PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL AND EXPERIMENTAL ANALYSIS & TESTING THE PROPERTY OF DIFFERENT BLENDS OF PRODUCED BIODIESEL

A Project Report Submitted in Partial Fulfillment of the Requirements

for the Degree of

BACHELOR OF TECHNOLOGY

IN

MECHANICAL ENGINEERING

Submitted by

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Under the Supervision of

Mr. Prem Shankar Yadav

JSS ACADEMY OF TECHNICAL EDUCATION, NOIDA

DR. A P J ABDUL KALAM TECHNICAL UNIVERSITY

(Formerly Uttar Pradesh Technical University)

LUCKNOW

June, 2020

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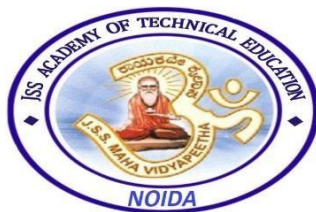**Submitted by**

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C-20/1, SECTOR-62, NOIDA 201301**

June, 2020

DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by any other person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

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CERTIFICATE

This is to certify that the project report entitled "**Production of biodiesel from waste cooking oil And experimental analysis & testing the property of different blends of produced biodiesel** " which is submitted by **Vivek kumar** (1609140180)**, Abhishek indradeo prasad** (1709140902), **Satyenda kumar** (1609140136) and **Shekhar verma** (1609140138) in partial fulfillment of the requirement for the award of **Bachelor of Technology** in the Department of Mechanical Engineering from Dr. APJ ABDUL KALAM Technical University, Lucknow is a record of the candidates under my supervision. The project report embodies results of original work, and studies are carried out by the student himself and the contents of the project report do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

Signature   Signature

Mr. Prem Shankar Yadav   **Dr. T.G. Mamatha**

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ABSTRACT

Increasing demand in transport fuel will eventually lead to complete depletion of fossils fuel .Development of alternative energy sources like solar energy ,wind energy, biofuels etc. can give the solution of such problem in future. Biodiesel is a fuel which is produced from different feedstock like plant based oil(soybeans oil, palm oil, jetropa oil, etc.) or animal fat. It is burning and renewable fuel. Biodiesel can be produced from a great variety of feedstock. To obtain biodiesel the vegitable oil or animal fat is subjected to a chemical reaction termed as transesterification. In that reaction, the vegitable oil reacted in the presence of the catalyst (usually a base)with an alcohol(usually methanol) to give the corresponding ester of the FA mixture that is found in the parent vegitable oil or animal fat.

 The main objective of the project is to produced biodiesel from the waste cooking oil, to analyze & test the engine performance by fuel as different blends of produced biodiesel with diesel.

ACKNOWLEDGEMENT

It gives us a great sense of pleasure to present the report of B.Tech project undertaken during B.Tech final year. We owe special debt and gratitude to **Mr. Prem Shankar Yadav (Assistant Professor at Department of Mechanical Engineering, JSS Academy of Technical Education, Noida)** for his constant support and guidance throughout the course of our work. His sincerity, thoroughness and perseverance have been a constant source of inspiration for us. It is only his cognizant efforts that our endeavor has seen light of the day.

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CHAPTER 1

INTRODUCTION

Energy is the prime mover for economic growth of any country and is vital to the sustenance of modern economy. Future economic growth crucially depends on the long-term availability of energy from sources that are affordable, accessible, and environmentally friendly as well. The major sources of energy in the world are fossil fuels (petroleum oil, coal, and natural gas), renewable energy (hydro, wind, solar, geothermal, marine energy, and combustible wastes), and nuclear energy. These primary energy sources are converted into secondary energy sources; that is, coal and crude oil are converted into electricity and steam.

Combustible wastes include animal products, biomass, and industrial wastes. Coal is the major source of energy for electric power generation where as petroleum products are for the transport sector. Energy consumption is unevenly divided across various sectors of industrialized economies, as it is unevenly divided across geographic regions.

Petroleum oil, which is the most important and abundantly available energy source, is largely consumed in the world. The price of crude oil is very volatile and supply is driven by market price. While developed industrialized countries consume around 43 million barrels daily on an average, developing countries consume only 22 million barrels per day (MBD). Coal is the second most abundant source of energy in the world and is mainly used in power generation. Natural gas has been the energy source with highest rates of growth in recent years. The high end-use efficiency of natural gas has made it a population choice for power generation projects. Hydroelectricity has been a major use of hydro sources of energy around the globe. Renewable sources of energy are gaining popularity. However, fuel prices and regulatory policies of different countries play important roles in the development of renewals (www.economywatch.com/energy-economy/scenario.html). The hydrocarbon industry across the world has been a major driver of economic growth and development for developed as well as developing countries. The commercial transportation sector uses a major share on diesel vehicles where as the public transportation—two wheelers and light commercial vehicles—auto market completely depend on gasoline-fueled engines. It is predicted that the global crude oil demand will rise by about 1.6% from 75 MBD in the year 2000 to 120 MBD in 2030 according to the IPCC assessment.
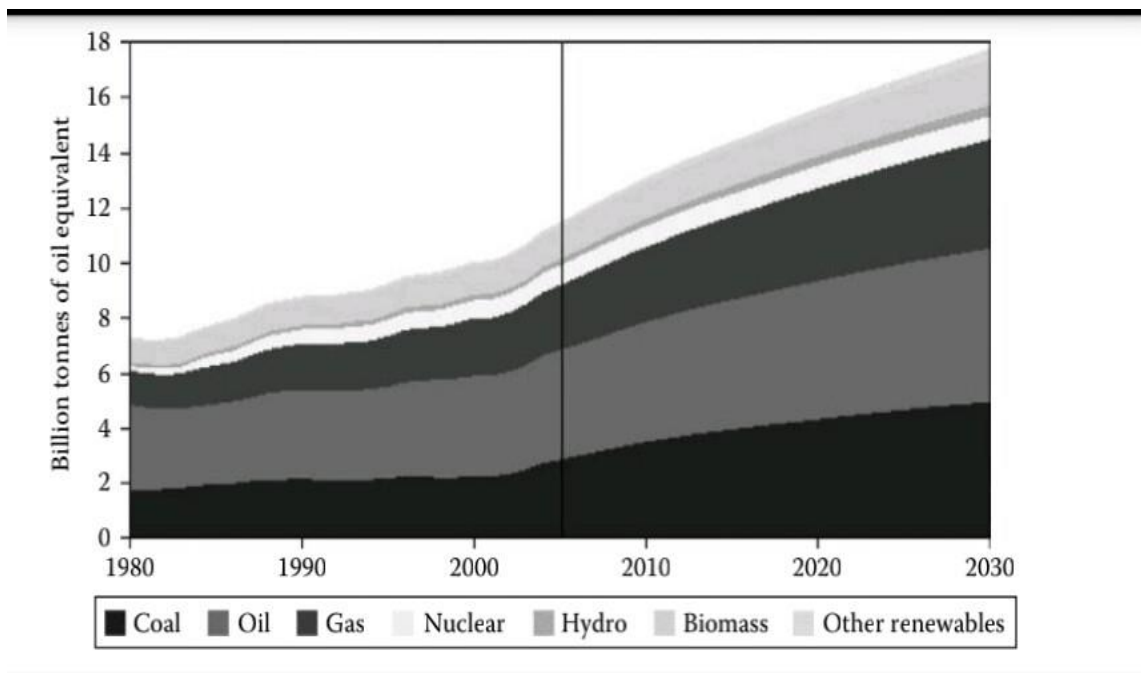
Figure 1.1 World energy consumption trend

1.1 ENERGY SECURITY

Energy is one of the important inputs for any country's economic growth and development. Although 80% of the world's population is in the developing countries, their energy consumption amounts to only 40% of the total energy consumption. The high living standards in the developed countries are attributable to high-energy consumption levels. Also, the rapid population growth in the developing countries has kept the per capita energy consumption low as compared with that of developed countries. Continuous availability of energy in various forms in sufficient quantity and at reasonable prices is required. Though the crude reserves are spread all over the world, the major petroleum resources are available only in selected regions particularly in Middle East countries (about 63%). The international trade in oil is subject to violent fluctuations and has often led to war-like situations in the past, especially involving supply from the Gulf countries. The amount of crude oil is finite being the product of burial and transformation of biomass over 200 million years. Even now fossil fuels are being created under pressure and temperature; however, they are more rapidly consumed than they are produced. So there is a chance of a fuel shortage in the near future. The petroleum resources around the world are continuously utilized and thus these resources are fast depleting. This fast depletion of the resources leads to one another global factor (i.e., the everincreasing cost of fuels). Hence, there is an urgent need to understand the energy crisis and transition from conventional to nonconventional sustainable energy sources. Countries having insufficient crude oil resources and depending upon the import of crude oil may seriously affect its economic

development and sovereignty in international political relations. Therefore, as a matter of necessity and national self-reliance, such countries strive to achieve self-sufficiency in fuel availability. In general, the world depends on the limited oil reserves (particularly Middle East countries) and if there is a reduction in the production of crude oil, it will affect the world economy.
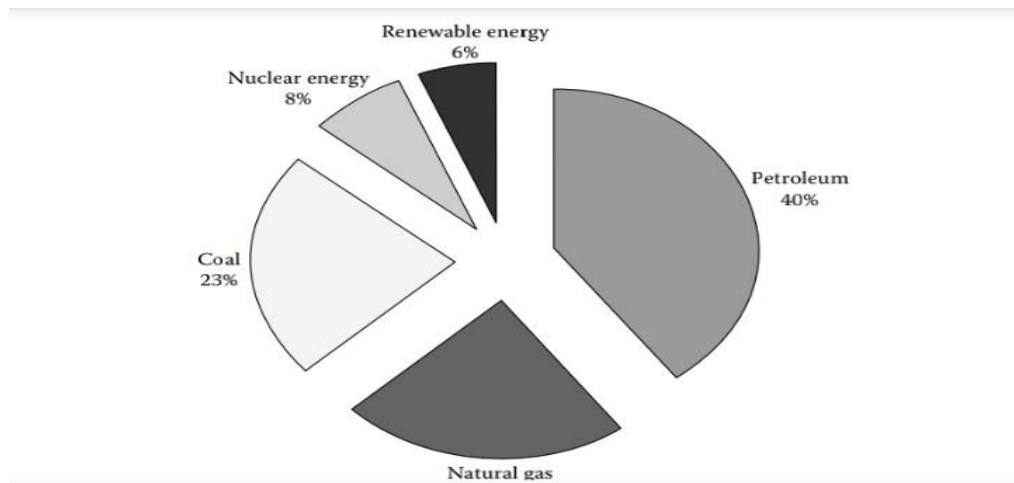
Figure 1.2 Energy consumption in the world

1.2 ENVIRONMENTAL POLLUTION

Presently the world is confronted with the twin crisis of fossil fuel depletion and environmental concern. Environmental pollution is an important public health problem in most cities of the developing world. Epidemiological studies show that air pollution in developing countries accounts for tens of thousands of excess deaths and billions of dollars in medical costs and lost productivity every year. These losses, and the associated degradation in quality of life, impose a significant burden on people in all sectors of society, but especially the poor .

Burning of any hydrocarbon fuel produces carbon dioxide, which is accumulated in the atmosphere. CO_2 is a greenhouse gas that is slowly building in quantity in the atmosphere and it is believed this will raise the temperature of the planet, causing dramatic climate changes. The majority of developed countries have committed to targeted emission reduction through the Kyota Protocol of 1997, which entered into force in February 2005.

Combustion of hydrocarbon fuel generates both "direct" and "indirect" greenhouse gases. Direct gases emitted by transport include carbon dioxide, methane, nitrous oxide, and carbonate fuel cells are radiatively active. The indirect greenhouse gases include carbon monoxide, other oxides of nitrogen, and nonmethanic volatile organic carbons.

These do not have a strong radiative effect in themselves, but influence atmospheric concentrations of the direct greenhouse gases by, for example, oxidizing to form CO_2 or contributing to the formation of ozone—a potent direct greenhouse gas.

The Human Development Report of 2007 says that developed countries should cut their carbon emissions by 20–30% before 2030 and at least by 80% by the year 2050. If emissions continue to rise following current trends, then stocks of the greenhouse emissions will be increasing at 4–5 ppm per year; by the year 2035, it may almost double the current rate. Accumulated stock will have risen to 550 ppm. Even without further increases in the rate of emissions, stocks would reach over 600 ppm by 2050 and 800 ppm by the end of the twenty-first century. India accounts for 5.5% of CO_2 emissions with the population of 17.2% world share. The report also says that the developing countries like India should cut their emissions by 20%. It would stabilize CO_2 equivalent concentration at 450 ppm in the atmosphere, which is currently at 379 ppm (Human Development Report 2007/2008).

It is expected that burning hydrocarbon fuel in the presence of air produces carbon dioxide and water. But, internal combustion engines do not completely burn petroleum products. Hence, these engines release unburned or partially burned/oxidized gases and nitrogen oxides into the atmosphere. The transport sector is a major contributor of air pollution particularly in cities and the vehicular pollution is the primary cause of air pollution in the urban areas (60%), followed by industries (20–30%), and fossil fuels. The pollutants released in the atmosphere interact with other pollutants (like photochemical reactions) and disturb the ecological balance. Faced with the growing air pollution related problems, a number of countries have established ambient air quality standards to protect their environment.

The main pollutants of internal combustion engines include particulate matter, unburned hydro carbons, CO, SO_2, and NO_x. These pollutants have serious effects on human health. Research is being carried out to produce alternative fuels, mainly directed toward reducing these harmful pollutant emissions. At this point, it would be appropriate to discuss the related health effects of various diesel pollutants.

The principal source of nitrogen oxides—nitric oxide (NO) and nitrogen dioxide (NO_2) are collectively known as NO_x. Nitric oxide (NO) emissions from engine exhaust is oxidized to nitrogen dioxides (NO_2), which can react with unburned hydrocarbon emissions and other sources allowing the concentration of ozone to increase around dense traffic. The NO and NO_2 concentrations are greatest in urban areas where traffic is heaviest. Exposure to NO_2 is linked with increased susceptibility to respiratory infection and viral infections such as influenza, lung irritation, edema of lungs, increased airway resistance in asthmatics, bronchitis and pneumonia, decreased pulmonary function, and increase in sensitivity to allergens. Nitrogen oxides combine with water vapor to form nitric acid and are removed from the atmosphere by direct deposition to the ground, or transferred to cloud or rainwater, thereby contributing to acid deposition.

Major sources of sulfur dioxide (SO2) emissions are diesel automobiles, powerhouses, and petroleum industries. The SO2 can impair lung function by constricting airways and damaging lung tissue, aggravate asthma and emphysema, and lead to suffocation and irritation to the throat. The SO2 in ambient air is also associated with asthma and chronic bronchitis. Sulfur dioxide is a corrosive acid gas, which combines with water vapor in the atmosphere to produce acid rain. It causes acidification of lakes and streams and can damage trees, crops, historic buildings, and statues.

Concern about the potential health impacts of PM10 has increased very rapidly over recent years. Airborne particulate matter varies widely in its physical and chemical composition, source, and particle size. The particulates in air of a very small size (<10 µm) are of major current concern as compared to larger particulates. The smaller particulates are small enough to penetrate deep into the lungs and so potentially pose significant health risks.

There are two main groups of hydrocarbons of concern: volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). Volatile organic compounds are released in vehicle exhaust gases either as unburned fuels or as combustion products, and are also emitted by the evaporation of solvents and motor fuels. The VOCs effects include eye irritation, respiratory irritation, and cancer. The VOC condense together with SO2 to create particulates, including smoke, soot, and dust. Benzene content in atmosphere is the main sources of emissions emitted in vehicle exhaust.

1.3 ALTERNATIVE FUELS

Fast dwindling reserves of fossil fuels, particularly petroleum products, cause hazards of environmental pollution by their combustion. Attempts were made to develop the future energy technologies that are energy efficient, environmentally friendly, and economically viable. Small incremental improvements in current energy technologies are sufficient to tackle the energy crisis and environmental problems. Alternative fuels are derived from other than crude oil resources. In general, alternative fuels include all the fuel used in vehicles other than gasoline and diesel. There are various alternative fuels that can be used with the current petrol or diesel internal combustion engine with little or no modification. The advantages with these fuels include cleaner burning than petroleum-derived fuels, producing lower emissions, and if it is derived from renewable biomass sources it will decrease the dependency on nonrenewable petroleum. However, alternative fuels, need not necessarily refer to a source of renewable energy. Each fuel has its own distinct advantages and disadvantages associated with cost, availability, environmental impact, vehicle/engine modification, safety and customer acceptance, and legislation.

Alternative fuels are receiving attention because of the following reasons:

i.   Alternative fuels are mostly produced from domestic resources that reduce the energy dependence.

Use of locally available resources for fuel purposes can reduce crude oil import bill. Most of the alternative fuels, for example, alcohols, biodiesel can be produced from biomass resources and agricultural wastes and electricity for battery operated vehicles can be produced from solar and fuel cells. Hydrogen can be produced from biomass gasification or electrolysis of water. Hence, even a small percentage substitution of different alternative fuels reduces the crude oil import significantly.

ii. Alternative fuels generally reduce the vehicle exhaust emission and hence improve the environmental air quality.

Alternative fuels are capable of reducing the engine emissions as compared to petroleum products. The molecular structure of alternative fuels (CH_3OH, C_2H_5OH, and CH_4, etc.) is much simpler than gasoline/diesel (mixture of different molecules). Moreover, a low C:H ratio of alternative fuels generates less hydrocarbon emissions on combustion. Hydrogen is the clean fuel and generates nil hydrocarbon emissions. Emissions released from a centralized plant can be more easily controlled than vehicular emissions.

iii. Some alternative fuels have the potential to operate at a lower cost compared to petroleum products.

Success of any new product or fuel depends on its cost. Currently, cost of the most alternative fuels is a little bit higher than conventional fuel. However, the cost of biodiesel and compressed natural gas (CNG) are cost competitive with petroleum. For the development of alternative fuels, government legislations and incentives are required to a certain extent. The large-scale production of alternative fuel could make these alternative fuels cost competitive.

The following parameters are to be considered while deciding the alternative fuel-

- The fuel should have high volumetric and mass energy density.
- Ease of transportation from production site to delivery points.
- Long-storage life of fuel, minimum handling, and distribution problems.
- Environmental compatibility: While using alternative fuel, the engine performance is expected to improve significantly with regard to regulated emissions and unregulated emissions.
- Manufacturer's warranty: The alternative fuel must guarantee the lifetime of the equipment; its reliability and operational capability are not modified.
- Investment cost: Additional investment on an existing engine must be small to ensure that the operation is competitive with petroleum fuel.
- Modification of existing engines: Engine modification should be simple, inexpensive, and easily reversible. Such modification should not affect the use of traditional fuel in order to preserve engine compatibility with the use of two fuels.

Switch over of operation from alternative fuel mode to conventional fuel mode should be done easily.

Some of the important fuels are listed here:

i. Alcohols (methanol and ethanol)
ii. Vegetable oils and biodiesel
iii. Gaseous fuels (natural gas, hydrogen, and liquefied petroleum gas)
iv. Ethers
v. Electric/fuel cell/hybrid vehicles

CHAPTER 2

BIODIESEL

2.1 INTRODUCTION: WHAT IS BIODIESEL

Biodiesel is a diesel replacement fuel for use in diesel engines. It is manufactured from plant oils (e.g., soybean oil, cottonseed oil, canola oil, corn oil); recycled cooking greases or oils (e.g., yellow grease); or animal fats (beef tallow, pork lard); and various combinations of these feedstocks. Used cooking oils are mostly plant based, but may also contain animal fats. Used cooking oils are both recycled and renewable.

The major component of vegitable oil and animal fat are triacylglycerols(TAG; often also called triglyceride). Chemically,TAG are esters of fatty acid with glycerol (1,2,3-Propanetriol; Glycerol is often also called glycerine. The TAG of vegitable oil and animal fats typically contains several different FA. Thus different FA can be attached to one glycerol backbone. The different FA that are contain in the TAG comprise the FA profile oil the vegitable oil or animal fat. Because different FA have different physical and chemical property, the FA profile is probably the most most important parameter influencing the corresponding properties of vegitable oil or animal fat.

Biodiesel can be produced from a great variety of feedstock. To obtain biodiesel the vegitable oil or animal fat is subjected to a chemical reaction termed as transesterification. In that reaction, the vegitable oil reacted in the presence of the catalyst (usually a base)with an alcohol(usually methanol) to give the corresponding ester of the FA mixture that is found in the parent vegitable oil or animal fat.

Feed stock include most common vegitable oil (e.g. soya bean, cotton seed, peanut, rapeseed- canola ,sunflower, coconut) and animal fat as well as waste oil. The choice of feed stock depends largely on geography. Depending on the origin and quality of feed stock, changes to the production process may be necessary

As biodiesel production and use increase, new feedstocks are being developed and may soon be introduced into the market. Some examples include pennycress, camelina, cuphea, brown grease, and various strains of algae. Although there is little biodiesel from these feedstocks currently available, there is great potential for these feedstocks to supplement the current feedstock supply.

Biodiesel can be produced from a great variety of feedstocks. These feedstocks include most common vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats (usually tallow) as well

as waste oils (e.g., used frying oils). The choice of feedstock depends largely on geography. Depending on the origin and quality of the feedstock, changes to the production process may be necessary.

Biodiesel is miscible with petrodiesel in all ratios. In many countries, this has led to the use of blends of biodiesel with petrodiesel instead of neat biodiesel. It is important to note that these blends with petrodiesel are not biodiesel. Often blends with petrodiesel are denoted by acronyms such as B20, which indicates a blend of 20% biodiesel with petrodiesel. Of course, the untransesterified vegetable oils and animal fats should also not be called "biodiesel." Methanol is used as the alcohol for producing biodiesel because it is the least expensive alcohol, although other alcohols such as ethanol or i s o-propanol may yield a biodiesel fuel with better fuel properties. Often the resulting products are also called fatty acid methyl esters (FAME) instead of biodiesel. Although other alcohols can by definition yield biodiesel, many now existing standards are designed in such a fashion that only methyl esters can be used as biodiesel if the standards are observed correctly.
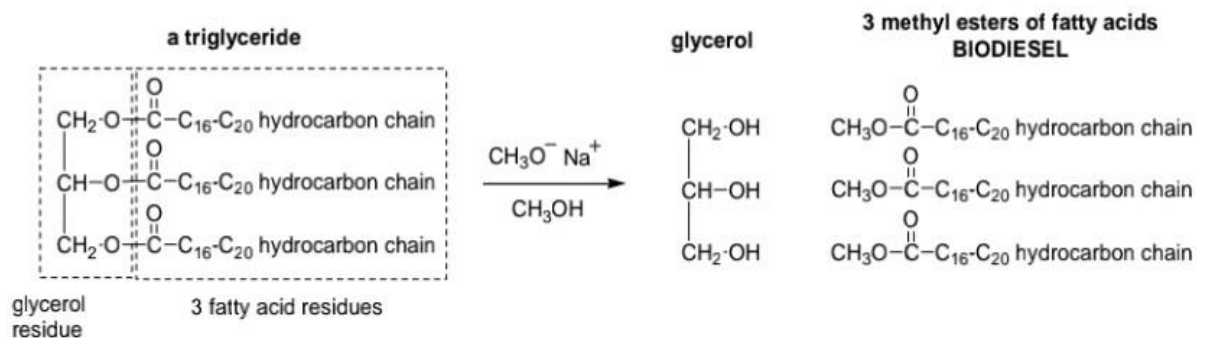
Fig. 2.1. The transesterification reaction.

Biodiesel has several distinct advantages compared with petrodiesel in addition to being fully competitive with petrodiesel in most technical aspects:

• Derivation from a renewable domestic resource, thus reducing dependence on and preserving petroleum.

• Biodegradability.

• Reduction of most exhaust emissions (with the exception of nitrogen oxides, NOx).

• Higher flash point, leading to safer handling and storage.

• Excellent lubricity, a fact that is steadily gaining importance with the advent of low-sulfur

petrodiesel fuels, which have greatly reduced lubricity. Adding biodiesel at low levels (1–2%) restores the lubricity.

Some problems associated with biodiesel are its inherent higher price, which in many countries is offset by legislative and regulatory incentives or subsidies in the form of reduced excise taxes, slightly increased NOx exhaust emissions (as mentioned above), stability when exposed to air (oxidative stability), and cold flow properties that are especially relevant in North America. The higher price can also be (partially) offset by the use of less expensive feedstocks, which has sparked interest in materials such as waste oils (e.g., used frying oils).

Why Are Vegetable Oils and Animal Fats Transesterified to Alkyl Esters (Biodiesel)?

The major reason that vegetable oils and animal fats are transesterified to alkyl esters (biodiesel) is that the kinematic viscosity of the biodiesel is much closer to that of petrodiesel. The high viscosity of untransesterified oils and fats leads to operational problems in the diesel engine such as deposits on various engine parts. Although there are engines and burners that can use untransesterified oils, the vast majority of engines require the lower-viscosity fuel.

Why Can Vegetable Oils and Animal Fats and Their Derivatives Be Used as (Alternative) Diesel Fuel?

The fact that vegetable oils, animal fats, and their derivatives such as alkyl esters are suitable as diesel fuel demonstrates that there must be some similarity to petrodiesel fuel or at least to some of its components. The fuel property that best shows this suitability is called the cetane number . In addition to ignition quality as expressed by the cetane scale, several other properties are important for determining the suitability of biodiesel as a fuel. Heat of combustion, pour point, cloud point, (kinematic) viscosity, oxidative stability, and lubricity are among the most important of these properties.

2.2 BIODIESEL PRODUCTION

Process of biodiesel production:

Step 1: Filter the oil using filter paper and heat the oil to 100°C to remove any moisture content.

Step 2: Check the FFA content of oil by taking 1 gram of the oil, 10 ml of isopropyl alcohol

and 2 drops of phenolphthalein indicator in the beaker and mix the content thoroughly using a glass bead. Now titrate the solution with N/10 sodium hydroxide solution till the color changes to dark pink.

Step 3: Calculate acid value using formula Acid number = (5.61× volume of NaOH consumed)/ wt. of oil sample

Step 4: Calculate free fatty acid using formula

FFA = 0.5× Acid number

If, FFA ≤ 2, proceed with transesterification reaction.

FFA > 2, proceed with esterification reaction followed by transesterification reaction.

Step 5: ESTERIFICATION REACTION

• Stir the oil continuously at 60°C. Prepare a catalyst solution of 0.5% (w/w) PTSA and 20% (w/w) methanol of oil in a separate beaker.

• Pour the catalyst solution in the oil and wait for the completion of the reaction till the FFA content get reduced to the desired values.

Step 6 : TRANSESTERIFICATION REACTION

• Stir the oil continuously at 60°C. Prepare a catalyst solution of 0.5% (w/w) KOH/NaOH pellets and 20%(w/w) methanol of oil in separate beaker

• Pour the catalyst solution in the oil and stir the solution for around 30 to 35 minutes till the glycerin layer gets deposited gradually in the solution.

Step 7 : GRAVITY SEPRATION METHOD

• Pour the solution in the separating funnel for gravity separation.

• Remove the glycerol setelled at the bottom of the seprating funnel.

Step 8: WATER WASHING

• Wash the biodiesel with warm water to remove dissolved impurity and glycerol.

• Repeat the procedure till the clean water is found in the bottom of seprating funnel

Step 9: Heat the biodiesel at 100°C for 15 minutes to remove any moisture content
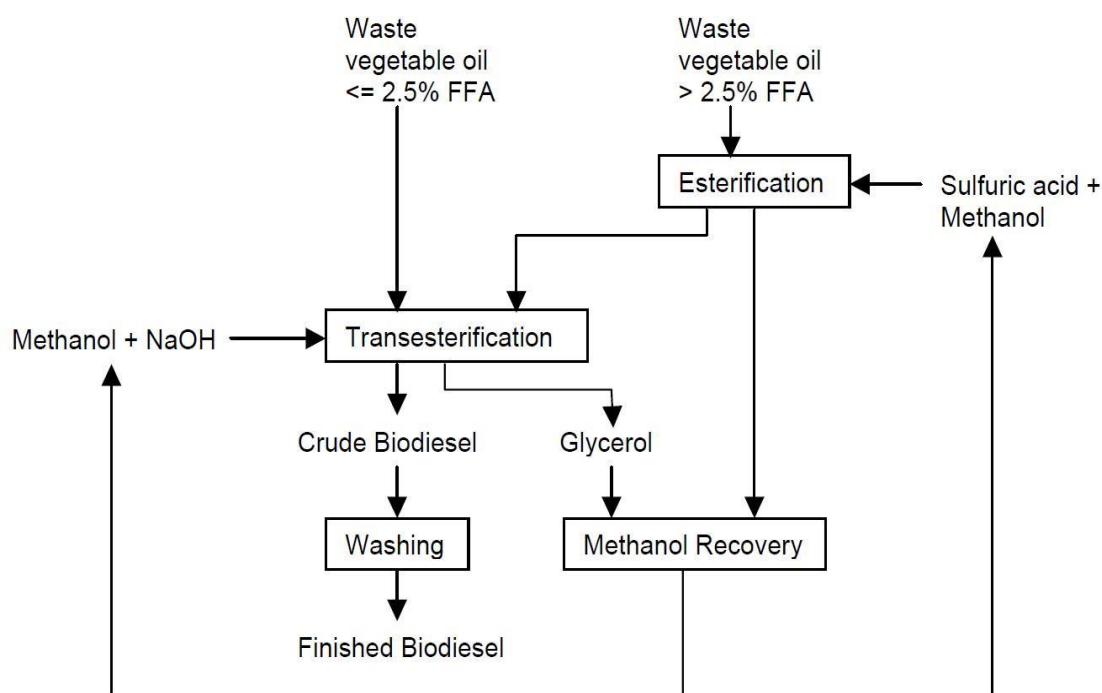
Fig 2.3 Flow diagram of biodiesel production

Four methods to reduce the high viscosity of vegetable oils to enable their use in common diesel engines without operational problems such as engine deposits have been investigated: blending with petrodiesel, pyrolysis, microemulsification (cosolvent blending), and transesterification.

Transesterification is by far the most common method and will be dealt with in this chapter. Only the transesterification reaction leads to the products commonly known as biodiesel, i.e., alkyl esters of oils and fats. The most commonly prepared esters are methyl esters, largely because methanol is the least expensive alcohol, although there are exceptions in some countries. In Brazil, for example, where ethanol is less expensive, ethyl esters are used as fuel. In addition to methanol and ethanol, esters of vegetable oils and animal fats with other low molecular weight alcohols were investigated for potential production and their biodiesel properties. Table 1 of this chapter contains a list of C1–C4 alcohols and their relevant properties.

In addition to vegetable oils and animal fats, other materials such as used frying oils can also be suitable for biodiesel production; however, changes in the reaction procedure frequently have to be made due to the presence of water or free fatty acids (FFA) in the materials. The present section discusses the transesterification reaction as it is most commonly applied to (refined) vegetable oils and related work. Alternative feedstocks and processes, briefly indicated here, will be discussed later. The general scheme of the transesterification reaction was presented in the introduction and is given here in Figure 2.1.

Di- and monoacylglycerols are formed as intermediates in the transesterification reaction. Figure 2.4 qualitatively depicts conversion vs. reaction time for a transesterification reaction taking into account the intermediary di- and monoacylglycerols. Actual details in this figure, such as the final order of concentration of the various glycerides at the end of the reaction and concentration maximums for di- and monoacylglycerols, may vary from reaction to reaction depending on conditions. The scale of the figure can also vary if concentration (in mol/L) is plotted vs. time instead of conversion.

TABLE 1

Properties of C_1–C_4 Alcohols[a]

	Formula	Molecular weight	Boiling point (°C)	Melting point (°C)	Density (g.mL)
Methanol	CH_3OH	32.042	65	–93.9	$0.7914^{20/4}$
Ethanol	C_2H_5OH	46.069	78.5	–117.3	$0.7893^{20/4}$
1-Propanol	$CH_2OH\text{-}CH_2\text{-}CH_3$	60.096	97.4	–126.5	$0.8035^{20/4}$
2-Propanol (iso-Propanol)	$CH_3\text{-}CHOH\text{-}CH_3$	60.096	82.4	–89.5	$0.7855^{20/4}$
1-Butanol (n-Butanol)	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$	74.123	117.2	–89.5	$0.8098^{20/4}$
2-Butanol	$CH_3\text{-}CHOH\text{-}CH_2\text{-}CH_3$	74.123	99.5	—	$0.8080^{20/4}$
2-Methyl-1-propanol (iso-butanol)	$CH_2OH\text{-}CH\text{-}CH_2\text{-}CH_3$ | CH_3	74.123	108	—	$0.8018^{20/4}$
2-Methyl-2-propanol (tert-butanol)	$CH_3\text{-}CHOH\text{-}CH_3$ | CH_3	74.123	82.3	25.5	$0.7887^{20/4}$

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Several reviews dealing with the production of biodiesel by transesterification have been published . Accordingly, the production of biodiesel by transesterification has been the subject of numerous research papers. Generally, transesterification can proceed by base or acid catalysis (for other transesterification processes, see the next section). However, in homogeneous catalysis, alkali catalysis (sodium or potassium hydroxide; or the corresponding alkoxides) is a much more rapid process than acid catalysis.

In addition to the type of catalyst (alkaline vs. acidic), reaction parameters of base-catalyzed transesterification that were studied include the molar ratio of alcohol to vegetable oil, temperature, reaction time, degree of refinement of the vegetable oil, and effect of the presence of moisture and FFA. For the transesterification to give maximum yield, the alcohol should be free of moisture and the FFA content of the oil should be <0.5% (12). The absence of moisture in the transesterification reaction is important because according to the equation (shown for methyl esters),

$$R\text{-}COOCH_3 + H_2O \rightarrow R\text{-}COOH + CH_3OH \qquad (R = alkyl)$$

hydrolysis of the formed alkyl esters to FFA can occur. Similarly, because triacylglycerols are also esters, the reaction of the triacylglycerols with water can form FFA. At 32°C, transesterification was 99% complete in 4 h when using an alkaline catalyst (NaOH or NaOMe) (12). At ≥60°C, using an alcohol:oil molar ratio of atleast 6:1 and fully refined oils, the reaction was complete in 1 h, yielding methyl, ethyl, or butyl esters (12). Although the crude oils could be transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils. These parameters (60°C reaction temperature and 6:1 methanol:oil molar ratio) have become a standard for methanol-based transesterification. Other alcohols (ethanol and butanol) require higher temperatures (75 and 114°C, respectively) for optimum conversion (12). Alkoxides in solution with the corresponding alcohol [made either by reacting the metal directly with alcohol or by electrolysis of salts and subsequent reaction with alcohol (18)] have the advantage over hydroxides that the water-forming reaction according to the equation

$$R'OH + XOH \rightarrow R'OX + H_2O \qquad (R' = alkyl; X = Na \text{ or } K)$$

cannot occur in the reaction system, thus ensuring that the transesterification reaction system remains as water free as possible. This reaction, however, is the one forming the transesterification-causing alkoxide when using NaOH or KOH as catalysts. The catalysts are hygroscopic; precautions, such as blanketing with nitrogen, must be taken to prevent contact with moisture. The use of alkoxides reportedly also results in glycerol of higher purity after the reaction.
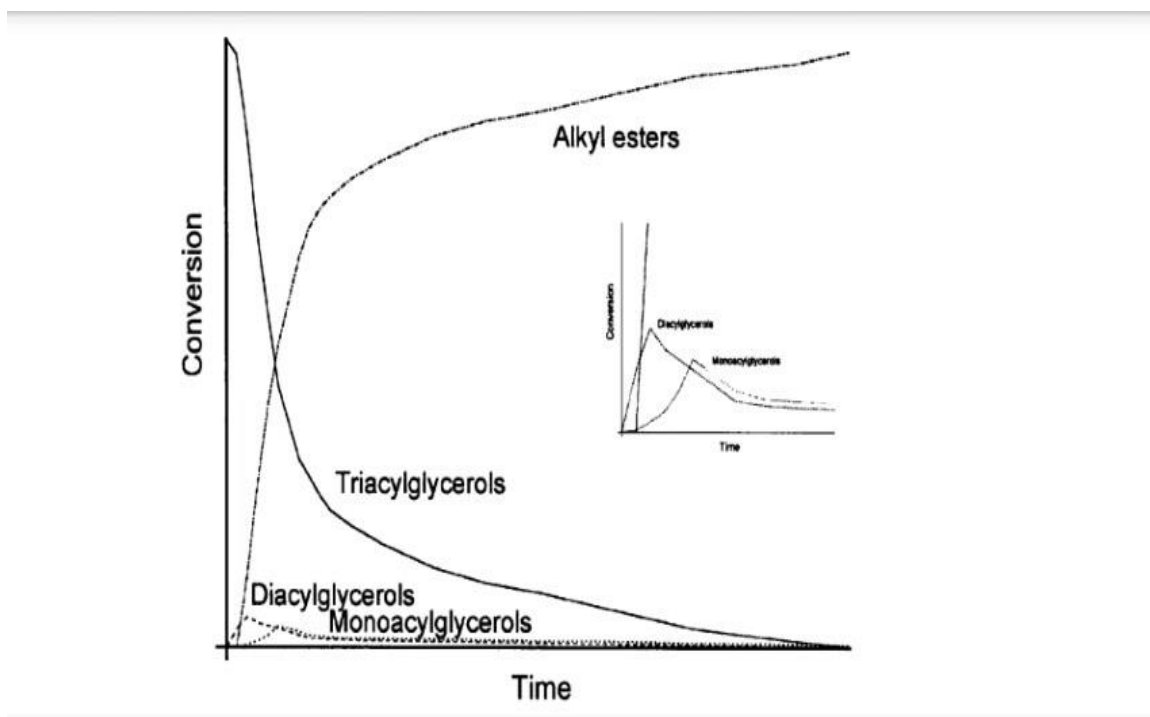
Fig. 2.4 Qualitative plot of conversion in a progressing transesterification reaction indicating relative concentrations of vegetable oil (triacylglycerols), intermediary di- and monoacylglycerols, as well as methyl ester product. Actual details can vary from reaction to reaction as mentioned in the text.

Effects similar to those discussed above were observed in studies on the transesterification of beef tallow. FFA and, even more importantly, water should be kept as low as possible. NaOH reportedly was more effective than the alkoxide; however, this may have been a result of the reaction conditions. Mixing was important due to the immiscibility of NaOH/MeOH with beef tallow, with smaller NaOH/MeOH droplets resulting in faster transesterification. Ethanol is more soluble in beef tallow which increased yield, an observation that should hold for other feedstocks as well.

Other work reported the use of both NaOH and KOH in the transesterification of rapeseed oil. Recent work on producing biodiesel from waste frying oils employed KOH. With the reaction conducted at ambient pressure and temperature, conversion rates of 80–90% were achieved within 5 min, even when stoichiometric amounts of methanol were employed. In two transesterifications (with more MeOH/KOH steps added to the methyl esters after the first step), the ester yields were 99%. It was concluded that an FFA content up to 3% in the feedstock did not affect the process negatively, and phosphatides up to 300 ppm phosphorus were acceptable. The resulting methyl ester met the quality requirements for Austrian and European biodiesel without further treatment. In a study similar to previous work on the transesterification of soybean oil, it was concluded that KOH is preferable to NaOH in the transesterification of safflower oil of Turkish origin. The optimal conditions were given as 1 wt% KOH at $69 \pm 1°C$ with a 7:1 alcohol:vegetable oil molar ratio to give 97.7% methyl ester yield in 18 min. Depending on the vegetable oil and its component fatty acids influencing FFA content, adjustments to the alcohol:oil molar ratio and the amount of catalyst may be required as was reported for the alkaline transesterification of Brassica carinata oil.

In principle, transesterification is a reversible reaction, although in the production of vegetable oil alkyl esters, i.e., biodiesel, the back reaction does not occur or is negligible largely because the glycerol formed is not miscible with the product, leading to a two-phase system. The transesterification of soybean oil with methanol or 1-butanol was reported to proceed with pseudo-first-order or second-order kinetics, depending on the molar ratio of alcohol to soybean oil (30:1 pseudo first order, 6:1 second order; NaOBu catalyst), whereas the reverse reaction was second order. However, the originally reported kinetics were reinvestigated and differences were found. The methanolysis of sunflower oil at a molar ratio of methanol:sunflower oil of 3:1 was reported to begin with secondorder kinetics but then the rate decreased due to the formation of glycerol . A shunt reaction (a reaction in which all three positions of the triacylglycerol react virtually simultaneously to give three alkyl ester molecules and glycerol) originally proposed as part of the forward reaction was shown to be unlikely, that second-order kinetics are not followed, and that miscibility phenomena play a significant role. The reason is that the vegetable oil starting material and methanol. are not well miscible. The miscibility phenomenon results in a lag time in the formation of methyl esters as indicated qualitatively in. The formation of glycerol from triacylglycerols proceeds stepwise v i a the di- and monoacylglycerols, with a fatty acid alkyl ester molecule being formed in each step. From the observation that diacylglycerols reach their maximum concentration before the monoacylglycerols, it was concluded that the last step, formation of glycerol from monoacylglycerols, proceeds more rapidly than the formation of monoacylglycerols from diacylglycerols.

The addition of cosolvents such as tetrahydrofuran (THF) or methyl tert-butyl ether (MTBE) to the methanolysis reaction was reported to significantly accelerate the methanolysis of vegetable oils as a result of solubilizing methanol in the oil to a rate comparable to that of the faster butanolysis. This is to overcome the limited miscibility of alcohol and oil at the early reaction stage, creating a single phase. The technique is applicable for use with other alcohols and for acid-catalyzed pretreatment of high FFA feedstocks. However, molar ratios of alcohol:oil and other parameters are affected by the addition of the cosolvents. There is also some additional complexity due to recovering and recycling the cosolvent, although this can be simplified by choosing a cosolvent with a boiling point near that of the alcohol being used. In addition, there may be some hazards associated with its most common cosolvents, THF and MTBE.

Other possibilities for accelerating the transesterification are microwave or ultrasonic irradiation. Factorial experiment design and surface response methodology were applied to different production systems and are also discussed in the next section. A continuous pilot plant-scale process for producing methyl esters with conversion rates >98% was reported as well as a discontinuous two-stage process with a total methanol:acyl (from triacylglycerols) ratio of 4:3. Other basic materials, such as alkylguanidines, which were anchored to or entrapped in various supporting materials such as polystyrene and zeolite, also catalyze transesterification. Such systems may provide for easier catalyst recovery and reuse.

FUEL QUALITY

The primary criterion for biodiesel quality is adherence to the appropriate standard. Generally, the fuel quality of biodiesel can be influenced by several factors, including the quality of the feedstock, the fatty acid composition of the parent vegetable oil or animal fat, the production process, the other materials used in this process, and postproduction parameters.

When specifications are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine's durability and reliability. Even when used in low-level blends with petrodiesel fuel, biodiesel is expected to meet the standard before being blended. Although some properties in the standards, such as cetane number and density, reflect the properties of the chemical compounds that make up biodiesel, other properties provide indications of the quality of the production process. Generally, the parameters given in ASTM D6751 are defined by other ASTM standards and those in EN 14214 by other European or international (ISO) standards. However, other test methods, such as those developed by professional oleochemical organizations, such as the American Oil Chemists' Society (AOCS), may also be suitable (or even more appropriate because they were developed for fats and oils and not for petroleum-derived materials addressed in the ASTM standards). This discussion will focus on the most important issues for ensuring product quality for biodiesel as it relates to production as well as some postproduction parameters.

PRODUCTION PROCESS FACTORS

The most important issue during biodiesel production is the completeness of the transesterification reaction. The basic chemical process that occurs during the reaction is indicated in Figure with the reaction proceeding stepwise from triacylglycerols to glycerol and alkyl esters with each step producing a fatty acid alkyl ester.

Even after a fully "complete" transesterification reaction, small amounts of tri-, di-, and monoacylglycerols will remain in the biodiesel product. The glycerol portion of the acylglycerols is summarily referred to as bound glycerol. When the bound glycerol is added to the free glycerol remaining in the product, the sum is known as the total glycerol. Limits for bound and total glycerol are usually included in biodiesel standards. For example, ASTM D6751 requires <0.24% total glycerol in the final biodiesel product as measured using a gas chromatographic (GC) method described in ASTM D 6584. Because the glycerol portion of the original oil is usually ~10.5%, this level of total glycerol corresponds to 97.7% reaction completion. Other methods can be used to measure total glycerol such as high-performance liquid chromatography (HPLC) (e.g., AOCS Recommended Practice Ca 14b-96: Quantification of Free Glycerine in Selected Glycerides and Fatty Acid Methyl Esters by HPLC with Laser Light-Scattering Detection) or a chemical procedure such as that described in AOCS Official Method Ca

(Total, Free and Combined Glycerol Iodometric Method). However, only the GC procedures are acceptable for demonstrating compliance with standards.

Free Glycerol- Glycerol is essentially insoluble in biodiesel so that almost all glycerol is easily removed by settling or centrifugation. Free glycerol may remain either as suspended droplets or as the very small amount that does dissolve in the biodiesel. Alcohols can act as cosolvents to increase the solubility of glycerol in the biodiesel. Most glycerol should be removed from the biodiesel product during the water washing process. Water-washed fuel is generally very low in free glycerol, especially if hot water is used for washing. Distilled biodiesel tends to have a greater problem with free glycerol due to glycerol carry-over during distillation. Fuel with excessive free glycerol will usually have a problem with glycerol settling out in storage tanks, creating a very viscous mixture that can plug fuel filters and cause combustion problems in the engine.

Residual Alcohol and Residual Catalyst- Because alcohols such as methanol and ethanol as well as the alkaline catalysts are more soluble in the polar glycerol phase, most will be removed when the glycerol is separated from the biodiesel. However, the biodiesel typically contains 2–4% methanol after the separation, which may constitute as much as 40% of the excess methanol from the reaction. Most processors will recover this methanol using a vacuum stripping process. Any methanol remaining after this stripping process should be removed by the water washing process. Therefore, the residual alcohol level in the biodiesel should be very low. A specific value for the allowable methanol level is specified in European biodiesel standards (0.2% in EN 14214), but is not included in the ASTM standard; however, the flash point specification in both standards limits the alcohol level. Tests showed that as little as 1% methanol in the biodiesel can lower its flashpoint from 170°C to <40°C. Therefore, by including a flashpoint specification of 130°C, the ASTM standard limits the amount of alcohol to a very low level (<0.1%). Residual alcohol left in biodiesel will generally be too small to have a negative effect on fuel performance. However, lowering the flashpoint presents a potential safety hazard because the fuel may have to be treated more like gasoline (which has a low flashpoint) than diesel fuel.

Most of the residual catalyst is removed with the glycerol. Like the alcohol, remaining catalyst in the biodiesel should be removed during the water washing. Although a value for residual catalyst is not included in the ASTM standard, it will be limited by the specification on sulfated ash. Excessive ash in the fuel can lead to engine deposits and high abrasive wear levels. The European standard EN 14214 places limits on calcium and magnesium as well as the alkali metals sodium and potassium.

POSTPRODUCTION FACTORS

Water and Sediment- These two items are largely housekeeping issues for biodiesel. Water can be present in two forms, either as dissolved water or as suspended water droplets. Although biodiesel is generally insoluble in water, it actually takes up considerably more water than petrodiesel fuel. Biodiesel can contain as much as 1500 ppm of dissolved water, whereas diesel fuel usually takes up only ~50 ppm. The standards for diesel fuel (ASTM D 975) and biodiesel (ASTM D 6751) both limit the amount of water to 500 ppm. For petrodiesel fuel, this actually allows a small amount of suspended water. However, biodiesel must be kept dry. This is a challenge because many diesel storage tanks have water on the bottom due to condensation. Suspended water is a problem in fuel injection equipment because it contributes to the corrosion of the closely fitting parts in the fuel injection system. Water can also contribute to microbial growth in the fuel. This problem can occur in both biodiesel and petrodiesel fuel and can result in acidic fuel and sludge that will plug fuel filters.

Sediment may consist of suspended rust and dirt particles or it may originate from the fuel as insoluble compounds formed during fuel oxidation. Some biodiesel users have noted that switching from petrodiesel to biodiesel causes an increase in sediment originating from deposits on the walls of fuel tanks that had previously contained petrodiesel fuel. Because its solvent properties are different from those of petrodiesel fuel, biodiesel may loosen these sediments and cause fuel filter plugging during the transition period.

Storage Stability- Storage stability refers to the ability of the fuel to resist chemical changes during long-term storage; it is a major issue with biodiesel. Contact with air (oxidative stability) and water (hydrolytic stability) are the major factors affecting storage stability. Oxidation is usually accompanied by an increase in the acid value and viscosity of the fuel. Often these changes are accompanied by a darkening of the biodiesel color from yellow to brown and the development of a "paint" smell. In the presence of water, the esters can hydrolyze to long-chain FFA, which also cause the acid value to increase. The methods generally applied to petrodiesel fuels for assessing this issue, such as ASTM D 2274, were shown to be incompatible with biodiesel, and this remains an issue for research. Discusses some methods for assessing the oxidative stability of biodiesel that were or are being evaluated.

Antioxidant additives such as butylated hydroxytoluene and t-butylhydroquinone were found to enhance the storage stability of biodiesel. Biodiesel produced from soybean oil naturally contains some antioxidants (tocopherols, e.g., vitamin E), providing some protection against oxidation (some tocopherol is lost during refining of the oil before biodiesel production). Any fuel that is going to be stored for an extended period of time, whether it is petrodiesel or biodiesel, should be treated with an antioxidant additive.

Quality Control- All biodiesel production facilities should be equipped with a laboratory so that the quality of the final biodiesel product can be monitored. To monitor the completeness of the reaction according to the total glycerol level specified requires GC analysis as called for in biodiesel standards.

It is also important to monitor the quality of the feedstocks, which can often be limited to acid value and water contents, tests that are not too expensive. Another strategy used by many producers is to draw a sample of the oil (or alcohol) from each delivery and use that sample to produce biodiesel in the laboratory. This test can be fairly rapid (1–2 h) and can indicate whether serious problems may occur in the plant.

2.3 PROPERTIES OF BIODIESEL & ITS ASTM RANGE :

1- Viscosity

The viscosity can be conceptualized as quantifing the fractional force that arises between adjacent layers of fluid that are in relative motion. In biodiesels it is generally calculated in the term of kinematic viscosity. Kinematic viscosity is ratio of dynamic viscosity to density. Its ASTM range for biodiesel is 1.9 to 6.0 (mm^2/S).

2- Flash point

The flash point of a volatile material is the lowest temp. at which vapoures of the materials will ignite when given an ignition source. Its ASTM range for biodiesel is 130° (minimum).

3- Cloud point

It refers to the temp. below which wax in diesel or bio wax in biodiesel form a cloud appearance. Its ASTM range for Biodiesel is -3 to -12 ^{o}C.

4- Density

The density of a substance is its mass per unit volume. Its ASTM range for Biodiesel is 1298 kg/m3(at 15° C).

5- Cetane number

It represents the knocking tendency in CI engine. A measure of the ignition value of a diesel fuel that represents the % by volume of cetane in a mixture of liquid methylnaphthalene that gives the same ignition lag as the oil being tested. Its ASTM range for biodiesel is 47 (minimum).

6- Calorific values

The calorific value is the total energy released as heat when a substance undergoes complete combustion with oxygen under the standard conditions. Mathematically it is defined as the amount of energy (heat) produced during complete combustion of unit mass of fuel. Its ASTM standard for biodiesel is 35 MJ/kg (minimum).

7- Acid value

Acid value is mass of KOH in milligrams that is required to neutralize 1 gram of chemical substance. The acid number is a measure of the number of carboxylic acid group in a chemical compound such as fatty acid or in mixture of compounds. Its ASTM range for biodiesel is 0.5(maximum)

Chemical Analysis of Biodiesel	
Parameters	**Test Result**
Flash Point	132°C
Viscocity	4.6 cSt
Pour Point	-15°C
Total Ash	0.01%
Cetan Number	48
Acidity	0.4 as KOH
Total Moisture	1.5%
Fire Point	140°C
Total Sulfur	Per Regulation
Carbon Monoxide	2.25%
Nitrogen Dioxide	17%
Calorofic Values	7940Kcal
Density	880
Carbon Content	290ppm
Hydrogen Content	2.5ppm
Oxygen Content	2.48ppm
Lead	1.5ppm
Arsenic	1.2ppm
Cadmium	1.1ppm
Mercury	ND
Cloud Point	-6°C

TABLE 2.1 property of produced biodiesel

2.4 BIODIESEL FUELS: BIODEGRABILITY, BIOLOGICAL AND CHEMICAL OXYGEN DEMAND AND TOXICITY

Biodegradability

The biodegradability of various biodiesel fuels in the aquatic and soil environments was examined by the CO_2 evolution method, gas chromatography (GC) analysis, and seed germination. The fuels examined included neat rapeseed oil (NR), neat soybean oil (NS), the methyl- and ethyl esters of rapeseed oil and soybean oil, and Phillips 2-D reference petroleum diesel. Blends of biodiesel/petrodiesel at different volumetric ratios, including 80/20, 50/50, 20/80, were also examined in the aquatic phase.

There are many test methods for accessing the biodegradability of an organic compound. Among them, the CO_2 evolution test (shaker flask system) and GC analysis are most common and were employed as the major method for the aquatic and soil experiments, respectively. One important difference between them is that $C O_2$ evolution measures ultimate degradation (mineralization) in which a substance is broken down to the final products, CO_2 and water, whereas GC analysis measures only primary degradation in which the substance is not necessarily transformed to the end products. Finally, because revegetation of soils contaminated by fuel spills is often a desirable goal, seed germination was employed to evaluate the toxicity of biodiesel on plants in the soil system.
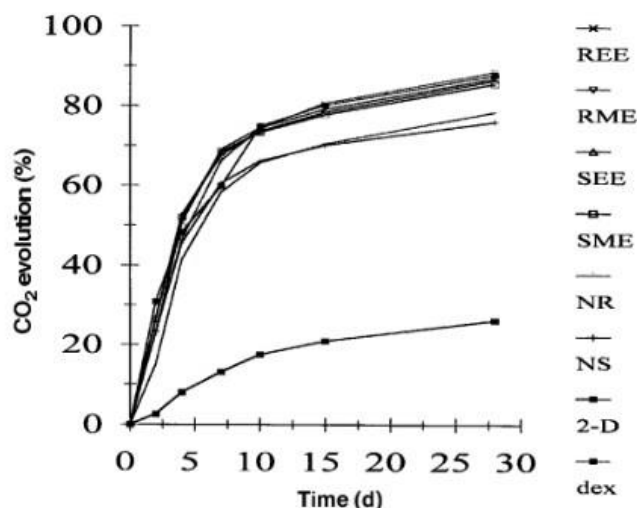

Fig. 2.5 Biodegradability of biodiesel compared with dextrose and 2-D reference fuel measured by the shake flask test.

BOD and COD

BOD is a measure of the dissolved oxygen consumed during the biochemical oxidation of organic matter present in a substance. In the current study, BOD5 w a s

used as a relative measure of the amount of organic matter subject to the microbially mediated oxidative processes present in biodiesel fuel. This may also serve as a relative measure of biodegradability. COD is a measure of the amount of oxygen required to chemically oxidize organic matter in a sample. COD values were used in the study as an independent measure of the total oxidizable organic matter present in the fuels.

BOD was determined using EPA Method 405.1. Dissolved oxygen is measured initially and after incubation. The BOD is computed from the difference between initial and final dissolved oxygen (DO). Replicate analyses were performed in triplicate (the method specifies that duplicate samples be used; thus, $n = 6$). Reference samples of glucose/glutamic acid solution, and a commercially available WasteWatRT M demand reference were also tested in duplicate. Fuels were tested at their appropriate water accommodated fraction (WAF: the highest concentration at which the test substance is maintained in the aqueous phase of the solution); WAF values were converted to pure substance for statistical comparison. COD was determined using EPA Method 410.1. Fuels were tested at their appropriate WAF, and these values were converted to pure substance for statistical comparison.
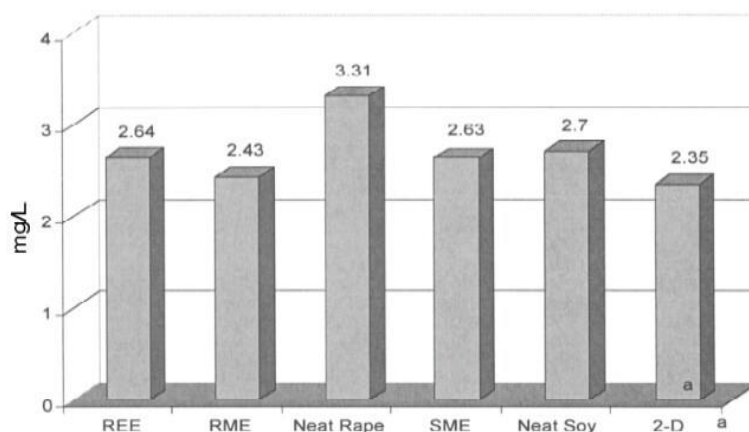

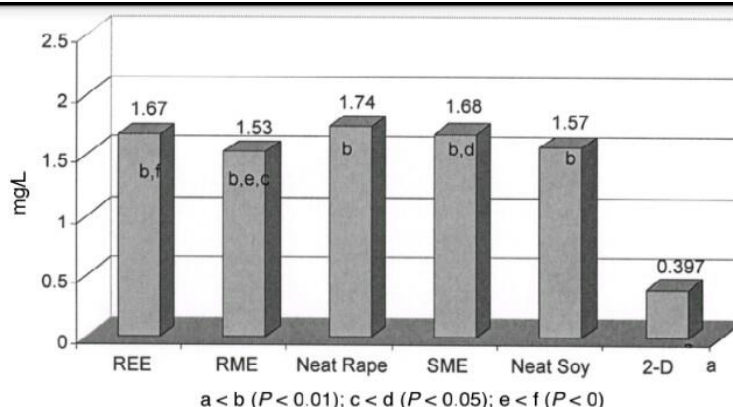Fig 2.6 Mean chemical oxygen demand (COD) values ($n = 3$).

a < b ($P < 0.01$); c < d ($P < 0.05$); e < f ($P < 0$)

Fig 2.7   Mean biochemical oxygen demand (BOD5) values ($n = 6$).

Toxicity

This section reports on acute oral and acute dermal toxicity tests and static acute aquatic toxicity tests with RME and REE and blends of each with diesel fuel. The acute oral toxicity tests were conducted with albino rats and the acute dermal toxicity tests were conducted with albino rabbits. Acute aquatic toxicity tests were performed with Daphnia magna and rainbow trout. Each of these studies was under contract with the University of Idaho. A separate set of studies with D. magna and juvenile rainbow trout was conducted by the University of Idaho.

The 50% lethal dose (LD50; the point at which 50% have died and 50% are still alive determined by interpolation) values for each of the substances tested were >5000 mg/kg when administered once orally to rats and >2000 mg/kg when administered once for 24 h to the clipped, intact skin of male and female albino rabbits. The LD50 values for acute aquatic toxicity with D. magna in mg/L were 3.7 for table salt, 1.43 for 2-D, 23 for RME, 99 for REE, and 332 for methyl soyate. Duplicate tests with rainbow trout were run with 10 organisms/replicate. The median lethal concentration (LC)50 values were not reported because of failure to kill a sufficient number of fish at the concentrations tested, even with petrodiesel. The 20 and 50% blends produced scattered losses of fish, but none of the tests had <85% survival at any concentration after 96 h.

2.5 SOYABEAN OIL COMPOSITION FOR BIODIESEL

The composition of soybean oil can be modified to improve the usefulness of soybeans for food and fuel applications. Molecular marker, traditional breeding, and transgenic technologies enable seed companies to incorporate modified oil traits into high-yielding germplasm. It takes several years to deliver a modified oil composition to the marketplace; thus, it is prudent to select the right targets in the early stages of development.

Benefits sought by the biodiesel industry are improved oxidative stability and improved cold flow properties. These two properties are linked. In some situations, neat biodiesel has to be heated to ensure flow. The warm temperatures increase the rate of fatty acid oxidation. Thus, improvements in cold flow can reduce the stability target required to meet commercial needs.

The key fatty acids limiting the cold flow quality of biodiesel are palmitic (16:0) and stearic acids (18:0) as illustrated by the melting point of the fatty acid methyl esters (FAME) (Table A-1 in Appendix A). Polyunsaturated fatty acids (PUFA) improve cold flow properties but are most susceptible to oxidation. Thus one has to identify an optimum level of PUFA. Food processors' demand for PUFA must be considered. If a large segment of the food processing industry rejects the oil, the costs of segregating the grain will prohibit the practical use of the extracted oil for fuel purposes. Linoleic acid is a primary source of fried food flavor compounds such as 2,4 decadienal, and oleic acid is a source of fruity, waxy, and plastic tasting odors such as 2-decenal. The proportions of these fatty acids have to be selected to balance flavor and shelf-life objectives. Good potato chip flavor was obtained with an oil having 68% oleic and 20% linoleic acid. PUFA are essential in the diet and play

a role in cardiovascular health particularly when they replace saturated fat. Thus, we hypothesized an optimized soybean oil composition for food and fuel use that retains ~24% PUFA(TABLE 2).

A synthesized biodiesel with the targeted composition was prepared from mixtures of pure FAME (>99% purity; modification from Table 1: 18:1 was 73.3% and the "other" category was 0%). The cold flow properties of the oil were compared with controls (Table 2). It was apparent from these data that the cold flow properties of the target biodiesel composition can be comparable to or better than those of petroleum diesel. Additional data from other biodiesel compositions were added to the data from this study, and an exponential relation was found between the saturated fat content of biodiesel and cloud point. The effect of lowering the saturated fat level of biodiesel from 15 to 10% on cloud point was relatively minor compared with a change to a 3.5% saturated fat content.

The oil of the target composition (Table 2) is suitable for use as a feedstock to produce biodiesel because biodiesel from the oil has improved cold flow, improved ignition quality (CN), improved oxidative stability, and presumably reduced nitrogen oxide emissions. The challenge is to create soybean oil near the target composition without sacrificing soybean yield. The composition also must be marketed successfully and tested in foods so that the soybeans are sought as an improved source of vegetable oil. These accomplishments will enable soybeans to be grown on a large percentage of the total acres and create value across the food and fuel chain.

TABLE 2 Compositions of Typical Soybean Oil (Control), a Modified Composition, and a Target Soybean Oil Composition

|	Control (%)	USDA[a] line (%)	Target (%)
18:1	21.8	31.5	71.3
18:2	53.1	52.7	21.4
18:3	8.0	4.5	2.2
16:0	11.8	5.2	2.1
18:0	4.6	4.1	1.0
Other	0.7	2.0	2.0

[a]United States Department of Agriculture.

2.6 CURRENT STATUS OF THE BIODIESEL INDUSTRY

Current Status of Biodiesel in the United States

The U.S. Department of Agriculture (USDA) and other researchers in the United States began investigating vegetable oils as a fuel source in the late 1970s and early 1980s after the Organization of Petroleum Exporting Countries (OPEC) oil crisis. The general conclusion at that time was that vegetable oils were too viscous to be used in modern diesel engines over long periods of time. Transesterifying the vegetable oil into its methyl ester yielded a fuel or blending component more similar to petrodiesel that could serve as a drop-in replacement in existing engines. This modified vegetable oil fuel was still uneconomical compared with conventional diesel and was viewed largely only as an emergency fuel; thus, research efforts dwindled. A small amount of technical research continued during the 1980s and early 1990s. The topic sprang up again in earnest in the early 1990s as Congress began investigating alternatives to imported petroleum fuels after the Desert Storm war. The subsequent passage of the Energy Policy Act of 1992 and the formation of the National Soydiesel Development Board by 11 soybean farmer-run Qualified State Soybean Boards were the beginning of the commercial biodiesel industry in the United States. The National Soydiesel Development Board embraced other biodiesel feedstocks in 1995, changing its name to the National Biodiesel Board (NBB) and focusing its efforts mainly on addressing the technical and regulatory needs to commercialize a new fuel in the United States.

From the first use of peanut oil in 1900 to today's stringent ASTM standards for vegetable oil methyl esters, i.e., biodiesel, the use of vegetable oils and animal fats as a source for diesel fuel applications has come a long way. The industry is currently enjoying exponential growth, and public policy will likely encourage further growth over time. The driving forces for biodiesel use are many and may become even more important as time goes on. Future technologies, such as ultraclean diesel engines or fuel cells, actually represent further opportunities for biodiesel—not threats. In our eyes, there is no longer a question of whether biodiesel will succeed; it is only a question of how large it will grow and how soon.
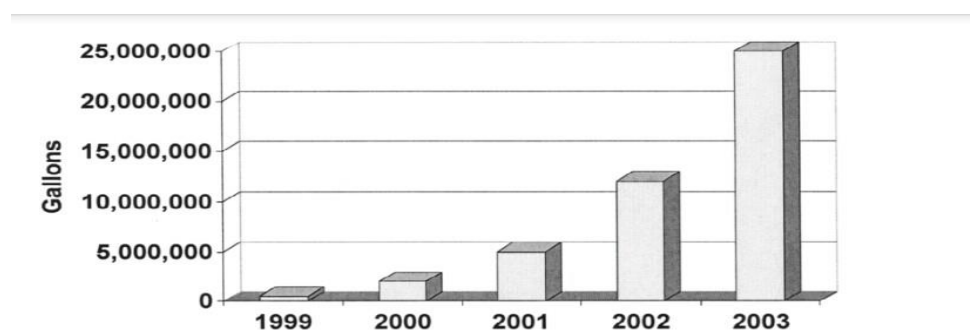
2.8 U.S. biodiesel sales by year.

Current Status of Biodiesel in the European Union

The current status of biodiesel production in the European Union (EU) as described in this chapter represents political measures with the fundamental objective of achieving full utilization of renewable energy sources in a stepwise manner. With these policies, the EU is pursuing a strategy directed toward utilizing renewable energy for the following reasons:

(i)   combating climate change;

(ii)   reducing local environmental loads;

(iii)   creating jobs and income in an EU increasing to 25 member countries;

(iv)   contributing toward a secure supply of energy.

To achieve these objectives, the following timeline was embodied in EU law:

• 1997—White Book COM (97)599: Energy for the Future: Renewable Sources of Energy.

• 2000—Green Paper COM (2000)769: Towards a European Strategy for the Security of Energy Supply.

• 2001—Directive 2001/77/EC on the Promotion of Electricity Produced from Renewable Energy Sources in the Internal Electricity Market.

• 2002—Directive 2002/91/EC on the Energy Performance of Buildings.

• 2003—Directive 2003/30/EC on the Promotion of the Use of Biofuels or Other Renewable Fuels for Transport.

• 2004—Directive 2003/96/EC Restructuring the Community Framework for the Taxation of Energy Products and Electricity.

In its white book, the EU and its member countries set the goal of increasing the production and use of renewable energy to a minimum of 12% of the total domestic energy consumption by the year 2010. The amounts of green power and biofuels should be 2.2 and 5.75%, respectively.

It should not be overlooked that these ambitious goals were not approved without reservations by representatives of commercial and political interests. The different conversions into national legislation by individual member countries reflect their different priorities regarding energy and climate policy. This is the result of intensive political discussions in the individual countries and at the EU level in which the variability provided in the EU directives is utilized in very different fashions relative to the individual climate protection responsibilities. The strategies of the member countries for promoting renewable energy, therefore, differ greatly and can be exemplified by the different tax advantages for biofuels described below. Thus, a well-balanced consensus of all political and economical parties is required to achieve the strategic objectives without conflict and without distorting competition. It is already clear that the speed at which the directives will be applied varies greatly, and it is possible that the desired proportions of biofuels according to the EU directive may not be attained. The German

example shows that technical problems concerning the commercialization of biodiesel and other biofuels (ethanol and sundiesel) can be solved only within existing economical and political conditions.

Status of Biodiesel in Asia, the Americas, Australia, and South Africa

China- The transportation sector was left out of China's economic plans for many years, and the resulting lack of infrastructure is a major obstacle for the country's energy sector and overall economy. Nevertheless, China is one of the largest consumers of fossil diesel oil worldwide. About 60–70 million tons of fossil diesel oil are used every year, with approximately one third of it being imported to balance the market. The Chinese government emphasized its support for biofuels some time ago, but it seems that with the construction of the world's largest Bioethanolproduction plant with ~600,000 t/yr in Changchun, Jilin Province, the development of this biofuel has a higher priority than biodiesel for the time being. In 1998, the Austrian Biofuels Institute completed a study together with the Centre for RenewableEnergy Development (CRED) in Beijing and the Scottish Agricultural College (SAC) within the INCO-programme of the European Union. This study evaluated the feedstock availability for biodiesel production from a variety of potential sources. There are no special regulations or tax exemptions for biodiesel in mainland China and Hong Kong, but following the example set for bioethanol, this may change in the near future.

India- At present, biodiesel initiatives are focused mainly on research, development, and demonstration projects. On September 12, 2002, the first biodiesel/ bioethanol conference was held in New Delhi, and was sponsored by the Ministry of Rural Development and the Petroleum Conservation Research Association. Because it is a tropical country, India has a wide variety of domestic plants that produce oil-bearing seeds of sufficient volume potential, e.g., Sal (Shorea robus ta), Neem (Azadirachta indica) and, specifically, the physic nut (J. curcas), to be considered as feedstock for biodiesel production. It is reported that in the near future, a 100 ton/d unit is expected to begin operation near Hyderabad in the state of Andhra Pradesh.

Japan- The city of Kyoto introduced biodiesel made from recycled frying oil into 220 garbage collection trucks in 1997, and has used the B-20 mixture for 81 city buses since 2000. If all of the edible-oil wastes are recycled and reused as biodiesel fuel (BDF), a market of ~30 billion yen will probably be created. To realize such amarket, however, it is necessary to establish an integrated recycling system involving citizens, companies, and local administrations.

Malaysia- As reported at the International Biofuel Conference in 1998, which was organized by PORIM (Palm Oil Research Institute of Malaysia), initial trials in production at PORIM's pilot plant and in utilization as a fuel in diesel engines had promising results. This included very detailed tests in bus fleets, which were started by Daimler-Benz as early as 1987. Malaysia's mineral oil company, PETRONAS, is carefully watching and studying further developments in Europe, but has not yet acted publicly. With feedstock limitations in Europe, the export of palm oil may become an

additional venue for Malaysia's palm oil industry.

Philippines- In 2001, the Philippine Coconut Authority announced the launch of a nation-wide program to develop the use of coconut oil biodiesel as an alternative fuel. Coconut oil contains 45–53% lauric acid, which is a saturated short-chain fatty acid (12:0) with a rather high level of oxygen of 14.9%. Although higher oxygen levels cause lower energy contents and therefore lower engine performance on the one hand, on the other hand, they give better combustion and therefore lower emission levels.

South Korea- Biodiesel is approved as an alternative fuel. It is expected that a tax exemption will be given in two to three years. Investigation showed that there are two small-scale biodiesel production plants with a total capacity of 8000 t/yr; one company has one large-scale plant (100,000 t/yr) under construction and intends to market a soy oil-based nonbranded biodiesel as a B-20 blend. Biodiesel was provided to vehicle fleets operated by several municipal governments for the test operation. The tests were completed in July 2004.

Thailand- Various mixes of unesterified vegetable (coconut and palm) oil blended with diesel oil or kerosene were introduced in the past year under the name of "biodiesel"; most of them did not meet official standards for commercial use. Other tests are in progress with "real" biodiesel from recycled cooking oils (called "super-biodiesel"), but the quality levels achieved cannot be reported as yet.

CHAPTER 3

LITERATURE REVIEW

• **K.A. Abed , et al.,** Biodiesel blends have ASTM standard of physical and chemical characterization near to diesel fuel. Diesel engine performance and exhaust emission were studied experimentally for burning waste cooking oil blends with diesel fuel. This experimental was on applied on diesel engine at different engine loads from zero to full load. Thermal efficiency for waste cooking oil biodiesel blends were lower than diesel oil. Specific fuel consumption, NOx emission were higher than diesel fuel.CO smoke opacity and HC emission for biodiesel blends were lower than diesel fuel.

• **Mjid Mohadesi,et al.,**The study investigated the transesterification of waste cooking oil with methanol in the presence of potassium hydroxide as catalyst.The acidicty of waste cooking oil was reduced to less than one mg KOH/g oil by using methanol at 60 degree celcius in the presence of 1% sulfuric acid.

• **Nur syakirah Talha,et al.,**Transeterification using heterogeneous base catalyst are found to be cost effective because of its reusability, widely availability, easy to separate from product and longer life time.

• **G. uguz et al.,**This study investigated the effect of anti oxidant addition on fuel stability at different concentration .In this study 3 synthetic anti oxidant namely Pyrogallol,Butylated Hydroxypoluene and tert-bueylhybroquinone were closed in waste cooking biodiesel at different concentration. The findings indicated the effectiveness of FT-IR and DSC as reliable method to assess the oxidation stability and to replace the conventional, time consuming and costly rancimat metrhod. TBHQ was found to be best option to enhance the stability of biodiesel.

• **Peng geng et al.,**This study investigated the influence of high biodiesel to diesel ratio on the combustion characteristics on NOx emission. Under 25%,50%,75% engine load at 1050 rpm and 1500 rpm condition .Experimental result indicated that the cylinder pressure decreases slightly with increasing the biodiesel content in the test fuels while the ignition advances, ignition delay reduces and combustion duration become longer. When test engine operated at low load the maximum % peak heat release rate decreases is about 14.3%, while the maximum % can reach to 21.3% at high load condition.

• **L.Wei et al.,** This study investigated the infkuence of waste cooking oil biodiesel on combustion ,unregulated gaseous emission and particulate emission of diesel engine. Experiment were carried out on direct injection diesel engine fuel with diesel, B20, B50, B75 and biodiesel Biodiesel increases the in-cylinder pressure, shorten the ignition delay and combustion duration, lower the maximum heat release rate. And increase of BSFC is also observed. For BTE no significant changes are found in most of the tested modes. No significant changes are observed for the ozone formation potential of these unregulated gaseous emission. The overall influence of biodiesel on the investigated emission is proportional to the biodiesel content in tested fuels.

- **A.K. Azad et al.,**

  The study investigated the engine performance and emission using biodiesel from soybean oil and waste cooking oil. The fuel properties of these biodiesels were determined using ASTM D6751and EN 14214 standards. The fuels were tested in a multi-cylinder diesel engine with an electromagnetic dynamometer and a 5-gas analyser was used for emission analysis. The result shows that the thermal performance of the engine slightly decreases with increase of the biodiesel blends ratio (i.e. B5, B10, B15, B20 and B50). On the other hand, emission decreases with the increase of biodiesel blends. The reduction in emissions was different for both biodiesels. Waste oil biodiesel showed better trends of emissions reduction with increase of the biodiesel percentage compared with soybean biodiesel. The brake specific fuel consumption (BSFC) of both biodiesels is (6.05%, 9.13%, 12.36% and 18.57% for soybean) and (8.17%, 11.40%, 17.71% and 14.96% for waste cooking oil) higher than diesel, respectively. However, soybean biodiesel consumed less fuel and produced more power and torque compared to waste oil biodiesel. The study concluded that B10 soybean biodiesel blend produced more consistent and expected results than waste oil biodiesel from the performance and emission point of view.

- **Diego Rodríguez et al .,**

  At present the production of biodiesel from castor oil (Ricinus communis L) has been restricted due to the high cost of vegetable oil. An alternative to reduce production costs is the blend of castor oil and waste cooking oil. This is a good alternative to improve the waste cooking oil which is a water contaminant and a health problem in many countries. Initially the two oils were characterized by density, viscosity, iodine index, saponification index and free fatty acids percentage, where the results were consistent with those reported in the literature. Subsequently the mixture between 0% and 20% of waste cooking oil with castor oil was conducted. The transesterification was performed under the conditions previously defined: temperature 60 ° C, molar ratio of 6 mol of methanol / 1mol of oil, catalyst potassium hydroxide (KOH) at 1% w/w with respect to oil. The highest yield was 99% for 85% mixture of castor oil and 15% waste cooking oil, since the results of the other mixtures used were up to 89% yield. The results obtained in gas chromatography showed an average composition of 97.6 of methyl esters. The calorific value was 36,645 J / g for the 85% blends of castor oil and 15% waste cooking oil, it was found that the above mixture was the best of all blends made. Through this work it is concluded that it is possible, from a technical point of view, to use the mixture of castor oil and waste cooking oil for biodiesel production, which can reduce costs in the production of biodiesel from castor oil.

- **Gaurav Dwivedi et al .,**

As a renewable, sustainable and alternative fuel for compression ignition engine, biodiesel instead of diesel has been increasingly fuelled to study its effects on engine performances and emissions in the recent 15 years. Biodiesel, derived from the transesterification of vegetable oils or animal fats, is composed of saturated and unsaturated long-chain fatty acid alkyl esters. In spite of having some application problems, recently it is being considered as one of the most promising alternative fuels in internal combustion engine. The aim of the present paper is to do a comprehensive review of engine performance and emissions using biodiesel from different feedstocks and to compare that with the diesel. From the review it is found that the use of biodiesel leads to the substantial reduction in PM, HC and CO emissions accompanying with the imperceptible power loss, the increase in fuel consumption and the increase in NOx emission on conventional diesel engine with no or fewer modification. However, many further researches about modification on engine, low temperature performance of engine, new instrumentation and methodology for measurements, etc., are recommended while using biodiesel as a substitute of diesel.

- **F. Ariani et al .,**

An observation was performed to evaluate the performance of direct injection stationary diesel engine which used a blends of biodiesel of Sunan pecan seed. The experiments were done with diesel oil, B5, B10, B15 and B20 in the engine speed variety. Results showed that the values of torque, power and thermal efficiency tend to decrease when the engine is using B5, B10, B15 and B20 , compared to diesel oil. It also shown that the specific fuel consumption is increased when using B5, B10, B15 and B20. From the results of experiments and calculations, the maximum power of 3.08 kW, minimum specific fuel consumption of 189.93 g/kWh and maximum thermal efficiency of 45.53% when engine using diesel oil. However, exhaust gases were measured include opacity, carbon monoxide and hydrocarbon when the engine using biodiesel B5, B10, B15 and B20 decreased.

- **S. Senthur Prabu et al .,** In this study, Waste cooking oil (WCO) biodiesel with Butylated hydroxytoluene (BHT) and n-butanol additive was used in a diesel engine and its effects on engine performance and exhaust emissions were studied. The biodiesel produced from waste cooking oil by transesterification process, Methanol, sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) catalyst were used in the reaction. Engine performance test were conducted with blends (B0, B20, B30, B40, and B100) and the results showed that, B30 is the superior blend among other biodiesel blends. Further to improve the performance characteristics of B30, antioxidants of BHT 2000ppm and n-butanol 20% by volume was added in the B30 blend. The results of BSFC for the B30+BHT is 7.3% higher whereas the BTE is 4.6% lower than diesel due to the lower heating value of biodiesel. The heat release rate of B20, B40 and B30+BHT are almost synchronous to diesel fuel, alongside at higher loads B30+n-butanol shows 37.5% less CO emission and 9% higher NOx emission was observed when compared to diesel fuel. WCO biodiesel and its blends with BHT and n-butanol can be used as a fuel in diesel engine.

CHAPTER 4

RESPONSE SURFACE METHODOLOGY

4.1 INTRODUCTION

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several independent variables (input variables). An experiment is a series of tests, called runs, in which changes are made in the input variables in order to identify the reasons for changes in the output response.

Originally, RSM was developed to model experimental responses, and then migrated into the modelling of numerical experiments. The difference is in the type of error generated by the response. In physical experiments,inaccuracy can be due, for example, to measurement errors while, in computer experiments, numerical noise is a result of incomplete convergence of iterative processes, round-off errors or the discrete representation of continuous physical phenomena. In RSM, the errors are assumed to be random.

The application of RSM to design optimization is aimed at reducing the cost of expensive analysis methods (e.g. finite element method or CFD analysis) and their associated numerical noise. The problem can be approximated as described in with smooth functions that improve the convergence of the optimization process because they reduce the effects of noise and they allow for the use of derivative-based algorithms. Venter et al. (1996) have discussed the advantages of using RSM for design optimization applications.

For example, in the case of the optimization of the calcination of Roman cement described in Section 6.3, the engineer wants to find the levels of temperature ($x1$) and time ($x2$) that maximize the early age strength (y) of the cement. The early age strength is a function of the levels of temperature and time, as follows:

$$y \;=\; f(x1, x2) \;+\; \varepsilon \tag{3.1}$$

The response can be represented graphically, either in the three-dimensional space or as contour plots that help visualize the shape of the response surface.Contours are curves of constant response drawn in the xi, xj plane keeping all other variables fixed. Each contour corresponds to a particular height of the response surface, as shown in Figure 4.1.
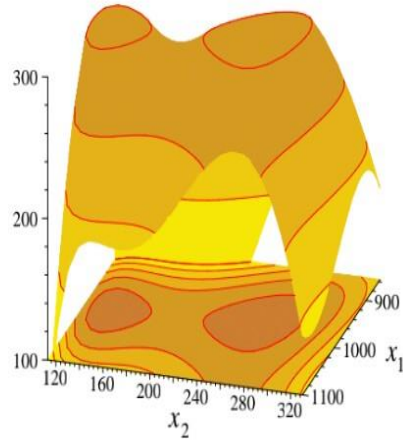
Figure 4.1 Three-dimensional response surface and the corresponding contour plot for the early age strength of Roman cement where x1 is the calcination temperature (°C) and x2 is the residence time (mins).

This chapter reviews the two basic concepts in RSM, first the choice of the approximate model and, second, the plan of experiments where the response has to be evaluated.

4.2 APPROXIMATE MODEL FUNCTION

Generally, the structure of the relationship between the response and the independent variables is unknown. The first step in RSM is to find a suitable approximation to the true relationship. The most common forms are low-order polynomials (first or second-order).

The advantage is that the structure of the approximation is not assumed in advance, but is given as part of the solution, thus leading to a function structure of the best possible quality. In addition, the complexity of the function is not limited to a polynomial but can be generalised with the inclusion of any mathematical operator (e.g. trigonometric functions), depending on the engineering understanding of the problem. The regression coefficients included in the approximation model are called the tuning parameters and are estimated by minimizing the sum of squares of the errors.

$$G(\boldsymbol{a}) \;=\; \sum_{p=1}^{P}\left\{ w_p \left(F_p - \tilde{F}_p(\boldsymbol{a}) \right)^2 \right\} \;\; -$$

where wp is a weight coefficient that characterizes the relative contribution of the information of the original function at the point p, p=1,...,P.

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The construction of response surface models is an iterative process. Once an approximate model is obtained, the goodness-of-fit determines if the solution is satisfactory. If this is not the case, the approximation process is restarted and further experiments are made or the GP model is evolved with different parameters, as explained in Chapter 4.

To reduce the number of analyses in computer simulations, sensitivity data may be used in the model fitting, although this information is not always available at low cost. If in addition to the values of the original function $F_p = F(x_p)$ their first order derivatives at point p

$$F_{p,i} = \frac{\partial}{\partial x_i} F_p \quad (i=1,\ldots,N, \ p=1,\ldots,P) \quad \varepsilon$$

are known, the problem (3.2) is replaced by the following one

$$G(a) = \sum_{p=1}^{P} \left\{ w_p \left(\left(F_p - \tilde{F}_p(a) \right)^2 + \gamma \frac{\sum_{i=1}^{N} \left(F_{p,i} - \tilde{F}_p(a)_{,i} \right)^2}{\sum_{i=1}^{N} F_{p,i}^2} \right) \right\}$$.

where $\gamma > 0$ is the parameter characterizing a degree of inequality of the contribution of the response and the sensitivity data. In this thesis, γ is taken as 0.5, following recommendations by Toropov et al. (1993).Van Keulen et al. (2000) have presented a methodology for the construction of responses using both function values and derivatives on a weighted least-squares formulation. The authors conclude that the use of derivatives provides better accuracy and requires a reduced number of data.

4.3 DESIGN OF EXPERIMENT

An important aspect of RSM is the design of experiments, usually abbreviated as DoE. These strategies were originally developed for the model fitting of physical experiments, but can also be applied to numerical experiments. The objective of DoE is the selection of the points where the response should be evaluated.

Most of the criteria for optimal design of experiments are associated with the mathematical model of the process. Generally, these mathematical models are polynomials with an unknown structure, so the corresponding experiments are designed only for every particular problem. The choice of the design of experiments can have a large influence on the accuracy of the approximation and the cost

ofconstructing the response surface.In a traditional DoE, screening experiments are performed in the early stages of the process, when it is likely that many of the design variables initially considered have little or no effect on the response. The purpose is to identify the design variables that have large effects for further investigation. Genetic Programming has shown good screening properties, which suggests that both the selection of the relevant design variables and the identification of the model can be carried out at the same time.

4.3.1 FULL FACTORIAL DESIGN

To construct an approximation model that can capture interactions between N design variables, a full factorial approach may be necessary to investigate all possible combinations. A factorial experiment is an experimental strategy in which design variables are varied together, instead of one at a time.

The lower and upper bounds of each of N design variables in the optimization problem needs to be defined. The allowable range is then discretized at different levels. If each of the variables is defined at only the lower and upper bounds (two levels), the experimental design is called 2N full factorial. Similarly, if the midpoints are included, the design is called 3N full factorial and shown in Figure 4.2.
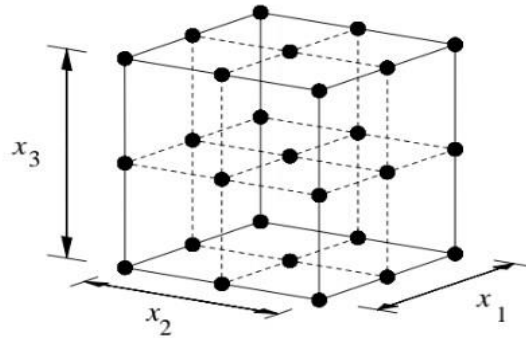

Figure 4.2 A 3ˇ3 full factorial design (27 points)

Factorial designs can be used for fitting second-order models. A second-order model can significantly improve the optimization process when a first-order model suffers lack of fit due to interaction between variables and surface curvature. A general second-order model is defined as

$$y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} a_{ii} x_i^2 + \sum_{i=1}^{n}\sum_{\substack{i=1 \\ i<j}}^{n} a_{ij} x_i x_j \qquad (3$$

where xi and xj are the design variables and a are the tuning parameters.

The construction of a quadratic response surface model in N variables requires the study at three levels so that the tuning parameters can be estimated. Therefore, at least (N+1) (N+2) / 2 function evaluations are necessary. Generally, for a large number of variables, the number of experiments grows exponentially (3N for a full factorial) and becomes impractical. A full factorial design typically is used for five or fewer variables.

If the number of design variables becomes large, a fraction of a full factorial design can be used at the cost of estimating only a few combinations between variables. This is called fractional factorial design and is usually used for screening important design variables. For a 3N factorial design, a fraction can be constructed, resulting in 3N-p points. For example, for p=1 in a 33 design, the result is a one-third fraction, often called 33-1 design, as shown in Figure 4.3 (Montgomery,1977).
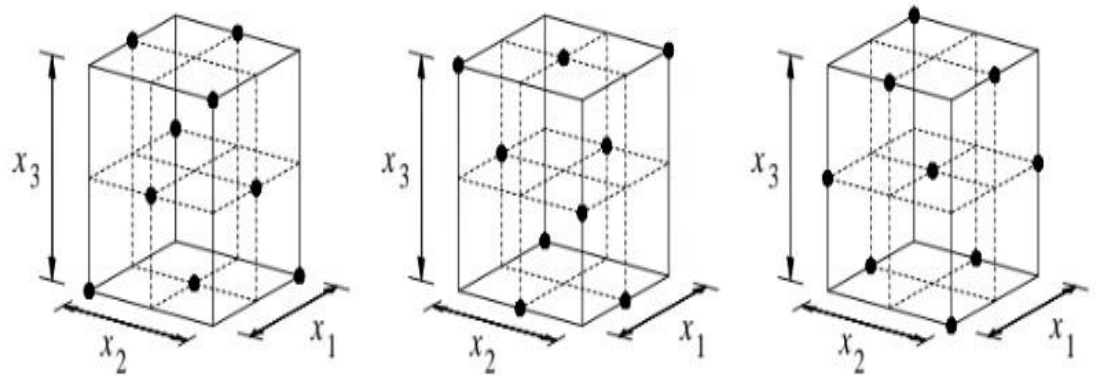

Figure 4.3 Three one-third fractions of the 3^3 design

4.3.2 CENTRAL COMPOSITE DESIGN

A second-order model can be constructed efficiently with central composite designs (CCD). CCD are first-order (2N) designs augmented by additional centre and axial points to allow estimation of the tuning parameters of a second-order model. Figure 4.4 shows a CCD for 3 design variables.
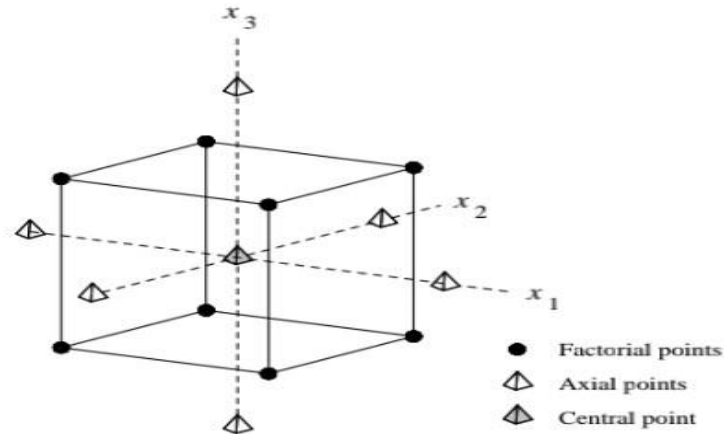
.

Figure 4.4 Central composite design for 3 design variables at 2 levels

In Figure 3.4, the design involves 2N factorial points, 2N axial points and 1 central point. CCD presents an alternative to 3N designs in the construction of second-order models because the number of experiments is reduced as compared to a full factorial design (15 in the case of CCD compared to 27 for a full-factorial design).

In the case of problems with a large number of designs variables, the experiments may be time-consuming even with the use of CCD.

4.3.3 TAGUCHI CONTRIBUTION TO EXPOERIMENTAL DESIGN

Taguchi's methods study the parameter space based on the fractional factorial arrays from DoE, called orthogonal arrays. Taguchi argues that it is not necessary to consider the interaction between two design variables explicitly, so he developed a system of tabulated designs which reduce the number of experiments as compared to a full factorial design. An advantage is the ability to handle discrete variables. A disadvantage is that Taguchi ignores parameter interactions.

4.3.4 LATIN HYPER CUBE DESIGN

Latin hypercube design can be viewed as an N-dimensional extension of the traditional Latin square design. On each level of every design variable only one point is placed. There are the same number of levels as runs and the levels are assigned randomly to runs.

This method ensures that every variable is represented, no matter if the response is dominated by only a few ones. Another advantage is that the number of points to be analyzed can be directly defined.

4.3.5 AUDZU –EGLAIS APPROACH

Audze and Eglais (1977) suggested a non-traditional criterion for elaboration of plans of experiments which, similar to the Latin hypercube design, is not dependent on the mathematical model of the problem under consideration. The input data for the elaboration of the plan only include the number of factors N (number of design variables) and the number of experiments K. The main principles in this approach are as follows:

1. The number of levels of factors (same for each factor) is equal to the number of experiments and for each level there is only one experiment. This is similar to the Latin hypercube design.

2. The points of experiments are distributed as uniformly as possible in the domain of variables. There is a physical analogy with the minimum of potential energy of repulsive forces for a set of points of unit mass, if the magnitude of these repulsive forces is inversely proportional to the distance squared between the points:

$$\sum_{p=1}^{P} \sum_{q=p+1}^{P} \frac{1}{L_{pq}^{2}} \rightarrow$$

where Lpq is the distance between the points having numbers p and q (p≠q).

The elaboration of the plans is time consuming, so each plan of experiment is elaborated only once and stored in a matrix characterized by the levels of factors for each of P experiments. For example, for a number of factors (design variables) N = 2 and P = 10, the matrix is

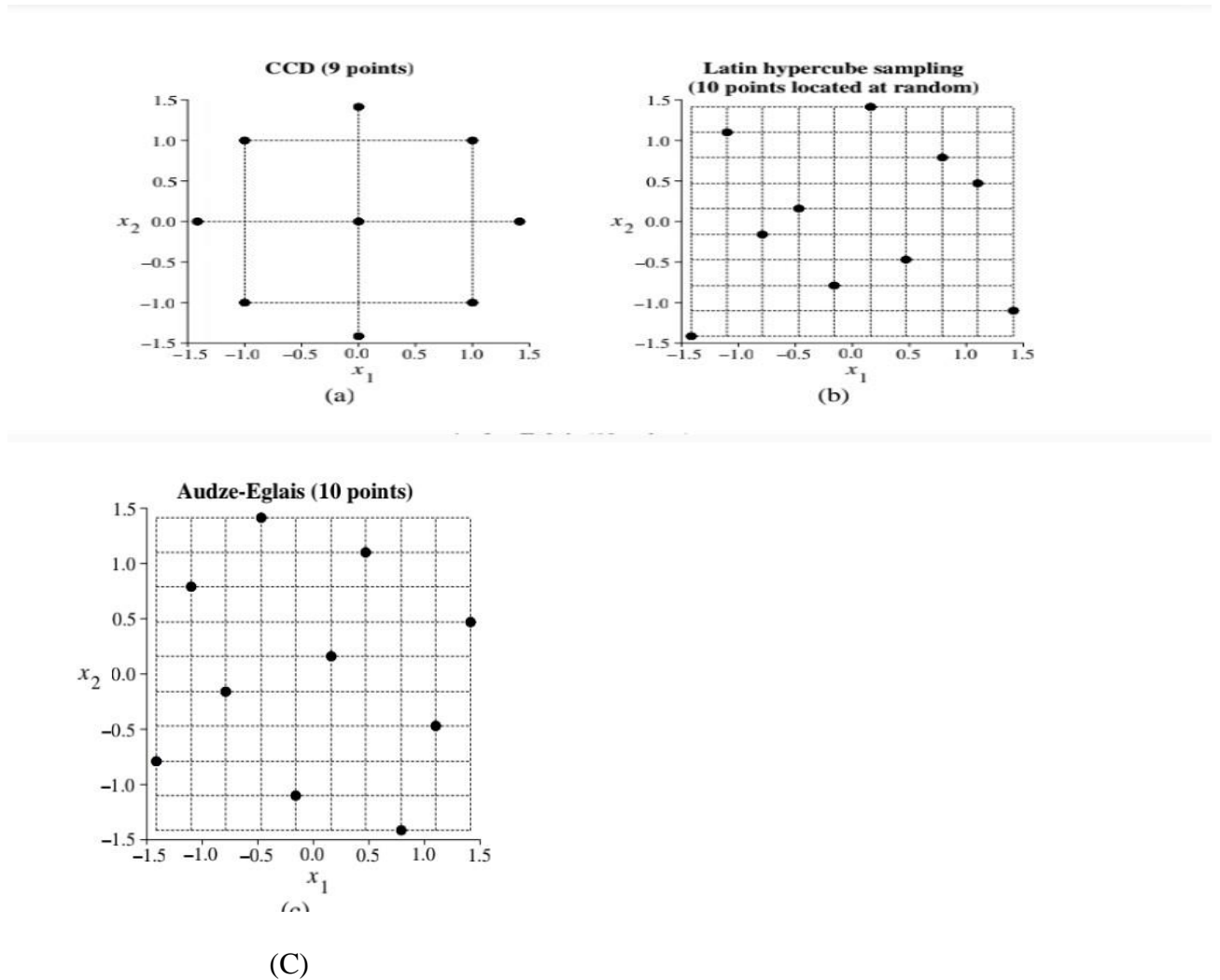$$\begin{vmatrix} 8 & 10 & 4 & 6 & 2 & 3 & 9 & 5 & 7 & 1 \\ 1 & 7 & 10 & 6 & 8 & 5 & 4 & 2 & 9 & 3 \end{vmatrix}$$

Figure 4.5 Comparison between CCD (a), Latin hypercube design (b) and AudzeEglais design (c)

4.3.6 VAN KEULENS APPROACH

In the course of an iterative optimization process modelled by approximations, new points must be generated in specified domains of the design variable space. A new scheme for the design of experiments (Van Keulen and Toropov, 1999) has been formulated with the following characteristics:

1. The scheme works efficiently even if only a single additional design point is generated to the existing plan. For a number of new design points, the algorithm is used several times.

2. The scheme remains effective if different types of functions are used within the same optimization task to approximate the objective function and the constraints.

The approach distributes points as homogeneously as possible in the sub domains of interest. This is done by the introduction of the following cost function:

$$Q = \sum_{p=1}^{P} \frac{n^2}{\| \bar{x}_p - \bar{d} \|} + \sum_{p=1}^{P} \sum_{i=1}^{n} \frac{1}{\left([\bar{x}_i]_p - \bar{d}_i \right)^2} + \sum_{i=1}^{n} \frac{1}{\left(2\,\bar{d}_i \right)^2} +$$
$$+ \sum_{i=1}^{n} \frac{1}{\left(2 - 2\bar{d}_i \right)^2} + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \frac{1}{\left(\bar{d}_i - \bar{d}_j \right)^2}$$

which is minimized with respect to the location of the new point d. Symbols denoted refer to coordinates which are normalized in the sub-domain of interest. The first term in the expression attempts to maximize the distance between points, and the second term promotes a homogeneous distribution along the coordinate axes. The third and fourth terms ensure that points do not belong to the boundary of the sub domain. The last term prevents points from aligning along the diagonal of the search sub-region when only a few points are available.

4.4 CONCLUSION

A review of different designs for fitting response surfaces has been given. A desirable design of experiments should provide a distribution of points throughout the region of interest, which means to provide as much information as possible on the problem. This "space-filling" property is a characteristic of three plans: Latin hypercube sampling, Audze-Eglais and van Keulen. All three plans are independent of the mathematical model of the approximation. However, Latin hypercube sampling distributes the points randomly in the space, while Audze-Eglais uses a distribution based on maximum separation between points.

It should be noted that if the model building is to be repeated within an iterative scheme (e.g. with mid-range approximations), van Keulen's plan would become an attractive alternative as it adds points to an existing plan. This thesis is primarily focused on building global approximations.

CHAPTER 5

RESULT AND CONCLUSION

 Parameter of Internal Combustion Engine

The performance of the internal combustion engine is specifically indicated by the value of the parameters of the engine. Some of these parameters can be described as follows

Power- The power is influenced by engine speed and torque that produced by the engine. In most cases, in the internal combustion engine, it is known two type of power that consist of shaft power and power indicator. As practice, it uses only the shaft power. The shaft power or effective power is the power that produced by an engine on the output shaft or it commonly known as brake horse power which is calculated by the equation:

$$\dot{W} = \frac{2\pi \cdot N \cdot \tau}{60000} \qquad \text{kW}$$

where N is engine speed (rpm) and τ is engine torque (Nm).

Specific Fuel Consumption- The specific fuel consumption is the amount of fuel that should consumed per unit of power which produced per hour of operation. Indirectly, the specific fuel consumption is an indication of the engine efficiency to generating power from fuel combustion. The value of specific fuel consumption can be defined as follows:

$$Sfc = \frac{\dot{m}_f}{\dot{W}} \cdot 3600000$$

where $\dot{m}_f$ is mass flow rate of fuel (kg/s).

Thermal Efficiency- The thermal efficiency of an internal combustion engine constituted the ratio between the output energy and the chemical energy of fuel, that can be stated as:

$$\eta_t = \frac{\dot{W}}{\dot{m}_f \cdot Q_{HV} \cdot \eta_c}$$

where Q_{HV} is calorivic value (kJ/kg) and η_c is combustion efficiency 0,97.

5.1 PERFORMANCE OF DIESEL ENGINE

5.1.1 POWER-

The experimental data in figure 5.1 shows that the maximum power occurs in 3.10 kW when the engine is using diesel oil at speed of 2800 rpm. The minimum engine power obtained 0.77 kW when engine using B20 at the speed of 1000 rpm.
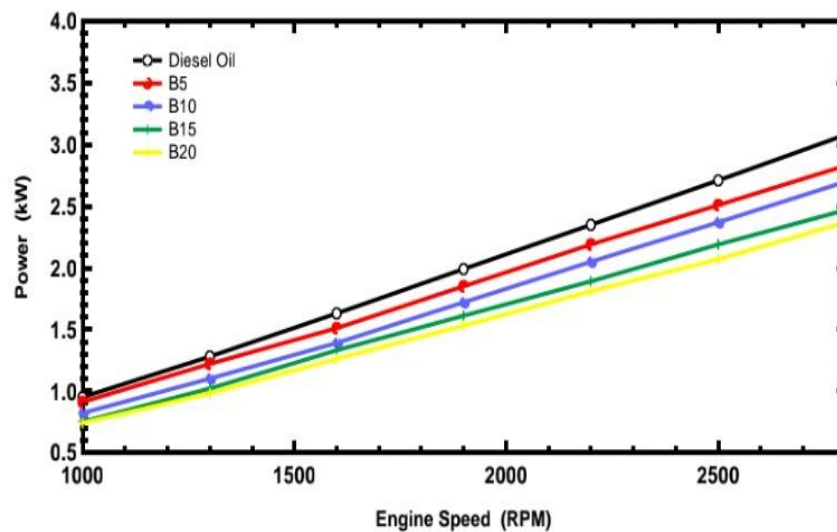

Figure 5.1 The engine power

The most influential of the power that generated by the engine shaft is torque. When the engine torque more greater, the engine power generated is also getting bigger and vice versa. This is due to the changing of engine power which is equally linier with engine torque. Another factor that allows the reduction in engine power is when the engine using B5, B10, B15 and B20 due to less precise injection timing settings.

5.1.2 SPCIFIC FUEL CONSUMPTION-

The experimental results in figure 4 shows that when the diesel engine using B20 at the speed of 1000 rpm, the maximum specific fuel consumption is obtained 443.26 g/kWh. The minimum value of specific fuel consumption when the engine using diesel oil at speed of 2800 rpm is obtained to 191.93 g/kWh. The average of specific fuel consumption during experiments is 286.38 g/kWh.
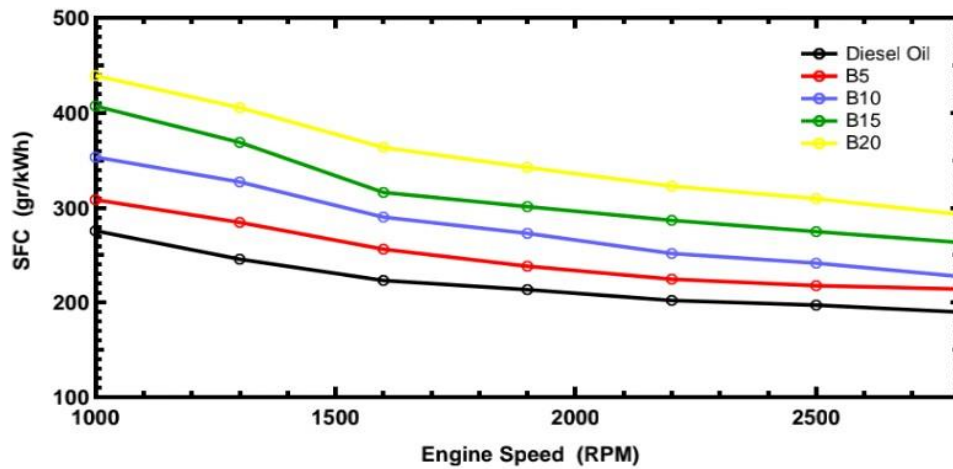
Figure 5.2. Specific fuel consumption

In general, the specific fuel consumption when the diesel engine using B5, B10, B15 and B20 increased. The calorific value of B5, B10, B15 and B20 were lower compared to the diesel oil because the presence of oxygen in biodiesel which result the air fuel ratio becomes a lean mixture. These conditions make the fuel becomes more needed than when using diesel oil.

5.1.3 THERMAL EFFICIENCY-

Figure 5.3 shows the value of maximum thermal efficiency 47.33% was reached by using diesel oil at the speed of 2800 rpm
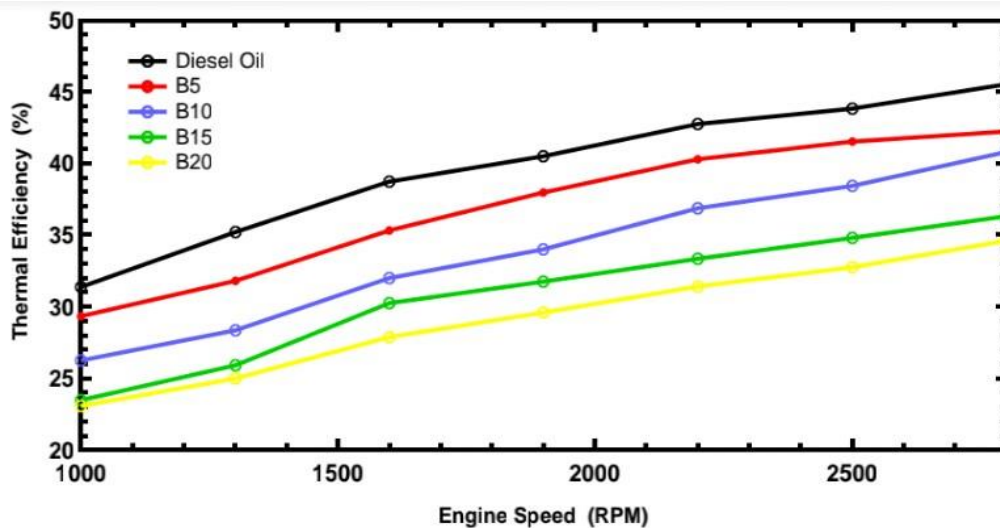

Figure 5.3. The thermal efficiency of engine

The value of minimum thermal efficiency is 22.41% by using B20 at speed of 1000 rpm. The average value of thermal efficiency resulting from the experiments conducted 33.18%. The decreasing of the thermal efficiency when the diesel engine is using blends fuel is about 9% - 35%. The average decreasing of the thermal efficiency occurs when the engine using blends fuel is 25.26%. As noted, that the thermal efficiency of the internal combustion engine are influenced by several parameters such as engine power, specific fuel consumption and the calorific value of the fuel that be used. The three parameters simultaneously affect the achievement of the engine thermal efficiency.

5.4 EMISSION MEASUREMENT

The emission factor of regulated matters in the exhaust is listed in below table. The biodiesel blends had lower PM, HC, and CO emissions when compared with those of ULSD.

Table 5.1 Mean emission factor of regulated matters from the HDDE.

Fuels	HC	CO	NO$_X$	PM
USLD	.89	2.07	6.82	.229
WCOB5	.805	1.86	6.87	.215
WCOB10	.71	1.84	6.90	.210
WCOB15	.65	1.83	6.91	.212
WCOB20	.59	1.72	6.94	.213

The above results indicate that WCOB, an oxygenated fuel, can increase combustion efficiency and reduce PM, HC, and CO emissions from HDDEs. The difference in reductions may be attributed to the different operation conditions and the products formed during frying, such as free fatty acids and some polymerized triglycerides, which affect the transesterification reaction and lead to various biodiesel properties. However, in previous research, the biodiesels produced slightly higher NO$_x$ emissions than diesel fuel at all tested engine operation conditions.

CHAPTER 6

FUTURE SCOPE

The experimental analysis and simulation model has proved soyabean oil fatty acid alkyl esters to be a suitable alternative for petroleum diesel. However, there are some difficulties in analysing the model to predict the performance of the engine. Therefore, the following are the recommendations for extending this work further.

- Investigations could be carried out to store biodiesel efficiently and use it after long time as diesel
- Efforts could be taken to perform experimental study to substitute pure biodiesel for petroleum diesel
- Implementation of artificial intelligent techniques to predict the performance of the engine with higher ratings and engines connected to grid
- In future there is much scope of biodiesel as alternative fuel.

REFRENCES

• K.A. Abed, A.K. El Morsi, " Effect of waste cooking oil biodiesel on performance and exhaust emission of a diesel engine". Egyptian journal of petroleum 27(2018) 985-989. 27 february 2018.

• Majid Mohadesi, Babak Aghel. "Production of biodiesel from waste cooking oil using homogeneous catalyst".Renewable energy, volume 136,june 2019

• G. uguz, A.E. Atabani, " Fuel stability of biodiesel from waste cooking oil". Biocatalysis and agricultural biotechnology,volume 21, september 2019.

• Peng geng , Hongjun moa, " Combustion characterstics and NOx emission of a waste cooking oil biodiesel blend in diesel engine". Applied thermal engineering volume 115, 25 march 2017.

• Nur syakirah Talha, Sarina Sulaiman,. "Overview of catalyst in biodiesel production" ,ARPN Journal of engineering and applied sciences,Vol. 11,No.1,January 2016

• L. Wei, C.S. Cheung, "Influence of waste cooking oil biodiesel on combustion, unregulated gaseous emission and particulate emission of a direct- injection diesel engine.". Energy , 24 march 2017

- Sajjad H, Masjuki H, Varman M, Kalam M, Arbab M and Imtenan S. 2014 *Comparative study of gas-to-liquid fuel, B5 diesel and their blends with respect to fuel properties, engine performance and exhaust emissions*. RSC Adv vol. 44 pp 452-459.

- Chih-Cheng Chou, Ying-Wei Lin, Chia-Jui Chiang and Yong-Yuan Ku 2014 *Experimental Analysis of a Turbo-Charged Common-Rail Diesel Engine Fueled with Biodiesel*. Energy Procedia. Vol 61 pp. 1167 - 1170.

- United States Environmental Protection Agency 2002 *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions.* EPA420-P-02-001.

- Mohd Hafizil Mat Yasina,Rizalman Mamata and Ahmad Fitri Yusop 2015 *Comparative study on biodiesel-methanol-diesel low proportion blends operating with a diesel engine*. Energy Procedia. Vol 75 pp. 10 - 16.

- Maman Herman, Muhammad Syakir, Dibyo Pranowo, Saefudin and Sumanto 2013 *Kemiri Sunan Tanaman Penghasil Minyak Nabati dan Konservasi Lahan*, ISBN : 978-602-1250-35- 2, IAARD Press.

- Gaurav dwivedi, siddharth jain "Diesel engine performance and emission analysis using biodiesel from various oil sources" J. Mater. Environ. Sci. 4 (4) (2013) 434-447.

- Yuvan chung lin, kuo hasing hsu, "Experimental investigation of the performance and emission of a heavy duty diesel engine fueled with soyabean oil biodiesel blend" Energy 36(2011) 241-258.

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