterification in which first oil is transesterified with basic catalyst and then with an acidic catalyst. The modifications in process included a slight reduction in reaction time for first step, catalyst concentration and the mixing of alcohol/acid solution, without any cooling between first and second step. The comparison between unwashed and washed biodiesel proved that for satisfactory results drying procedure is necessary after the final washing. The modified procedure higher conversion index was resulted in a (98% for linseed oil and 97% for waste cooking and soybean oil) and higher methyl ester yield ($93\pm 3\%$ for linseed oil, $87\pm 5\%$ for waste cooking oil and $92\pm 3\%$ for soybean). The methyl esters produced by using the modified transesterification double step process met ASTM and EN ISO standards.

Jawalkar *et al.* [22] studied and compared the performance characteristics (brake thermal efficiency, brake specific fuel consumption etc) and emissions characteristics (HC, CO and CO₂) of a single cylinder variable compression ratio direct injection diesel engine fuelled by different blends of linseed and mahua oil biodiesels. They founded that the brake thermal efficiency was increased with an increase in injection pressure and brake specific fuel consumption was reduced

more in case of mahua biodiesel with comparison to linseed oil biodiesel. They observed a decrease in brake thermal efficiency with increase in proportion of blend and brake specific fuel consumption was also decreased with the increase in proportion of blend. They also observed that the brake thermal efficiency of M50 was nearly 13% lower than L50 at full load conditions and 160 bar pressure. Their results showed that CO emissions were higher for linseed oil biodiesel than from mahua oil biodiesel. They also observed that, the HC emissions of the engine were slightly higher for mahua oil at 20% load than the linseed oil.

Jimenez *et al.* [23] investigated the different injection characteristics like injection delay, injection timing, injection pressure, injection duration, and mean injection rate with the diesel engine. They operated the engine by fuelling it with different fuels like pure diesel, pure biodiesel produced from rapeseed oil, bioethanol and biodiesel blends up to 15% and bioethanol and diesel fuel. According to the results they got the effect of the bioethanol in biodiesel was more significant for all injection characteristics than the pure diesel fuel. They observed that E15B85 blend showed the best results because injection characteristics for it were very close to those of conventional diesel fuel. They also observed that in terms of the fuel consumption bioethanol blended with biodiesel fuel was found to be more effective than conventional diesel. They concluded that with the addition of bioethanol biodiesel fuelling was decreased. According to the results of their study injection delay was increased and injection timing was retarded with the addition of bioethanol. According to them this was because of lower viscosity of bioethanol and this was also the reason for reduced NO_x emissions. They also observed slight increase in injection duration with the bioethanol addition in diesel. The reduction in injection pressure was less in case of the bioethanol addition in diesel than addition of bioethanol in biodiesel which was explained to be the second main reason for the reductions of NO_x emissions. At last they concluded that the blends of bioethanol in diesel and biodiesel up to 15% were more effective than the higher amounts of blending.

Kaya *et al.* [24] – produced peanut methyl esters by using the transesterification reaction of peanut oil with methanol. They extracted the peanut (*Arachis hypogea* L.) seed oil from the peanut seeds of that grows in SE Anatolia which is a state of Turkey. Peanut oil was extracted in 50 wt/wt.%, by

using the solvent extraction. Peanut (*A. hypogea* L.) seed oil was used as a raw material for the production of a biodiesel fuel and was considered as a good alternative for petroleum fuels to be used in compression ignition engines. Biodiesel was produced from peanut oil by the transesterification reaction of crude oil and methanol (methanol was used as alcohol because of its low cost) in the presence of NaOH as alkaline catalyst. A maximum production yield of methyl ester was found to be 89%. The viscosity of peanut oil biodiesel was observed to be close to that of the mineral diesel fuel but the calorific value was observed to be about 6% less than the diesel. The heating value of peanut seed oil was about 8.3% less than the mineral diesel fuel due to the more oxygen contents in their molecules. As the quality of every biodiesel is most important part to be checked therefore various standards had been specified to evaluate the quality of biodiesel fuel. The important fuel characteristics of peanut oil and biodiesel obtained from it (methyl esters) such as, iodine number, density, flash point, kinematic viscosity, neutralization number, cloud point, pour point and cetane number were found out and compared with petroleum diesel, EN and ASTM biodiesel standards. The study showed that the methyl esters of peanut seed oil have fuel properties relatively close to the mineral diesel fuel than that of the raw peanut seed oil.

Kim *et al.* [25] – optimized the values of parameters, such as molar ratio (oil/alcohol), catalyst concentration (wt%), catalyst type and reaction temperature controlling the production yield of rapeseed methyl ester by using transesterification reaction. The Taguchi's methodology was used to design the experiments which were sufficient to understand the effects of various controlling parameters and then to optimize the values of experimental parameters from these less number of experiments. The optimal combination of experimental conditions resulted by taguchi's approach in this study was at a catalyst concentration of 1.5 wt %, potassium hydroxide used as the catalyst and having 60°C reaction temperature. According to the results of Taguchi method, the catalyst concentration was found to be most important parameter significantly affecting the rapeseed methyl ester production yield. Finally by using optimized values of parameters rapeseed methyl ester yield was improved and was checked to be 96.7% which was much higher than all the experiments performed.

Kumar *et al.* [26] - used chemical transformations of linseed oil by transesterification to improve their properties and to make it usable as an alternative fuel in existing diesel engines.

Transesterification process reduced the poly free fatty acid contents of linseed oil which results in fuel (biodiesel) similar to petroleum diesel. Alkali catalyzed transesterification process was used for this conversion of linseed oil. In their study, the kinetics and simulation of transesterification reaction for linseed oil biodiesel production in the batch reactor by alkaline catalyst is reported. The effects of reaction temperature, molar ratio (oil to alcohol) and catalyst concentration were investigated experimentally. The average conversions of triglycerides into methyl esters were achieved 88–96%. The reaction time of 40 minutes was given to all experiments. Increase in conversion yield was observed in their study with the increase in molar ratio and reaction temperature whereas catalyst concentration was found to be having no significant effect. They applied the reversible kinetic model to resulted conversion data. For backward and forward reactions model parameters were evaluated and optimized. At different conditions simulations were carried out which showed that after a critical molar ratio there was no significant effect observed on transesterification kinetics. Fuel properties of biodiesel obtained from linseed oil were found to be quite similar to mineral diesel.

Lapuerta *et al.* [27] - Collected and analyzed the body of work published mainly in various scientific journals about the diesel engine emission characteristics when using biodiesel instead of mineral diesel fuel. Although biodiesel is being prepared by most countries following international policies related to energy issues, biodiesel is currently facing some resistance from some car and engines manufacturing companies. This somehow makes it difficult to achieve the target of increased use of biodiesel in internal combustion diesel engines. One of the main reasons for the resistance is lack of knowledge related to the various effects on engine emissions while using the biodiesel. The basis of their study was to maintain the engine performance, so first section was devoted to the effect of use of biodiesel on thermal efficiency, engine power and fuel consumption. Most of the studies were showing an increase in the fuel consumption in proportion to heating value loss. In the second section the engine emissions using biodiesel and diesel fuels were compared, concentrating mainly on: nitric oxide emissions and particulate matter emissions. Particulate matter emissions were analyzed not only in composition and mass but also in the size distribution. In most of the studies a sharp reduction was observed in the particulate emissions.

Liaquat *et al.* [28] – told in their review article that the demand of fossil fuels is continuously increasing day by day resulting in rapid depletion of these fuel deposits and according to the US energy department, the world’s fossil fuel deposits will face the midpoint of depletion around the year 2020. They also study the investigations that discussed human health hazards which are related to exposure to the diesel exhaust emissions. According to their study because of limited fossil fuels and their intensified environmental polluting effects, it has become a necessity to develop a clean, technically feasible, environmentally acceptable and domestically available fuel. Biodiesel, which is an is a renewable, oxygenated, biodegradable and environmental friendly bio-fuel, is produced by transesterification of different animal fats or vegetable oils and therefore is recommended as a clean alternative for petroleum-based fuels. According to their study most of the results obtained by most of the researchers around the globe reported that biodiesel fuelled engine showed a very little loss of performance with the use of biodiesel as fuel.

Lin and Li [29] - In their study, the waste parts of various marine fish species were transformed into biodiesel by using transesterification reaction with methanol. Marine fish oil, which was used as a raw material for transesterification, was extracted from discarded parts of the mixed marine fish. These discarded parts were refined by using some pretreatment processes. Transesterification reaction of this refined fish oil was completed by reacting with methyl alcohol to obtain biodiesel. A direct injection diesel engine was operated by using this biodiesel and performance and emission characteristics of engine were investigated. They observed that, fish oil biodiesel possess a large heating value, hydrogen content, elemental carbon, cetane index, brake fuel conversion efficiency, exhaust gas temperature, O₂ and NO_x emissions and a lower elemental oxygen content, brake-specific fuel consumption rate, fuel consumption rate and CO emission as compared to biodiesel obtained from waste cooking oil. When compared to petroleum diesel fuel both waste cooking-oil biodiesel and marine fish-oil biodiesel have lower gross heating value, exhaust gas temperature, cetane index, black smoke opacity, equivalence ratio, CO emissions and elemental carbon content and higher elemental oxygen content and fuel consumption rate.

Nabi *et al.* [30] – targeted the non edible vegetable oil (cotton seed oil) because use of edible oil increases the cost of biodiesel production and imposes challenges to global food supply. Different parameters affecting the production yield of cotton seed methyl ester were optimized in the first

part of their study, while in the second part of their study performance and emission characteristics of diesel engine were evaluated running it with biodiesel blends and pure diesel fuel. Biodiesel was produced by using transesterification of cottonseed oil as cottonseed oil is non-edible oil, thus fuel versus food conflict was solved. They observed that biodiesel production was effected with the variation of methanol or ethanol and variation of catalyst. In their study a maximum of 77% yield of methyl ester production was observed with the use of 20% methanol and using 0.5% sodium hydroxide as catalyst. The results of experiments made on direct injection diesel engine showed that emissions including particulate matter (PM), carbon monoxide (CO) and smoke were reduced significantly for all biodiesel blends. However, there was a slight increase observed in nitrogen (NO_x) emissions for all biodiesel blends. Engine performance was affected a little with a little decrease in brake power and increase in brake specific fuel consumption. They concluded that the cotton seed biodiesel can be used in diesel engines with or without little modifications.

Patel et al. [31] - studied the various performance and emission characteristics of diesel engine coated with thermal barrier using biodiesel produced from rice bran oil. They observed that the performance of the engine was improved and there was a little decrease in engine emissions by coating the walls of combustion chamber with thermal barriers. They investigated in their study that there was a increase in the brake thermal efficiency with load for all blends of biodiesel. The average brake thermal efficiency of engine was observed to be lower with the use of rice bran oil biodiesel blends than neat diesel fuel. The BTE (brake thermal efficiency) of B10, B20 and B40 blends was found to be close to that of mineral diesel. The BTE (brake thermal efficiency) was observed to be maximum 20.0 % among all experiments. They observed that with the increase in blending of biodiesel in the engine there was an increase in fuel consumption. The brake specific fuel consumption (bsfc) was observed to be higher for all blends of rice bran biodiesel (B10, B20, B40 and B100) than the petroleum diesel. The mechanical efficiency for all blends of biodiesel of B10, B20, B40 and B100 fuel was slightly decreased than that of the pure diesel fuel with load. The maximum efficiency was observed at full load conditions for pure diesel fuel and was found to be 10-15 % increased. They also observed that the decrease in specific fuel consumption with brake power for different biodiesel blends. According to results of their study the brake specific fuel consumption of B100 blend was observed to be higher than that of the diesel fuel and with

comparison to pure diesel fuel a slight increase (10-15 %) in specific fuel consumption was found in the case of rice different blends of biodiesel (B10, B20, B40, B100) for all loads. The indicated thermal efficiency was found to be high in case of rice bran oil biodiesel than the pure diesel fuel. Maximum value of indicated thermal efficiency was for pure rice bran oil biodiesel (B100) and was found to be 44.8 %. According to the results of their study the HC emissions were increased with the brake power and these emissions were decreased with the increase in rice bran oil blending. The HC emissions for pure use of biodiesel were lowest than all other blends. CO emissions were also observed to be lower in case of the rice bran oil biodiesel than that of pure diesel fuel. The CO emissions were found to be lowest in case of pure rice bran oil biodiesel (B100 blend). The NO_x emissions were observed to be high for higher loads and low for lower loads in the case of all blends of rice bran oil biodiesel

Patil et al. [32] - studied the biodiesel production from non-edible and edible oils. Their study was concentrated on optimization of transesterification reaction and to maximize the biodiesel production from both non-edible and edible oils. In their study for non edible oils two step transesterification reaction was used to produce methyl esters and for edible oils they used single step transesterification reaction with methanol to get methyl esters. Production yield of biodiesel in the range of 90-95% for Jatropha, 80-95% canola, 80-85% for Pongamia and 85-96% for corn were observed using KOH as an alkaline catalyst. It was observed that oils having high free fatty acid contents were difficult to transesterified by using alkali catalyst. Molar ratio (oil to alcohol) of 1:6, 0.5% catalyst concentration with H₂SO₄ catalyzed esterification at 40-50°C reaction temperature, and molar ratio 1:9, with 2% catalyst concentration with KOH alkali catalyzed esterification at 60°C reaction temperature were found to be optimal conditions for jatropha oil. An alkali catalyzed transesterification reaction was applied to transform the corn seed and canola oil to its esters. The maximum production yield for corn seed and canola was obtained at 2% and 1% alkali catalyst concentrations, 9:1 molar ratio (methanol to oil) and at 80°C and 60°C reaction temperatures respectively. They suggested further research on advanced methods such as supercritical methanol methods to use as conversion processes to convert vegetable oils into their esters.

Puhan *et al.* [33] – use transesterification reaction to prepare the biodiesel from mahua (*madhuca indica*) oil by lowering its viscosity and free fatty acid contents because vegetable oils cannot be used straight in diesel engines because of their low volatilities, high viscosities and poor cold flow properties. So efforts have been made in their study to lower the viscosity and to raise the volatilities by using the transesterification. In this study, Mahua (*madhuca indica*) seed oil was transesterified by reacting it with methanol in the presence of sodium hydroxide (alkaline catalyst) to produce mahua oil methyl ester. The biodiesel produced by this process was tested in a single cylinder, four stroke, compression ignition diesel engine (Kirloskar) running at a constant speed and various performance and emissions characteristics were evaluated. They observed an increase in brake specific fuel consumption and a little decrease in brake thermal efficiency of the engine in the case of mahua oil biodiesel. There was a decrease in CO, HC, CO₂ and particulate emissions with the use of mahua oil biodiesel. They concluded that mahua oil biodiesel can be used as a fuel in diesel engines with little modification.

Puhan *et al.* [34] - investigated a linseed oil (high linolenic) methyl ester in a constant speed, direct injection diesel engine by varying fuel injection pressures (200, 220 and 240 bar). The main goal of their study was to investigate and analyze the effect of injection pressures on various combustion, performance and emissions characteristics of the engine operating on linseed methyl ester. The results of their study showed that by using the linseed methyl ester as a fuel the optimum value of fuel injection pressure was 240 bar. At this optimized pressure thermal efficiency was observed to be quite similar to that of pure diesel fuel. There was a reduction in unburned hydrocarbon, carbon monoxide and smoke emissions and there was an increase in the nitrogen oxide with the use of linseed methyl ester as compared to petroleum diesel. The combustion analysis of linseed methyl ester showed that, the ignition delay was higher at lower injection pressures compared to the diesel and at full load conditions the peak pressure was also higher. The combustion duration was almost same at all the injection pressures. It was concluded that the linseed methyl ester at an injection pressure of 240 bar is more efficient than 200 and 220 bar, except for emissions of nitrogen oxides.

Raheman and Ghadge [35] - studied the performance characteristics high speed E6 Ricardo diesel engine fuelled with biodiesel produced by transesterification of mahua oil and its blends along with its fuel properties. These properties were observed to be comparable to petroleum diesel fuel and confirming to the European and American standards. Engine performance characteristics (brake thermal efficiency, exhaust gas temperature and brake specific fuel consumption) and emissions characteristics (CO, NO_x and smoke density) were observed to analyze and predict the characteristics of the diesel engine operating on biodiesel. The reductions were observed in brake specific fuel consumption and exhaust emissions and an increase was noted in brake thermal efficiency and brake power. It was concluded that the 20% blend of biodiesel (B20) is a suitable substitute fuel for petroleum diesel and can help in lowering the air pollution.

Sharma *et al.* [36] - discussed the various aspects and latest developments observed in production of biodiesel. Effect of reaction temperature, molar ratio, specific gravity, moisture content, stirring had been evaluated in their study. Apart from this satiability and biodegradability of bio-fuels had also been evaluated. In their study methanol was the used alcohol during the transesterification reaction because of its low cost. They observed that homogeneous catalysts such as sodium hydroxide, sulphuric acid, potassium hydroxide are commonly used at commercial level of biodiesel production among all other catalysts. They investigated heterogeneous catalysts such as magnesium oxide, calcium oxide. The main goal of their study was to decrease the catalyst amount and production cost of biodiesel. According to their study transesterification process can be achieved even without using the catalyst by using supercritical methanol method but the production cost of bio-fuel will be increased as it was an energy intensive method. According to their observations the molar ratio of oil to alcohol required for acidic transesterification reaction was from 1:6 and 1:18 and for alkaline transesterification reaction it was ranged from 1:5 and 1:12. According to them the reaction temperature should be between 45°C and 65°C as boiling temperature of methanol is 64.7°C and using the temperature above this will burn the methanol. However, higher temperatures were employed while using the supercritical methanol method (200°C–300°C). They concluded that a balance must be maintained between unsaturated and saturated fatty acid compositions in biodiesel fuel. According to them higher unsaturated content increased the cloud point and pour point but oxidative stability was

decreased. Whereas high saturated fatty acids content increased the oxidative stability and increased the cloud point and pour point which is not desirable.

Singh *et al.* [37] - prepared the hybrid fuels consisting of aqueous ethanol, coconut oil and a surfactant (butan-1-ol) and tested these fuels in a direct injection compression ignition engine. After determining the fuel properties like, viscosity, density and gross heating values of these fuels the engine performance and emission characteristics of engine operated on these fuels were investigated and comparison was made with the pure diesel. The experimental results showed that the performance of these hybrid fuels was comparable to the petroleum diesel. With the decrease in viscosity of these hybrid fuels and becoming close to that of diesel, there was progressive increase in efficiency towards the diesel fuel. There was a decrease observed in exhaust emissions than the diesel, except the carbon monoxide emissions. A little increase was observed for carbon monoxide emissions. Hence, it was concluded that hybrid fuels can be successfully used as alternative fuels without any modifications in diesel engines. Their renewable nature ensures the environmental friendly operation of engine with regard to emissions characteristics.

Sivalakshmi *et al.* [38] – performed the transesterification of neem oil and prepared biodiesel and different blends of biodiesel with pure diesel from it. A diesel engine was operated by fuelling it with neem oil biodiesel and its blends. The evaluation of the performance and emission characteristics of the engine was made by them. They observed the improved BTE (brake thermal efficiency) by using the neem oil–alcohol blends as compared to that of pure neem oil. The average smoke intensity was found to be lowered with the increase in blends. The NO_x emissions were slightly reduced by using the neem (oil–alcohol) blends. At higher loads the HC and CO emissions were found to be lower with the use of neem (oil– alcohol) blends as compared to neat neem oil.

Sivaramakrishanan and Ravikumar [39] – tried to optimize the performance of single cylinder direct injection (DI) diesel engine with respect to its brake power, emissions and fuel economy through the experimental investigations and design of experiments methods. A single cylinder four stroke having 5.2 kW power rating diesel engine was opted for experiments. Five different parameters, Static injection pressure (IP), Power (P), Fuel fraction (B), Injection timing (IT) and

Compression ratio (CR) were varied at four different levels and the output brake power, emissions and fuel economy were investigated. The optimal values of the outputs were estimated by using the Signal to Noise ratio (S/N ratio) and optimal combination of the control parameters were specified. Results observed from confirmation experiments showed valid agreement with those of predicted quantities. So the relationship between diesel engine parameter, brake specific fuel consumption, brake power and emissions was evaluated using the design of experiments. The best results for brake thermal efficiency (BTHE), brake specific fuel consumption (BSFC) were recorded at increased compression ratio, indicated pressure, and ignition timing. The emissions of HC and CO were reduced significantly while there was an increase in NO_x emissions. The results of their study showed that the combination of blend of 30% karanja biodiesel (B30), a nozzle opening pressure of 230 bar, a compression ratio of 17.9, injection timing of 27° bTDC and with 70% load conditions produces maximum performance of the diesel engine with reduced emissions from the diesel engine.

Swaminatan and Sarangan [40] -studied the increasing demand for fossil petroleum fuels in India for use in the transport sector with constraints of environmental concerns, international commitments, limited resources and legal requirements. As bio-fuels prepared from ethanol and vegetable oils/animal fats (biodiesel) are accepted as alternate solution for the problems of energy security, environmental degradation and agricultural economy. In their study biodiesel was produced from bio fish oil by its transesterification and experiments were performed on a single cylinder four stroke diesel engine and generator set to make a close study on its performance and emission characteristics and to check its usage as a substitute fuel for petroleum diesel. It was blended with other advance techniques such as, oxygenate and EGR techniques to improve its performance and to reduce the exhaust emissions of the engine. Encouraging results were observed from their investigation. The significant reductions were observed in CO, CO₂, NO_x and UHC by running the engine at maximum load conditions with the use of bio fish oil biodiesel with 2% additive with exhaust gas recirculation and similar results were observed for the other load conditions. According to their observation there was an increase in NO_x emissions at maximum load and other load conditions for bio fish oil biodiesel as compared with the pure diesel fuel, for obvious reasons but that was reduced by the addition of oxygenates and using EGR technique. The optimum values of blending biodiesel were observed with 2% of additive.

With the increase or decrease in this percentage of additives the emissions were observed to be increased.

Yamin *et al.* [41] – completed a comparative study on the production of biodiesel from unused and waste cooking oil and tested its fuel properties by testing the produced bio-fuel in direct injection CI engine. The performance and emission characteristics of engine were evaluated and were compared with characteristics of pure diesel fuel. According to their results a loss was observed in the calorific value of fuel of about 7.24% for biodiesel obtained from unused oil and 13.43% for biodiesel obtained from waste cooking oil. Further, they observed that there was about 4.75% increase in density of the fuel as compared to the pure reference fuel. According to their observation for the performance characteristics, biodiesel showed a little increase in the thermal efficiency, torque and power but there was reduction observed in the specific fuel consumption. This was accomplished for both low load as well as full load conditions. Exhaust emissions were significantly reduced for both of the biodiesels except NO_x emissions. NO_x emissions were high for biodiesel fuel obtained from waste cooking oil than that of obtained from unused oil and were lowest for pure diesel fuel. At last they concluded that both biodiesels produced from waste cooking oil as well as un used oil can be used as a suitable alternative fuel for diesel engine but as production cost for biodiesel from unused oil is high and it causes fuel versus food conflict therefore biodiesel should be produced from waste cooking oil.

CONCLUSION

It is seen that extensive work has been done already on production of biodiesel from various edible oils. In developing countries cost and consumption of the edible oils is very high and in countries like India there is fuel versus food conflict for biodiesel feed stocks therefore biodiesel production using edible oils is not considered as an economically feasible idea. So biodiesel should be produced by using non edible oils as it is economically because of low cost of non-edible oils. However enough work has been reported on non-edible oils such as mahua, jatropha, karanja, neem but not enough work has been done on biodiesel production using linseed oil. India is on third position India is on third position in global production of linseed oil but awareness

about production of linseed oil biodiesel is very less. Limited work has been performed on optimization of linseed oil biodiesel production and performance and emission characteristics of a diesel engine fuelled with linseed oil biodiesel. In this work optimization of parameters, such as molar ratio, catalyst concentration, catalyst type, reaction temperature and reaction time, controlling the production yield of linseed oil methyl ester was achieved. Taguchi approach of orthogonal arrays (L18) was used to design the experiments and perform optimization by considering fewest experiments. Only 18 experiments were performed which were equivalent to 243 experimental situations. The optimal combination of controlling parameters was found to be 1.5% catalyst concentration by weight, 60°C reaction temperature, 60 minutes reaction time and by the use of KOH as catalyst. Statistical technique ANOVA (analysis of variance) was used to study the influence of different parameters on biodiesel production yield.

The technique of laying out the designs of experimental situations involving multiple parameters was first carried out in 1920 by Sir R.A. Fisher called full factorial design. In this technique all possible combinations of parametric values are considered but most industrial experiments involve significant number of factors so full factorial design results in large number of experiments. For example, in an experimental design having seven parameters, each at two levels, total number of experiments will be $128 (2)^7$. To reduce the number of experiments only a small set of possible combinations is selected. This technique is called partial factorial design and produces most information but there are no general guidelines for the use of this technique. Taguchi's approach considered both important areas by clearly defining a set of orthogonal arrays to design the experiments and by devising a standard method to analyze the results obtained. Design of experiments by orthogonal arrays offers great experimental efficiency.

3.1 DESIGN OF EXPERIMENT

The main aim of experimental design is to develop a layout of the different conditions to be studied. An experimental design must fulfill two objectives. First, the number of experimental trails must be determined. Second, the conditions for all the trails must be specified. In Taguchi's approach there are pre-defined orthogonal arrays which are used to select fewest possible experimental conditions. Before designing the experiments, wide knowledge of the product or process under investigation is of prime importance for identifying the factors likely to affect the output. Consider an example of biodiesel production yield in which there are four parametric variations (let us say molar ratio, catalyst type, catalyst concentration and reaction temperature) which influence the production yield each varying at three levels. The controlling parameters and their levels are shown in table 3.1. In general the levels of factors are decided on the basis of pre judgment experiments. Pre judgment experiments are performed to determine the range of parametric values within which the parameters affect the output considerably. But this can also be done on the basis of previous researches and studies. After selection of levels experiments are designed on the basis of orthogonal arrays.

Table 3.1 Parameters and their levels to design the experiments

Parameters	Levels		
	1	2	3
Molar ratio (oil/methanol)	1:6	1:8	1:10
Reaction temperature (°C)	40	50	60
Catalyst type	NaOH	NaOCH ₃	KOH
Catalyst concentration (wt %)	0.5	1.0	1.5

3.2 SELECTION OF ORTHOGONAL ARRAY

Taguchi has established orthogonal arrays to describe large number of experimental situations. Orthogonal arrays are a set of tables of numbers which can be used to efficiently accomplish optimal design. The symbolic designation of the array carries the information on the size of the experiments. For example an L8 array indicates that 8 trials are required.

Every orthogonal array must satisfy balancing property. According to balancing property the interactions between two levels of factors in experimental design must be occurred equal number of times. For example if interaction between level 1 and level 2 of two different factors occurs thrice then the interactions between level 2 and level 1 of these factors must occur thrice.

Selection of a proper orthogonal array is must to accomplish the accurate results. To select suitable orthogonal array first degree of freedom is calculated by the following equation.

$$\text{degree of freedom} = p \times (l - 1) \quad (3.1)$$

Where p = number of parameters

l = number of levels

For example in above case there are four parameters and three number of levels so degree of freedom becomes 8. Now we must perform minimum eight experiments to achieve the require results. This can be done by selecting an L9 array. But to avoid the error one should use Taguchi's array selector to select the suitable array and the experiments must be designed according to the predefined orthogonal arrays. For the above example of table 3.1 the suitable L9 array is shown below in table 3.2.

Table 3.2 Design of experiments using L9 (3⁴) orthogonal array with four parameters varied at three levels

Experiment no.	Molar Ratio (oil/methanol)	Reaction temperature (°C)	Catalyst type	Catalyst concentration (wt %)
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

3.3 ANALYSIS OF RESULTS

In Taguchi's approach results are analyzed on the basis of three basic quality characteristics.

1. The bigger the better
2. The nominal the better
3. The smaller the better

The bigger the better is used where our prime motive is to maximize the output, the nominal the better is used when output should be nominal and the smaller the better is used when to minimize the output is primary concern. The output of nine experiments given by orthogonal array is recorded and results are obtained according to the quality characteristic the bigger the better because here maximum output of the biodiesel is requirement in the above example. Minimum three repetitions of each experiment are recommended to reduce the error in results. Mean standard deviation and signal to noise ratio is calculated by using the following equations.

$$MSD = \frac{1}{n} \sum_i^n \left(\frac{1}{y_i} \right)^2 \quad (3.2)$$

Where n represents the repetition of experiment and y_i represents the methyl esters yield. Then S/N ratio of performed experiments was calculated by using the following equation.

$$\frac{S}{N}ratio = -10 \log(MSD) \quad (3.2)$$

S/N ratio is a generalized term which denotes the output to error ratio. So to have the maximum output, an experiment must produce the highest S/N ratio. Let us say the nine experiments of above example produces the following results as shown in table 3.3. A,B,C,D,E,F,G,H and I are showing the yields of experiments, M showing the mean yield and S is representing the S/N ratio obtained from all experiments.

Table 3.3 Output yield and S/N ratios of 9selected experiments

Experiment no.	Yield of Linseed oil methyl ester				S/N Ratio
	Sample 1	Sample 2	Sample 3	Mean yield	
1	A1	A2	A3	M1	S1
2	B1	B2	B3	M2	S2
3	C1	C2	C3	M3	S3
4	D1	D2	D3	M4	S4
5	E1	E2	E3	M5	S5
6	F1	F2	F3	M6	S6
7	G1	G2	G3	M7	S7
8	H1	H2	H3	M8	S8
9	I1	I2	I3	M9	S9

Now to determine the optimum values of controlling parameters and the contribution of each parameter towards the production yield these results are to be analyzed by Taguchi's methodology. Let us say S_A is the mean S/N ratio of all the nine experiments. Now to check the optimum value of molar ratio the variations in S/N ratio for each level of molar ratio can be calculated by taking the mean of S/N ratios of experiments having that level. For example for experiments 1, 2 and 3 level of molar ratio is 1:6. So the mean of s/n ratios of these experiments gives the mean S/N ratio for level1 of molar ratio say

S_{A1} . Similarly mean S/N ratios for each level of each parameter can be calculated. Consider we got the results as shown in table 3.4.

Table 3.4 Mean S/N ratio of each level, difference between S/N ratios of levels and contribution of each parameter on methyl ester production.

Parameters	Level			Difference			Contribution (%)
	1	2	3	L ₂₋₁	L ₃₋₁	L ₃₋₂	
Molar ratio (oil/methanol)	S_{A1}	S_{A2}	S_{A3}	W1	W2	W3	P1
Reaction temperature (°C)	S_{B1}	S_{B2}	S_{B3}	X1	X2	X3	P2
Catalyst type	S_{C1}	S_{C2}	S_{C3}	Y1	Y2	Y3	P3
Catalyst concentration (wt %)	S_{D1}	S_{D2}	S_{D3}	Z1	Z2	Z3	P4

Now from these results the level of any parameter producing highest mean S/N ratio is the optimum value of parameter which will produce highest output. Let us say among S_{A1} , S_{A2} and S_{A3} the highest S/N ratio is produced for S_{A2} . So the optimum value for molar ratio is 1:8. Similarly the optimum values of all parameters are evaluated. Now to evaluate the contribution of each parameter for output, difference between mean S/N ratios of all three levels is calculated. For example W1 is the difference between mean S/N ratios for level 1 and level 2 of molar ratio ($S_{A2} - S_{A1}$). The maximum positive value of these differences is used to calculate the percentage contribution of all the parameters say P1, P2, P3 and P4. For example if W1, X1, Y1 and Z1 are maximum positive differences between mean S/N ratios of individual parameters. Then percentage contribution for molar ratio is calculated by the following equation.

$$P1 = \frac{W1}{W1+X1+Y1+Z1} \quad (3.3)$$

CHAPTER 4

EXPERIMENTAL SETUP AND METHADODOLOGY

In this chapter procedure and different steps acquired for the optimization of parameters affecting production yield of linseed methyl ester by using the design of experiments via Taguchi's approach and methods used measure the different fuel characteristics of optimally produced linseed biodiesel and its three different blends (B10, B15, B20) is discussed. These three blends of linseed biodiesel were used as fuel in a compression ignition (C.I.) engine. Then performance parameters such as, Brake Thermal Efficiency (BTHE), brake power (BP), Brake Specific Fuel Consumption (BSFC), Mechanical efficiency (MechEff) and Brake mean effective pressure (BMEP) and are measured. Afterwards various emission parameters such as, Carbon Dioxide (CO₂), Carbon Monoxide (CO), Nitrogen Oxides (NO_x) and Un-burnt Hydro carbon (UHC) were also evaluated. The resulted performance and emission characteristics of Linseed oil biodiesel were then compared to those of the pure diesel.

4.1 DESIGN OF EXPERIMENTS VIA TAGUCHI'S METHOD

In Taguchi's method the experiments are designed to get the optimal combination of parameters controlling the production yield by performing fewest experiments. The effect of individual parameters can be evaluated by using orthogonal arrays as proposed by Taguchi. An orthogonal array is a subset of all experimental possibilities which can be used to efficiently determine the optimum values of parameters by considering a small no of experimental situations [42]. The main controlling parameters (molar ratio, catalyst type, catalyst concentration, reaction temperature and reaction time) and their levels were decided on the basis of previous studies [7, 43, and 44]. Table 4.1 is showing five selected parameters varying at three levels. Here L18 (3⁵) orthogonal array is suitable to study the effect of parametric variation on methyl ester production. Set of 18 performed experiments at different levels are shown in Table 4.2. Automatic design software Design Expert 8.0 was used to design and analyze the results and to optimize the levels of controlling parameters.

Table 4.1 Parameters and their levels to design the experiments

Parameters	Levels		
	1	2	3
A Molar ratio (oil/methanol)	1:6	1:8	1:10
B Reaction time (minutes)	40	60	80
C Reaction temperature (°C)	40	50	60
D Catalyst type	NaOH	NaOCH ₃	KOH
E Catalyst concentration (wt %)	0.5	1.0	1.5

Table 4.2 Design of experiments using L18 (3⁵) orthogonal array with five parameters varied at three levels

Experiment no.	Levels of parameters				
	Molar Ratio (oil/methanol)	Reaction time (minute)	Reaction temperature (°C)	Catalyst type	Catalyst concentration (wt %)
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	2	1	2	3	3
5	2	2	3	1	1
6	2	3	1	2	2
7	3	2	3	2	3
8	3	3	1	3	1
9	3	1	2	1	2
10	1	3	2	2	1
11	1	1	3	3	2
12	1	2	1	1	3
13	2	2	1	3	2
14	2	3	2	1	3
15	2	1	3	2	1
16	3	3	3	1	2
17	3	1	1	2	3
18	3	2	2	3	1

4.2 PRODUCTION OF BIODIESEL

As linseed oil is readily available and possess considerable unsaturated groups so it is suitable to use as raw material for biodiesel production [45]. Linseed oil was provided by Pardeep Traders, Ludhiana. Biodiesel preparation was performed in laboratory at Mechanical Engineering Research and Development Organization (MERADO), Ludhiana (India). Various materials like KOH, NaOH, NaOCH₃ and methanol were used in methyl ester conversion reaction.

Various steps acquired for biodiesel production from linseed oil are described as following:

- For methyl ester conversion linseed oil sample (200 ml) was first preheated to 60°C. Methanol (by volume) and solid catalyst (by weight) were mixed and stirred in a separate conical flask.
- After that the stirred sample was added in preheated linseed oil sample.
- A batch reactor immersed in a water bath, capable to maintain ($\pm 1^\circ\text{C}$) required reaction temperature, was used for transesterification. To mix the reactants properly a continuous shaker, which converts the electric power into mechanical shaking, was used at impeller running at 300 rpm. This was done for different reaction times (40,50 and 60 minutes) for required samples.
- After transesterification the sample was taken in a separating funnel having a drainage valve. The mixture was made to settle for twenty four hours and then the glycerol was separated.
- Excess methanol and impurities were removed by washing the methyl ester with distilled water at 40°C.
- All of the above steps were repeated for different values of parameters controlling production yield such as, different molar ratios (10:1, 8:1, 6:1), different reaction times (40,50 and 60 minutes), different reaction temperatures (40,50 and 60°C) and using different catalysts at different concentrations (0.5,1.0 and 1.5 by wt%) of catalyst. Fig 4.1 is showing glycerol separation from methyl ester by using separating funnel.



Fig 4.1: Separation of methyl ester at different KOH concentration

4.3 DETERMINATION OF PROPERTIES OF THE BIODIESEL

Determination of the following fuel properties of linseed biodiesel is discussed as below:

- Kinematic viscosity
- Calorific value
- Flash point
- Fire point
- Cloud point
- Pour point.
- Ash content
- Carbon residue

4.4 APPARATUS USED FOR ESTIMATION OF PROPERTIES

The apparatus used for the determination of fuel properties of linseed biodiesel are discussed as below.

4.4.1. The redwood viscometer: The redwood viscometer, as shown in Fig 4.2, is a commonly used device for the determination of viscosity of any lubricating oil. It does not produce a direct measure of the oil viscosity in absolute units. Rather it measures the efflux of 50 ml oil under standard conditions through the standard orifice of the instrument and thus enables the viscosities of oils to be compared.

The complete procedure to estimate the viscosity by using redwood viscometer is as below:

First of all level the instrument properly by using the leveling screws provided on the tripod. Then fill the water bath to the tip of the indicator with clean water up to which the oil will be filled in the cylindrical cup. To seal the orifice Keep the brass ball in proper position. Then pour the oil, of which the viscosity is to be measured, carefully into the cylindrical oil cup again up to the tip of indicator. Keep a 50 ml flask in accurate position below the jet. Keep stirring the oil and water properly and note the temperatures of both. When temperature of the water and oil becomes steady, raise the valve of brass ball and suspend it from thermometer bracket. Simultaneously start running a stop watch .When level of the oil spilling into the flask touches the 50 ml mark note the reading on stopwatch in seconds. Replace the brass ball valve in initial position to properly seal the cup and to prevent any overflow of the oil. Refill the oil under test into the cylindrical cup up to the indicator tip and repeat this experiment for two more times. Mean of three readings from stopwatch is calculated as $t_m(s)$.



Fig 4.2: The Redwood Viscometer

$$\text{If } tm < 34 \quad V = .24 \times tm - \frac{50}{tm} \quad (4.1)$$

$$\text{If } tm(s) > 34 \quad V = .26 \times tm - \frac{179}{tm} \quad (4.2)$$

Where tm is mean time in seconds

V is the kinematic viscosity in centistokes.

4.4.2 Bomb calorimeter: The total heat of combustion of the biodiesel samples was as per IS: 1448 [P: 6]: 1984 and was determined with the help of Isothermal Bomb Calorimeter (Plate 3.4). made by Widson Scientific Works. Fig 4.3 is showing the isothermal bomb calorimeter which was used to determine the calorific value of biodiesel extracted from linseed oil. A fuel sample of 1 ml was combusted in the bomb of the calorimeter in presence of pure oxygen. The fuel sample was electrically ignited and as the heat was produced, there was rise in the temperature. This rise was measured accurately. The water equivalent (effective heat capacity of the calorimeter) was also determined by using the dry and pure benzoic acid as test fuels. This was repeated three times for each sample. The total heat of combustion of biodiesel samples was determined by using the following equation:

$$H_C = \frac{(W_C \times \Delta T)}{M_S} \quad (4.3)$$

H_C = Heat of combustion of the fuel sample, Cal / g

W_C = Water equivalent of the calorimeter, Cal /OC

ΔT = Rise in temperature, OC

M_S = Mass of sample burnt



Fig 4.3: The bomb calorimeter

4.4.3 Pensky Martin (closed) apparatus: The fire and flash point of the biodiesel samples were determined as per IS: 1448. The oil sample was poured into the cylindrical oil cup and was filled up to the mark. The use of Pensky Martin apparatus to determine the fire and flash point is shown in Fig 4.4.



Fig 4.4: Pensky Martin apparatus

The biodiesel sample was continuously stirred at a constant rate. The whole apparatus is heated in such a way that the temperature of the oil increases by 5 to 6°C per minute when the stirrer rotation is kept at 60 revolutions per minute approximately. The temperature of oil was measured by using the thermometer of -10 to 400°C range. At every 1°C rise, flame was ignited for a short moment by using a shutter provided in apparatus. The flash point was recorded as the minimum temperature at which distinct flash was observed on introducing test flame into cylindrical oil cup. The fire point was determined as the temperature at which vapors of fuel sample catches fire which stays for minimum five seconds.

4.4.4 Cloud and pour point apparatus: The Cloud point and Pour point of biodiesel samples were found out as per IS: 1448 [P: 10]: 1970. Cloud and Pour point apparatus was used for this purpose. This apparatus consists of 12 cm long glass tubes each having diameter 3 cm. These tubes are fitted in an air jacket, which is filled with the freezing mixture of sodium chloride crystals and crushed ice. The oil was poured to a height of 5 cm into the test jar. Thermometers were installed in the cooling bath and oil. With every fall of 1°C in the oil temperature, the jar was momentarily drawn for examination and was replaced immediately. This process was continued until cloudiness appeared in the oil sample near the bottom of test jar at particular temperature of oil sample. This temperature was recorded as the cloud point temperature of the oil sample under test. The apparatus and procedure to determine the pour point are same as used for cloud point determination; but the sample was first pre-heated to 48°C to determine pour point and then cooled to 35°C in the air before filling it into the glass tube. Thereafter, these cooled samples were poured in the glass tube of the apparatus and withdrawn at every 10°C fall to check its flow ability. The pour point was recorded as the temperature at which there was no motion of the fuel observed for five seconds by tilting the glass tube to a horizontal plane. This was repeated three times for every sample. The apparatus used to determine the pour and cloud point is illustrated in Fig 4.5.



Fig 4.5: cloud and pour point apparatus.

4.4.5 Ash content apparatus: There can be ash content in a fuel because of oil, water soluble compounds or extraneous solids like dirt and rust. The ash content of biodiesel samples, pure diesel and blends of both was measured as per ASTM D482-IP 4 standards of Institute of Petroleum, London. A Wiswo make electric muffle furnace was used in this experiment. In order to determine the ash content, fuel sample was first taken in a silica dish. First the dish was weighed empty and then was weighted with the fuel sample. The sample weight was determined from the difference between final and initial weight readings of the dish. The sample was placed in the electric muffle furnace and was heated at $775 \pm 25^{\circ}\text{C}$ for two hours. The dish was then cooled and brought to room temperature by putting it in a desiccator. Afterthat the dish was weighed again to the nearest 0.01 mg by using an electronic balance. This was repeated three times for each sample. The ash content was determined by using the following equation.

$$A_S = \left(\frac{W_A}{W_S} \right) \times 100 \quad (4.4)$$

Where

A_S = Ash content in percentage

W_A = Weight of ash in miligrams

W_S = Weight of sample in miligrams.

4.4.6 Rams bottom apparatus. The measurements were made in accordance with ASTM D189IP 13 standards of Institute of Petroleum, London. This procedure estimates the amount of residual carbon left after the evaporation of an oil. To determine the relative weight of oil sample electronic balance was used and the bulb was placed in a sheath having an iron tube about 76 mm long and 25.5 mm internal diameter, with a flat closed end. The sheath was then immersed in a bath of molten lead to depth of more than 72 mm. The lead bath then was heated to 550°C for minimum of 20 minutes. The bulb was withdrawn then and was made to cool. Bulb was weighed again by using the electronic balance. The result was recorded as % residual carbon for the weight of the linseed oil taken. To determine the % residual carbon in the oil the following equation is used.

$$\% \text{ of carbon residue in the oil} = \left(\frac{W_2}{W_1} \right) \times 100 \quad (4.5)$$

W_1 = weight of the oil taken for test, g

W_2 = weight of the carbon residue deposited, g

The apparatus used to determine the residual carbon content in the oil sample is shown in the Fig 4.6.



Fig 4.6: Carbon residue (rams bottom) apparatus

4.4.7 Acid value: The acid value or acid number is defined as the mg KOH required to make the free fatty acids neutral present in the one gram of sample. The total acid value was measured for the different fuel samples by using the method described by Cox and Pearson, 1962. The procedure followed to determine the total acidity of different fuel samples selected for the study is described as below:

- Dissolve 1-10 grams of oil in the 50 ml of neutral solvent (mixture of 25 ml ether, 25 ml alcohol and 1 ml of 1% phenolphthalein solution and neutralize with N/10 alkali) in a 250 ml capacity conical flask.
- Add a few drops of phenolphthalein and titrate the contents against 0.1N KOH.
- Shake it continuously until a pink color of the solution is obtained which persists for atleast 15 seconds.

During the study, three replications were made for each sample. The total acidity of fuel samples was calculated by using the following equation:

$$A_V = \frac{(56.1 N \times T_V)}{W_S} \quad (4.6)$$

A_V = Acid value, mg of KOH/g

T_V = Titrate value, ml

N = Normality of the potassium hydroxide solution

W_S = Weight of sample in grams.

4.5 EQUIPMENTS USED FOR EVALUATION OF THE ENGINE PERFORMANCE

The experiments to determine the engine performance and emissions were carried out in internal combustion engines lab and sophisticated analytical instruments (SAI) lab at THAPAR UNIVERSITY PATIALA. The following engine and accessories were used for the experiments.

4.5.1 The variable compression ratio ignition engine: A single cylinder, variable compression ratio, water cooled diesel engine was used. The variable compression ratio diesel engine used to perform the experiments is shown in Fig 4.7.

The engine performance parameters evaluated are listed below:

- Brake power (BP)
- Brake mean effective pressure (BMEP)
- Mechanical efficiency (MechEff)
- Brake thermal efficiency (BthEff)
- Brake specific fuel consumption. (BSFC)



Fig 4.7: variable compression ratio engine

Table 4.3 The specifications of engine used in the present study.

Engine specifications	
Model	TV1(KIRLOSKAR)
Type	Single cylinder 4 strokes, Water cooled.
Compression ratio	12 to 18
Bore	87.5 mm

Stroke	110 mm
Rated power	3.5 KW @1500 rpm
Connecting rod length	234 mm
Orifice diameter	20 mm
Dynamometer	Eddy current type
Dynamometer arm length	145 mm
Load sensor	Load cell, type strain gauge, range 0-50Kg
Load indicator	Digital, Range 0-50 Kg, Supply 230V AC
Speed indicator	Digital with non contact type speed sensor
Rota meter	Engine cooling 40-400 LPH; Calorimeter 25-250 LP
Temperature sensor	Thermocouple, Type K

4.5.2 Eddy current dynamometer: The engine used was coupled to an eddy current dynamometer in order to measure the power and torque. With the help of load cell connected with dynamometer, various engine loads i.e. 0, 2, 4 and 6 kg were applied. Load sensor was connected to load cell which indicates load on the indicator. The SAJ make AG20 eddy current dynamometer was used in the present evaluation. The construction of eddy-current dynamometer consist a rotor driven by the prime mover (such as engine, etc.) and the magnetic poles (stators) located outside with a gap. To excite the magnetic pole a coil is wound in circumferential direction. When current starts running through the coil, a magnetic flux loop starts to form around the coil through stators and rotor. The rotor rotation produces density difference, then eddy-current flows through stator. An electromagnetic force is applied by the product of this eddy-current opposite to the direction of rotation. Fig 4.8 illustrates eddy current dynamometer.



Fig 4.8: eddy current dynamometer

4.5.3 Horiba analyzer: Hydrocarbon (HC) emissions of the fuel were evaluated by horiba analyzer. It consist its own individual sensors. In this device, one end of the cable is directly connected to the analyzer inlet and the other is connected to the exhaust gas outlet end. The horiba analyzer used to evaluate Hydrocarbon emissions is illustrated in Fig 4.9.



Fig 4.9: Horiba gas analyzer

4.5.4 Flue gas analyzer (KM9106): The emission gases such as carbon monoxide (CO), Carbon dioxide and Nitrogen oxide (NO) were analyzed by using this analyzer. The flue gas analyzer is illustrated in Fig 4.10



Fig 4.10: Flue gas analyzer

4.6 PROCEDURE OF EXPERIMENT

The experiments were performed firstly by using the pure diesel and then by using three blends of linseed biodiesel (B10, B15, and B20). The steps followed are described as below:

- Firstly the fuel tank was filled with diesel.
- Initially the compression ratio of engine was adjusted to 12:1.
- Then the calorimeter and cooling water flow was set to 70 LPH and 300 LPH respectively.
- After checking all the electrical connections properly the electric supply was started.
- Engine performance analysis software "Engine soft" was opened for on screen analysis of engine performance.
- Then valve provided at burette was opened to start the supply of the diesel to engine.
- After starting, the engine was run for few minutes without application of load.
- After selecting the log option of the software, supply of the fuel was turned on. After one minute of operation the display was switched to input mode and the value of water flow in

cooling jacket and the calorimeter was entered. The first reading of engine was noted at zero load condition. After that the fuel knob was again turned back to its regular position.

- The same procedure was repeated for different loads.
- All the readings for different loads were saved. by changing the screw arrangement
- Then the compression ratio was set to 14:1 16:1 compression ratio and the same procedure was repeated again.
- After noting the readings for all experiments, the engine was brought to zero load conditions. After that the engine and the computer was turned off and the experiment was completed. The fuel supply was stopped after some time.

4.7 Precautions taken during experiment.

- All the nuts, bolts and connections are checked properly before starting the engine.
- Oil level was checked properly in the fuel tank of the engine.
- The engine was attended continuously to ensure the proper supply of cooling water to the engine and dynamometer during the power failure.
- Fuel lines and fuel tank was cleaned properly.
- Sensitive instruments such as, pressure crank angle and sensors were handled very carefully.

4.8 Exhaust emission evaluation

The exhaust emissions of the engine were analyzed by using the flue gas analyzer and horiba analyzer. The emissions parameters of the engine are given in Table 4.4 along with their test methods.

Table 4.4 Emission parameter test method

S. No.	Parameters	Test methods
1	Hydro carbon as HC (ppm)	Horiba analyzer.
2	Carbon monoxide as CO (ppm)	Flue gas analyzer(KM9106)
3	Nitrogen oxides (NO) as NOX (ppm)	Flue gas analyzer(KM9106)
4	Carbon dioxide as CO2 (%)	Flue gas analyzer(KM9106)

Experimental procedure to evaluate the exhaust emissions:

- Sensors were carefully inserted into provided outlet for exhaust gases at the required load condition.
- The analyzer was then attached to exhaust outlet and with the help of various sensors the exhaust gases were made to pass to the analyzer.
- After this the three displayed readings on the digital analyzer screen were noted.
- Mean value of three noted readings were calculated.
- Then the sensors were carefully removed.
- The above steps were repeated at different load conditions for different fuel samples.

CHAPTER 5

RESULT AND DISCUSSIONS

5.1 Experimental Results

The experiments results are grouped into five categories as given below:

- Optimization of parameters affecting production of linseed oil using Taguchi's approach.
- Optimum yield of biodiesel production by transesterification of linseed oil under optimum conditions obtained by Taguchi's approach.
- Validation studies by ANOVA and study of the effects of various control parameters on production of linseed methyl ester.
- Comparison of performance parameters of linseed biodiesel blends with pure diesel.
- Comparison of emission parameters of linseed biodiesel blends with pure diesel.

5.2 DETERMINATION OF OPTIMUM CONDITIONS BY DESIGN OF EXPERIMENTS

The mean yields of linseed methyl ester and respective S/N (Signal to Noise Ratio) ratios of selected experimental conditions are shown in Table 5.1. To minimize the error each experiment was performed under three repetitions. In Taguchi approach S/N ratio measures the deviation of quality characteristic from a desired value. There are three characteristic types of S/N ratio i.e. larger the better, nominal the better and smaller the better [42]. The mean square deviation (MSD) was calculated for larger the better case by using following equation.

$$MSD = \frac{1}{n} \sum_i^n \left(\frac{1}{y_i} \right)^2 \quad (5.1)$$

Where n represents the repetition of experiment and y_i represents the methyl esters yield. Then S/N ratio of performed experiments was calculated by using the following equation.

$$\frac{S}{N} \text{ ratio} = -10 \log(MSD) \quad (5.2)$$

Experiment number 3 offered highest yield and highest S/N ratio (38.740) whereas mean S/N ratio for all the performed experiments was 37.673. The mean S/N ratio for each level of each parameter was calculated as shown in table 5.2. The mean S/N ratio for any level of a parameter

was average of all the S/N ratios of experimental conditions having that parametric level. For example the mean S/N ratio for reaction temperature at value 40°C was calculated by taking the average of S/N ratios of experiments 1,6,8,12,13 and 17 as reaction temperature was 40°C for all these experiments. Similarly the mean S/N ratio for catalyst concentration at value 0.5% (by weight) was calculated by considering S/N ratios of experiments 1,5,8,10,15 and 18. The level having maximum mean S/N ratio gives the optimum value of parameter under consideration. The catalyst concentration was the parameter having highest mean S/N ratio of 38.119 at value 1.5% (by weight). So to maximize the methyl ester production yield, 1:6 molar ratios, 1.5% (by weight) catalyst concentration, 60°C reaction temperature, 60 minutes reaction time and use of KOH as catalyst were the optimum values of controlling parameters. The maximum difference between the mean S/N ratios of each level for any parameter was used to calculate the contribution of that parameter as shown in Table 5.2. Molar ratio and reaction time were least significant and catalyst concentration was most significant parameter for methyl ester production.

Table 5.1 Methyl ester yields from linseed oil and S/N ratios of 18 performed experiments

Experiment no.	Yield of Linseed oil methyl ester				S/N Ratio
	Sample 1	Sample 2	Sample 3	Mean yield	
1	67.1	68.3	66.8	67.4	36.572
2	82.4	84.2	80.9	82.5	38.326
3	84.9	90.1	84.8	86.6	38.740
4	77.9	78.8	81.6	79.4	37.995
5	84.5	79.4	83.9	82.6	38.329
6	65.3	65.4	67.2	66.0	36.384
7	80.3	78.7	83.1	80.7	38.131
8	71.1	75.6	72.8	73.2	37.278
9	78.3	74.7	75.2	76.1	37.618
10	66.2	67.2	64.6	66.0	36.387
11	86.2	86	81.1	84.4	38.520
12	79.7	83.5	84.3	82.5	38.321
13	79.7	83.4	78.6	80.6	38.115
14	77.6	79.2	84.5	80.4	38.092
15	69.3	65.4	66.3	67.0	36.513
16	79.3	76.5	81.4	79.1	37.951
17	76.4	72.8	74.2	74.5	37.434
18	73.3	77.2	72.3	74.3	37.405

Table 5.2 Mean S/N ratio of each level, difference between S/N ratios of levels and contribution of each parameter on methyl ester production.

Parameters	Level			Difference			Contribution (%)
	1	2	3	L ₂₋₁	L ₃₋₁	L ₃₋₂	
Molar ratio (oil/methanol)	37.811	37.571	37.636	-0.240	-0.175	0.065	1.99
Reaction time (minutes)	37.442	38.104	37.472	0.662	0.030	-0.632	20.32
Reaction temperature (°C)	37.351	37.637	38.031	0.286	0.680	0.394	20.87
Catalyst type	37.814	37.196	38.009	-0.618	0.195	0.813	24.95
Catalyst concentration (wt %)	37.081	37.819	38.119	0.738	1.038	0.300	31.86

5.3 EXPECTED YIELD FROM OPTIMUM VALUES OF PARAMETERS

The contribution of parameters in S/N ratio for all the parameters is shown in Figure 5.6. Catalyst concentration was found to be most effecting parameter with .446 parametric contributions. The parametric contribution is modification which can be obtained by optimum values of parameters and is calculated from the difference between S/N ratios of parameter under optimum value and mean S/N ratio (37.673). As shown in Table 5.3 the contribution for catalyst concentration was calculated by subtracting the average value of S/N ratio (37.673) from 38.119 which is highest S/N ratio for 1.5 (wt %) catalyst concentration. Similarly the contribution for catalyst type was found to be .336 and total contribution of all the parameters was 1.709 which was added to average S/N ratio to calculate expected S/N ratio under optimum conditions. Theoretically, the expected yield of linseed oil methyl ester was determined by equations (5.1) and (5.3).

$$y_{exp} = (MSD)^{-0.5} \quad (5.3)$$

For expected S/N ratio (39.382) the MSD was found to be .0001190 and 93.13% expected yield was calculated by using equation (5.3) which was higher than all the experiments performed under orthogonal array.

Table 5.3 Contribution of all parameters and expected S/N ratio under optimum conditions.

Parameters	Levels	Description	Contribution
A Molar ratio (oil/methanol)	3	1:6	0.138
B Reaction time (minutes)	3	60	0.431
C Reaction Temperature (°C)	3	60	0.358
D Catalyst type	3	KOH	0.336
E Catalyst concentration (wt %)	3	1.5	0.446
Total contribution from all parameters			1.709
Average S/N ratio			37.673
Expected S/N ratio for optimum conditions			39.382

The various fuel properties of optimized linseed biodiesel were compared with the pure diesel and in accordance with the specifications as per the ASTM standards. According to the observations made by experimental results the properties of linseed biodiesel shown in Table 5.4 were in confirmation with the latest biodiesel standards. The calorific value of linseed biodiesel was 9271 kcal/kg which is about 7.9 % lower than the diesel fuel. The fire and flash point of optimized linseed biodiesel were recorded to be higher than that of diesel fuel. The pour and cloud point for linseed biodiesel were observed to be lower than the pure diesel.

Table 5.4 Properties of diesel and linseed biodiesel according to ASTM standards.

Property of oil	ASTM standards	Diesel	Linseed biodiesel (B100)
Density (kg/m ³)	-----	850	875.8
Kinematic viscosity (centistokes)	1.9-6.0	2.049	4.322
Flash point (°C)	>130	78	153
Fire point (°C)	>53	83	158
Cloud point (°C)	-3 to 12	<10	-2

Pour point (°C)	-15 to 10	-6	-6
Calorific value, (kJ/kg)	> 33000	42000	38904.2
Carbon residue, (%)	<0.050	0.0214	0.0179%
Ash content, (%)	0.02% max	0.02	0.02
pH	-----	-----	7.7
FFA, (%)	<2.5	-----	0.0702

5.4 VALIDATION STUDIES BY ANOVA (ANALYSIS OF VARIANCE)

The results obtained from Taguchi method for optimization of linseed oil methyl ester production were statistically verified by ANOVA (analysis of variance). The term variance ratio, which is ratio of variance of factor to error variance, distinguishes the more significant factors from less significant. More than 9 variance ratio for a factor represents that the factor is having an important effect on linseed oil methyl ester production yield [44]. Table 5.5 shows the analysis of variance using S/N ratios of performed experiments for all parameters.

The various terms of ANOVA such as variance (v), variance ratio (F), sum of squares (S), total sum of squares (S_T), correction factor ($C.F.$), pure sum of squares (S_p) and percentage contribution (P) are calculated for all parameters by using the following equations.

$$C.F. = \frac{T^2}{n} \quad (5.4)$$

$$S_T = \sum_i^n y_i^2 - C.F. \quad (5.5)$$

$$S = \frac{A_1^2}{N_1} + \frac{A_2^2}{N_2} + \frac{A_3^2}{N_3} - C.F. \quad (5.6)$$

$$V = \frac{S}{f} \quad (5.7)$$

$$F = \frac{V}{V_e} \quad (5.8)$$

$$S_p = S - f \times V_e \quad (5.9)$$

$$P = S \times 100/S_T \quad (5.10)$$

Where T is total of all the yields obtained, n is total number of experiments, A_1 is sum of all the S/N ratios under level 1 of any parameter, N_1 is number of experiments having level 1 of any parameter, A_2 is sum of all the S/N ratios under level 2 of any parameter, N_2 is number of experiments having level 2 of any parameter, A_3 is sum of all the S/N ratios under level 3 of any parameter, N_3 is number of experiments having level 3 of any parameter, f is the degree of freedom of parameter and V_e is the error variance.

For example to calculate the sum of squares for catalyst concentration A_1 was calculated from the sum of all the S/N ratios from experiments 1,5,8,10,15 and 18 because these experiments were carried out for 0.5 (wt %) catalyst concentration (level 1) and N_1 is 6 here as total 6 experiments are having .5 (wt %) catalyst concentration. From values of A_1, N_1, A_2, N_2, A_3 and N_3 the sum of squares was calculated by using the equation (5.6) which was found to be 5.294. By the same manner sum of square was calculated for each parameter.

Table 5.5 ANOVA Table to determine influence of parameters.

Parameters	Degree of freedom	Sum of Squares	Variance	Variance ratio	Pure sum of squares	Contribution (%)
Molar ratio (oil/methanol)	2	0.184	0.092	0.534	-0.16	1.83
Reaction time (minutes)	2	1.679	0.839	4.877	1.335	16.70
Reaction temperature (°C)	2	1.399	0.699	4.064	1.055	13.91
Catalyst type	2	2.162	1.081	6.285	1.818	21.50
Catalyst concentration (wt %)	2	3.426	1.713	9.959	3.082	34.07
Error	7	1.204	0.172	1.000	2.925	11.97
Total	17	10.055	4.596			100

The error in ANOVA table is because of uncontrollable factors which were not considered in experiment. Modified ANOVA table (Table 5.6) was prepared by pooling. Neglecting the effect of an individual parameter and using it to determine error variance is called pooling. As contributions of molar ratio, reaction temperature and reaction time were in the range of experimental error so these parameters were pooled with error and there was a little modification in percentage contribution of dominant parameters. The detailed concept of pooling and its use is discussed by Roy [44]. Catalyst concentration was found to be most effecting parameter having variance ratio more than 9. This was with agreement of results from Taguchi approach.

Table 5.6 ANOVA Table to determine influence of parameters (with pooling).

Parameters	Degree of freedom	Sum of Squares	Variance	Variance ratio	Pure sum of squares	Contribution (%)
Molar ratio (oil/methanol)				Pooled		
Reaction time (minutes)	2	1.679	0.839	5.448	1.371	13.63
Reaction temperature (°C)	2	1.399	0.699	4.539	1.091	10.85
Catalyst type	2	2.162	1.081	7.019	1.854	18.44
Catalyst concentration (wt %)	2	3.426	1.713	11.123	3.118	31.01
Error	9	1.388	0.154	1.000	2.621	26.07
Total	17	10.055	4.486			100

5.5 Effects of parameters on methyl ester production

5.5.1 Effect of Molar ratio (oil/ methanol)

As shown in Figure 5.1 mean S/N ratio was 37.571 for molar ratio 1:8 and was 37.636 for molar ratio 1:10. The maximum mean S/N ratio (37.811) was for molar ratio 1:6. Performance was reduced for higher molar ratios because excessive methanol was dissolved in byproduct glycerin reducing the methyl ester yield. Molar ratios less than 1:6 were not suitable as some excess methanol is required to shift the equilibrium of reversible reaction to product side. So to maximize the methyl ester yield 1:6 is optimum value of molar ratio. Colluci et al. [49] recorded about 10% increase in methyl ester yield with change in molar ratio from 1:3 to 1:6 and slight

decrease with change from 1:6 to 1:9. Hanh et al. [47] also recorded 1:6 as optimum value of molar ratio for biodiesel production. As shown in Figure 6 the molar ratio has 1.99% contribution in linseed oil methyl ester production.

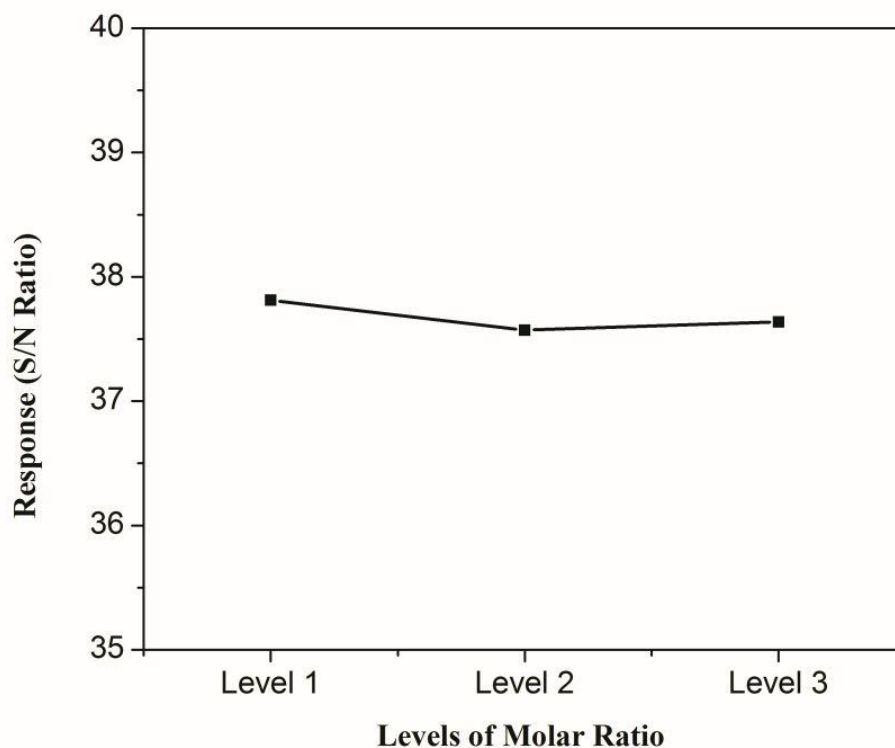


Figure 5.1 Variation of S/N ratio with molar ratio.

5.5.2 Effect of reaction time:

As shown in Figure 5.2 the mean S/N ratio increased from 37.442 to 38.104 with increase in reaction time from 40 minutes to 60 minutes and was decreased to 37.472 for 80 minutes reaction time. As heterogeneous mixture is formed by oil and methanol because of their immiscibility towards each other so methyl ester yield was improved with increase in reaction time. As shown in Figure 5.6 reaction time has 20.32% contribution in linseed oil methyl ester production.

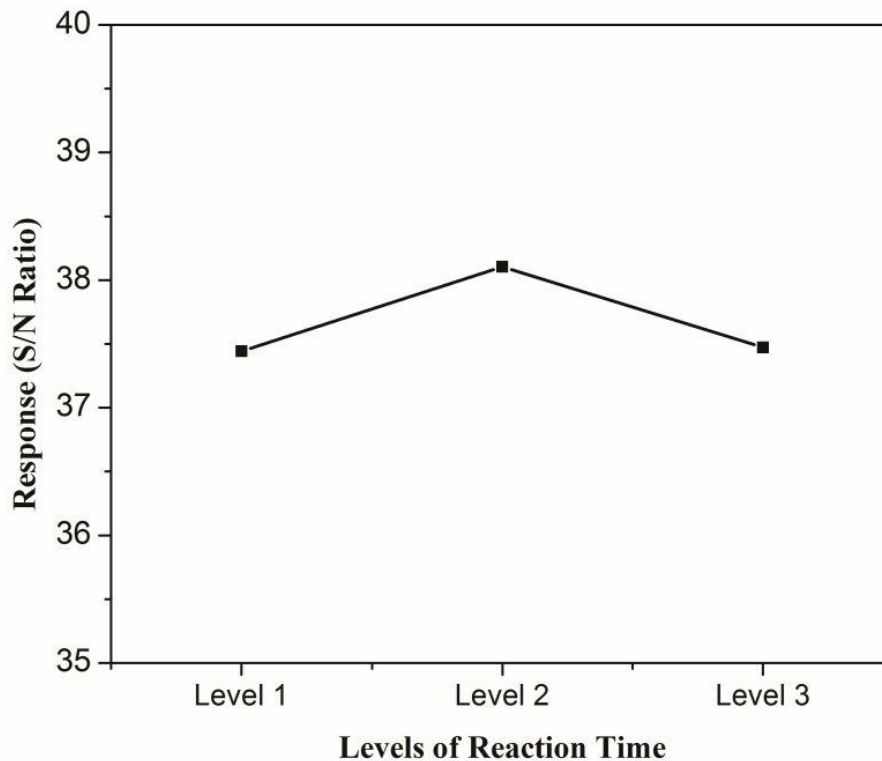


Fig. 5.2: Effect of reaction time on S/N ratio

5.5.3 Effect of reaction temperature:

Rate of transesterification reaction increases at higher temperatures and was reported optimal at 60°C [46c]. In this study reaction temperature was seen as an important parameter after catalyst concentration and catalyst type for biodiesel production from linseed oil having 20.87% contribution in production yield as shown in Figure 6. Because of improved reaction rate at higher temperatures mean S/N ratio increases from 37.351 to 37.637 with increase in reaction temperature from 40°C to 50°C. The optimum value of reaction temperature was 60°C with mean S/N ratio of 38.031 as shown in Figure 5.3.

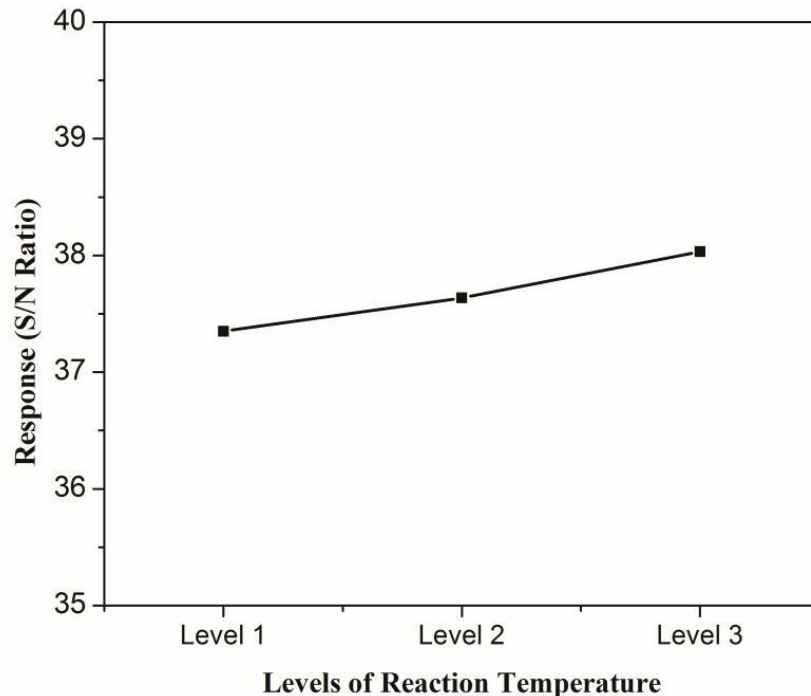


Fig. 5.3: Effect of reaction temperature on S/N ratio

5.5.4 Effect of catalyst type and concentration:

Percentage contribution of type of catalyst was 24.95% and KOH was the catalyst having highest mean S/N ratio as shown in Figure 5.4 proving it the most suitable catalyst among all three. The mean S/N ratio increases linearly with increase in catalyst concentration from level 1 to level 2 and from level 2 to level 3. Lower cost of KOH provides an additional benefit of its use.

As shown in Figure 5.6 catalyst concentration was most dominant parameter with 31.86% contribution (Figure 5.5) in methyl ester production. Some researchers have also recorded similar effects [47]. Methyl ester yield was seen improved with increase in catalyst loading. As shown in Figure 4 mean S/N ratio was maximum for 1.5% (by weight) catalyst concentration. The increase in production yield with increase in catalyst loading was with agreement of previous researches [48] Catalyst loading more than 1.5% (by weight) is not suitable because soap formation occurs at higher catalyst concentrations which cause incomplete reaction. This is because high FFA content deactivates the catalyst and addition of excess catalyst gives rise to emulsification which leads to the formation of gels reducing methyl ester yield.

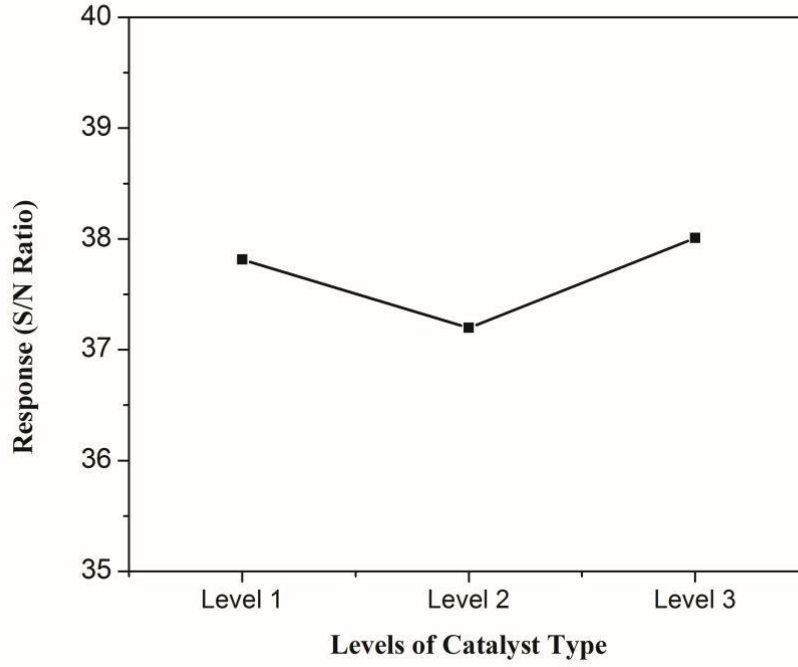


Fig. 5.4: Effect of catalyst type on S/N ratio.

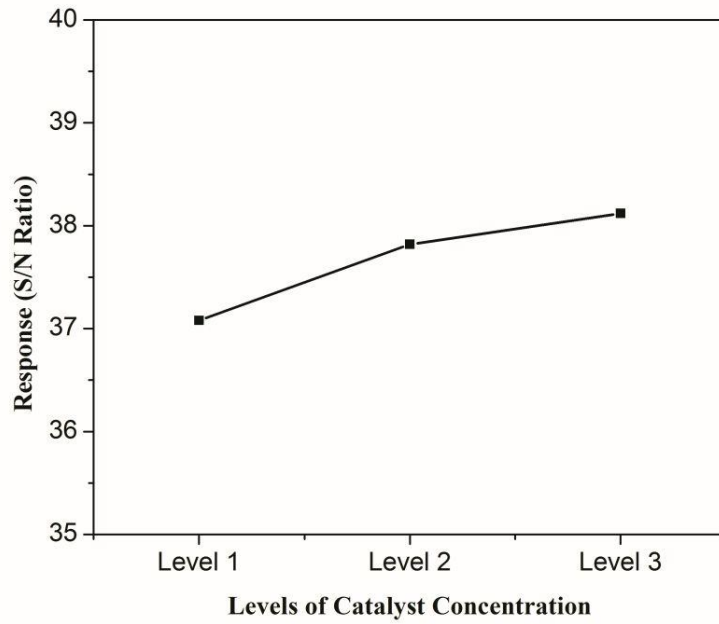


Fig 5.5: Effect of catalyst concentration on S/N ratio.

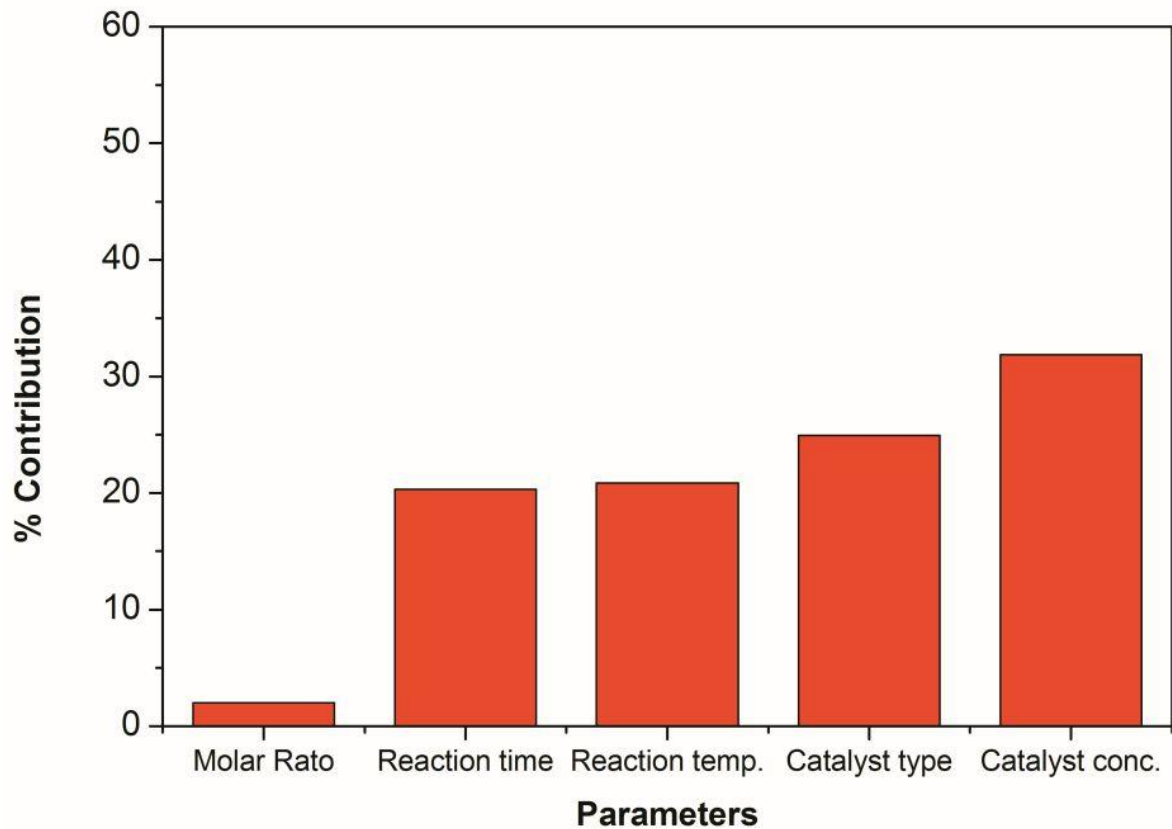


Fig. 5.6: Percentage contribution of each parameter on biodiesel production.

5.6 ENGINE PERFORMANCE AND EMISSION PARAMETERS OF LINSEED OIL AND ITS BLENDS

The experiments were carried out with the pure diesel, B10, B20 and B30 blends of biodiesel at three different compression ratios (CR12, CR14, CR16) in the single cylinder four stroke variable compression ratio engine. The performance parameters such as, brake power (BP), brake thermal efficiency (BthEff), brake specific fuel consumption (BSFC), mechanical efficiency (MechEff), cylinder pressure and brake mean effective pressure (BMEP) were evaluated

5.6.1 Performance parameters

5.6.1.1 BRAKE POWER (BP)

- **Effect of blend**

The variation of brake power with the amount of blend and load at different compression ratios is represented in the figures below. It was observed that with the increase in amount of blend in the diesel BP was decreased. This is because of the low calorific or heating value of blends. The BP of the biodiesel blends was observed to be lower than that of pure diesel. The BP of B10 blend was higher than all the other blends of biodiesel due to more calorific value. According to the experimental observations the variation in BP is less at higher loads because of less losses of heat at higher loads. It was observed that with the increase in load the brake power increases, due to increase in the torque with load. The variation of the brake power (BP) with blend and load proportion at CR12, CR 14 and CR 16 is illustrated in fig 5.7, 5.8, 5.9 respectively.

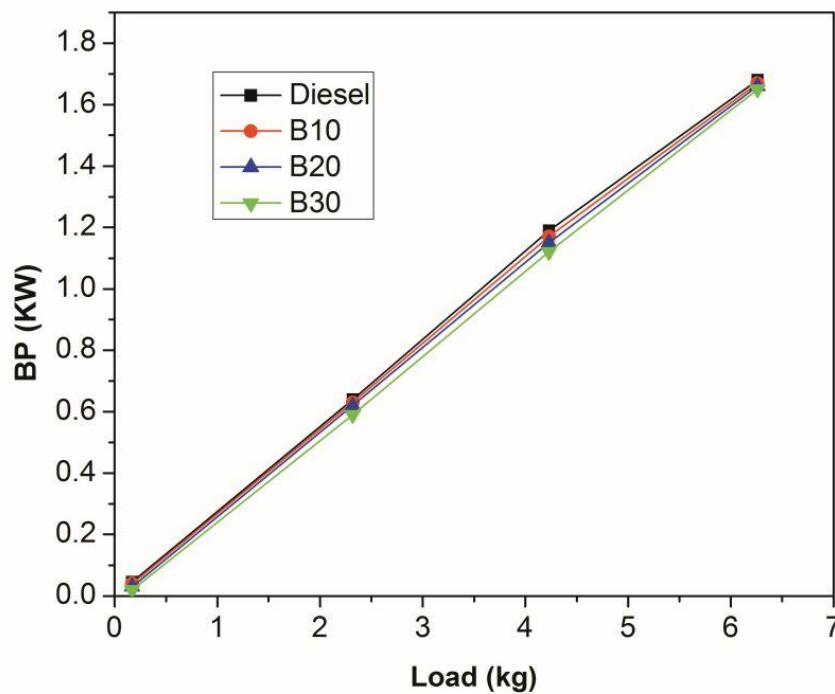


Fig 5.7: Variation of brake power with load at compression ratio 12

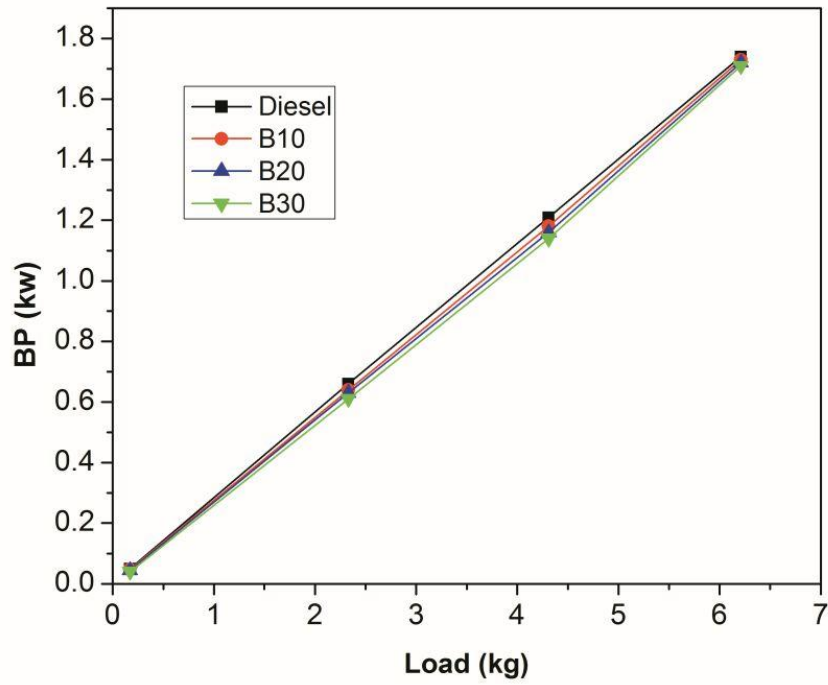


Fig 5.8: Variation of brake power with load at compression ratio 14

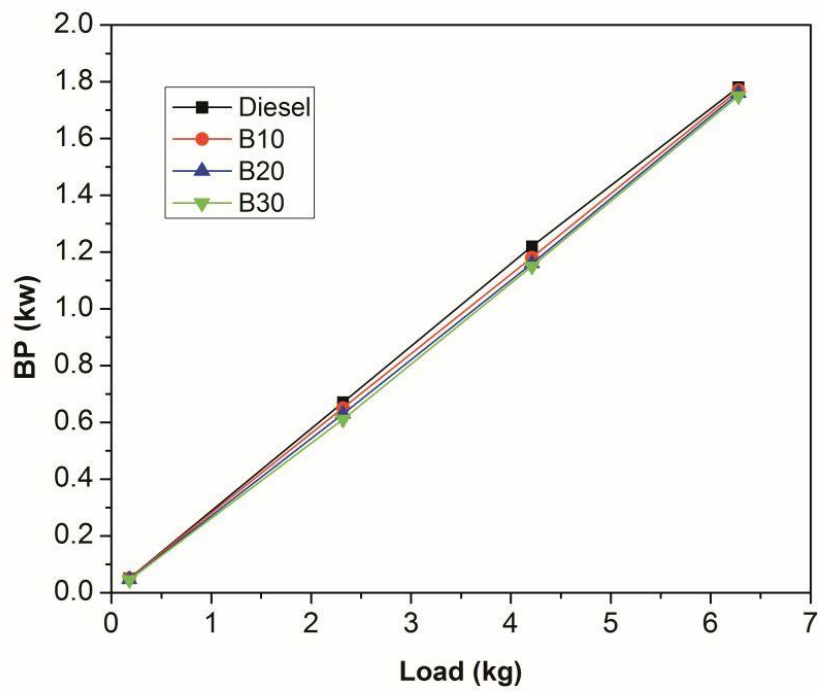


Fig 5.9: Variation of brake power with load at compression ratio 16

- **Effect of compression ratio**

It was seen that the break power of engine increases, with the increase in compression ratio. This is mainly because of increase in torque at higher compression ratios. Increase in the compression ratio induces more turning effect on cylinder crank. This means that the combustion is causing more push on the piston of engine, and thus more torque is generated. The effects of varying the compression ratio on BP of B10 blend of biodiesel is illustrated in fig 5.10. It was observed by the experimental results that among CR12, CR14 and CR16 brake power was higher with CR16 for all load conditions.

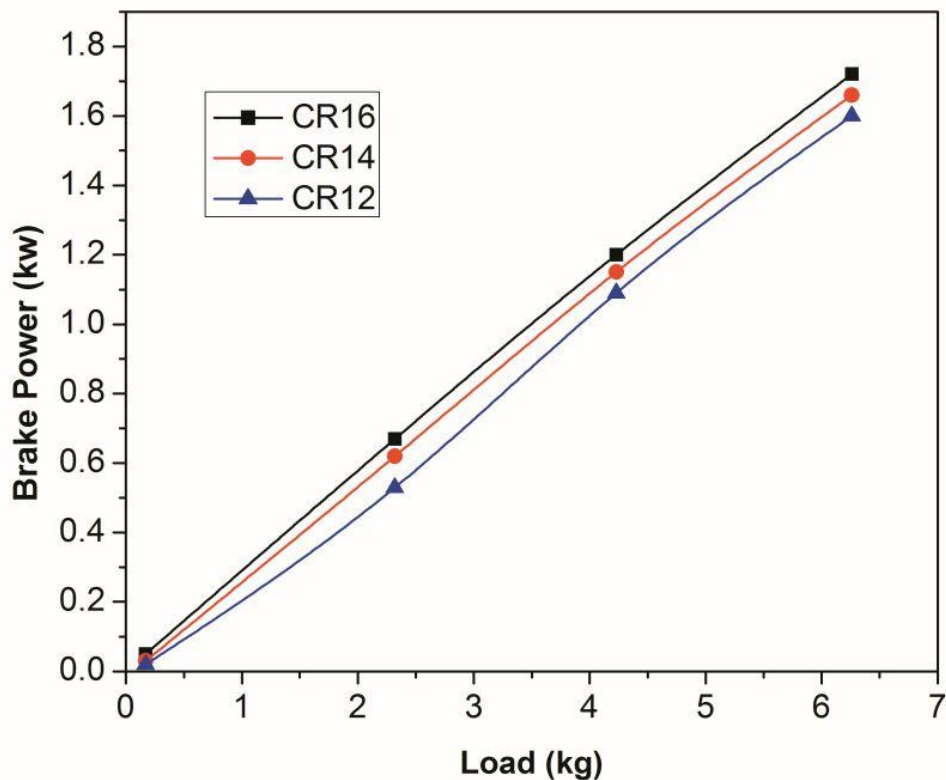


Fig 5.10: Variations of brake power with compression ratio

5.6.1.2 BRAKE SPECIFIC FUEL CONSUMPTION (BSFC)

- **Effect of load and blend**

The brake specific fuel consumption of pure diesel fuel and three different linseed biodiesel blends i.e. B10, B20, and B30 were compared. According to the experimental observations BSFC

decreases sharply with increase in load for all compression ratios and fuels. This was mainly because of the reason that percent increase in the fuel required to operate the engine is less than the percent increase in brake power due to relatively less portion of the heat losses at higher loads. The brake specific fuel consumption of diesel fuel was observed to be lower than all the blends of biodiesel. As the amount of blend increased, an increase in the brake specific fuel consumption of the engine was observed. The BSFC of B30 was observed to be higher than all other blends. The higher density of linseed oil biodiesel is the main reason for this. So, density of fuel increases with the increases in amount of blend. The higher densities of blended fuel caused higher mass injections for the same volume. Therefore because of high density of biodiesel fuel consumption is more. The variation of brake specific fuel consumption of different blends and pure diesel with load at CR16 is illustrated in the fig. 5.11.

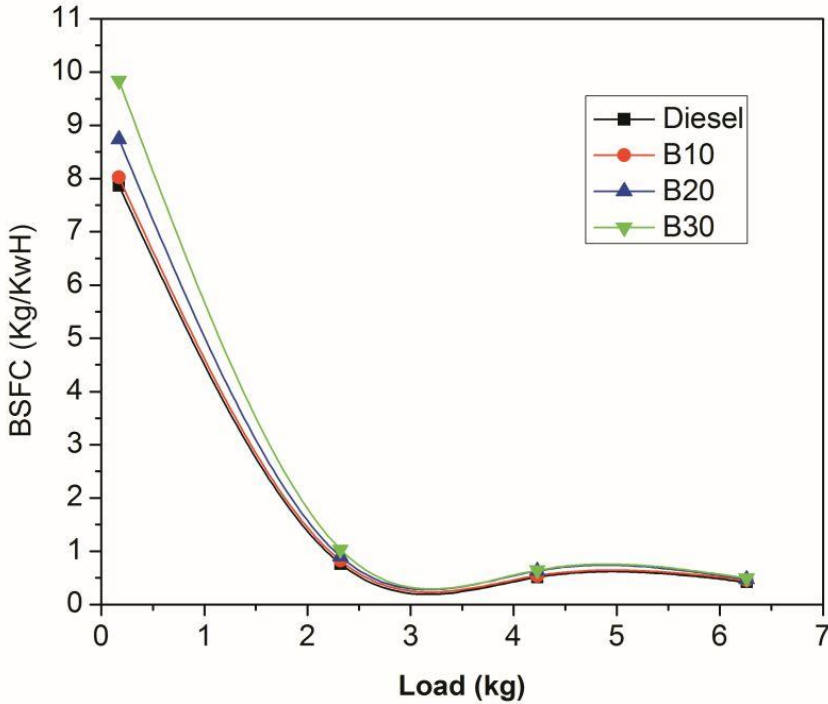


Fig 5.11: Variation of BSFC with load at compression ratio 16

The variation of brake specific fuel consumption at full load was observed to be less as compared to the part loads. This was due to the less variation in brake power (BP) of engine at full loads. The variation of brake specific fuel consumption with load for CR14 and CR12 is shown in fig 5.12 and 5.13 respectively.

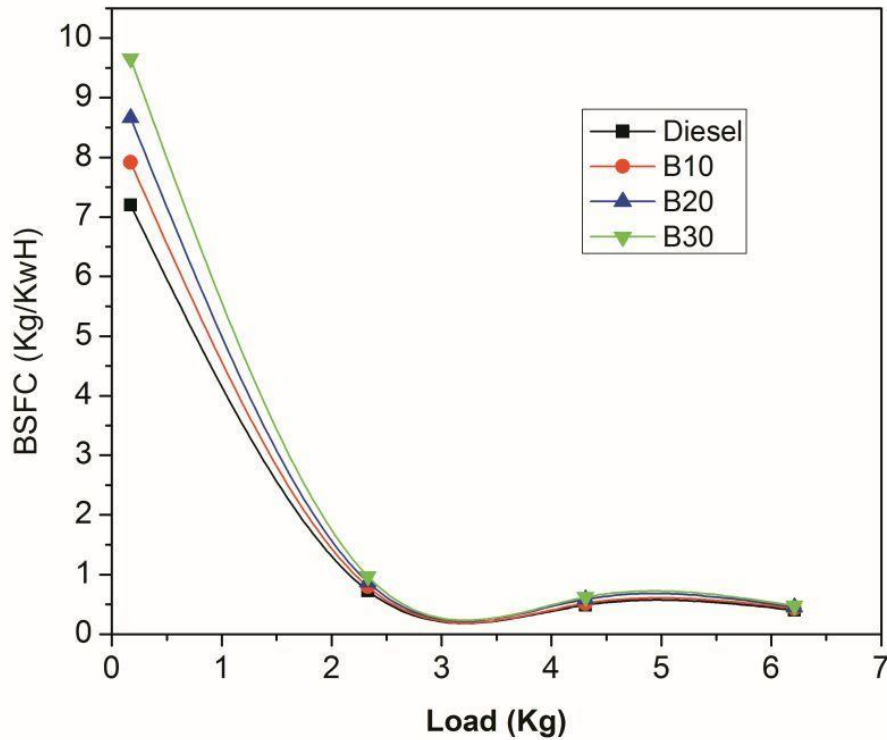


Fig 5.12: Variation of BSFC with load at compression ratio 14

Effect of compression ratio on brake specific fuel consumption

According to the experimental observations the brake specific fuel consumption was decreased with increase in compression ratio of engine from 12 to 16. The BSFC with CR 16 was observed to be less than CR12 and CR14. This is mainly because of the increase in brake power with increase in compression ratio. The higher compression ratio causes better combustion due to rise in temperature in the combustion chamber of engine which led to improved combustion of the fuel and hence causes increase in the brake power and therefore decrease in BSFC. The effects of increase in compression ratio on the variation of the brake specific fuel consumption of B10 blend is illustrated in fig 5.14.

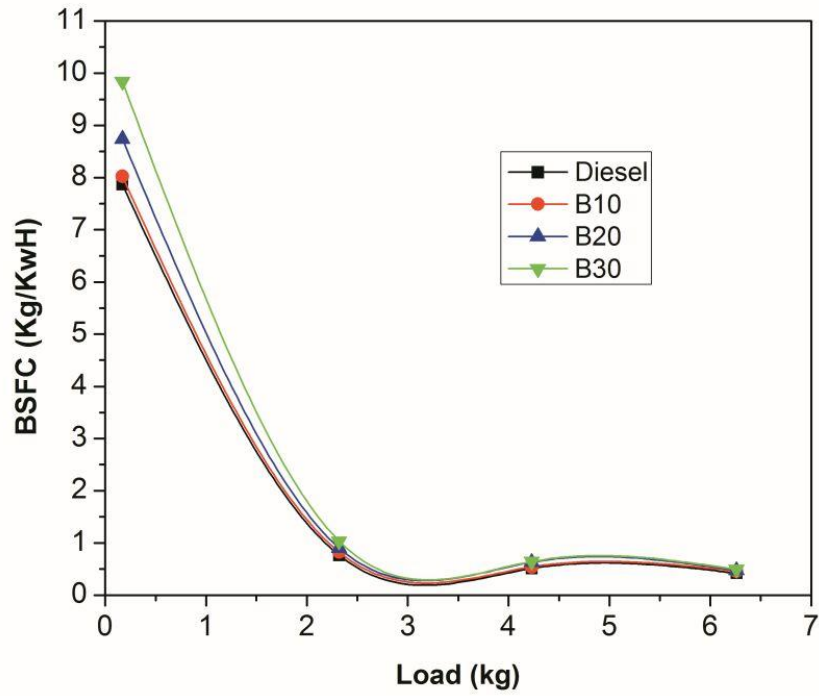


Fig 5.13: Variation of BSFC with load at compression ratio 12

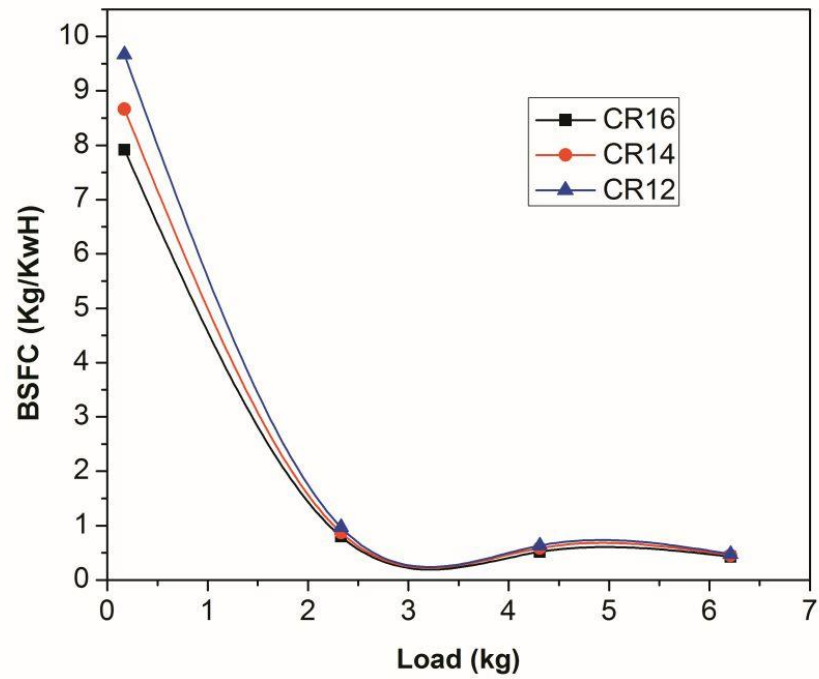


Fig 5.14: Variation of BSFC with load and compression ratio

5.6.1.3 BRAKE THERMAL EFFICIENCY

Effect of load and blend: The brake thermal efficiency of the engine was low at part load conditions. An improve was observed in the brake thermal efficiency with the increase in load and this was mainly because of relatively less power loss with increasing load. Also, brake thermal efficiency was observed to be decreased with the increase in amount of blend content. This is due to higher viscosity of biodiesel blends which led to the poor atomization of the fuel and poor combustion. The other reason for this decreased brake thermal efficiency of the engine with the amount of blend content is because of the increased fuel consumption which is due to higher density of blended fuel. The variation of brake thermal efficiency with blend content and load at different compression ratios is illustrated in fig 5.15.

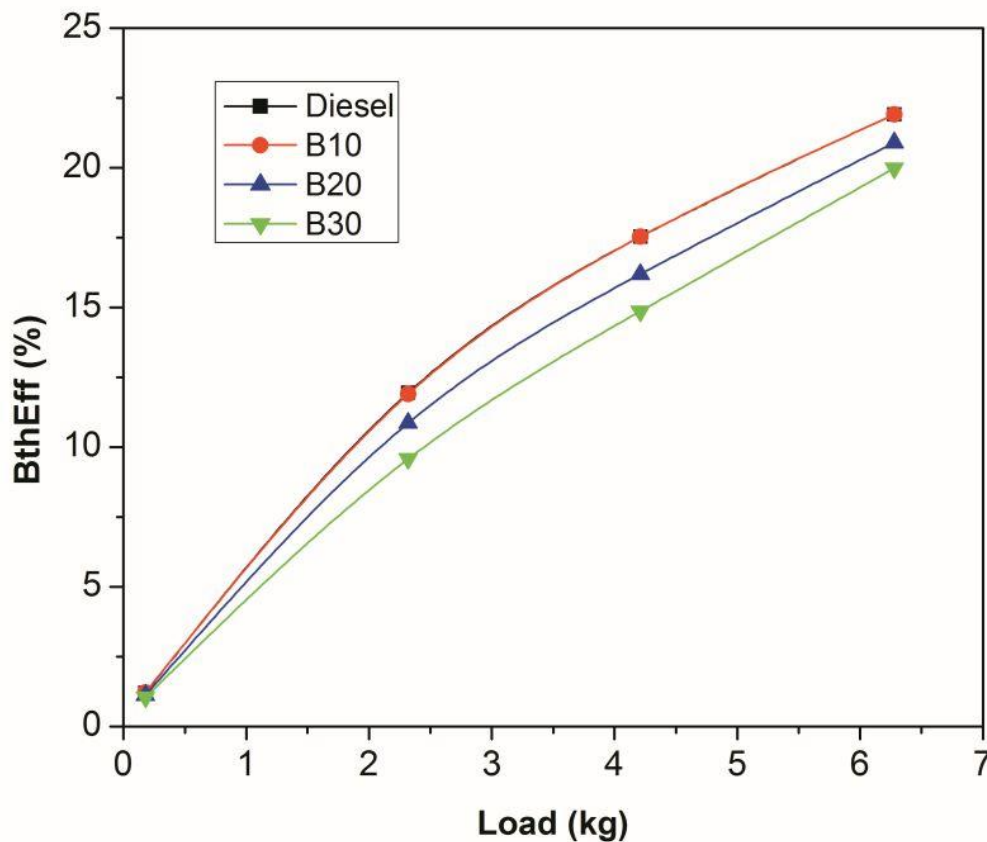


Fig 5.15: Variation of Brake Thermal Efficiency with load at compression ratio 16

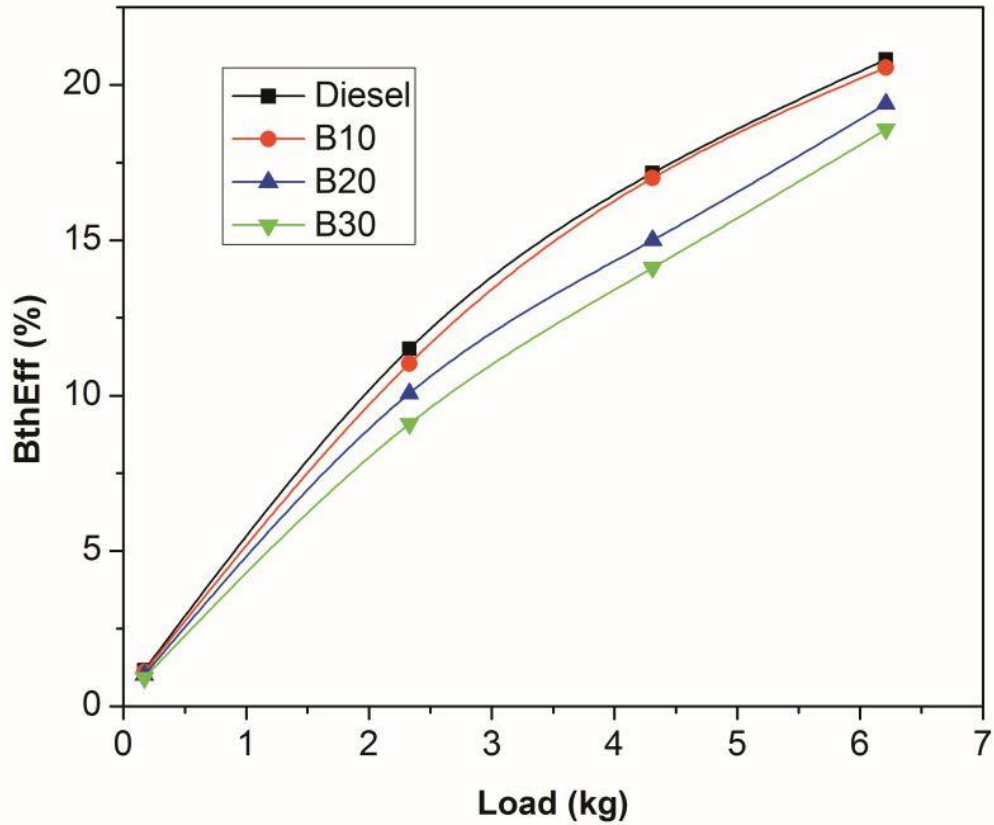


Fig 5.16: Variation of Brake Thermal Efficiency with load at compression ratio 14

At CR 16 the highest value of brake thermal efficiency was observed to be 21.9% for pure diesel fuel. Among blends, the brake thermal efficiency was observed to be highest for B10 blend and was 21.6%.

Effect of compression ratio

The brake thermal efficiency of engine was observed to be increased with increase in compression ratio. The brake thermal efficiency was observed to be highest with the compression ratio 16 at all load conditions. This trend is observed because air temperature is high at higher compression ratio, which results in better combustion of the fuel. The brake thermal efficiency variation with compression ratio and load for B10 blend is illustrated in fig 5.18.

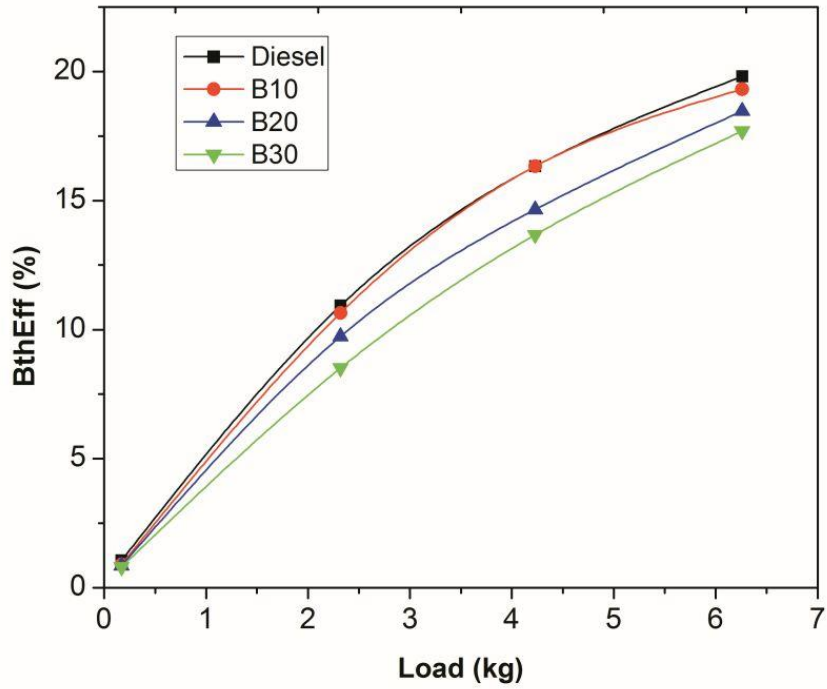


Fig 5.17: Variation of Brake Thermal Efficiency with load at compression ratio 12

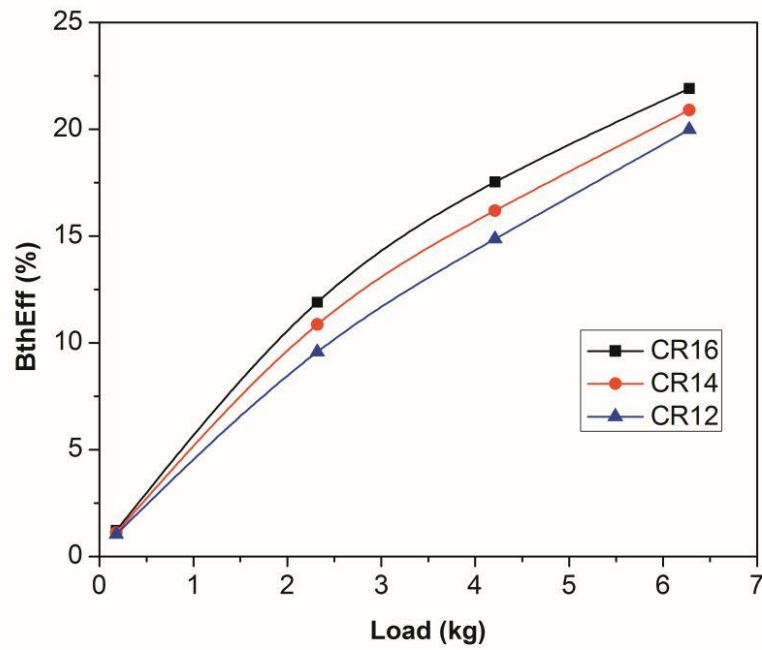


Fig 5.18: Variation of Brake Thermal Efficiency with load and compression ratio

5.6.1.4 MECHANICAL EFFICIENCY

Effect of blend

At all load conditions the mechanical efficiency of engine was observed to be lowest for the diesel fuel. With increase in load there was increase in mechanical efficiency because of the increase in brake power. Biodiesel blends exhibited better mechanical efficiency than the pure diesel fuel. This is mainly due to better lubrication properties of blended fuels than that of diesel fuel. The mechanical efficiency of B30 blend of linseed biodiesel was the highest among all fuel samples i.e. Diesel, B10, and B20. This is mainly due to more viscosity and better lubricity properties B30 blend have. The mechanical efficiency of B30 blend was observed to be 35.9% while that of the diesel was 34.4% at full load and CR14. At CR16 it was 39.4% for B30 blend and 36.5% for the diesel respectively. The variation in the mechanical efficiency with the variation of load at CR16, CR14 and CR12 is illustrated in figures 5.19, 5.20, 5.21.

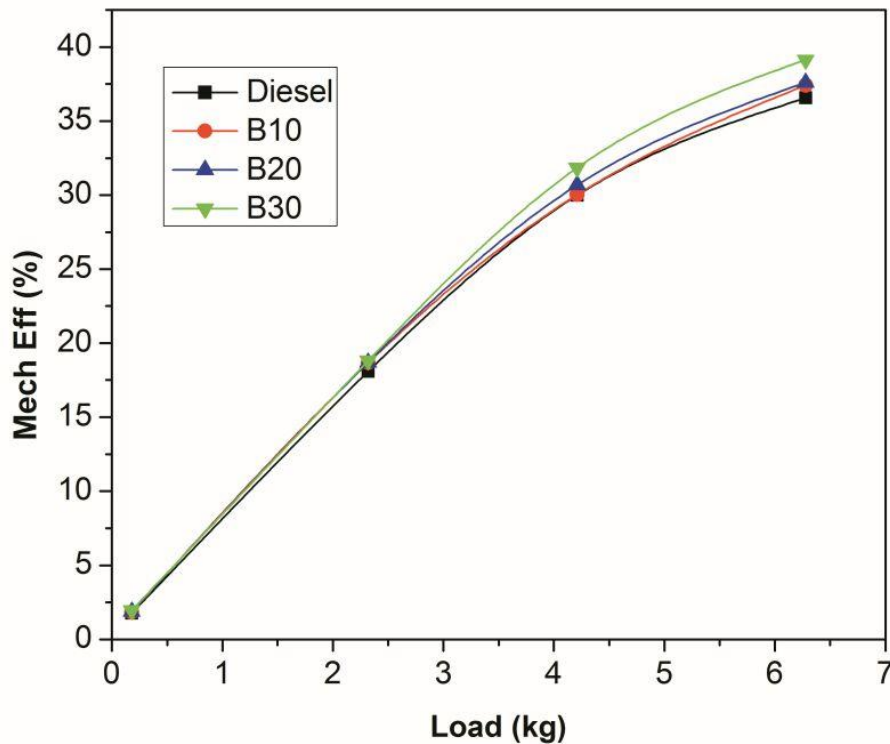


Fig 5.19: Variation of Mechanical Efficiency with load at compression ratio16

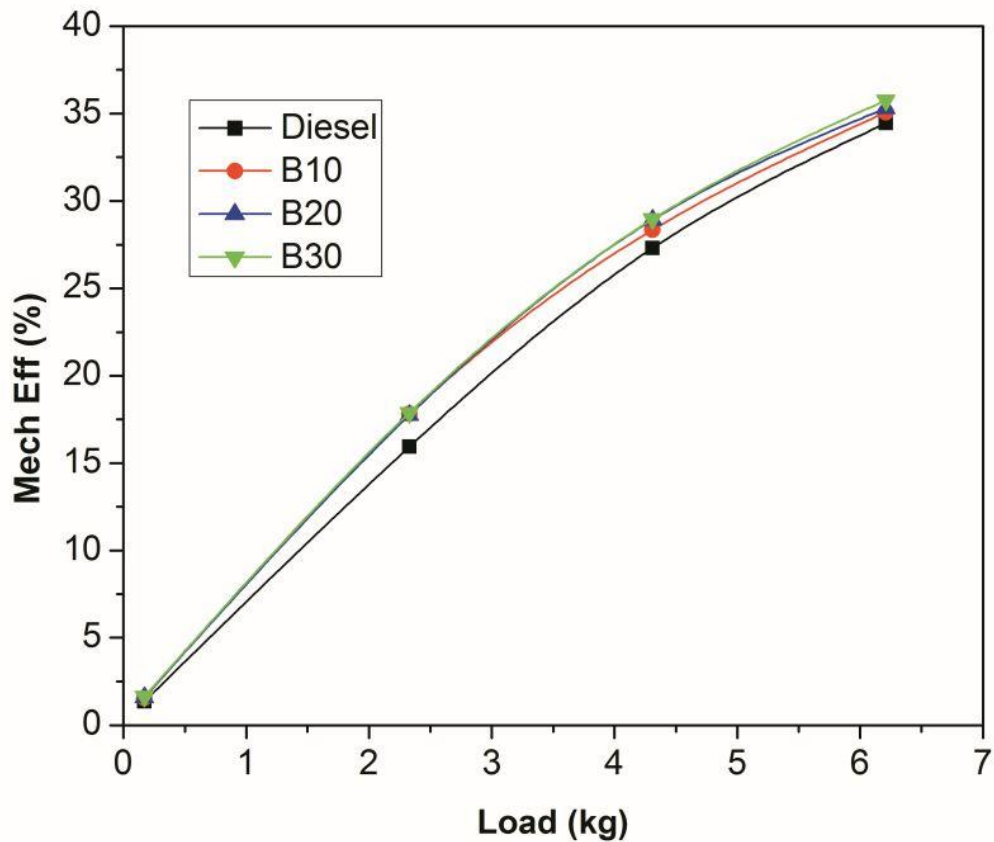


Fig 5.20: Variation of Mechanical Efficiency with load at compression ratio14

Effect of compression ratio

According to the observations there was an increase in the mechanical efficiency with the increase in compression ratio the increases. The mechanical efficiency of B30 blend was highest for CR 16 at all loads. The mechanical efficiency of B30 blend at CR 16 and at full load application was observed to be 39.3% while at CR14 and CR12 was 35.8% and 34.2% respectively. The variation of mechanical efficiency at all compression ratios for B30 blend of linseed biodiesel is illustrated in fig 5.22. This increase observed in mechanical efficiency is mainly due to the increase in BP with increase in compression ratio. Since the brake power of the engine at CR 16 is higher than at CR12 and CR 14 therefore the mechanical efficiency is also higher at CR 16.

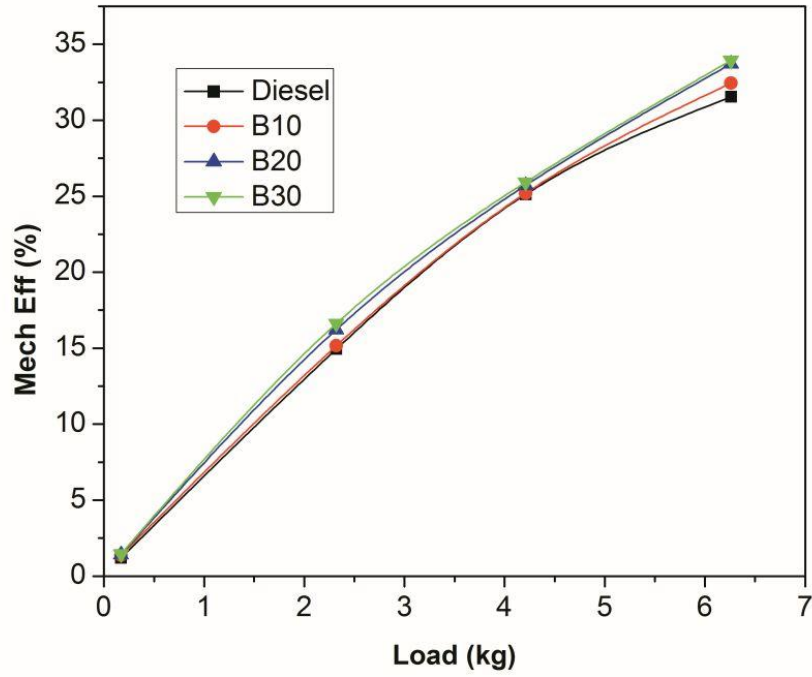


Fig 5.21: Variation of Mechanical Efficiency with load at compression ratio 12

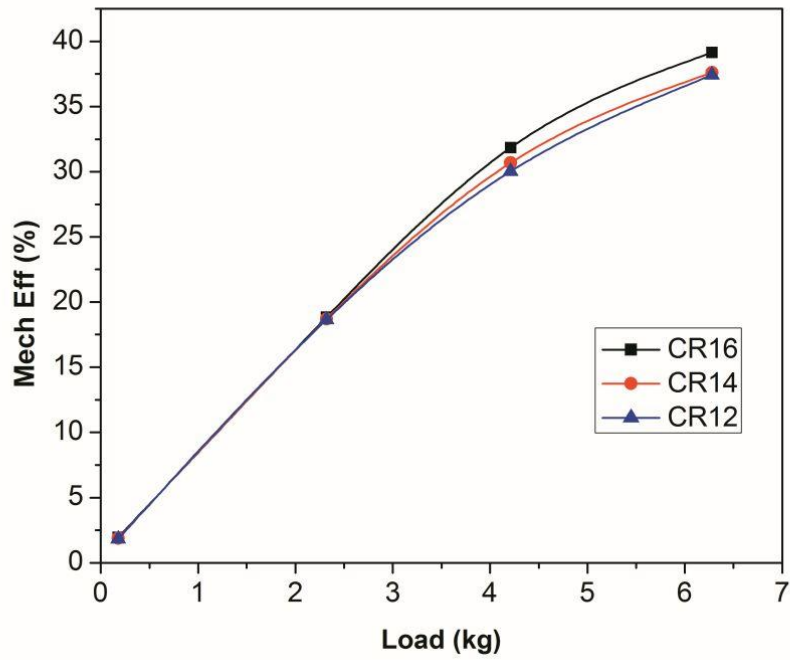


Fig 5.22: Variations in mechanical efficiency with compression ratio of B20 blend.

5.6.1.5 BRAKE MEAN EFFECTIVE PRESSURE

The mean effective pressure is defined as the average pressure on piston head over a cycle in combustion chamber of the engine, which measures the capacity of the engine to do work.

Effect of blend and compression ratio

Slight variations were observed in brake mean effective pressure with amount of biodiesel blend. An increase was observed in BMEP with the increase in load application. The lower BMEP was observed at higher loads for pure diesel fuel as compared to B10 blend. It may be because of the proper burning of the fuel due to more oxygen content in biodiesel molecule. The BMEP was observed to be increased by increasing the compression ratio. For all load conditions the BMEP with CR16 was observed to be higher than the CR12 and CR14. The BMEP for B10 blend was found to be nearly same as the pure diesel fuel. The variation of brake mean effective pressure at CR16, CR14, and CR12 is illustrated in Figures 5.23, 5.24, 5.25 respectively.

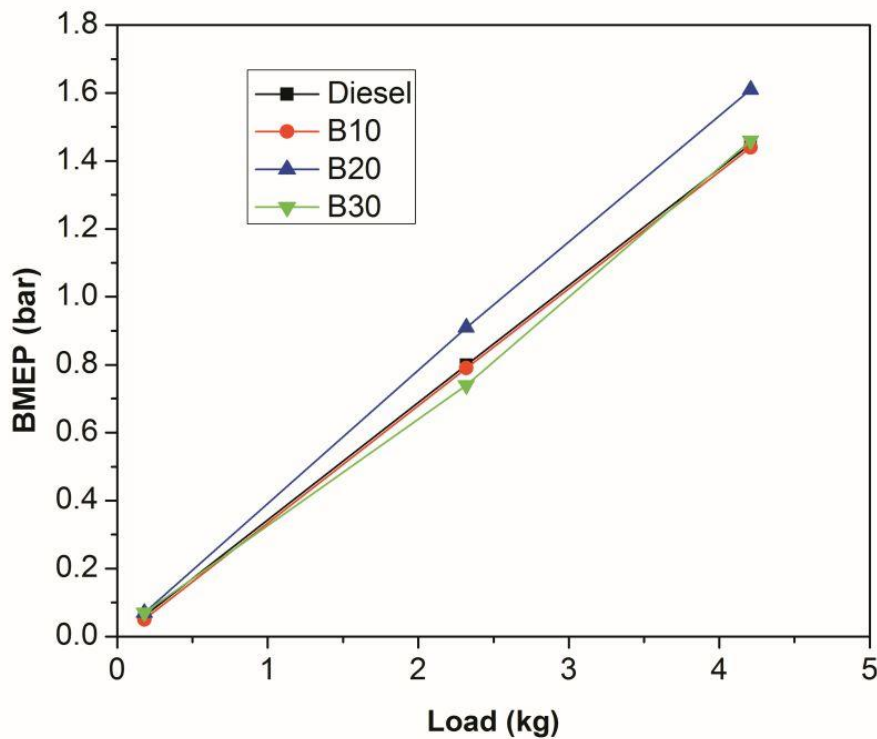


Fig 5.23: Variation of Brake Mean Effective Pressure with load at compression ratio 16

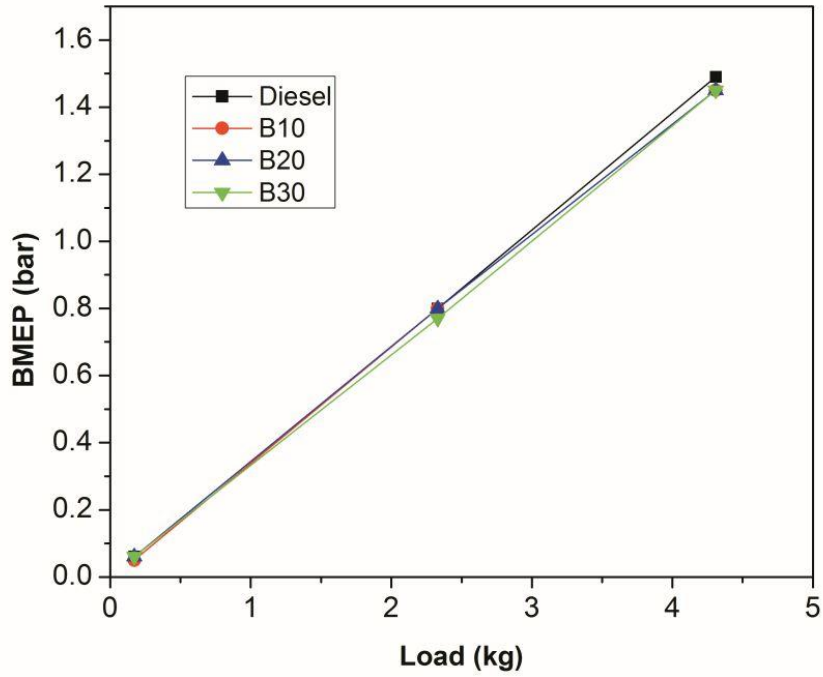


Fig 5.24: Variation of Brake Mean Effective Pressure with load at compression ratio 14

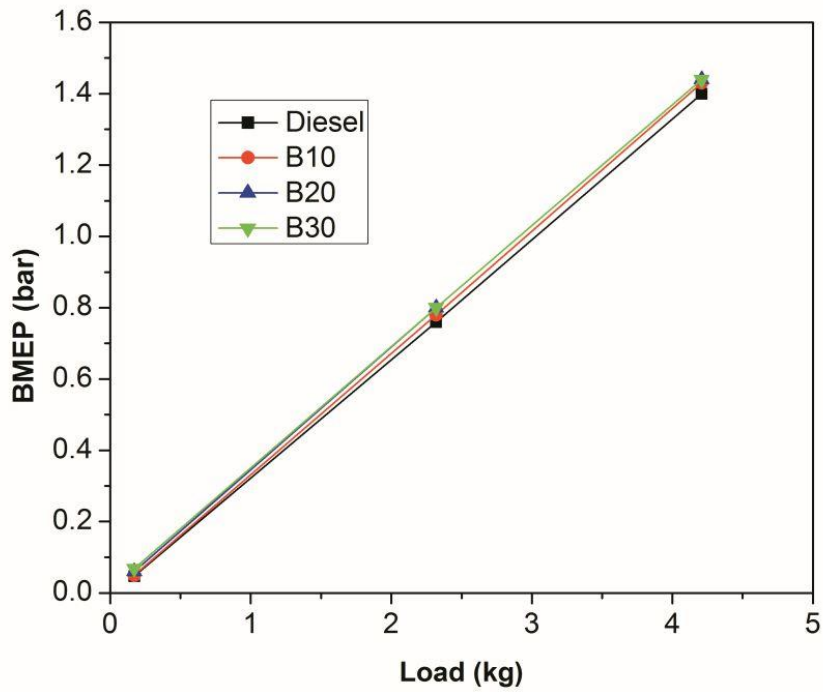


Fig 5.25: Variation of Brake Mean Effective Pressure with load at compression ratio 12

5.6.1.6 Variation in cylinder pressure

The variation of the cylinder pressure for diesel, B10, B20 and B30 with the crank angle at CR16, CR14, and CR12 was compared. According to experimental observations the peak pressure in combustion chamber was obtained between 300° to 450° crank angle. The maximum peak pressure for B10 blend was found to be nearly close to diesel fuel for all compression ratios. This may be because of higher calorific value of B10 blend than other blends which results in better combustion. The cylinder pressure was observed to be lowered with the amount of blend. This is due to higher viscosity of biodiesel blend due to which the proper atomization of fuel may not take place. On increasing the compression ratio cylinder pressure or the peak pressure was observed to be increased. This may be because of the better combustion of the fuel at higher compression ratios. The variation of cylinder pressure with CR16, CR14, and CR12 is shown in the figures 5.26, 5.27 and 5.28 respectively.

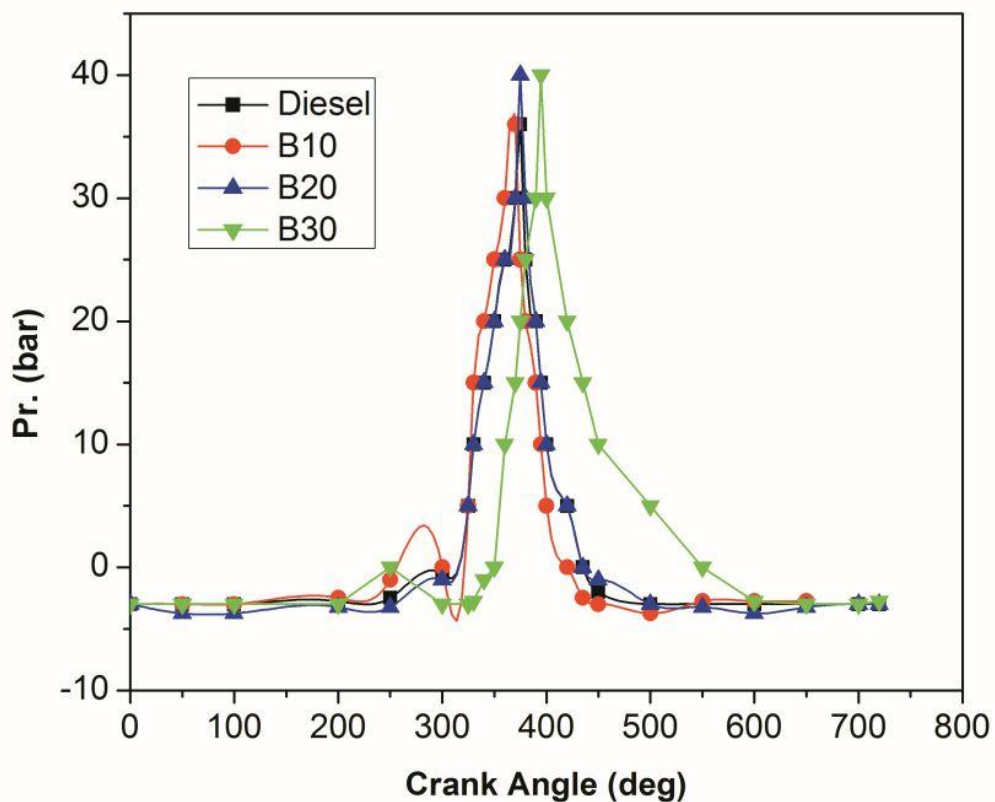


Fig 5.26: Variation of cylinder pressure with crank angle at compression ratio16

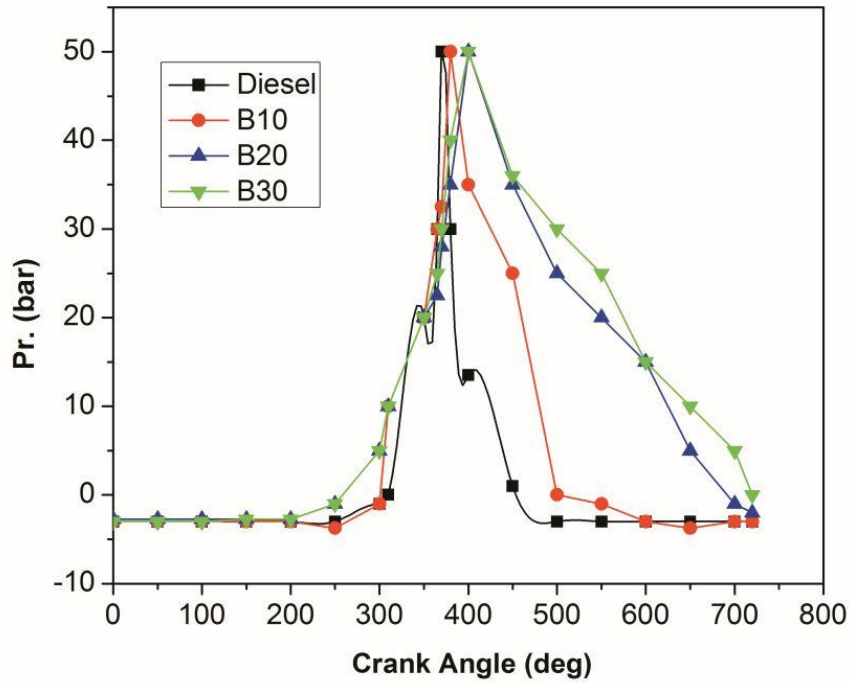


Fig 5.27: Variation of cylinder pressure with crank angle at compression ratio 14

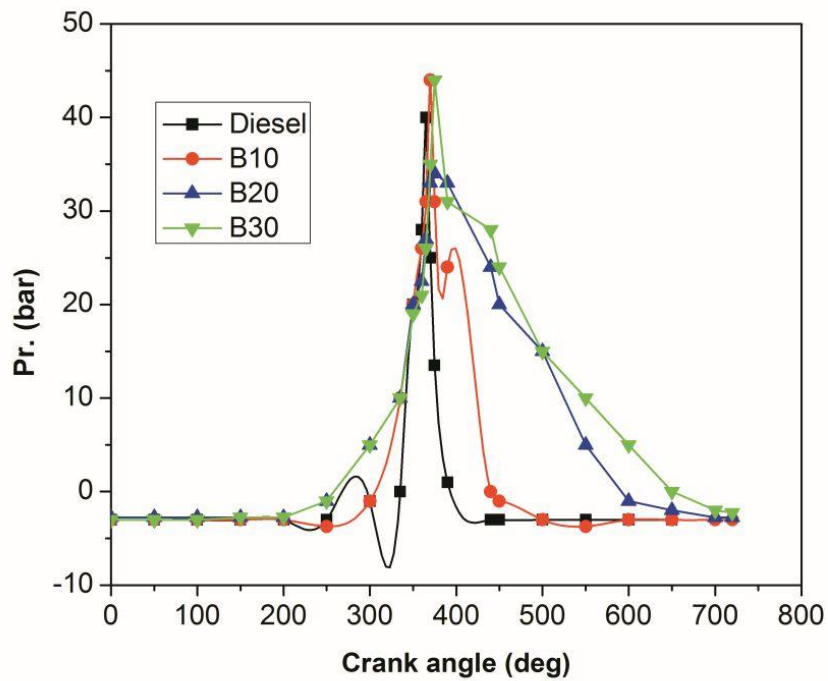


Fig 4.28: Variation of cylinder pressure with crank angle at compression ratio 12

5.7 EMISSION PARAMETERS

5.7.1 HYDROCARBON EMISSIONS (HC)

The variation of hydrocarbon exhaust emissions with load are compared for diesel, B10, B20, and B30 blends of biodiesel at two different compression ratios. It was observed in the experiments that with increase in the load hydrocarbon emissions increase. The main reason for that is entering of rich mixture of fuel and air in the combustion chamber of engine because of increase in the fuel consumption. This causes improper combustion of fuel which in turn increases the un-burnt hydrocarbon emissions. It was observed that HC emissions decrease with increase in amount of blend content. This is because of higher cetane number of biodiesel blends. Higher cetane number lowers the combustion delay and therefore the combustion is improved. Another reason for decreased hydrocarbon emissions with the increase in amount of blend is due to higher oxygen content of biodiesel than the diesel. According to observations made HC emissions for pure diesel fuel were highest and for B30 blend of biodiesel it was lowest. The variation in HC emissions for all fuel samples with the load at CR16 and CR14 are illustrated in the figures 5.29 and 5.30 respectively.

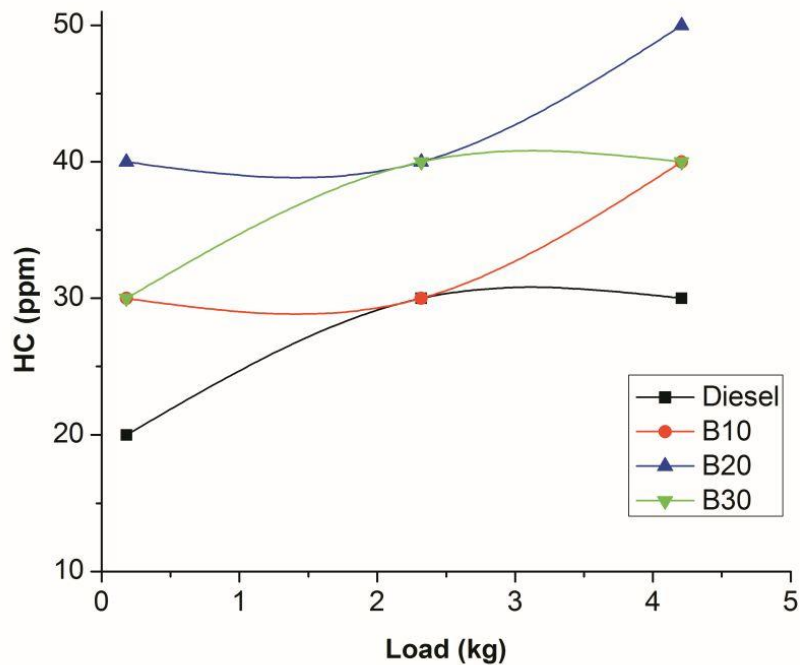


Fig 5.29: Variation of hydrocarbon emissions with compression ratio 16

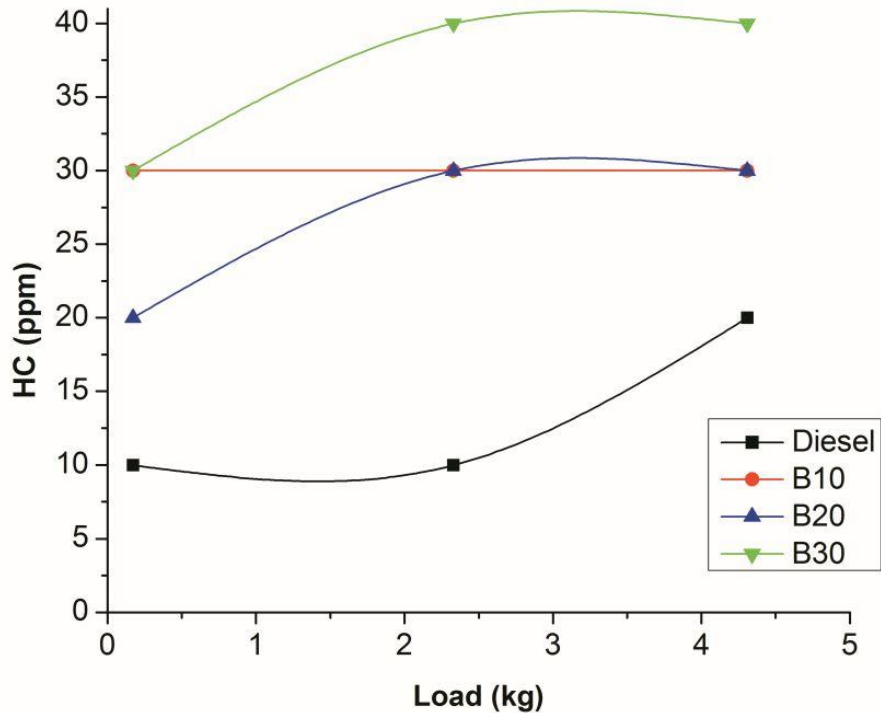


Fig 5.30: Variation of hydrocarbon emissions with load at compression ratio 14

5.7.2 CARBON MONOXIDE (CO) EMISSIONS

The carbon monoxide emissions mainly results from incomplete combustion of fuel in the combustion chamber. The CO emissions for pure diesel fuel, B10, B20 and B30 are compared for different loads at CR16 and CR14. It was found that with the increase in load CO emissions increased. This is because of the injection of rich fuel air mixture which causes incomplete combustion of fuel in combustion chamber. It was also observed the CO emissions for B10 blend were nearly close to that of the diesel fuel. But with the further increase in amount of blend the CO emissions were found to be decreased. This may because of the higher oxygen content of biodiesel which leads to the complete combustion of fuel. The CO emissions were observed to be decreased with the increase in compression ratio. This is because of increase in temperature of the air which lowers delay period and improves combustion of the fuel. The CO emissions were observed to be lowest for the B30 blend at CR16 among all fuels. The CO emissions for pure diesel, B10, B20, and B30 blends with load at CR16 and CR14 compression ratios are illustrated in the fig 5.31 and 5.32.

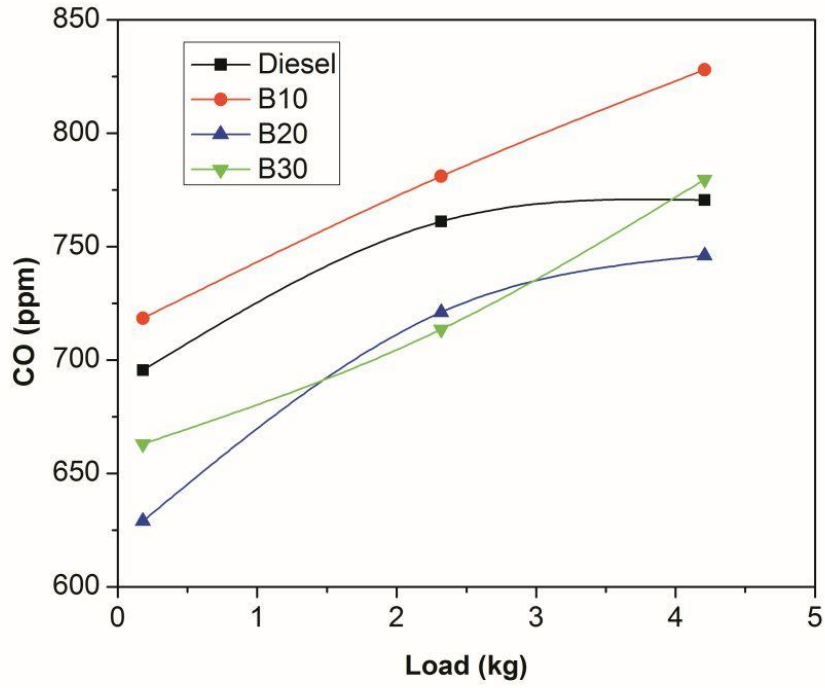


Fig 5.31: Variation of CO emissions with load at compression ratio 16

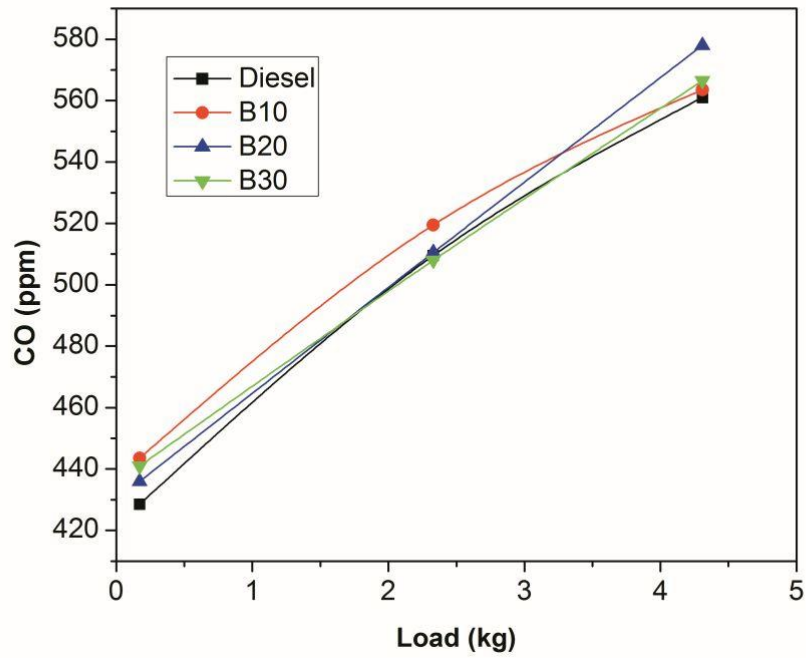


Fig 5.32: Variation of CO emissions with load at compression ratio 14

5.6.3 NO_x EMISSIONS

The NO_x emissions of pure diesel, B10, B20 and B30 were compared with load at compression ratios of CR14 and CR16. NO_x emissions are dependent of temperature of the combustion chamber. It was observed that with the increase in load NO_x emissions increase due to increase in temperature inside the combustion chamber at higher loads. NO_x emissions were also observed to be increased with the increase in amount of blend content. This is mainly because of higher oxygen content of biodiesel fuels. Nitrogen from the air can mix with the oxygen easily and causes the NO_x emissions. These emissions were found to be increased with the increase in compression ratio because of lower ignition delay which in turn increases the temperature and peak pressure. The comparison of NO_x emissions for pure diesel, B10, B20 and B30 blends with load at CR16 and CR14 is illustrated in the figures 5.33 and 5.34 respectively.

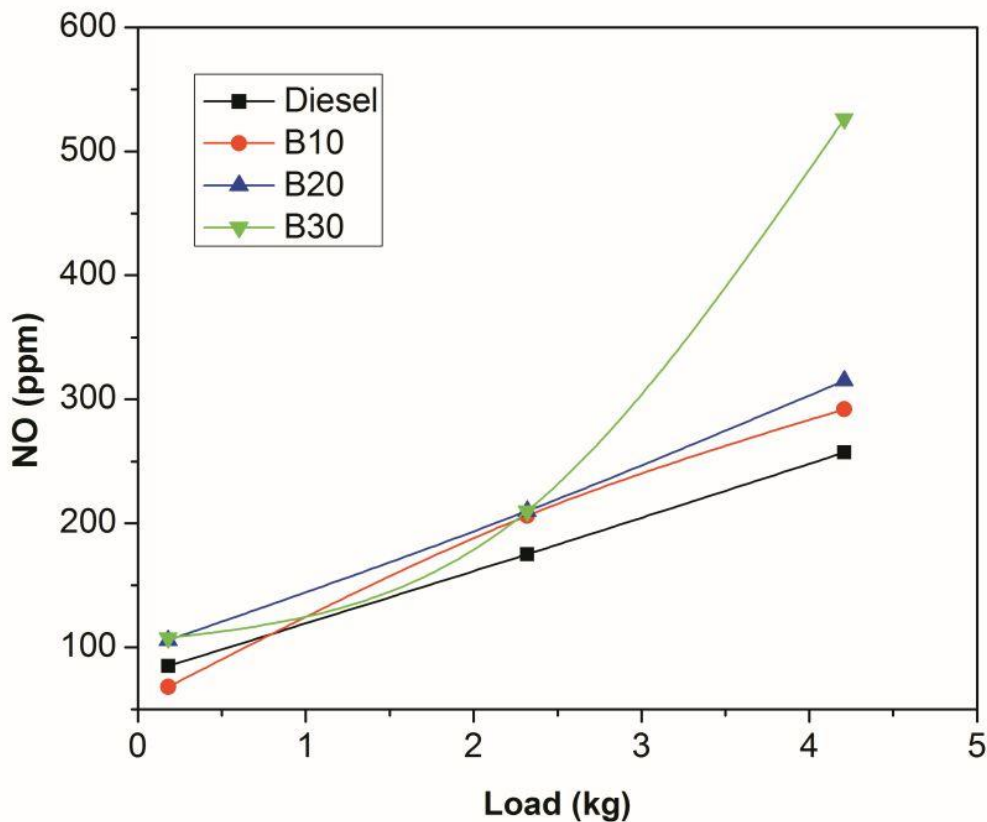


Fig 5.33: Variation of NO_x emissions with load at compression ratio 16

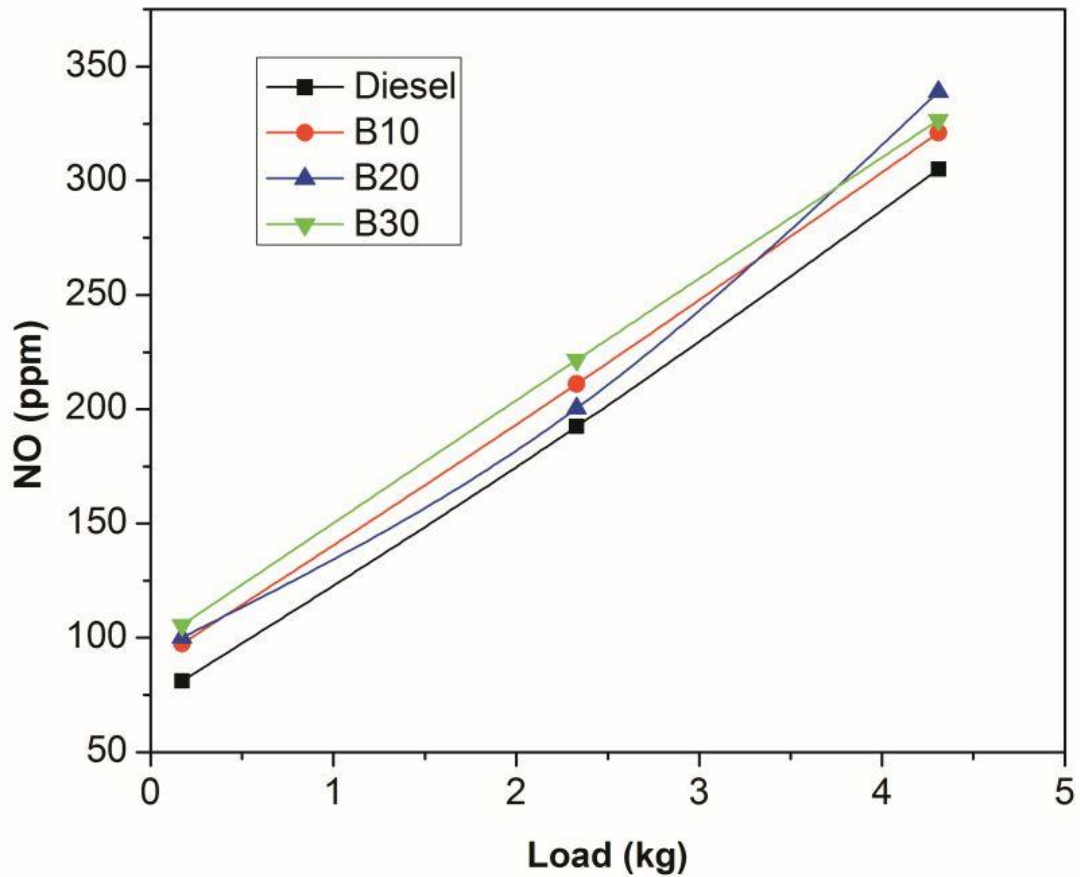


Fig 5.34: Variation of NO_x emissions with load at compression ratio 14

It can be observed from the figures above that NO_x emissions for pure diesel were lowest for both compression ratios. The NO_x emissions of B30 blend were found to be highest for all loads and for both compression ratios.

5.6.4 CARBON DIOXIDE (CO₂) EMISSIONS

The CO₂ emissions for pure diesel, B10, B20 and B30 were compared with load at CR16 and CR14. According to the experimental observations the CO₂ emissions increases with increase in load due to the better combustion of fuel at higher loads. The CO₂ emissions for diesel were highest. As the amount of blend increased, the CO₂ emissions were observed to be decreased. Carbon dioxide is formed by complete combustion of fuel in oxygen. Here, carbon dioxide

formation is less because of the fact that in general biodiesel is a fuel having low carbon content and has lower elemental carbon to hydrogen ratio than the diesel fuel. The CO₂ emissions were found to be increased with compression ratio this due to lower ignition delay that causes better combustion. The variations of CO₂ emissions with load at CR16 and CR14 are shown in figures 5.35 and 5.36 respectively.

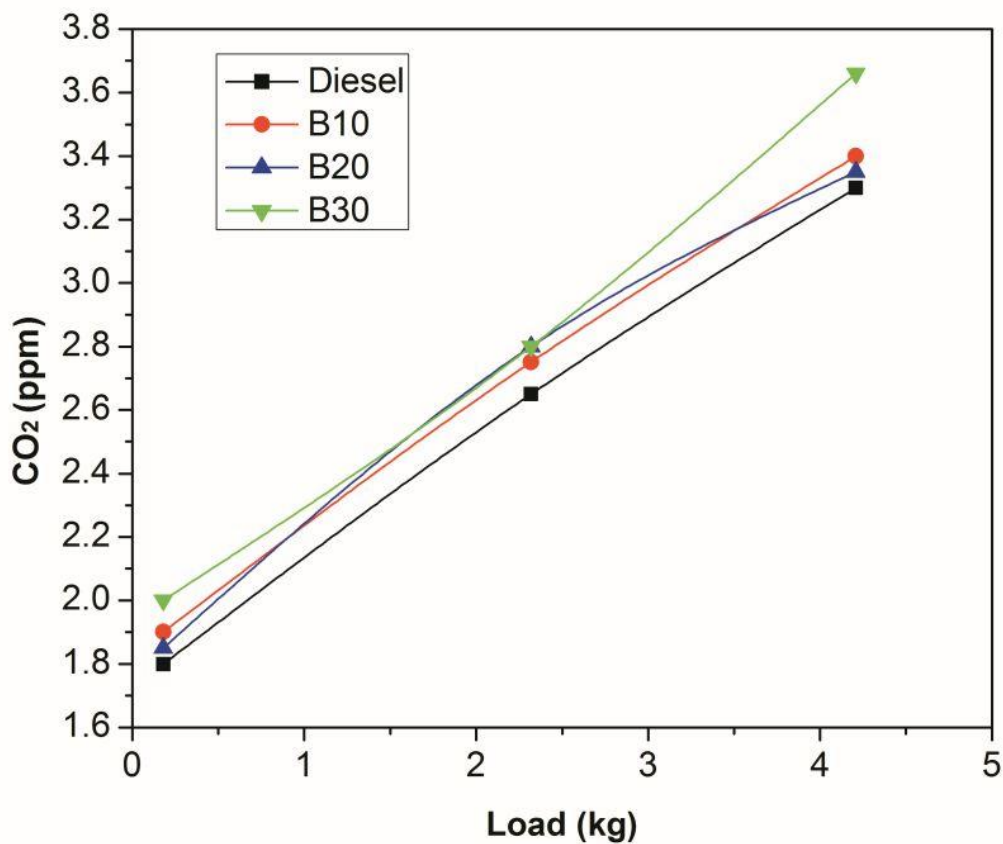


Fig 5.35: Variation of CO₂ emissions with load at compression ratio 16

According to the observations CO₂ emissions were found lowest for B30 blend for all loads and both compression ratios.

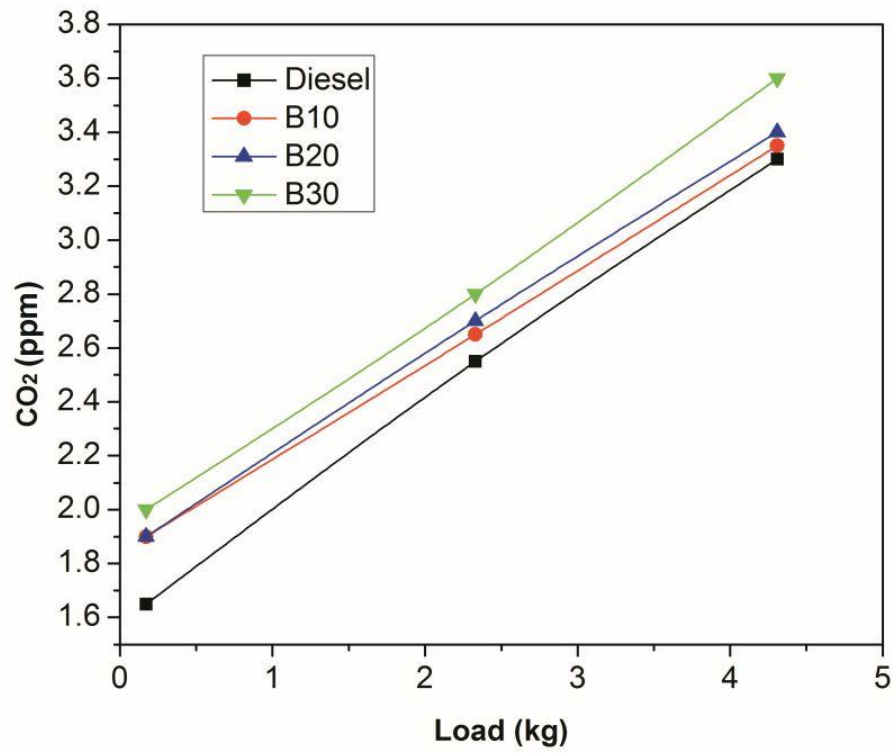


Fig 5.36: Variation of CO₂ emissions with load at compression ratio 14

CHAPTER 6

CONCLUSIONS AND FUTURE SCOPE

6.1 CONCLUSIONS

The optimization of parameters effecting production yield of linseed methyl ester was evaluated using design of experiments by Taguchi's approach. The performance and emission characteristics for pure diesel were compared with B10, B20 and B30 blends of linseed biodiesel. The following conclusions can be drawn from the present study:

- By using the Taguchi's approach optimum conditions to maximize the production of linseed biodiesel were obtained at molar ratio of 6:1, reaction time of 60 minutes, at 60°C reaction temperature and 1.5% KOH concentration. An expected yield of 93.13% was estimated and by using optimum conditions production yield of 98.04% was obtained.
- The fuel properties of optimally produced linseed biodiesel were observed to be comparable to that of pure diesel and were also conforming to latest biodiesel standards.
- The calorific value of optimally produced linseed biodiesel was 9273 Kcal/Kg which is 7.7% lower than the pure diesel fuel.
- The fire and flash point of biodiesel produced from linseed oil were determined to be 160°C and 154°C respectively both being higher than the diesel fuel whereas the pour and cloud point were observed to be lower for linseed biodiesel fuel.
- The performance parameters of linseed biodiesel such as BP, brake thermal efficiency and BMEP with B10 blend were found to be nearly similar to that of diesel at all loads. B10 blend showed better performance parameters than all other blends of biodiesel. At higher compression ratios the performance of engine was observed to be better. The brake specific fuel consumption of engine was lowest for B10 blend among all the blends.
- The different emissions parameters of engine such as CO, CO₂, and HC were observed to be nearly similar to the diesel fuel for B10 blend. With increase in amount of blend these emissions were decreased. Among all the blends, these emissions were found to be lowest for B30 blend while the NO_x emissions were found to be lowest for B10 blend. The CO and HC emissions were observed to be decreased at higher compression ratios while NO_x and CO₂ emissions were increased for higher compression ratios.

6.2 FUTURE SCOPE

Biodiesel obtained from various non-edible feed stocks such as mahua oil and linseed oil are found to be feasible choices to avoid food versus fuel conflicts in developing countries including India where cost and consumption of edible oil is high. Selection of a feedstock for biodiesel production is the major concern because of the cost and availability of feedstock within the country. Linseed oil is relatively less expensive and readily available feedstock for biodiesel production in India as India is 3rd largest producer of linseed oil in the world. Before introducing linseed biodiesel as a fuel in India following points must be considered:

- Attempts and research for making proper use of linseed oil for biodiesel production should be undertaken by the Indian government.
- The research for long term stability of biodiesel blends should be carried out as the different blends prepared for present study were utilized within short time.
- Further research and development on the additional fuel property measures, long-term run and wear analysis of biodiesel fueled engine is necessary along with injection timing and duration for better combustion of biodiesel in diesel engines.
- The optimization of linseed biodiesel production was performed by varying five parameters i.e. molar ratio, catalyst concentration, catalyst type, reaction temperature and reaction time. The effect of other controlling parameters like different alcohols and stirring rate should also be studied.

REFERENCES

1. Meher LC, Vidya Sagar D, Naik SN. Technical aspects of biodiesel production by transesterification – a review. *Renewable and Sustainable Energy Reviews* 2006;10:248-268.
2. Gerpen JV. Biodiesel processing and production. *Fuel Process Technol.* 2005;86:1097-1107.
3. Pinzi S, Garcia IL, Lopez-Gimenez FJ, Luque de Castro MD, Dorado G, Dorado MP. The ideal vegetable oil-based biodiesel composition: a review of social, economical and technical implications. *Energy & Fuels* 2009;23:2325-2341.
4. Demirbas A. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey. *Energy Conversion and Management* 2003;44:2093-2109.
5. Ma F, Hana MA, Biodiesel production: a review. *Bioresource technology* 1999;70:1-15.
6. Jegannathan K, Seng C, Ravindra P. Economic assessment of biodiesel production: Comparison of alkali and biocatalyst processes. *Renew Sust Energy Rev.* 2011;15:745-751.
7. Meher LC, Dharmagadda Vidya SS, Naik SN. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. *Bio-resource Technology* 2006;97:1392-1397.
8. Cvengros J, Povazanec F. Production and treatment of rapeseed oil methyl esters as alternative fuels for diesel engines. *Bioresour. Technol.* 1996;55:145-150.
9. National council of applied economic research (NCAER) & the solvent extractors. overview of Indian oilseed sector, outlook for India's edible oil sector issues and challenges 15 March, 2013, Delhi.
10. Schwab AW, Dykstra GJ, Selke E, Sorenson SC, Pryde EH. Diesel fuel from thermal decomposition of soybean oil. *Jaocs* 1988;65:1781-1786.
11. Weisz PB, Haag WO, Rodeweld PG. Catalytic production of high grade fuel (gasoline) from biomass compounds by shape selective catalysis: *Science* 1979;206:57-58.
12. Aggarwal DK and Aggawal AK. Performance evaluation of a vegetable oil fuelled CI engine. *Renewable energy* 2007;23:351-357.

13. Alcantara R, Amores J, Canoira L, Fidalgo E, Franco MJ, Navarro A. Catalytic production of biodiesel from soy-bean oil, used frying oil. *Biomass and Bioenergy* 2000;18: 515-527.
14. Antolin G, Tinaut FV, Briceno Y, Castano V, Perez C, Ramirez AI. Optimisation of biodiesel production by sunflower oil transesterification. *Bioresource Technology* 2002;83: 111–114.
15. Behçet R. Performance and emission study of waste anchovy fish biodiesel in a diesel engine. *Fuel Processing Technology* 2011;92:1187–1194.
16. Chongkhong S, Tongurai C, Chetpattananondh P, Bunyakan C. Biodiesel production by esterification of palm fatty acid distillate. *Biomass and bioenergy* 2007;32:254-260.
17. Demirbas A. Production of biodiesel fuels from linseed oil using methanol and ethanol in non-catalytic SCF conditions. *Biomass and Bioenergy* 2009;33:113–118.
18. Dhar A, Kevin R, Agarwal AK. Production of biodiesel from high-FFA neem oil and its performance, emission and combustion characterization in a single cylinder DIC I engine. *Fuel Processing Technology* 2012;97:118–129.
19. Ghadge SV and Raheman H. Process optimization for biodiesel production from mahua oil using response surface methodology. *Bioresource Technology* 2006;97:379–384.
20. Godiganur S, Suryanarayana CH, Reddy RR. Engine performance and emission tests using methyl ester mahua oil/diesel blends. *Renewable Energy* 2009;34:2172–2177.
21. Guzzatto R, Martini TL, Samios D. The use of a modified TDSP for biodiesel production from soybean, linseed and waste cooking oil. *Fuel Processing Technology* 2011;92:2083–2088.
22. Jawalkar A, Mahantesh K, Jagadish M. Performance and Emission Characteristics of Mahua and Linseed Biodiesel Operated at Varying Injection Pressures on CI Engine. *International Journal of Modern Engineering Research (IJMER)*. 2012;2:1142-1149.
23. Jimenez ET, Dorado MP, Breda Kegl. Experimental investigation on injection characteristics of bioethanol–diesel fuel and bioethanol–biodiesel blends. *Fuel* 2010;90:1968–1979.
24. Kaya C, Hamamci C, Baysal A, Akba O, Erdogan S, Saydut A. Methyl ester of peanut seed oil as a potential feedstock for biodiesel production. *Renewable Energy* 2009;34:1257–1260.

25. Kim ST, Yim B, Park Y. Application of Taguchi Experimental Design for the Optimization of Effective Parameters on the Rapeseed Methyl Ester Production Environ. Eng. Res. 2010;15:129-134.
26. Kumar R, Tiwari P, Garg S. Performance of compression ignition engine with mahua biodiesel. Fuel 2013;104:553–560.
27. Lapuerta M, Armas O, Fernandez JR. Effect of biodiesel fuels on diesel engine emissions. Progress in Energy and Combustion Science 2008;34:198–223.
28. Liaquat AM, Masjuki HH, Kalam MA, Rizwanul Fattah IM, Hazrat MA, Varman M, Mofijur M, Shahabuddin M. Effect of coconut biodiesel blended fuels on engine performance and emission characteristics. Procedia Engineering 2013;56:583–590.
29. Lin CY and Li RJ. Engine performance and emission characteristics of marine fish-oil biodiesel produced from the discarded parts of marine fish. Fuel Processing Technology 2009;90:883–888.
30. Nabi MN, Rahman MM, Akhter MS. Biodiesel from cotton seed oil and its effect on engine performance and exhaust emissions. Applied Thermal Engineering 2009;29:2265–2270.
31. Patel SI, Gosai DC, Vandana Y. Performance and exhaust emission analysis of thermal barrier coated diesel engine using rice bran oil biodiesel. International Journal of Engineering and Advanced Technology (IJEAT) 2013;2:2249 – 2258.
32. Patil PD and Deng S. Optimization of biodiesel production from edible and non-edible vegetable oils. Fuel, 2007;88:1302–1306.
33. Puhana S, Vedaraman N, Boppana, Rama VB, Sankarnarayananb G, Jeychandran K. Mahua oil methyl ester as biodiesel-preparation and emission characteristics. Biomass and Bioenergy 2005;28:87–93.
34. Puhan S, Jegan R, Balasubbramanian K, Nagarajan G. Effect of injection pressure on performance, emission and combustion characteristics of high linolenic linseed oil methyl ester in a DI diesel engine. Renewable Energy 2009;34:1227–1233.
35. Raheman H and Ghadge SV. Performance of compression ignition engine with mahua biodiesel. Fuel 2007;86:2568–2573.
36. Sharma YC, Singh B, Upadhyay SN. Advancements in development and characterization of biodiesel: A review. Fuel, 2008;87:2355–2373.

37. Singh PJ, Khurma J, Singh A. Preparation, characterisation, engine performance and emission characteristics of coconut oil based hybrid fuels. *Renewable Energy* 2010;35: 2065-2070.
38. Sivalakshmi S, Balusamy A, Balusamy T. Performance and emission characteristics of a diesel engine fuelled by neem oil blended with alcohols. *International Journal of Ambient Energy* 2011;32:170-178.
39. Sivaramakrishnan K and Ravikumar P. Performance optimization of karanja biodiesel engine using Taguchi approach and multiple regression. *ARPN journal of engineering and applied sciences* 2012;7:506-516.
40. Swaminathan C and Sarangan J. Performance and exhaust emission characteristics of a CI engine fueled with biodiesel fish oil. *Biomass and bioenergy* 2012;39:168-174.
41. Yamina JA, Sakhninib N, Sakhrieha A, Hamdan MA. Environmental and performance study of a 4-Stroke CI engine powered with waste oil biodiesel. *Sustainable Cities and Society* xxx (2013) xxx–xxx.
42. Roy RK. Design of experiments using the Taguchi approach: 16 steps to product and process improvement. New York: Wiley; 2001.
43. Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Soc.* 1984;61:1638-1643.
44. Roy, R. A primer on the Taguchi method; Van Nostrand Reinhold: Newyork,1990.
45. Samios D, Pedrotti F, Nicolau A, Reiznautt QB, Martini DD, Dalcin FM. A transesterification double step process – TDSP for biodiesel preparation from fatty acid triglycerides. *Fuel Processing Technology* 2009;90:599-605.
46. Piyanuch N, Sasiwimol W. High free fatty acid coconut oil as a potential feedstock for biodiesel production in Thailand. *Renewable Energy* 2010;35:1682-1687.
47. Hanh H, Dong N, Starvarache C, Okitsu K, Maeda Y, Nishimura R. *Energy Convers. Manage.* 2008;49:276-280.
48. Mahamuni N, Adewuyi Y. *Energy. FUELS* 2009;23:2757-2766.