# Extraction of Biodiesel from Castor Oil and Study of Its Properties

by

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A Project submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering in the Department of Energy Science and Engineering
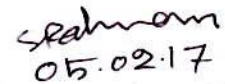
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# Declaration

This is to certify that the project work entitled "*Extraction of Biodiesel from Castor Oil and Study of Its Properties*" has been carried out by *Mohammad Siddiqur Rahman* in the *Department of Energy Science and Engineering*, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above project work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

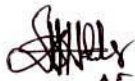Signature of Supervisor

Signature of Candidate

# DEDICATION

This project work is dedicated to my parents.

# Approval

This is to certify that the project work submitted by *Mohammad Siddiqur Rahman* entitled *"Extraction of Biodiesel from Castor Oil and Study of Its Properties"* has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of *Master of Engineering* in the Department of *Energy Science and Engineering*, Khulna University of Engineering & Technology, Khulna, Bangladesh in February' 2017.

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# Acknowledgements

# Abstract

Energy demand is increasing worldwide with expected fossil fuel shortages, alternative energy resources need to be explored. Moreover, the high fossil energy utilization with its unfavorable impact on environment and climate changes entitle for bio-fuels. In Bangladesh energy consumption is increasing at a rapid rate due to rapid industrialization, transportation and mechanization. Increasing pressure of population and increasing use of energy in agriculture, industrial, domestic and public sectors is an area of concern. At the same time, the need to meet energy demand has created huge capital requirements needed for setting up power plants, pipe-lines, ports, terminals, railway tracks to move fuel etc.

Biodiesel fuel can be defined as medium length ($C_{16}$ to $C_{18}$) chains of fatty acids, and is comprised mainly of mono-alkyl fatty acid esters. It is made through a chemical process called transesterification where by the glycerin is separated from the fat or vegetable oil. The process leaves behind two products: methyl esters (biodiesel) and glycerin.

In the present work the production of biodiesel from castor oil by transesterification of the raw oil with methanol in the presence of $H_2SO_4$ and NaOH as catalyst. Castor oil (*Ricinus Communis L.*) enclosed high value of fatty acid which makes transesterification process be converted into methyl esters (biodiesel) due to high solubility in methanol. Biodiesel produced from castor oil has been one of the most significant studies for current researcher. Also methyl esters are transformed from castor oil by etherification process. Various fuel properties of biodiesel produced from castor oil like density, viscosity, flash point, fire point, pour point, calorific value were characterized and compared with the properties of standard petro-diesel. It could be concluded that these oil from castor oil can be used as a viable alternative to the diesel fuel.

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# Nomenclature

| | |
|---|---|
| °C | Degree Celsius |
| ASTM | American Society for Testing Materials |
| FFA | Free Fatty Acid |
| B20 | 20% biodiesel and 80% diesel |
| B30 | 30% biodiesel and 70% diesel |
| B70 | 70% biodiesel and 30% diesel |
| B100 | 100% biodiesel |
| g/ml | Gram per mili Liter |
| $mm^2/s$ | mili meter square per second |
| MJ/kg | Mega Joule per kilogram |

# CHAPTER I

# INTRODUCTION

## 1.1 General

Energy is the basic need for economic development of any country. Renewable energy is now a burning issue in both developed and developing countries such as energy security, climate change and emission mitigation. Energy demand and environmental concerns have significantly constrained sustainable development. Biofuel in particular, as an energy source have attracted great attention in USA, European countries, China, Japan, and even in Bangladesh for significant advantages over diesel as biofuel consumption generates less environmental pollutants such as SOx and NOx and mitigates $CO_2$ emission. Bangladesh, however, has been detached from this issue till recent times. In Bangladesh energy consumption is increasing at a rapid rate due to rapid industrialization, transportation and mechanization. Increasing pressure of population and increasing use of energy in agriculture, industrial and the domestic and public sectors is an area of concern. At the same time, the need to meet energy demand has created huge capital requirements needed for setting up power plants, pipe-lines, ports, terminals, railway tracks to move fuel etc.

Nowadays, petroleum products derived from crude oil and natural gas are important world energy resources. These resources are limited and non-renewable. If these resources continue to be consumed at the current rate, their shortage can be expected. Moreover, the widespread use of petroleum based fuels causes environmental problems, especially the global warming and pollution. Consequently, there has been a considerable interest in the development of some alternative energy.

The Demand of fuel is increasing and conventional sources are diminishing with the passage of time, which creates a large difference between its demand and supply. The future generation needs alternatives or renewable sources of energy. Therefore, biodiesel has been proposed as an alternative to the normal diesel to overcome this problem to some extent. It is

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non-petroleum fuel derived from non-conventional resources that contain alkyl esters produced from the process of transesterification of triglycerides (TG) or the esterification of free fatty acids (FFA) with low molecular weight alcohols [1-2]. It is produced from vegetable oils, such as soya, castor, corn, etc. Technically, it is described as a vegetable oil or animal fat-based fuel which constitutes long-chain alkyl esters and reacting lipids with an alcohol [3]. It can be used as alternative fuel as well as an additive for petroleum based diesel fuel. After burning of biodiesel, it acts as clean fuel; it leads to a major reduction in many types of contaminants contributing to smog and global warming. It has been approved as non-contaminated fuel by the Environmental Protection Agency (EPA) and Clean Air Act of California Air Resources Board (CARB) [4].

Biodiesel has significantly lower emissions than petroleum-based diesel when it is burned, whether used in its pure form or blended with petroleum diesel. It does not contribute to a net rise in the level of carbon dioxide in the atmosphere and leads to minimize the intensity of greenhouse effect [5].

Biodiesel is the product one gets when organically derived oil such as vegetable oil or animal fat chemically reacts with an alcohol to produce a fatty acid alkyl ester. It has become an interesting alternative to be used in diesel engine, because it has similar properties to the traditional diesel fuel and may, thus, substitute conventional fuel with none or very minor engine modification. One of the attractive features of biodiesel is its biodegradability and being more environmental friendly than the fossil fuels, resulting in less environmental impact upon release on harmful emission to the environment [6]. Emissions such as total hydro carbons and CO are usually found significantly low with biodiesel as compared to petroleum diesel. This may be due to more complete combustion caused by the increased oxygen content in the flame coming from the biodiesel molecules. It is always recommended to produce biodiesel from used waste edibles oil or non-edibles oil such as jatropha, castor, pongamia pinnata, rubber seed and mango.

Castor oil plant (*Ricinus communis L.*) is a non-food, drought resistant, energy crop gaining attention for producing biofuel as biodiesel in developed as well as in developing countries. As an oil bearing biomass feedstock, it can ensure an alternative source of energy and reduce

the dependency on fossil fuel. This plant can grow anywhere including soil considered infertile for food production.

## 1.2 Biodiesel

Biodiesel is not vegetable oil. It is derived oil. It is intended to be used as a replacement for petroleum diesel fuel, or can be blended with petroleum diesel fuel in any proportion. It does not require modifications to a diesel engine to be used. It has reduced exhaust emissions compared to petroleum diesel fuel. It has lower toxicity compared to petroleum diesel fuel. It is safer to handle compared to petroleum diesel fuel. It quality is governed by ASTM D 6751 quality parameters.

Biodiesel fuel can be defined as medium length ($C_{16}$ to $C_{18}$) chains of fatty acids, and is comprised mainly of mono-alkyl fatty acid esters. Biodiesel fuel has the benefits of being non-toxic, biodegradable and essentially free of sulphur and carcinogenic ring components [7]. Considerable research has been done on vegetable oils as diesel fuel. That research includes palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil and tung oil [8].

Biodiesel can be produced from vegetable oil, animal oil/fats, tallow and waste cooking oil and from oil seed plants. It is made through a chemical process which converts oil and fats of natural origin into fatty acid methyl esters (FAME). The process used to convert these oil to biodiesel is called transesterification.

## 1.3 Advantages of using Biodiesel

Biodiesel is better for the environment because it is made from renewable resources and has lower emissions compared to petroleum diesel. It is less toxic than table salt and biodegrades as fast as sugar. Produced domestically with natural resources, its use decreases the dependency on imported fuel and contributes to our economy. Biodiesel is more lubricating than diesel fuel, it increases the engine life and it can be used to replace sulfur, a lubricating agent that, when burned, produces sulfur dioxide. It is safe to handle because it is biodegradable and non-toxic. According to the national bio-diesel board, "neat diesel is as biodegradable as sugar and less toxic than salt." It is safe to transport. It has a high flash point, or ignition temperature, of about 150°C compared to petroleum diesel fuel, which has a

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flash point of 52°C. It is the only alternative fuel that runs in any conventional, unmodified diesel engine. It can be used alone or mixed in any ratio with petroleum diesel fuel. The most common blend however is a mixture of 20% biodiesel with 80% petroleum diesel, or "B20". It is about 10% oxygen by weight and contains no sulfur. The lifecycle production and use of biodiesel produces approximately 80% less carbon dioxide emissions, and almost 100% less sulfur dioxide.

### 1.3.1 Easy to Use

One of the great advantages of biodiesel is that it can be used in existing engines, vehicles and infrastructure with practically no changes. Biodiesel can be pumped, stored and burned just like petroleum diesel fuel, and can be used pure, or in blends with petroleum diesel fuel in any proportion. Power and fuel economy using biodiesel is practically identical to petroleum diesel fuel, and year round operation can be achieved by blending with diesel fuel.

### 1.3.2 Emissions and Greenhouse Gas reduction

Biodiesel is the only alternative fuel to successfully complete the EPA's rigorous emissions and health effects study under the Clean Air Act. It provides significantly reduced emissions of carbon monoxide, particulate matter, unburned hydrocarbons, and sulfates compared to petroleum diesel fuel. Additionally, it reduces emissions of carcinogenic compounds by as much as 85% compared with petro-diesel. When blended with petroleum diesel fuel, these emission reductions are generally directly proportional to the amount of biodiesel in the blend [9].

### 1.3.3 A Clean Alternative Fuel for New and Old Engines

Diesel engine has a reputation of being "dirty" engine. However, with the advent of newer diesel engine equipped with exhaust gas recirculation (EGR), particulate filters, and catalytic converters, clean diesel technology provides incredible fuel efficiency with ultra low emissions levels. When coupled with the use of biodiesel, both new and old diesel engine can significantly reduce emissions, including particulate matter (black smoke).

### 1.3.4 A Closer Look at Emissions Reduction

Studies on biodiesel emissions have been conducted for almost 20 years. In that time biodiesel has undergone the most rigorous testing of any alternative fuel, having been the first and only fuel to be evaluated by the EPA under the Clean Air Act Section 211(b). This study examined the impact of hundreds of regulated and non-regulated exhaust emissions, as well as the potential health effects of these emissions. Some of these results are summarized below.

Average Exhaust Emissions are reduced for 100% Biodiesel Compared to Petroleum Diesel Fuel shown in Table 1.1 [9].

Table 1.1: Regulated and Non Regulated Exhaust Emissions reduced for B100

| Regulated Exhaust Emissions reduced for B100 | |
|---|---|
| Particulate Matter | 47% |
| Carbon Monoxide | 48% |
| Total Unburned Hydrocarbons | 67% |
| Nitrogen Oxides | 18% |
| Non Regulated Emissions reduced for B100 | |
| Sulfates | 100% |
| Polycyclic Aromatic Hydrocarbons (PAH) | |
| Nitrated Polycyclic Aromatic Hydrocarbons (nPAH) | 90% |
| Special Hydrocarbons Ozone Forming Potential | 50% |

### 1.3.5 Economic Development

Energy dollars stay in communities. Since biodiesel is a fuel which can be created from locally available resources, its production and use can provide a host of economic benefits for local communities. The community-based model of biodiesel production is particularly beneficial. In this model, locally available feed stocks are collected, converted to biodiesel, then distributed and used within the community. This model keeps energy dollars in the community instead of sending them to foreign oil producers and refineries outside the community.

### 1.3.6 Sustainable Farming and Value Added Agriculture

Biodiesel feedstock can come from a variety of agricultural crops. When these crops are grown in a sustainable manner, using good stewardship practices, there are long term benefits to farmers, farming communities and the land. Many crops which yield oil used for biodiesel production can be a beneficial rotation for other food crops, including soybeans when used in a traditional corn rotation, and canola when used in a wheat rotation. Using crops in rotation can improve soil health and reduce erosion. The overall impacts of growing energy crops are

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complex, with thousands of variables. However, the added value created for oilseed crops by the production of biodiesel is a tangible benefit for farming communities, and when coupled with sustainable farming practices can provide benefits to farming communities and the environment.

## 1.4 Scope of Present Investigation

Biodiesel is a promising diesel fuel substitute because it is a clean renewable fuel which can be used in any direct injection engine without the need to redesign the current technology. Biodiesel is derived from renewable and domestic feedstock and shows higher biodegradability than fossil fuels excellent lubricity and negligible sulfur content [10-11]. For biodiesel-diesel blends, comparable engine efficiency was showed. From an environmental point of view, in spite of higher emission level of NOx, the emission from biodiesel combustion contained lower amounts of $CO$, $CO_2$, HC and smoke [12].

Castor plant is a sustainable source of second generation biodiesel feedstock species and the overall supply can be increased with different propagation technologies. In addition, the plant can grow in drought as well as in flooding condition and the land use patterns in Bangladesh are suitable for its cultivation.

The peripheral benefits of this type of model are different for each case, but can include:
- Increased tax base from biodiesel production operations.
- Jobs created for feedstock farming and collection.
- Skilled jobs created for biodiesel production and distribution.
- Income for local feedstock producers and refiners.

## 1.5 Objectives of the Research Work

The main objective of the proposed project is the extraction of biodiesel from castor oil and study of its properties. The specific objectives of this project are-
1. Filtration of Castor oil, collected from local market.
2. To analyze the properties of Castor Oil.
3. Design and construction of a reactor for transesterification process.
4. Conversion of biodiesel from castor oil.
5. Separation of Biodiesel and glycerol produced from transesterification.
6. To analyze the properties of biodiesel produced by transesterification.
7. Comparison of the properties of biodiesel with that of conventional diesel fuel.

# CHAPTER II

## LITERATURE REVIEW

### 2.1 General

Biodiesel is a promising nontoxic and biodegradable renewable fuel comprised of mono-alkyl esters of long chain fatty acids, which are derived from vegetable oil or animal fat [13]. It is a viable alternative fuel for diesel engine due to its non toxicity, biodegradability and low emission. It is oxygenated and essentially free of sulfur making it a cleaner burning fuel than petroleum diesel which reduced emissions of sulfur, carbon monoxide, unburnt hydrocarbons and particulate matter. Traditionally, vegetable oil including canola, soybean, and corn are used as feedstock for biodiesel production. However, increasing concern of food shortage throughout the world due to usage of edible oil for biodiesel production that conflicts with human consumption has developed a contradictory situation of food vs fuel. Inedible oil meet the requirement for these considerations because they are inedible and can be grown in waste land with low fertilizer and pesticide inputs. Therefore, it is crucial to develop environmental friendly processes with low cost feedstock containing high net energy ratios. The high cost of vegetable oil, especially edible oil, is the main barrier for expansion of biodiesel applications. By using low cost feedstock is necessary for producing biodiesel's long term commercial viability. One way to reduce the cost of this fuel is to use less expensive feedstock including vegetable oil (castor oil) and waste cooking oil that are non-edible and require low harvesting cost [14].

An excellent review has described various vegetable oil feedstocks, which are used for producing biodiesel. These may be classified as edible vegetable oils, inedible vegetable oils and others. Edible oil include soybean, rapeseed, sunflower, palm, peanut, corn, camelina, canola, pumpkin while non-edible oil are jatropha, pongamia, sea mango, Palanga, tallow, Nile tilapia, cotton seed, castor seed and used cooking oil fall in the category of others[15]. Biodiesel produced from this edible oil is a suitable substitute for diesel fuel. In Bangladesh as well as in other countries, edible oil is not recommended to be used as raw material for

biodiesel. Its use is likely to increase the cost of edible oil, which is used by human beings. Therefore, it is desirable and preferred to use non-edible oil for this purpose.

The significant amount of research work has been done on non-edible oil, namely Jatropha curcas, Pongamia pinnata, sea mango, Palanga, tallow, Nile tilapia, etc. and used cooking oil [15]. Several excellent reviews have been published recently on biodiesel from vegetable oil. After critical assessment of published work, it has been observed that relatively less amount of research work has been done on the transesterification of castor oil, a non-edible vegetable oil [16-18].

## 2.2 History of Development of Biodiesel

Biodiesel was first developed in the 1890s by inventor Rudolph Diesel. After its development the diesel engine has become the engine of choice for power, reliability, and high fuel economy, worldwide. Early experimenters on vegetable oil fuels included the French government and Dr. Diesel himself, who envisioned that pure vegetable oils could power early diesel engines for agriculture in remote areas of the world, where petroleum was not available at the time. Modern biodiesel fuel, which is made by converting vegetable oils into compounds called fatty acid methyl esters, has its roots in research conducted in the 1930s in Belgium, but today's biodiesel industry was not established in Europe until the late 1980s.Dr. Diesel became famous for his innovative engine which could use a variety of fuels.

### 2.2.1 Early Work

The early diesel engines had complex injection systems and were designed to run on many different fuels, from kerosene to coal dust. It was only a matter of time before someone recognized that, because of their high energy content, vegetable oil would make excellent fuel. The first public demonstration of vegetable oil based diesel fuel was at the 1900 World's Fair, when the French government commissioned the Otto Company to build a diesel engine to run on peanut oil. The French government was interested in vegetable oil as a domestic fuel for their African colonies. Rudolph Diesel later did extensive work on vegetable oil fuels and became a leading proponent of such a concept, believing that farmers could benefit from providing their own fuel. However, it would take almost a century before such an idea became a widespread reality. Shortly after Dr. Diesel's death in 1913 petroleum became widely

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available in a variety of forms, including the class of fuel we know today as "diesel fuel". With petroleum being available and cheap, the diesel engine design was changed to match the properties of petroleum diesel fuel. The result was an engine which was fuel efficient and very powerful. For the next 80 years diesel engines would become the industry standard where power, economy and reliability are required.

### 2.2.2 Modern Engine, Modern Fuel

Due to the widespread availability and low cost of petroleum diesel fuel, vegetable oil-based fuels gained little attention, except in times of high oil prices and shortages. World War II and the oil crises of the 1970's saw brief interest in using vegetable oils to fuel diesel engine. Unfortunately, the newer diesel engine design could not run on traditional vegetable oil, due to the much higher viscosity of vegetable oil compared to petroleum diesel fuel. A way was needed to lower the viscosity of vegetable oils to a point where they could be burned properly in the diesel engine. Many methods have been proposed to perform this task, including pyrolysis, blending with solvents, and even emulsifying the fuel with water or alcohols, none of which have provided a suitable solution. It was a Belgian inventor in 1937 who first proposed using transesterification to convert vegetable oil into fatty acid alkyl esters and use them as a diesel fuel replacement. The process of transesterification converts vegetable oil into three smaller molecules which are much less viscous and easy to burn in a diesel engine. The transesterification reaction is the basis for the production of modern biodiesel, which is the trade name for fatty acid methyl esters. In the early 1980s concerns over the environment, energy security, and agricultural over production once again brought the use of vegetable oils to the forefront, this time with transesterification as the preferred method of producing such fuel replacements.

### 2.2.3 Biodiesel Goes Worldwide

Pioneering work in Europe and South Africa by researchers such as Martin Mittelbach furthered development of the biodiesel fuel industry in the early 1990s, with the U.S. industry coming on more slowly, due to lower prices for petroleum diesel. Pacific Biodiesel became one of the first biodiesel plants in the United States in 1996, establishing a biodiesel production operation to recycle used cooking oil into biodiesel on the island Maui in Hawaii.

The biodiesel industry became a household name in the U.S. after the terrorist attacks of 9/11/2001 resulted in historically high oil prices and an increased awareness of energy security. As of 2005, worldwide biodiesel production had reached 1.1 billion gallons, with most fuel being produced in the European Union, although biodiesel projects worldwide have been on the rise due to rising crude oil prices and concerns over global warming.

## 2.2.4 The Future of Biodiesel Fuel

Due to its clean emissions profile, ease of use, and many other benefits, biodiesel is quickly becoming one of the fastest growing alternative fuels in the world. With minimal subsidy biodiesel is cost competitive with petroleum diesel, and millions of users have found and enjoyed the benefits of the fuel. The future of biodiesel lies in the world's ability to produce renewable feedstock such as vegetable oils and fats to keep the cost of biodiesel competitive with petroleum, without supplanting land necessary for food production, or destroying natural ecosystems in the process. Creating biodiesel in a sustainable manner will allow this clean, renewable, and cost effective fuel to help ease the world through increasing shortages of petroleum, while providing economic and environmental benefits well into the 21st century.

## 2.3.1 Properties of Biodiesel

The transesterification process of castor oil is carried out with a basic catalyst and a single reaction step is required because of its favourable acidity level. Properties of biodiesel were tested according to ASTM D 6751 standard. The Properties of biodiesel produced from Castor oil are shown in Table 2.1.

Table 2.1: Properties of biodiesel produced from Castor oil [19].

| Properties | Units | B10 | B20 | B100 |
|---|---|---|---|---|
| Density | kg/m³ | 864.3 | 870.3 | 926.8 |
| Kinematic viscosity | mm²/s | 4.54 | 4.97 | 15.98 |
| Flash point | °C | 85.3 | 88.7 | 190.7 |
| Heating value | KJ/kg | 44427.6 | 44780.4 | 37900.8 |
| Copper strip corrosion | 1 a | 1 a | 1 a | 1 b |
| Carbon residue | mass% | 0.009 | 0.007 | 0.037 |
| Cloud point | °C | -5 | -7 | -23 |
| Pour point | °C | -26 | -30 | - 45 |

Castor oil properties indicate a very low pour and cloud points which make this bio-fuel a good alternative in winter conditions. Also, mixtures of 20 (B20) and 10 (B10) percent biodiesel-petroleum diesel showed good flow properties. It indicates that castor oil biodiesel also could be used as petroleum diesel additive improving both environmental and flow behaviour of the mineral fuel.

The properties of biodiesel were analyzed according to ASTM Standards presented in Table 2.2. Biodiesel was produced from castor oil using KOH or $H_2SO_4$ as catalyst in transesterification process. About 25 ml of oil was kept in three necked round bottom flask and heated to $65^0C$. Then, calculated amount of methanol and catalyst (KOH or H2SO4) were added with stirring system. The experiment prolonged for three hour and then the sample was monitored by running TLC to conform the completion of reaction. After cooling, two layers were separated by separator funnel. The upper layer was methyl ester (biodiesel) while the lower layer was glycerol. The obtained methyl ester was purified by successive rinse with 2.5% (w/w) sulphuric acid and distilled water. The properties of biodiesel are shown in Table 2.2.

Table 2.2: Properties of biodiesel [20].

| SN. | Properties | Biodiesel | Mineral Diesel | ASTM Std. |
|-----|-----------|-----------|----------------|-----------|
| 1 | Methyl Ester Content % | 88 | - | 97 |
| 2 | Density (Kg/m$^3$) at $15^0$C | 900 | 850 | 860-890 |
| 3 | Specific gravity | 0.9 | 0.85 | 0.86-0.89 |
| 4 | Viscosity (Cst) @$40^0$C | 20.62 | 3.2 | 1.9-6.0 |
| 5 | Moisture content % | 0.37 | - | 0.05 |

Methyl ester content at 6:1 ratio was 88% while for 9:1 ratio it was 92% which are near to ASTM limits. The density and specific gravity were key properties of fuel which directly affect the engine performance. The denser fuel has greater mass which influences in the engine output. The density and specific gravity of the biodiesel found to be within the limits. Viscosity is another parameter of the fuel which depends on the flow of its liquid. Higher viscosity is a major problem of biodiesel in diesel engines. The high value of viscosity of fuel

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causes depositions on engine which effect on its function. Though the viscosity of oil has been decreased up to 93% after conversion to biodiesel but this value is still high as compared to reported value. Thus, the biodiesel cannot be directly used in diesel engine. To minimize the viscosity of fuel, it can be used by blending with other methyl ester or mineral diesel up to 10 to 20%.

## 2.3.2  Properties of furnace oil

Furnace oil is a dark viscous residual product used as a fuel in different types of combustion equipment. It conforms to ISO: 1593-1982 for fuel oils. It is a residual fuel oil which is obtained by blending residual products from various refining processes with suitable diluents usually middle distillates to obtain the required fuel oil grades. The fuel oil grades are similar in nature and are being marketed under different specifications in various countries.

Furnace oil is used mainly in different furnaces of the steel plant, in power plant boilers for raising steam and for injection in the blast furnace. It is also sometimes used in air pre-heaters. Furnace oil is having flash point above $66^0C$. Since this is a residual fuel, there has to be gradual filtration system to prevent the choking of filter and fuel nozzles. Due to its viscous nature, it is normally to be heated to improve its flow ability and to a proper temperature for proper atomization. Usually for furnace oil, gear pumps are preferred to avoid cavitations problems. Typically the calorific value of the furnace oil is 10,500 kcal per kg.

For direct burning, furnace oil is viscous as well as not suitable for complete combustion. It is pre-heated to $55^0$ C onwards, depending upon application. The flow increases with temperature and it improves the combustion also. A water based scrubber is used in the exhaust chimney of furnace, which arrests considerable amount of carbon soot and improves the emissions. Furnace oil is a complex mixture of hydrocarbons. Its CAS number is 68476-33.5 and UN number is 1223. It has a colour ranging from brown to black with a diesel like smell. It is a flammable liquid. Its boiling point ranges from 185 deg C to 500 deg C. Its vapour density is 3.0 to 5.0 (air=1). It is insoluble in water and is also lighter than water. It is a neutral liquid (neither acidic nor basic).

Typical properties of furnace oil are shown in Table 2.3.

Table 2.3: Typical properties of furnace oil.

| Sl. No. | Property | Value |
|---------|----------|-------|
| 1 | Inorganic acidity | Nil |
| 2 | Ashes, % wt., max. | 0.1 |
| 3 | Gross calorific value, kcal/ kg | 10350 |
| 4 | Net calorific value, kcal/ kg | 9600 |
| 5 | Density at 15 deg C | 0.96 |
| 6 | Flash point deg C , min. | 66 |
| 7 | Kinematic viscosity, cst at 50 deg C | 125-180 |
| 8 | Sediment, % wt., max. | 0.25 |
| 9 | Sulphur, total % wt., max. | 4 |
| 10 | Water content, % v/v, max. | 1 |
| 11 | Pour point, deg C | + 27 |
| 12 | Cleanliness, ASTM D 4740 | No. 1 |
| 13 | Micro carbon residue (MCR), % mass | 16 |
| 14 | Asphaltenes, % mass | 9 |

# CHAPTER III

# THEORETICAL ASPECTS

## 3.1 Technical Definition for Biodiesel (ASTM D 6751)

Biodiesel is comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100 and meeting the requirements of ASTM D6751.

Biodiesel blend is a blend of biodiesel fuel meeting ASTM D6751 with petroleum-based diesel fuel, designated BXX, where XX represents the volumetric percentage of biodiesel fuel in the blend. It can be used 100% (B100) or in blends with petroleum diesel fuel. Blends are indicated by B20, which correspond to the percentage of biodiesel in the blended fuel. For example, a 20% blend of biodiesel with 80% diesel fuel is called B20.

## 3.2 Problem Statement

Traditionally, vegetable oil including canola, soybean and corn are used as feedstock for biodiesel production. However, increasing concerns of food shortage throughout the world due to usage of edible oil for biodiesel production that conflict with human consumption has developed a contradictory situation of food vs fuel. In this study, castor oil has been chosen as feedstock. Castor oil is non-edible oil and low-cost feedstock. High free fatty acids (FFAs) feedstock reacts with the catalyst and easily forms soaps. Conventional operation for production of biodiesel usually takes place in two steps. The first step is acid esterification where the free fatty acids (FFAs) content of the oil reduces to less than 2%. The second step is alkali transesterification where the products of first step are converting to monoesters and glycerol. This study is combining the two steps transesterification process (acid esterification followed by alkali transesterification) to single step of transesterification to produce biodiesel from high free fatty acids (FFAs) feedstock. Finding a suitable catalyst that is active, selective and stable under the high FFA content is the major challenge. The use of homogenous base catalysts for transesterification is problematic because the alkali can produce large amounts of

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unwanted soap by product, which creates serious problems of product separation and ultimately decreases substantially the yield. Heterogeneous catalysts are easily removed from the reaction mixture, making the purification step easier.

## 3.3 High Free Fatty Acid Systems

High free fatty acid feedstock will react with the catalyst and form soaps if they are fed to a base catalyzed system. The maximum amount of free fatty acids acceptable in a base catalyzed system is less than 2 percent, and preferably less than 1 percent [21]. Some approaches to using high free fatty acid feedstock use this concept to "refine" the free fatty acids out of the feed for disposal or separate treatment in an acid esterification unit. The caustic is added to the feedstock and the resulting soaps are stripped out using a centrifuge. This is called caustic stripping. Some triglycerides are lost with the soaps during caustic stripping. The soap mixture can be acidulated to recover the fatty acids and lost oil in a separate reaction tank. The refined oil is dried and sent to the transesterification unit for further processing. Rather than waste the free fatty acids removed in this manner, they can be transformed into methyl esters using an acid esterification process. As described earlier, acid catalyzed processes can be used for the direct esterification of high free fatty acids (FFAs) feedstock. Less expensive feedstock, such as tallow or yellow grease, are characteristically high in free fatty acids. The standard for tallow and yellow grease is ≤ 15 percent FFA. Some lots may exceed this standard. Direct acid esterification of a high free fatty acid feed requires water removal during the reaction, or the reaction will be quenched prematurely. Also, a high alcohol to FFA ratio required, usually between 20:1 and 40:1. Direct esterification may also require rather large amounts of the acid catalyst depending on the process used. The esterification reaction of FFAs with methanol produces byproduct water that must be removed, but the resulting mixture of esters and triglyceride, can be used directly in a conventional base catalyzed system. The water can be removed by vaporization, settling, or centrifugation as a methanol-water mixture. Counter-current continuous-flow systems will wash out the water with the exiting stream of acidic methanol.

These free fatty acids react with the alkaline catalyst to produce soaps, which inhibit the separation of the product from glycerin and wash water. In addition, soap increases the viscosity of the reactants and results in the lower yield of methyl ester [22].

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A minimal content of water and free fatty acids in oil or fat is important for obtaining optimal results in the transesterification process. The existing water in oil promotes the decomposition of esters in glycerol and fatty acids, which, combined with the fatty acids already free. It is saponified with the basic catalyst (soap formation) thus decreasing the efficiency of the transesterification. The importance of using dry oil and free fatty acid content is less than 0.5% by weight [23]. A basic catalyst is used in the transesterification of triglycerides with a low content of FFA. However, if the water and free fatty acid contents are high, either an acid catalyst must be used or two transesterification must be done, one with an acid catalyst and another with a basic one.

Base catalyzed transesterification reaction is widely used for biodiesel production from vegetable oil due to its faster kinetics than that of acid catalyzed process. But if FFA content in the oil is more than 2%, the base catalyzed process is not feasible. The main problem for the non-edible oil sources is its high FFA content which limits the use of single step transesterification reaction. To overcome this problem, two-step procedures were used to prepare biodiesel from different oils, which have high content of free fatty acids [24-25].
In these works the first step is the acid catalyzed esterification, which reduces the FFA content of the oil and minimizes the soap formation in the second step (base catalyzed transesterification).

### 3.3.1 Acid Catalysis

This technique uses a strong acid such as sulfuric acid to catalyze the esterification of the FFAs and the transesterification of the triglycerides. The reaction does not produce soaps because no alkali metals are present. The esterification reaction of the FFAs to alcohol esters is relatively fast, proceeding substantially to completion in one hour at 60°C. However, the transesterification of the triglycerides is very slow, taking several days to complete. Heating to 130°C can greatly accelerate the reaction but reaction times will still be 30-45 minutes. Another problem with acid catalysis is that the water production from the following reaction

FFA + methanol → methyl ester + water
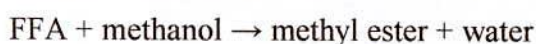
stay in the reaction mixture and ultimately stops the reaction, usually well before reaching completion.

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### 3.3.2 Acid catalysis followed by alkali catalysis

This approach solves the reaction rate problem by using each technique to accomplish the process for which it is best suited. Since acid catalysis is relatively fast for converting the FFAs to methyl esters, it is used as a pretreatment for the high FFAs feedstock. Then, when the FFAs level has been reduced to 0.5%, or lower, an alkali catalyst is added to convert the triglycerides to methyl esters. This process can convert high free fatty acid feedstock quickly and effectively. Water formation is still a problem during the pretreatment phase. One approach is to simply add so much excess methanol during the pretreatment that the water produced is diluted to the level where it does not limit the reaction. Molar ratios of alcohol to FFAs are high as 40:1 may be needed. The disadvantage of this approach is that more energy is required to recover the excess methanol. Another approach would be to let the acid-catalyzed esterification proceed as far as it will go until it is stopped by water formation. Then, boil off the alcohol and water. If the FFAs level is still too high, then additional methanol and, if necessary, acid catalyst can be added to continue the reaction. This process can be continued for multiple steps and will potentially use fewer methanols than the previous approach. Again, the disadvantage is the large amount of energy required by the distillation process. A less energy intensive approach is to let the acid-catalyzed reaction mixture settle. After a few hours, a methanol-water mixture will rise to the top and can be removed. Then, additional methanol and acid can be added to continue the reaction.

### 3.3.3 Catalyst Selection

The transesterification reaction can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base or enzymatic) catalysts. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts, but it is considerably more costly to separate homogeneous catalyst from the reaction mixture. Heterogeneous catalyst has many advantages such as being noncorrosive, being environmentally and presenting fewer disposal problems. These catalysts are also much easier to separate from liquid products, and they can be designated to give a higher activity and selectivity and to have longer catalyst lifetimes. Many types of heterogeneous catalysts, such as alkaline earth metal compounds supported on alumina or zeolite, can catalyze many types of chemical reactions. In transesterification of

vegetable oils to biodiesel, most supported alkali catalysts and anion exchange resins exhibit a short catalyst lifetime because the active ingredients are easily corroded by methanol [26].

The most commonly used technology for fats and oil transesterification is based on the use of batch reactor, in which a basic homogeneous catalyst is used. The use of homogeneous catalysts requires extensive conditioning and purification step for the reaction products to separate the catalysts. In contrast, heterogeneous catalysts are easily removed from the reaction mixture, making the purification step easier. Biodiesel production costs could certainly be reduced by using a heterogeneous catalyst for transesterification reaction instead of a homogeneous catalyst. This heterogeneous process provides higher quality esters and glycerol, which are more easily separated and further expensive refining operations are not needed [26-27]. Heterogeneous solid base catalysts, able to catalyze the transesterification of alkyl esters could solve these problems, they can be easily separated from the reaction mixture without the use of solvent, and they are easily regenerated and have a less corrosive character, leading to safer ,cheaper and more environment friendly operations[27].

In my research heterogeneous catalysts are used. Sulfuric acid ($H_2SO_4$) are used as acid catalyst and Solid Sodium Hydroxide (NaOH) are used as base catalyst.

### 3.4 Production of Biodiesel

Biodiesel is made through a chemical process called transesterification where by the glycerin is separated from the fat or vegetable oil. The process leaves behind two products -- methyl esters (the chemical name for biodiesel) and glycerin (a valuable byproduct usually sold to be used in soaps and other products).

### 3.4.1 Castor Oil as Feedstock

A variety of oils both edible and non-edible oils can be used to produce biodiesel but most are derived from edible oils such as sunflower, soybean, and palm oil. Since the prices of edible vegetable oils are high, the less expensive raw materials containing free fatty acids, such as non-edible crude oils, waste food oils, animal fats and byproducts of the refining vegetable oils, are preferred.

Castor seed is the source of castor oil, which has a wide variety of uses. The seeds contain between 40% to 60% oil. A Photographic view of Castor seeds is shown in figure 3.1.

Figure 3.1: Photographic view of Castor seeds

The extraction of castor oil is about 35 to 55% of the weight of the castor seeds. Castor oil, like currently less expensive vegetable oils, can be used as feedstock in the production of biodiesel. This oil is highly viscous, its coloration ranges from a pale yellow to colorless and it has a soft and faint odor and a highly unpleasant taste. Average composition of fatty acid chains in castor oil are shown in Table 3.2.

Table 3.1: Average composition of fatty acid chains in castor oil [28].

| Fatty acid name | Average Percentage (%) |
|---|---|
| Ricinoleic acid | 90% |
| Oleic acid | 4% |
| Linoleic acid | 3% |
| α-Linolenic acid | 0.75% |
| Stearic acid | 0.75% |
| Palmitic acid | 0.75% |
| Dihydroxystearic acid | 0.4% |
| Others | 0.35% |

This vegetable oil is comprised almost entirely (90% wt) of triglycerides of ricinoleic acid in which the presence of hydroxyl group at $C_{12}$ imparts several unique chemical and physical properties. Thus, castor oil and its derivatives are completely soluble in alcohols at room temperature [29- 30].

It has been thought to be an alternative source of biodiesel because it's unique chemical and physical properties. Typical of vegetable oils and most fats, castor oil is a triglyceride of various fatty acids. Its uniqueness stems from the very high (87-90% wt) content of ricinoleic acid, $C_{18}H_{34}O_3$, structurally $cis_{12}$ hydroxyoctaeca-$_9$-enoic acid, $CH_3(CH_2)sCH(OH)$ $CH_2CH=CH (CH_2)_7COOH$, an eighteen-carbon hydroxylated fatty acid having one double bond. This oil, sometimes described as a triglyceride of ricinoleic acid, is one of the few commercially available glycerides that contain hydroxyl functionality in such a high percentage of one fatty acid [31]. It has a good shelf life and it does not turn rancid unless subjected to excessive heat. The presence of ricinoleic acid, which is a complex fatty acid that contains both a double bond and a hydroxyl group, can impart increased lubricity to the castor oil and its derivatives as compared to other vegetable oils and makes of it a prime candidate as an additive for diesel fuel [32].

Castor oil is the only significant oil composed mainly of the ricinoleic acid of a hydroxylated fatty acid. Ricinoleic acid cannot be distilled unless special precautions are taken via derivative formation to protect the hydroxyl group. It is distinguished from other triglycerides by its high specific gravity, viscosity and hydroxyl value. Another unique feature is alcohol solubility, one volume of castor oil dissolves on two volumes of 95% ethyl alcohol at room temperature, and the oil is miscible in all proportions with absolute ethyl alcohol [31].

The sulfur content of commercial diesel fuel causes a decrease in its lubricity, causing possible damage to the engine and fuel injection systems. Biodiesel can be used as an additive in diesel fuel increasing lubricity. Castor oil has shown a better performance as an additive with more effective lubricity than oils that do not contain any hydroxylated fatty acids. The hypothesis was that the hydroxylated fatty acids of ricinoleic acid in castor oil which represent approximately 90% of oil composition give it better performance as a lubricity enhancer that other common vegetable oil esters. Besides the use as an additive in diesel fuel, castor oil is highly valuable for industrial purposes due to this chemical composition. However, depending

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on the reaction conditions, the products obtained by transesterification of castor oil do not form two liquid phases. Glycerol showed low solubility in the biodiesel phase. The solubility was considered temperature insensible [33]. Castor oil is a nontraditional raw material for production of biodiesel. It is inedible, inexpensive and environmental friendly.

This oil was collected from Local Market of Jamalpur due to availability. It was filtered by filter paper. This oil was used as raw materials of biodiesel.

### 3.4.2 Properties of Castor Oil

The properties of the raw castor oil were measured by standard method and presented in Table 3.3.

Table 3.2: Properties of Raw Castor Oil

| Properties of Raw Castor Oil | Value |
| --- | --- |
| Density (g/ml) @ 15°C | 0.953 |
| Density ( g/ml) @ 30°C | 0.944 |
| Viscosity (mm$^2$/s) @ 40°C | 154.678 |
| Pour point (°C) | -11 |
| Flash point (°C) | 230 |
| Molecular Weight (g/mol) * | 928.30 |
| Color | Pale yellow |
| Calorific Value (MJ/kg) | 36.319 |

*Determination of Castor Oil Molecular Weight by Vapour Pressure Osmometry Technique [34].

### 3.4.3 Transesterification Process

Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow, waste oil and castor oil. There are three basic routes to biodiesel production from oil and fats.

1. Base catalyzed transesterification of the oil.
2. Direct acid catalyzed transesterification of the oil.
3. Conversion of the oil to its fatty acids and then to biodiesel.

The Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerin molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerin. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalyzed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production; either base can be used for the methyl ester. A common product of the transesterification process is methyl ester produced from raw castor oil reacted with methanol.

A successful transesterification reaction is signified by the separation of the methyl ester and glycerol layers after the reaction time. The heavier, co-product, glycerol settles out and may be sold as it is or it may be purified for use in other industries, e.g. the pharmaceutical, cosmetics etc.

Five distinct stages will be involved,
1. Preparation of feedstock.
 2. Adding of alkaline alcohol to feedstock and stirring the mixture.
3. Heating of oil.
4. Settling of separation of glycerol.
5. Washing of ethyl ester with water.


The biodiesel can be obtained by transesterification of castor oil using either ethanol or methanol as the Transesterification agent. The extraction of biodiesel from castor oil, in the presence of the catalysts faster with methanol as the transesterification agent compared with ethanol. The maximum yield of esters depends on the reaction time and that is 2 hour with methanol or of 5 hours with ethanol. However, while similar yields of fatty acid esters may be obtained following ethanolysis or methanolysis, the reaction times required to attain them are very different, with methanolysis being much more rapid [35]. The transesterification of castor oil via ethanolysis or methanolysis can be improved through the development of more

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efficient catalytic systems and processes, to maintain kinetic control of the reaction, and by optimization of purification procedures.

### 3.4.4 Transesterification Reaction

Biodiesel is monoalkyl esters of long chain fatty acids derived from vegetable oils or animals' fats. It is produced through a chemically reversible reaction called transesterification or alcoholysis which has been widely used to reduce the high viscosity of triglyceride [29].

The transesterification reaction can be expresses by the following general equation.

Triglyceride + 3 ROH $\longrightarrow$ 3 R'COOR + Glycerol

The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

The reaction is carried out in the presence of catalyst [29]. The overall reaction of triglyceride transesterification to produce biodiesel is shown below.

$$
\begin{array}{c}
\quad\quad O \\
\quad\quad || \\
CH_2O\text{-}C\text{-}R_1 \\
|\quad\quad O \\
|\quad\quad || \\
CH\text{-}O\text{-}C\text{-}R_2 \;+\; 3CH_3\,OH \\
|\quad\quad O \\
|\quad\quad || \\
CH_2\text{-}O\text{-}C\text{-}R_3
\end{array}
\xrightarrow[\longleftarrow]{\text{Catalyst}}
\begin{array}{c}
CH_2\text{-}OH \\
| \\
CH\text{-}OH \\
| \\
CH_2\text{-}OH
\end{array}
\quad
\begin{array}{c}
CH_3COOR_1 \\
\\
+\; CH_3COOR_2 \\
\\
CH_3COOR_3
\end{array}
$$

Triglyceride     Methanol          Glycerol         Methyl Ester (Biodiesel)
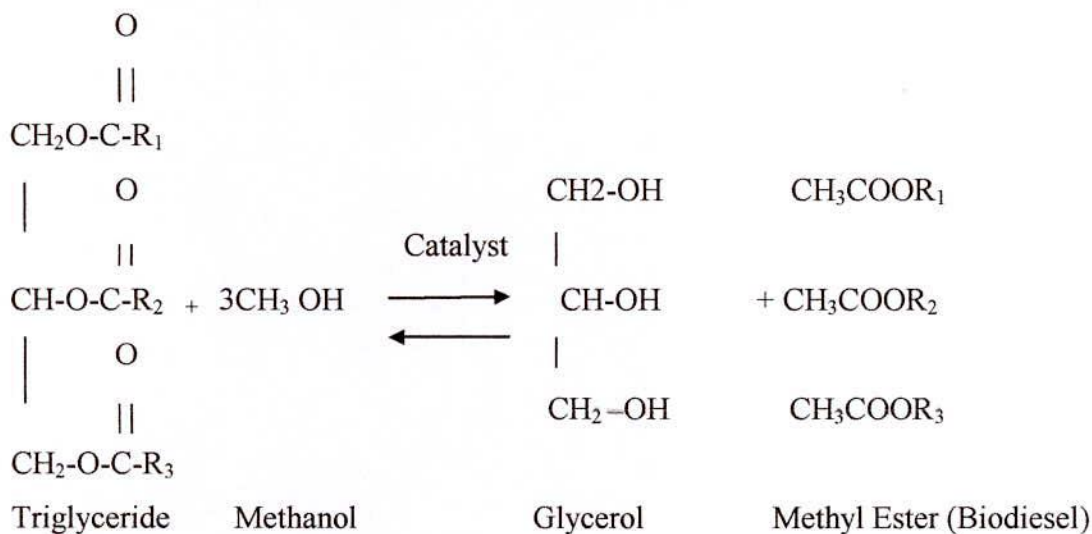
The products of the reaction are the biodiesel and glycerol.

The transesterification reaction is completed via a transition state, in which ring formation consisting of the carbon of the carboxyl and alkoxyl groups appears, even if a long chain alcohol is used as a reactant. The properties of the biodiesel fuel are strongly influenced by the structure and concentration of the fatty acid esters, which depend on the source, such as palm, soybean, corn or sunflower. Normally, the triglyceride consists of one glycerol and various types of fatty acid esters which vary in carbon chain length and in number of unsaturated

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bonds. Therefore, a transesterification reaction can be rather complex. A typical transesterification of a triglyceride consisting of consecutive reversible reactions, where R 1, R2 and R3 represent long-chain alkyl groups [36] .The overall process is normally a sequence of three consecutive steps, which are reversible reactions. The triglyceride is converted stepwise to a diglyceride, a monoglyceride and finally, to glycerol by removal of an alkaline each step [36-37]. Transesterification reaction of castor oil takes place at a significantly lower temperature when compared to other vegetable oils [33].

## 3.5 Effect of various parameters on the product

The products are affected by various parameters such as temperature, molar ratio, and reaction time.

### 3.5.1 Effect of molar ratio of alcohol to oil

The practical range of the molar ratio between methanol and a vegetable oil is 3.3 to 5.5:1[38]. The transesterification will be carried out by reacting castor oil with methanol in the presence of a basic catalyst (NaOH).

The stoichiometric ratio for the reaction requires 3 mol of alcohol and 1 mol of triacyglycerol to yield 3 mol fatty acid ester and 1mol of glycerol However, because of the reversibility if the reaction, an excess of alcohol is usually needed to force the equilibrium to the product side .In practice, 6 mol of alcohol and 1mol of triacyglycerol are use to raise the product yield. Hence, the reaction rate depends on ethanol solubility in the oil phase [39]. The stoichiometric ratio alcohol/oil has been identified as a crucial variable and has been studied in the range of 1:1 and 6: 1. An excess of alcohol has been recognized to improve the reaction toward the desired product [7].

### 3.5.2 Effect of Temperature

A trials were performed with peanut, soy, and sunflower oils at 60°C using methanol and sodium methoxide as a catalyst and found that around 80% of the conversion of esters occurs within the first few minutes of the reaction and after one hour it reaches a range of about 93-98% [40]. When an acid catalyst is used, reaction time can be much longer. The temperature of the transesterification, its catalyst and quantity, the alcohol and its moral relation with the triglyceride depends on the oil or fat that is being used.

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Solvent reuse would also lead to water accumulation in ethanol, affecting the initial stage of the reaction. One factor of particular importance in the alcoholysis process is the degree of mixing between the alcohol and the triacyglycerol phases [39]. The reaction temperature effect on the yield was studies in the temperature range of 40-100°C for jatropha curcas oil at atmospheric pressure. The maximum yield was obtained at a temperature of 60° C for jatropha oil. A decrease in yield was observed when the reaction temperature was above 60°C. Other researchers have achieved optimum yield at temperature above 60°C and 70°Cwhile using refined linseed oil and brassica carinata oil respectively. The reaction temperature for processing jatropha oil should be maintained below 60°C because saponification of glycerides by the alkali catalyst is much faster than the alcoholysis at temperature above 60°C [7].

The transesterification process is generally carried out at 40°C to 70°C, because the reaction temperature is limited by the boiling point of the alcohol and the low mutual solubility of vegetable oil and mehanol at atmospheric pressure. The reaction mixture is usually mechanically stirred to enhance mass transfer [39].

### 3.5.3 Effect of reaction time on the conversion

Reaction conditions: methanol/oil molar ratio 5:1, catalyst amount 7.5% and methanol reflux temperature. The conversion increases steadily with the reaction time and then reached a plateau value representative of a nearly equilibrium conversion. A nearly maximum conversion of 65% is obtained after 9 hour reaction time [41].

The reaction was very fast in the first few minutes, a product of more than 90% ester content was formed within the first 5 min. After that (the time of a clear phase being formed), the reaction slowed down and entered a slow rate stage till the reaction equilibrium was reached eventually. As can be observed, the ester content increased with reaction time at the beginning, reached a maximum at a reaction time of 15 min at 70°C, and then remained relatively constant with increasing further the reaction time. Based on this, the product yield under the case of a reaction time larger than 15 min was examined. The results indicated that an extension of the reaction time from 15 min to 30 min had no significant effect on the conversion of triglycerides, but led to a reduction in the product yield, the yield of the product with the same ester content decreased from 87.5% to 85.3%, dropped by about 2.2%. This is because longer reaction enhanced the hydrolysis of esters (reverse reaction of

transesterification), resulted in a loss of esters as well as causing more fatty acids to form soap. More visible soaps were observed experimentally with gradually extending the reaction time. Accordingly, it can be concluded that the reaction time was also a controlling factor of product yield and extending the reaction time had a negative effect on the product yield. The optimal reaction time for the transesterification of used frying oil is 15 min at 70 °C with the maximum mixing degree currently available, which is similar to that of neat Canola oil [42].

## 3.6 Properties of Biodiesel

To study the behavior of any chemical substance its properties are determined. These are two type of properties i.e, Physical and chemical properties. The analyses of the properties of biodiesel are briefly explained below.

### 3.6.1 Physical Properties

The physical properties of biodiesel can be determined by following the standard test methods for Kinematic viscosity, Density, Flash point, Pour point, etc. These are briefly described below:

### 3.6.2 Kinematic Viscosity

The kinematic viscosity is a measure of the resistance to gravity flow of a fluid. Viscosity of oil is an important property since it affects for example the flow of the liquid through the pipelines. The lower the viscosity of the oil, the easier it is to pump and to atomize and achieve finer droplets. This is the major criterion upon which the oil is graded. The kinematic viscosity of the biodiesel was determined using Glass Capillary Kinematic Viscometer, according to ASTM D445 test methods.

### 3.6.3 Density

The density, or the volumetric mass density, of a substance is its mass per unit volume. The symbol most often used for density is $\rho$, although the Latin letter $D$ can also be used. Mathematically, density is defined as mass divided by volume.

Density, $\rho = \dfrac{m}{v}$

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Where $\rho$ is the density, $m$ is the mass, and $V$ is the volume.

### 3.6.4 Flash point

The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Measuring a flash point requires an ignition source. At the flash point, the vapor may cease to burn when the ignition source is removed. This is a measure of the volatility of the oil as well as its ease of ignition. The higher this number, the safer the oil is to handle because the risk of accidental vapor ignition is reduced. The flash point of the liquid was determined according to ASTM D93 test methods.

### 3.6.5 Pour point

The pour point is the lowest temperature at which the liquid is observed to flow under prescribed conditions. The parameter is an indication of the minimum temperature at which the oil can be pumped without heating of the storage tank. The standard test method for the determination of the pour point is ASTM D97.

### 3.6.6 Chemical Properties

The chemical properties of biodiesel can be determined by the following the tests such as Gross calorific value (GCV). These are briefly described below:

### 3.6.7 Gross Calorific Value (GCV)

The gross calorific value is a measure of the quantity of heat released in total combustion and therefore measure the energy content of a fuel. It is the most important fuel property of any fuel. The Gross calorific value (GCV) of the biodiesel was determined by an Oxygen bomb calorimeter.

## 3.7 Cost Analysis

Cost analysis is the process of developing and analyzing cost data from separate business elements and estimating incremental and total resources needed to support current and future business strategies. A decision making tool is used to evaluate and prioritize resource needs at based on cost estimates and their expected return on investment. The cost analysis of a biodiesel plant is described in the following section.

### 3.7.1 Capital Costs

The capital cost of a plant is determined by summing the costs related to the major pieces of base equipment. The Total Capital Requirement (TCR) for a plant was determined by adding to the Fixed Capital Investment (FCI), the start-up costs, 10% of FCI and the working capital [43]. The capital charges were determined by the formula given by Eq. No. (1)

$$ACC = \frac{TCR}{\{1-(1+i)^{-N}\}} \times i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where ACC, the annual capital cost, i, the interest rate and N, the plant life time.

The production cost was determined by estimating the capital cost and the operating costs for biodiesel process of castor oil.

### 3.7.2 Total cost of Biodiesel Production

Total cost of biodiesel is generally depends upon the feed stock cost, total fixed cost, variable cost. The fixed cost which includes building rent, machine depreciation value it was calculated with depreciable life of 15 years. The Production cost of biodiesel from pongamia seeds is shown in Table 3.4.

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Table 3.3: Production cost of biodiesel from pongamia seeds [44].

| Sl. | Description/ Particulars | Qty. | Rate (Rs) | Amount (Rs.) |
|---|---|---|---|---|
| I. Total cost of production | | | | |
| 1 | Pongamia seeds | 6000 kg | 15 | 90000 |
| 2 | Transportation charges | 6000 kg | 1 | 6000 |
| 3 | Chemicals and reagents | - | - | 24862 |
| 4 | Electricity | 4 1520 units | 6.50 | 9880 |
| 5 | Man Power (6-days) Helpers (2 No's) | 2 | 5000 | 10000 |
| 6 | Office supervision | - | - | 5000 |
| 7 | Production Unit building Rent/month | - | - | 2000 |
| 8 | Depreciation value @ 1%/month | - | - | 1000 |
| Total | | | | 148742 |
| II. Income from the by-products: | | | | |
| 9 | Seed cake | 4200 kg | 15 | 63000 |
| 10 | Glycerin | 240 Liter | 25 | 6000 |
| Total | | | | 69000 |
| III. Net production cost of biodiesel for 1410 Liter: | | | | |
| 11 | Total cost of Biodiesel production | - | - | 148742 |
| 12 | Profits from by products | - | - | 69000 |
| Total | | | | 79742 |

The net production cost of biodiesel from Pongamia seeds was of Rs. 56.54 per Liter or Tk. 65.92 Per Liter.

# CHAPTER I V

## EXPERIMENTAL SET UP AND PROCEDURES

### 4.1 Materials and methods

The raw materials used as feedstock for the transesterification was the castor oil. The castor oil was collected from the Melandah, Jamalpur, Bangladesh. Castor oil was kept in a bottle to settle down. The sediment portion of this oil was separated. It was filtered by filter paper. Filtrate oil was ready for using as feedstock. Methanol was used with castor oil. $H_2SO_4$ and NaOH were used as the catalyst; $H_2SO_4$ was in the liquid form and NaOH was in the pellet form, which was purchased from Khulna Scientific Store.

### 4.2 Experimental set-up

Batch type reactor was selected for the study. It was made of MS sheet having a length of 31.5cm; the outer diameter of the unit was 27cm and inner diameter of 25cm. One end of the unit was closed and the other end was connected to the feeding system with flange. The major components of the unit are

(i)     A batch reactor
(ii)    An electric heater
(iii)   Motor
(iv)    Agitator
(v)     Bearing
(vi)    Oil seal
(vii)   Temperature indicator
(viii)  K-type thermocouples, with temperature controller
(ix)    Level gage
(x)     Oil collecting beaker
(xi)    Measuring Cylinder
(xii)   Pressure gage

(xiii)  Ball Valve

(xiv)  Globe Valve

(xv)  Pressure relief valve (PRV)

(xvi)  Separating bottle

(xvii)  Washing vessel

(xviii) Funnel

A schematic diagram of the experimental set-up is shown in Figure 4.1 which consists of an electric heater for maintaining temperature inside the reactor and an agitator with motor for properly mixing the reaction mixture.
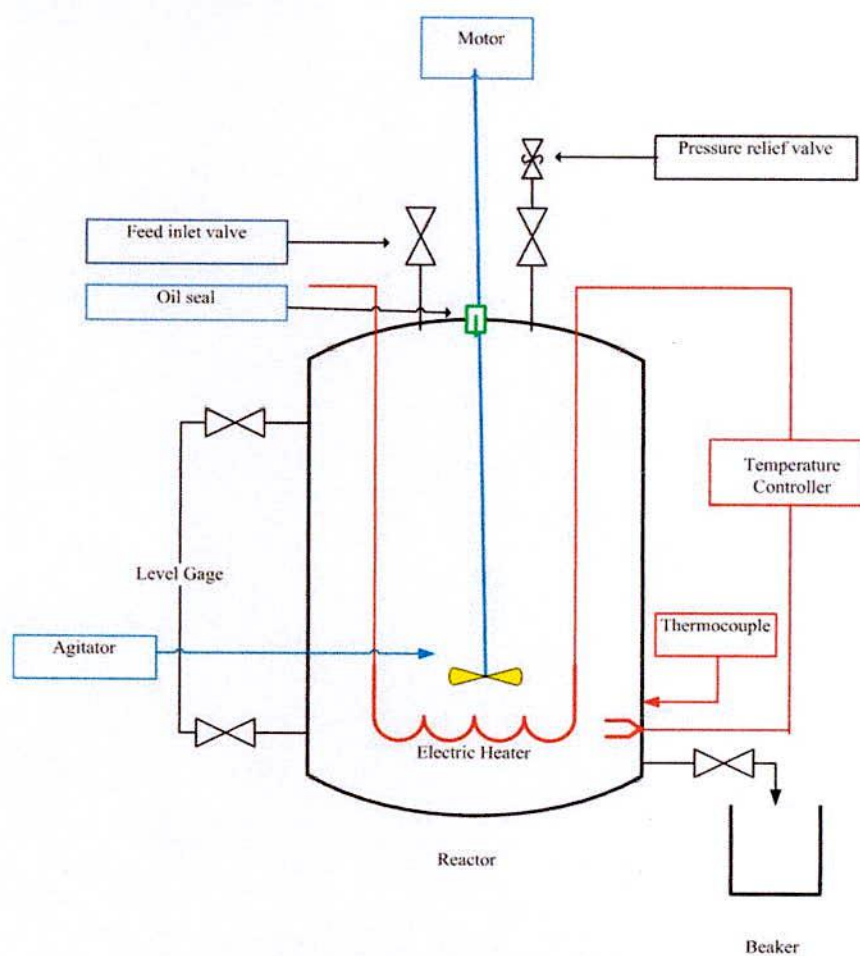


Figure 4.1: Schematic diagram of the experimental set-up

The first aspect with respect to the design of the reactor was the total volume of the reactor. As was decided that a maximum output of 8 liter of bio-diesel was required from a single batch, the total required volume of the reactor was estimated to 15 liter. This volume is required to accommodate all the reactants vise versa Castor oils, methanol, Sulfuric acid and sodium

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hydroxide in the recommended ratio. Hence with the required volume in consideration a cylindrical shape was sought to be appropriate.

The system require is being closed system and hence a flange was designed to prevent any leakage of methanol which could vaporize due to heating and potentially be health hazard. Hence the whole system was designed to be air tight with the use of a flange and gasket to prevent any leakage. Oil seals and bearing are used with agitator shaft to air tight the reactor. Since it was observed that methanol has tendency to vaporize and MS sheet could be explosion due to increase in pressures. A pressure relief valve (PRV) was used due to release high pressure. A photographic view of Reactor is shown in Figure 4.2.



Figure 4.2: Photographic view of Reactor

As the reaction requires vigorous stirring and heating, the design was involved to integrate the stirring and the heating systems into the reactor for higher mixing sufficiency and more uniform temperature during the reactions. A motor (0.5 hp) was attached with agitator for

stirring reaction mixture. A heater was inserted into the reactor to heating castor oil properly. A pressure gage was installed on the top of reactor to observed pressure during reaction. A level gage was installed beside of reactor to see the level of product.

The washing vessels are designed to be cylindrical in shape with a capacity to accommodate more than 15 liters to hold water necessary for bubble washing. A Photographic view of Washing vessel and Separator is shown in Figure 4.3.



Figure 4.3: Photographic view of Washing vessel and Separator

The washing system was designed using a compressor to deliver air through a pipe to a diffuser inside the washing/separating vessel. The diffuser used for this purpose is to be integrated into the tank with the help of the appropriate piping from the compressor.
This is necessary to prevent reverse flow of fluid from the vessel into the pipe providing the compressed air. A one way check valve is also provided at the diffuser attachment in the vessel to prevent flow of liquid into the same Pipe.

A temperature Controller was used to maintain temperature at 45°C to 70°C in the reactor. A thermocouple with display is used to show temperature. Temperature controlling is very

important for proper reaction to obtained desired product. A Photographic view of Temperature controller is shown in Figure 4.4.



Figure 4.4: Photographic view of Temperature controller

The Photographic view of Overall Experimental Setup is shown in Figure 4.5.



Figure 4.5: Photographic view of Overall Experimental Setup

## 4.3 Experimental Procedure

The batch type Reactor as described in section 4.2 was constructed and installed in the Heat Engine Laboratory of Department of Mechanical Engineering, Khulna University of Engineering & Technology. The experiments were conducted for different castor oil and methanol ratios. The thermocouple sensors were placed in the reactor chamber to record the temperatures inside the reactor. The loading of raw materials were made by the action of gravity through a ball valve. The methanol was taken into the reactor through a ball valve by the action of gravity. The catalysts ($H_2SO_4$ and NaOH) were taken into reactor by the action of gravity after loading feed materials. The reactor heater was switched on and the temperature of the reactor was allowed to rise to a desired value of 45°C to 70°C indicated by the temperature recorder. The temperatures were noted from the digital recorder during the experiment. The samples were collected at every 5°C interval and measured the amount of biodiesel and glycerol.

For the present research biodiesel was prepared from castor oil by two step method. Acid catalyzed esterification reaction was carried out to reduce the FFA (Free Fatty Acid) content of raw oil and partially convert the castor oil to biodiesel. The first step for acid catalyzed esterification was carried out at 45°C to 70°C and atmospheric pressure. The esterification reaction was carried out at oil to methanol molar ratio 1:6. Catalyst (Sulfuric acid) was mixed 3wt% of oil with reaction mixture. The reaction continued for 3 hours.

The second step for base catalyzed transesterification, Sodium hydroxide pellets were mixed with reaction mixture. Molar ratio of methanol to oil was taken 6:1 for the total conversion of Triglyceride to biodiesel. Sodium hydroxide pellet was used as base catalyzed 0.5wt% of oil and Temperature maintained 45°C to 70°C. The reaction continued for 3 hours. Various Reaction parameters that affect the esterification and transesterification reaction are oil to methanol molar ratio, catalyst concentration, reaction temperature and time shown in Table 4.1.

Table 4.1: Reaction Parameters

| Reaction Parameters | Esterification | Transesterification |
| --- | --- | --- |
| Oil : Methanol | 1.02:6.6 | 1.02:6.6 |
| Catalyst Conc. | 3 wt% ($H_2SO_4$) of castor oil | 0.5 wt% (NaOH) of castor oil |
| Temperature | 45-70°C | 45-70°C |
| Time | 3 hrs | 3 hrs |

After the reaction, the reaction mixture should be allowed to cool and settle in measuring cylinder. The settling period allows for the reaction mixture to separate into the two products namely glycerol and the biodiesel. The separation occurs over a period of about 7 or more hours. A photographic view of measuring cylinder is shown in Figure 4.6.



Figure 4.6: Photographic view of measuring cylinder

Measuring Cylinder was used to measure the amount of biodiesel and glycerol after layer separation.

The methodology developed / processes adopted for production of biodiesel was given below. Whole process was described for one liter of castor oil. During processing of multiple quantity of castor oil, chemical constituents were changed in the same proportion however timing for heating, settling and washing remain same.

**First step**

• One liter of castor oil was taken into the Reactor.

• 250 ml of methanol & 16 ml of concentrated sulphuric acid was added to oil.

• The temperature of this mixture was maintained 45°C to 70°C and data was collected at every 5°C temperature interval.

• This temperature of the mixture was maintained for about 3 hours and stirred continuously.

• The mixture was allowed to settle for 8 hours after completion of this reaction and cooling the reaction mixture.

**Second step**

• 5g NaOH was added to oil mixture.

• This temperature of the mixture was maintained 45°C to 70°C and data was collected at every 5°C temperature interval.

•The mixture stirred continuously for about 3 hours.

Chemical reaction of Triglyceride with Methanol is shown below.

$$
\begin{array}{llll}
& O & & \\
& \| & & \\
CH_2O\text{-}C\text{-}R_1 & & & \\
| & O & CH2\text{-}OH & CH_3COOR_1 \\
& \| & | & \\
CH\text{-}O\text{-}C\text{-}R_2 + 3\,CH_3\,OH & \xrightarrow{\text{Catalyst}} & CH\text{-}OH & + CH_3COOR_2 \\
| & O & | & \\
& \| & CH_2\text{-}OH & CH_3COOR_3 \\
CH_2\text{-}O\text{-}C\text{-}R_3 & & &
\end{array}
$$

Triglyceride     Methanol          Glycerol          Methyl Ester (Biodiesel)
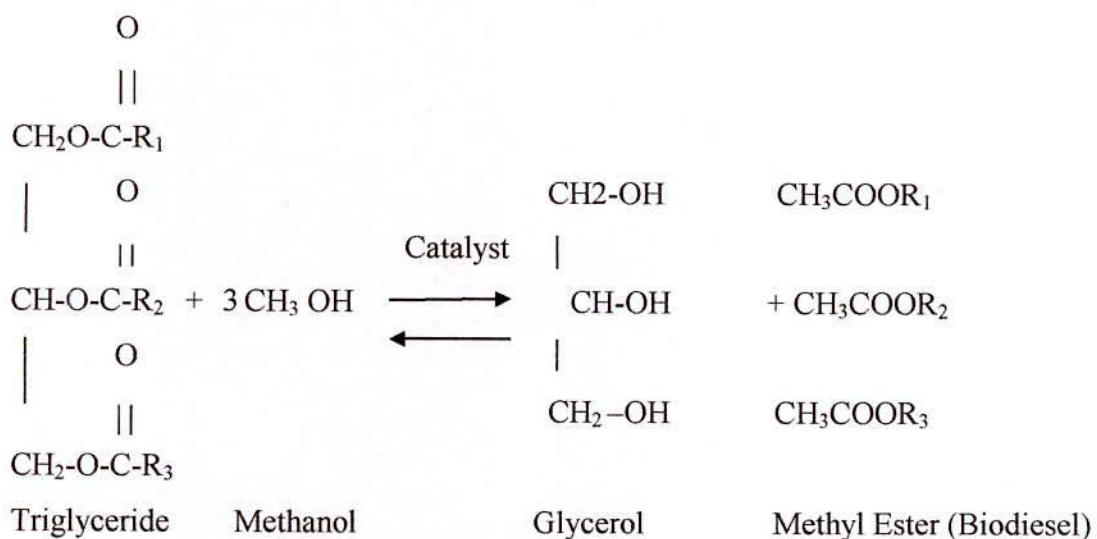
• The mixture was collected from reactor after reaction completion.

•The mixture was allowed to settle for 8 hours in separating bottle. This settled reactant mixture would consist of two layers.

a. Upper layer as biodiesel and traces of glycerin etc.

b. Bottom layer as glycerin and gums etc.

A photographic view of biodiesel and glycerol separation is shown in Figure 4.7.



Figure 4.7: Photographic view of biodiesel and glycerol separation

• The Biodiesel was collected from the separating bottle by using pipette and filler.

• The biodiesel separated in this stage still impure and needs to be bubble washing. This pre-washed biodiesel was taken in a washing vessel. Water was added in washing vessel as 2:1 ratio of biodiesel.

• This process involves cleaning the fuel with water by using agitation which was provided by compressed air through the water and biodiesel mixture.

•After bubble wash this mixture should be allowed more than 8 hours for settle down. After two layer separation biodiesel was collected in beaker.

•For further purification 600 ml of hot water at approximately 40° C was added per liter of crude biodiesel in separating bottle and shaken well and allowed to settle to separate two layers for nearly 7-8 hours.

• Above process was repeated two times so that the traces of glycerin and soap get removed and the biodiesel produced from castor oil was ready for use. A Photographic view of Methyl Ester (Biodiesel) was produced from castor oil is shown in Figure 4.8.
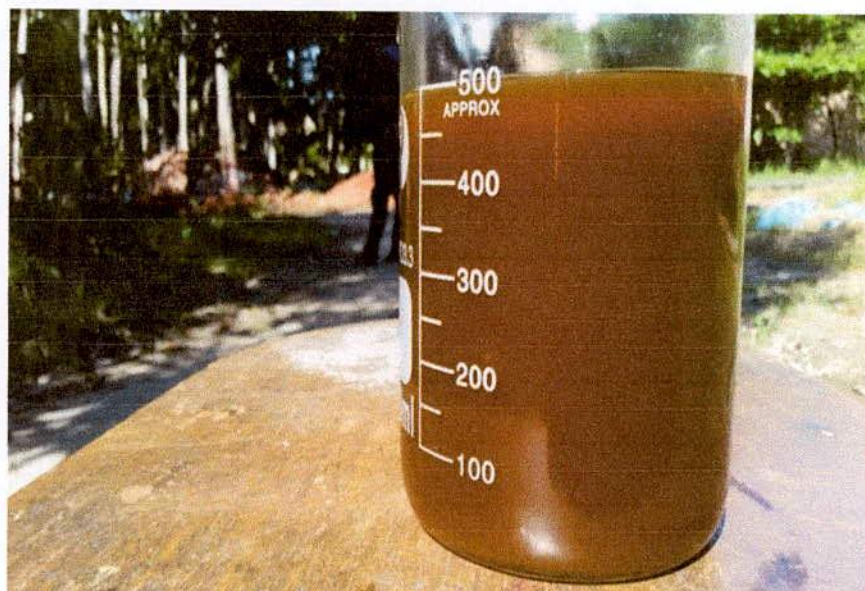
Figure 4.8: Photographic view of Methyl Ester (Biodiesel)

## 4.4 Experimental Data

During the experiments, Castor oil was charged in the reactor chamber in different ratio of castor oil and methanol. Details of Sample was used in various run is shown in Table 4.2.

Table 4.2: Details of Sample was used in various run.

| Sample N0. | Castor Oil | | Methanol | | Molar ratio= | Total Volume (L) |
|---|---|---|---|---|---|---|
| | Liter | Mole | Liter | Mole | Castor Oil : Methanol | |
| 1 | 3.0 | 1.02 | 1.0 | 8.23 | 1.02: 8.23 | 4.00 |
| 2 | 2.8 | 0.96 | 0.85 | 7.00 | 0.96: 7.00 | 3.65 |
| 3 | 2.9 | 0.98 | 0.73 | 6.00 | 0.98: 6.00 | 3.63 |
| 4 | 3.0 | 1.02 | 0.75 | 6.17 | 1.02: 6.17 | 3.75 |
| 5 | 3.0 | 1.02 | 0.80 | 6.60 | 1.02: 6.60 | 3.80 |

The experiments were performed by varying the temperature within the range of 45-70°C at every 5°C interval for each feed. The data collected during esterification and transesterification of castor oil to biodiesel shown in Table 4.3 through 4.12.

Table 4.3: Experimental data for esterification of 4.0 liter feed Materials for Various Temperatures using $H_2SO_4$ as catalyst.

| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
|---|---|---|---|---|---|
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 1.20 | 2.69 | 0.110 | 50 |
| 2 | 50 | 1.40 | 2.47 | 0.135 | 75 |
| 3 | 55 | 1.65. | 2.21 | 0.144 | 100 |
| 4 | 60 | 2.00 | 1.85 | 0.150 | 125 |
| 5 | 65 | 2.32 | 1.53 | 0.155 | 150 |
| 6 | 70 | 2.31 | 1.53 | 0.160 | 175 |

**Sample-1: (3 wt% $H_2SO_4$ as catalyst)**
Feed Materials: 4.00 Liter , Molar ratio= 1.02: 8.23

Table 4.4: Experimental data for esterification of 3.65 liter feed Materials for Various Temperatures using $H_2SO_4$ as catalyst.

**Sample-2: (3 wt% $H_2SO_4$ as catalyst)**
Feed Materials: 3.65 Liter, Molar ratio= 0.96: 7.00

| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
|---|---|---|---|---|---|
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 1.02 | 2.54 | 0.095 | 50 |
| 2 | 50 | 1.22 | 2.33 | 0.105 | 75 |
| 3 | 55 | 1.45 | 2.09 | 0.114 | 100 |
| 4 | 60 | 1.74 | 1.785 | 0.125 | 125 |
| 5 | 65 | 2.15 | 1.36 | 0.137 | 150 |
| 6 | 70 | 2.14 | 1.36 | 0.145 | 175 |

Table 4.5: Experimental data for esterification of 3.629 liter feed Materials for Various Temperatures using $H_2SO_4$ as catalyst.

| Sample-3: (3 wt% $H_2SO_4$ as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.63 Liter, Molar ratio= 0.98: 6.00 | | | | | |
| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 1.12 | 2.42 | 0.090 | 50 |
| 2 | 50 | 1.22 | 2.31 | 0.102 | 80 |
| 3 | 55 | 1.44 | 2.08 | 0.110 | 110 |
| 4 | 60 | 1.72 | 1.79 | 0.122 | 140 |
| 5 | 65 | 2.14 | 1.35 | 0.140 | 170 |
| 6 | 70 | 2.13 | 1.35 | 0.148 | 200 |

Table 4.6: Experimental data for esterification of 3.85 liter feed Materials for Various Temperatures using $H_2SO_4$ as catalyst.

| Sample-4: (3 wt% $H_2SO_4$ as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.75 Liter, Molar ratio= 1.02: 6.17 | | | | | |
| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 1.16 | 2.45 | 0.092 | 50 |
| 2 | 50 | 1.24 | 2.40 | 0.106 | 80 |
| 3 | 55 | 1.48 | 2.16 | 0.112 | 110 |
| 4 | 60 | 1.90 | 1.73 | 0.125 | 140 |
| 5 | 65 | 2.25 | 1.37 | 0.134 | 170 |
| 6 | 70 | 2.24 | 136 | 0.144 | 200 |

Table 4.7: Experimental data for esterification of 4.7 liter feed Materials for Various Temperatures using $H_2SO_4$ as catalyst.

| Sample-5: (3 wt% $H_2SO_4$ as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.80 Liter, Molar ratio= 1.02: 6.60 | | | | | |
| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 1.17 | 2.53 | 0.096 | 50 |
| 2 | 50 | 1.27 | 2.42 | 0.110 | 80 |
| 3 | 55 | 1.50 | 2.19 | 0.114 | 110 |
| 4 | 60 | 2.00 | 1.68 | 0.124 | 140 |
| 5 | 65 | 2.28 | 1.39 | 0.135 | 170 |
| 6 | 70 | 2.27 | 1.38 | 0.146 | 200 |

Table 4.8: Experimental data for transesterification of 4.0 liter feed Materials for Various Temperatures using NaOH as catalyst.

| Sample-6: (0.5 wt% NaOH as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 4.00 Liter, Molar ratio= 1.02: 8.23 | | | | | |
| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 2.35 | 1.49 | 0.165 | 50 |
| 2 | 50 | 2.60 | 1.23 | 0.175 | 75 |
| 3 | 55 | 2.80 | 0.98 | 0.215 | 100 |
| 4 | 60 | 3.12 | 0.63 | 0.245 | 125 |
| 5 | 65 | 3.40 | 0.34 | 0.264 | 150 |
| 6 | 70 | 3.39 | 0.34 | 0.270 | 175 |

Table 4.9: Experimental data for transesterification of 3.65 Liter feed Materials for Various Temperatures using NaOH as catalyst.

| Sample-7: (0.5 wt% NaOH as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.65 Liter, Molar ratio= 0.96: 7.00 | | | | | |
| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 2.25 | 1.25 | 0.150 | 50 |
| 2 | 50 | 2.41 | 1.08 | 0.156 | 75 |
| 3 | 55 | 2.63 | 0.86 | 0.162 | 100 |
| 4 | 60 | 3.00 | 0.43 | 0.220 | 125 |
| 5 | 65 | 3.20 | 0.20 | 0.255 | 150 |
| 6 | 70 | 3.19 | 0.19 | 0.262 | 175 |

Table 4.10: Experimental data for transesterification of 3.63 liter feed Materials for Various Temperatures using NaOH as catalyst.

| Sample-8: (0.5 wt% NaOH as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.63 Liter, Molar ratio= 0.98: 6.00 | | | | | |
| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 2.25 | 1.23 | 0.152 | 50 |
| 2 | 50 | 2.50 | 0.97 | 0.162 | 80 |
| 3 | 55 | 2.72 | 0.73 | 0.185 | 110 |
| 4 | 60 | 2.94 | 0.48 | 0.214 | 140 |
| 5 | 65 | 3.19 | 0.19 | 0.250 | 170 |
| 6 | 70 | 3.18 | 0.19 | 0.260 | 200 |

Table 4.11: Experimental data for transesterification of 3.85 liter feed Materials for Various Temperatures using NaOH as catalyst.

| Sample-9: (0.5 wt% NaOH as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.75 Liter, Molar ratio= 1.02: 6.17 | | | | | |
| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 2.35 | 1.25 | 0.150 | 50 |
| 2 | 50 | 2.55 | 1.04 | 0.160 | 80 |
| 3 | 55 | 2.96 | 0.63 | 0.165 | 110 |
| 4 | 60 | 3.18 | 0.37 | 0.205 | 140 |
| 5 | 65 | 3.37 | 0.15 | 0.228 | 170 |
| 6 | 70 | 3.36 | 0.14 | 0.246 | 200 |

Table 4.12: Experimental data for transesterification of 4.7 liter feed Materials for Various Temperatures using NaOH as catalyst.

| Sample-10: (0.5 wt% NaOH as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.80 Liter, Molar ratio= 1.02: 6.60 | | | | | |
| No. of Observation | Temperature (°C) | Product yield, L | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 2.40 | 1.25 | 0.152 | 50 |
| 2 | 50 | 2.62 | 1.02 | 0.163 | 80 |
| 3 | 55 | 2.96 | 0.66 | 0.184 | 110 |
| 4 | 60 | 3.26 | 0.33 | 0.214 | 140 |
| 5 | 65 | 3.42 | 0.14 | 0.238 | 170 |
| 6 | 70 | 3.41 | 0.13 | 0.258 | 200 |

# CHAPTER V

## RESULTS AND DISCUSSION

### 5.1 Presentation of Results

Under the study of transesterification of castor oil in batch type reactor, the experiments were conducted in the temperature range of 45°C to 70°C. The experiments were conducted to examine the effect of temperature on product yield by esterification and transesterification reaction with $H_2SO_4$ and NaOH as catalyst. The experimental data are shown in Table 4.3 to Table 4.12 and the results calculated from these data are shown in Table 5.1 to 5.10, from which Figure 5.1 to 5.13 have been drawn for convenience of analysis. They will be discussed in details in the following sections.

Table 5.1: Effect of Temperature on Product yield of esterification reaction using $H_2SO_4$ as catalyst.

| Sample-1: ($H_2SO_4$ as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 4.00 Liter, Molar ratio= 1.02: 8.23 | | | | | |
| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 30.00 | 67.25 | 2.75 | 50 |
| 2 | 50 | 35.00 | 61.75 | 3.38 | 75 |
| 3 | 55 | 41.25 | 55.25 | 3.60 | 100 |
| 4 | 60 | 50.00 | 46.25 | 3.75 | 125 |
| 5 | 65 | 58.00 | 38.25 | 3.88 | 150 |
| 6 | 70 | 57.75 | 38.25 | 4.00 | 175 |

Table 5.2: Effect of Temperature on Product yield of esterification reaction using $H_2SO_4$ as catalyst.

| Sample-2: ($H_2SO_4$ as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.65 Liter, Molar ratio= 0.96: 7.00 | | | | | |
| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 27.94 | 69.58 | 2.60 | 50 |
| 2 | 50 | 33.42 | 63.83 | 2.87 | 75 |
| 3 | 55 | 39.72 | 57.26 | 3.12 | 100 |
| 4 | 60 | 47.67 | 48.76 | 3.42 | 125 |
| 5 | 65 | 59.00 | 37.26 | 3.75 | 150 |
| 6 | 70 | 58.75 | 37.25 | 4.00 | 175 |

Table 5.3: Effect of Temperature on Product yield of esterification reaction using $H_2SO_4$ as catalyst.

| Sample-3: ($H_2SO_4$ as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.63 Liter, Molar ratio= 0.98: 6.00 | | | | | |
| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 30.85 | 66.68 | 2.47 | 50 |
| 2 | 50 | 33.60 | 63.64 | 2.80 | 80 |
| 3 | 55 | 40.00 | 57.30 | 3.03 | 110 |
| 4 | 60 | 47.38 | 49.31 | 3.36 | 140 |
| 5 | 65 | 59.00 | 37.19 | 3.85 | 170 |
| 6 | 70 | 58.67 | 37.19 | 4.07 | 200 |

Table 5.4: Effect of Temperature on Product yield of esterification reaction using $H_2SO_4$ as catalyst.

| Sample-4: (3 wt% $H_2SO_4$ as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.75 Liter, Molar ratio= 1.02: 6.17 | | | | | |
| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 31.00 | 65.33 | 2.45 | 50 |
| 2 | 50 | 33.06 | 64.00 | 2.82 | 80 |
| 3 | 55 | 39.47 | 57.60 | 2.98 | 110 |
| 4 | 60 | 50.66 | 46.13 | 3.33 | 140 |
| 5 | 65 | 60.00 | 36.53 | 3.57 | 170 |
| 6 | 70 | 59.73 | 36.26 | 3.84 | 200 |

Table 5.5: Effect of Temperature on Product yield of esterification reaction using $H_2SO_4$ as catalyst.

| Sample-5: ($H_2SO_4$ as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.80 Liter, Molar ratio= 1.02: 6.60 | | | | | |
| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 30.78 | 66.57 | 2.52 | 50 |
| 2 | 50 | 33.42 | 63.68 | 2.89 | 80 |
| 3 | 55 | 39.47 | 57.63 | 3.00 | 110 |
| 4 | 60 | 52.63 | 44.21 | 3.26 | 140 |
| 5 | 65 | 60.00 | 36.57 | 3.55 | 170 |
| 6 | 70 | 59.73 | 36.31 | 3.84 | 200 |

Table 5.6: Effect of Temperature on Product yield of transesterification reaction using NaOH as catalyst.

| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
|---|---|---|---|---|---|
| | | biodiesel | Unreacted feed | glycerol | |
| **Sample-6: (0.5 wt% NaOH as catalyst)** | | | | | |
| **Feed Materials: 4.00 Liter, Molar ratio= 1.02: 8.23** | | | | | |
| 1 | 45 | 58.75 | 37.25 | 4.12 | 50 |
| 2 | 50 | 65.00 | 30.75 | 4.37 | 75 |
| 3 | 55 | 70.00 | 24.50 | 5.37 | 100 |
| 4 | 60 | 78.00 | 15.75 | 6.12 | 125 |
| 5 | 65 | 85.00 | 8.50 | 6.60 | 150 |
| 6 | 70 | 84.75 | 8.50 | 6.75 | 175 |

Table 5.7: Effect of Temperature on Product yield of transesterification reaction using NaOH as catalyst.

| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
|---|---|---|---|---|---|
| | | biodiesel | Unreacted feed | glycerol | |
| **Sample-7: (0.5 wt% NaOH as catalyst)** | | | | | |
| **Feed Materials: 3.65 Liter, Molar ratio= 0.96: 7.00** | | | | | |
| 1 | 45 | 61.64 | 34.24 | 4.11 | 50 |
| 2 | 50 | 66.02 | 29.58 | 4.27 | 75 |
| 3 | 55 | 72.05 | 23.56 | 4.44 | 100 |
| 4 | 60 | 82.19 | 11.78 | 6.02 | 125 |
| 5 | 65 | 87.67 | 5.47 | 6.98 | 150 |
| 6 | 70 | 87.40 | 5.20 | 7.12 | 175 |

Table 5.8: Effect of Temperature on Product yield of transesterification reaction using NaOH as catalyst.

| Sample-8: (0.5 wt% NaOH as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.63 Liter, Molar ratio= 0.98: 6.00 | | | | | |
| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 61.98 | 33.88 | 4.18 | 50 |
| 2 | 50 | 68.87 | 26.72 | 4.46 | 80 |
| 3 | 55 | 74.93 | 20.11 | 5.09 | 110 |
| 4 | 60 | 81.00 | 13.22 | 5.89 | 140 |
| 5 | 65 | 87.87 | 5.23 | 6.88 | 170 |
| 6 | 70 | 87.60 | 5.23 | 7.16 | 200 |

Table 5.9: Effect of Temperature on Product yield of transesterification reaction using NaOH as catalyst.

| Sample-9: (0.5 wt% NaOH as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.75 Liter, Molar ratio= 1.02: 6.17 | | | | | |
| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 62.66 | 33.34 | 4.00 | 50 |
| 2 | 50 | 68.00 | 27.74 | 4.26 | 80 |
| 3 | 55 | 78.93 | 16.67 | 4.40 | 110 |
| 4 | 60 | 84.80 | 9.74 | 5.46 | 140 |
| 5 | 65 | 90.00 | 3.92 | 6.08 | 170 |
| 6 | 70 | 89.60 | 3.84 | 6.56 | 200 |

Table 5.10: Effect of Temperature on Product yield of transesterification reaction using NaOH as catalyst.

| Sample-10: (0.5 wt% NaOH as catalyst) | | | | | |
|---|---|---|---|---|---|
| Feed Materials: 3.80 Liter, Molar ratio= 1.02: 6.60 | | | | | |
| No. of Observation | Temperature (°C) | Product yield (Vol%) | | | Operating Time (min) |
| | | biodiesel | Unreacted feed | glycerol | |
| 1 | 45 | 63.15 | 32.85 | 4.00 | 50 |
| 2 | 50 | 68.94 | 26.78 | 4.28 | 80 |
| 3 | 55 | 77.89 | 17.27 | 4.84 | 110 |
| 4 | 60 | 85.78 | 8.59 | 5.63 | 140 |
| 5 | 65 | 90.00 | 3.74 | 6.26 | 170 |
| 6 | 70 | 89.73 | 3.49 | 6.78 | 200 |

The tabular values shown in Table 5.1 to 5.10 are plotted on Figures 5.1 to 5.13 and are discussed below:
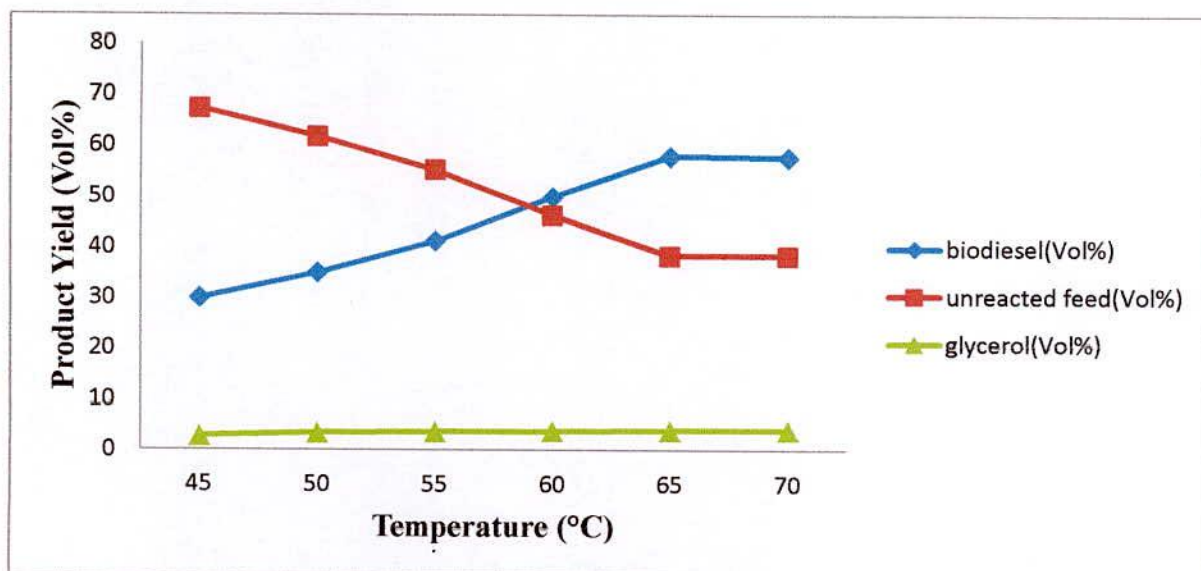


Figure 5.1: Effect of temperature on product yields of esterification of castor oil using $H_2SO_4$ as catalyst with Molar ratio= 1.02: 8.23
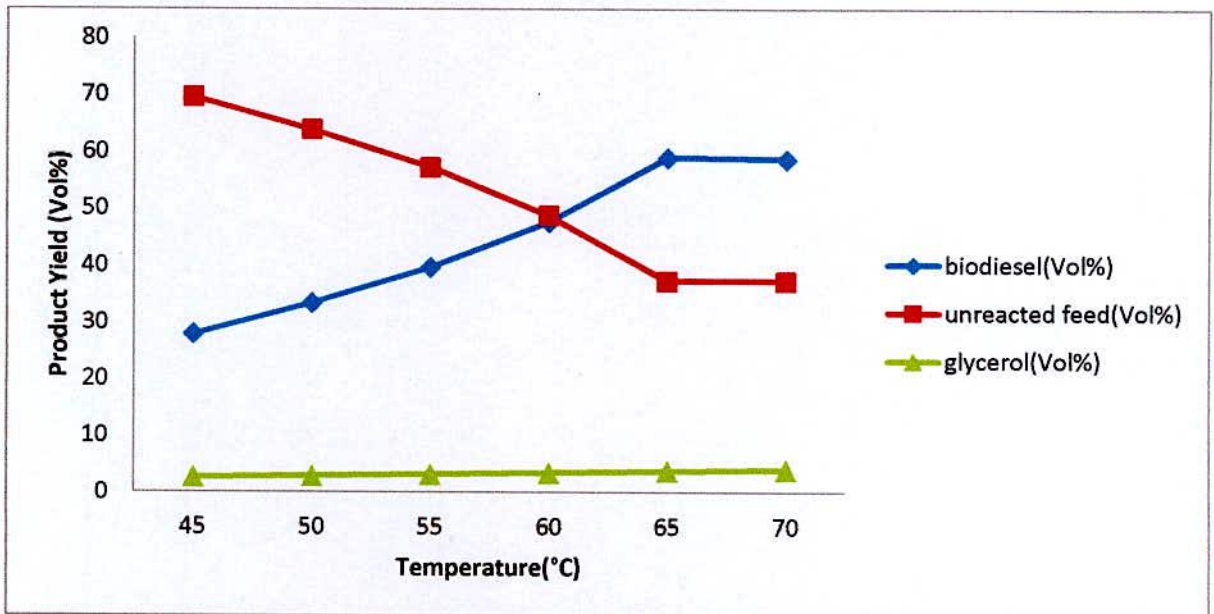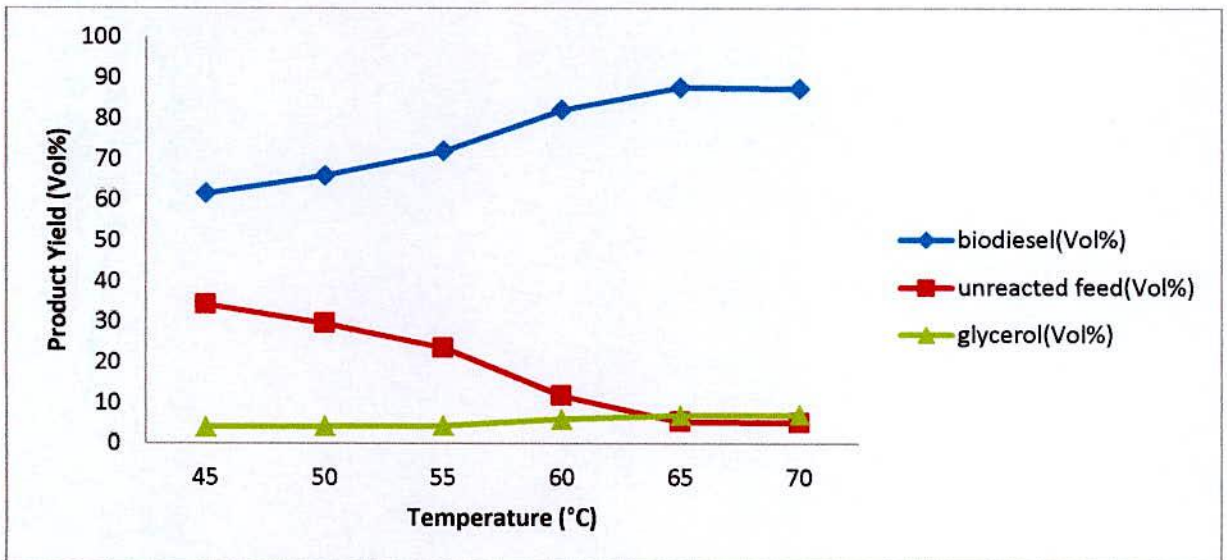
Figure 5.2: Effect of temperature on product yields of esterification of castor oil using $H_2SO_4$ as catalyst with molar ratio= 0.96: 7.00
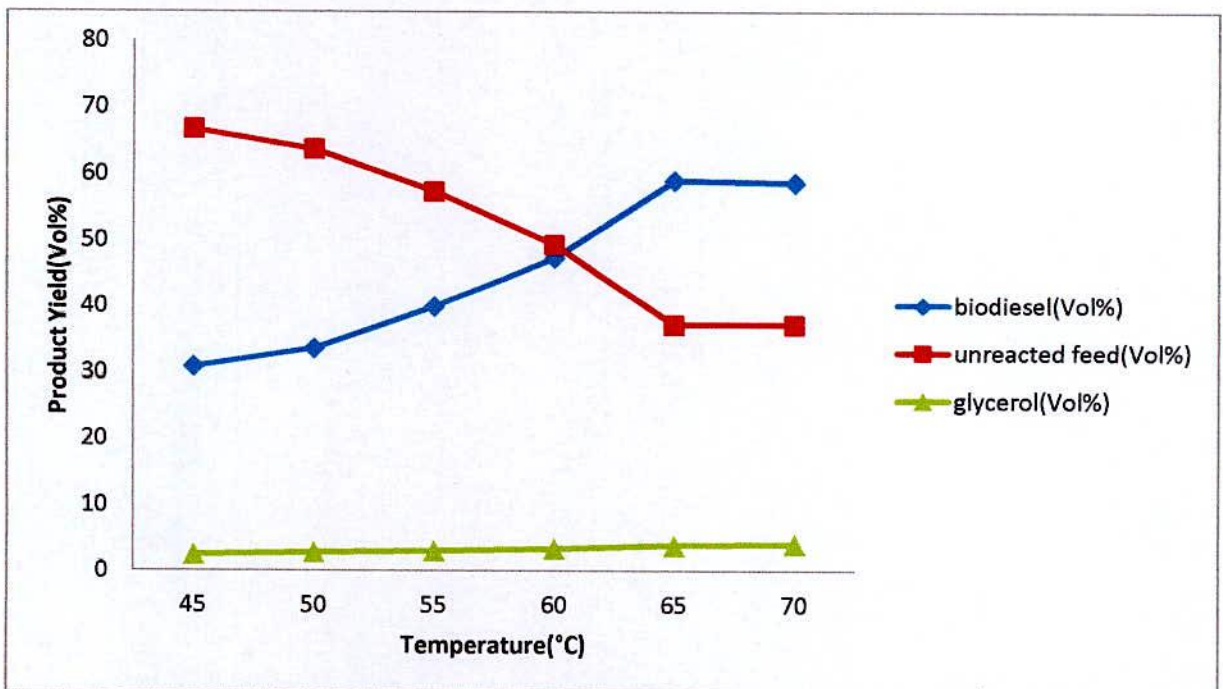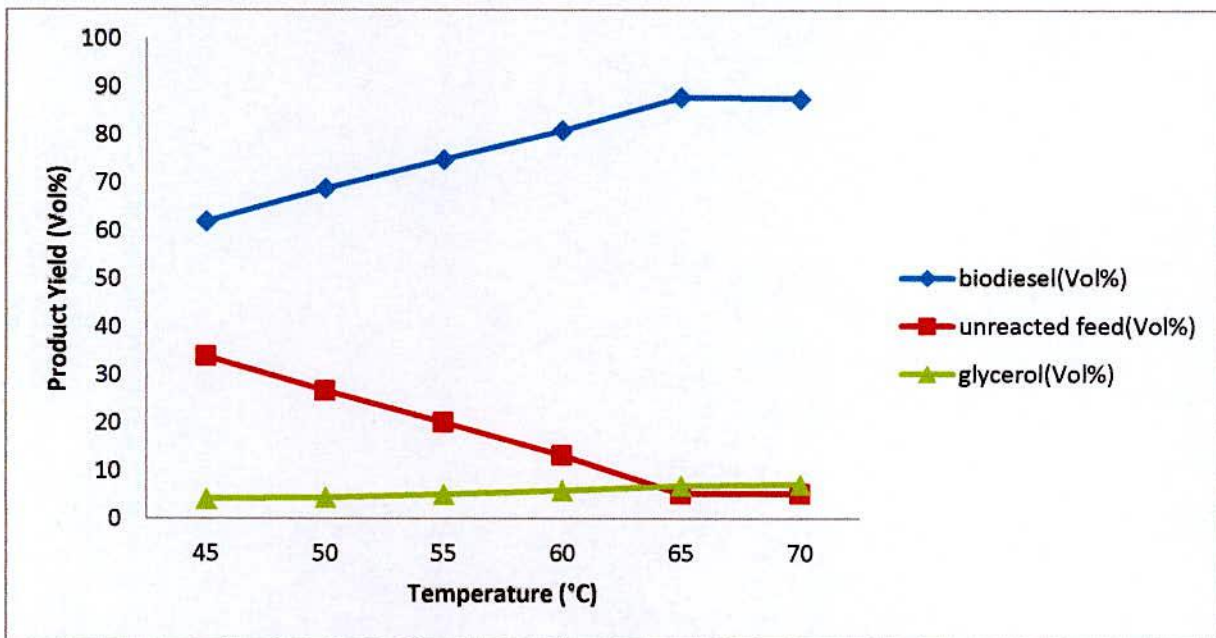


Figure 5.3: Effect of temperature on product yields of esterification of castor oil using $H_2SO_4$ as catalyst with molar ratio= 0.98: 6.00
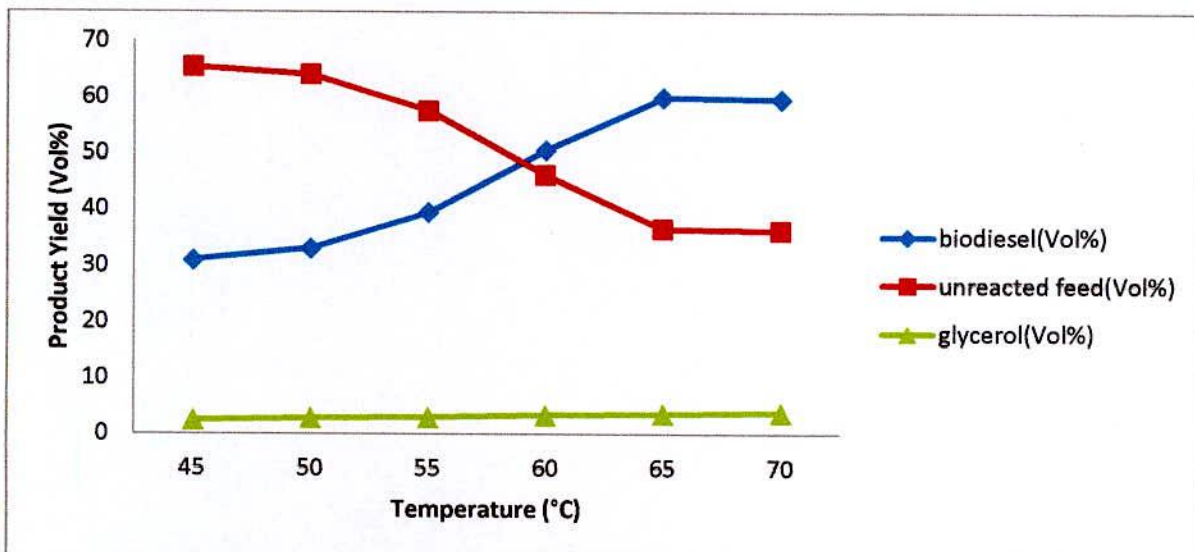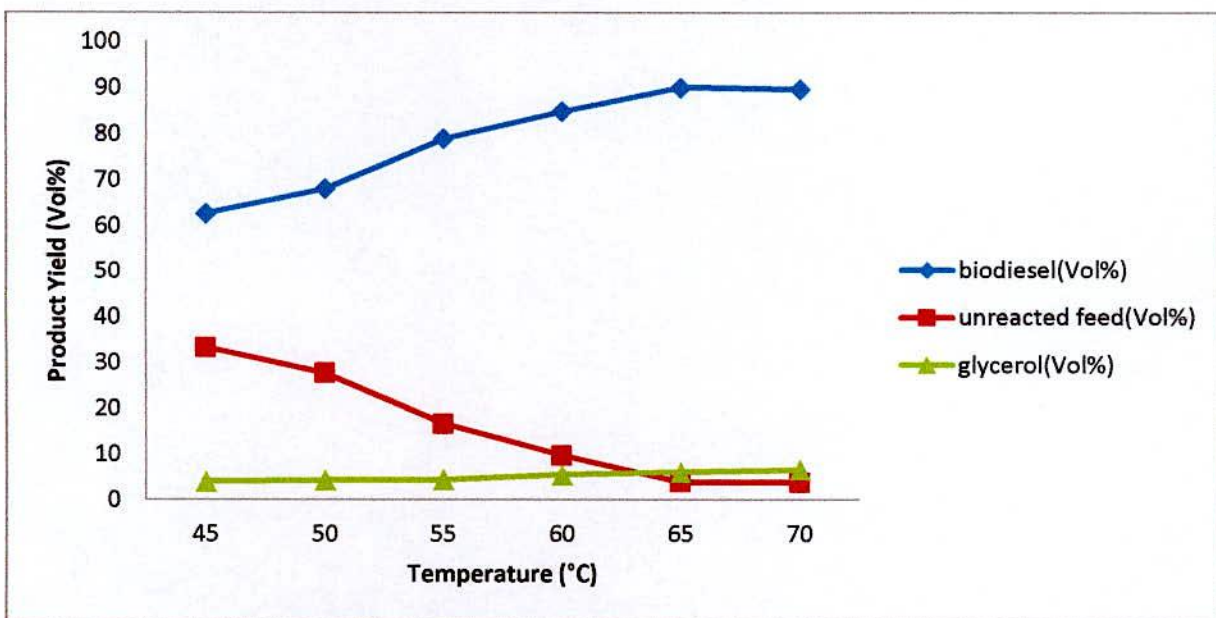
Figure 5.4: Effect of temperature on product yields of esterification of castor oil using $H_2SO_4$ as catalyst with molar ratio= 1.02: 6.17
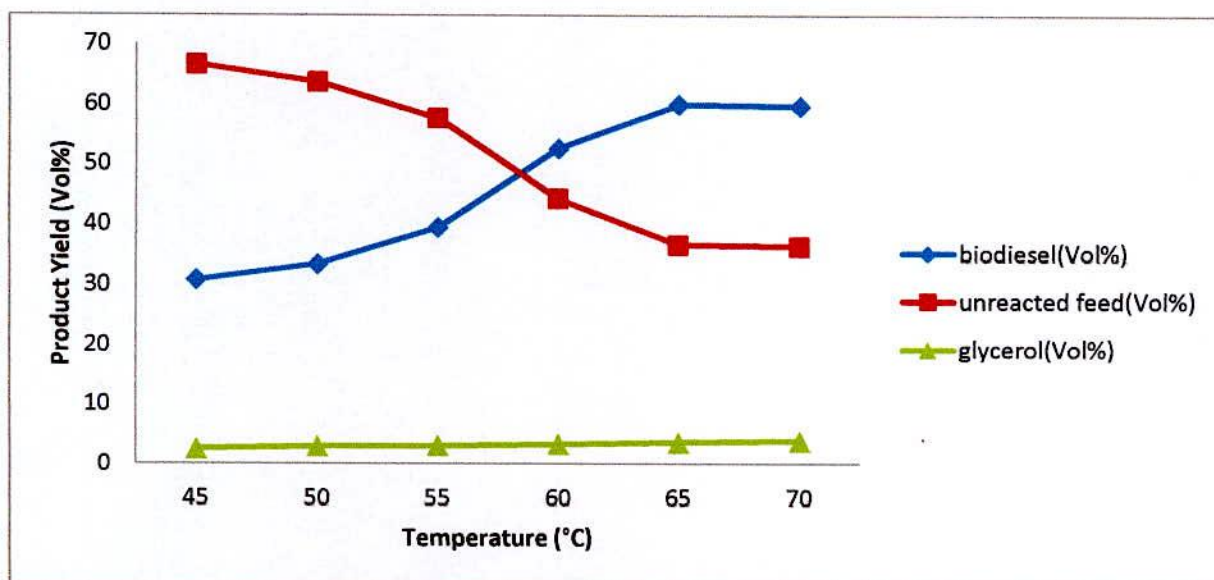


Figure 5.5: Effect of temperature on product yields of esterification of castor oil using $H_2SO_4$ as catalyst with molar ratio= 1.02: 6.60
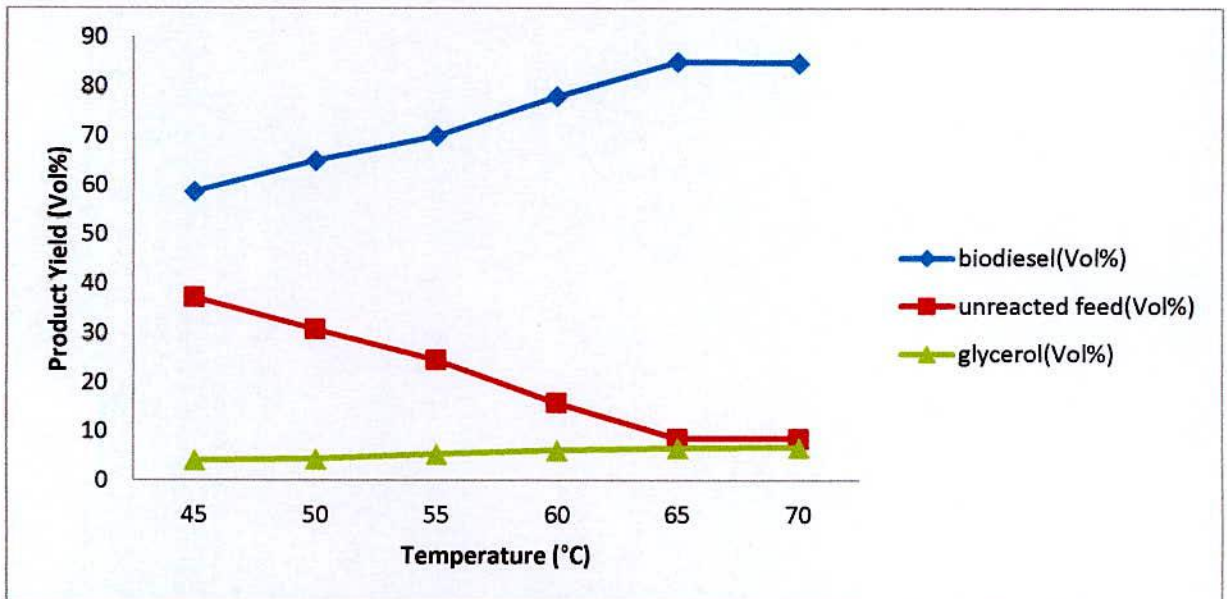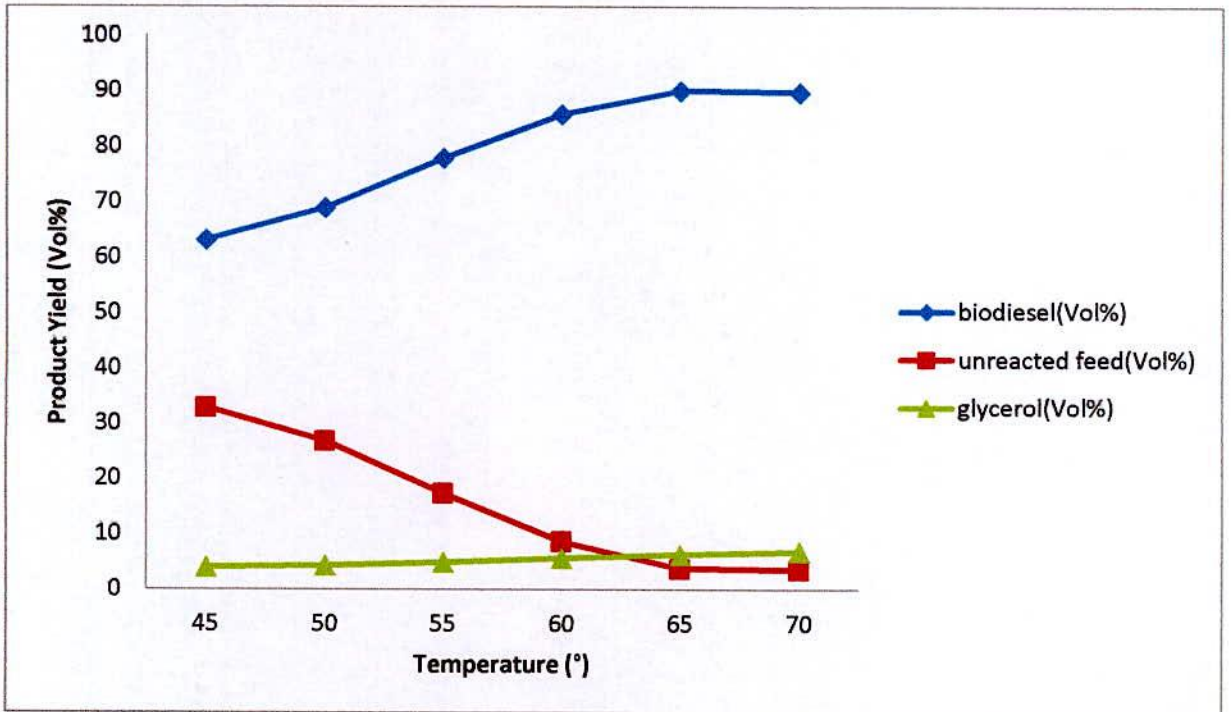
Figure 5.6: Effect of temperature on product yields of transesterification of castor oil using NaOH as catalyst with molar ratio= 1.02: 8.23



Figure 5.7: Effect of temperature on product yields of transesterification of castor oil using NaOH as catalyst with molar ratio= 0.96: 7.00

Figure 5.8: Effect of temperature on product yields of transesterification of castor oil using NaOH as catalyst with molar ratio= 0.98: 6.00



Figure 5.9: Effect of temperature on product yields of transesterification of castor oil using NaOH as catalyst with molar ratio= 1.02: 6.17

Figure 5.10: Effect of temperature on product yields of transesterification of castor oil using NaOH as catalyst with molar ratio= 1.02: 6.60
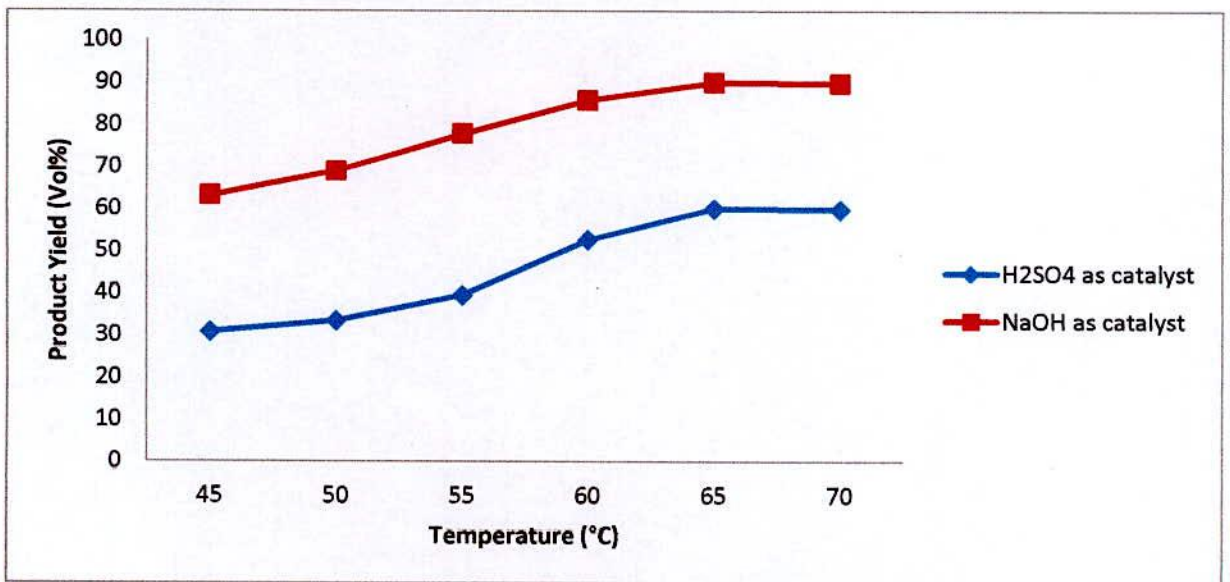


Figure 5.11: Effect of Catalyst on product yields with molar ratio= 1.02: 6.60
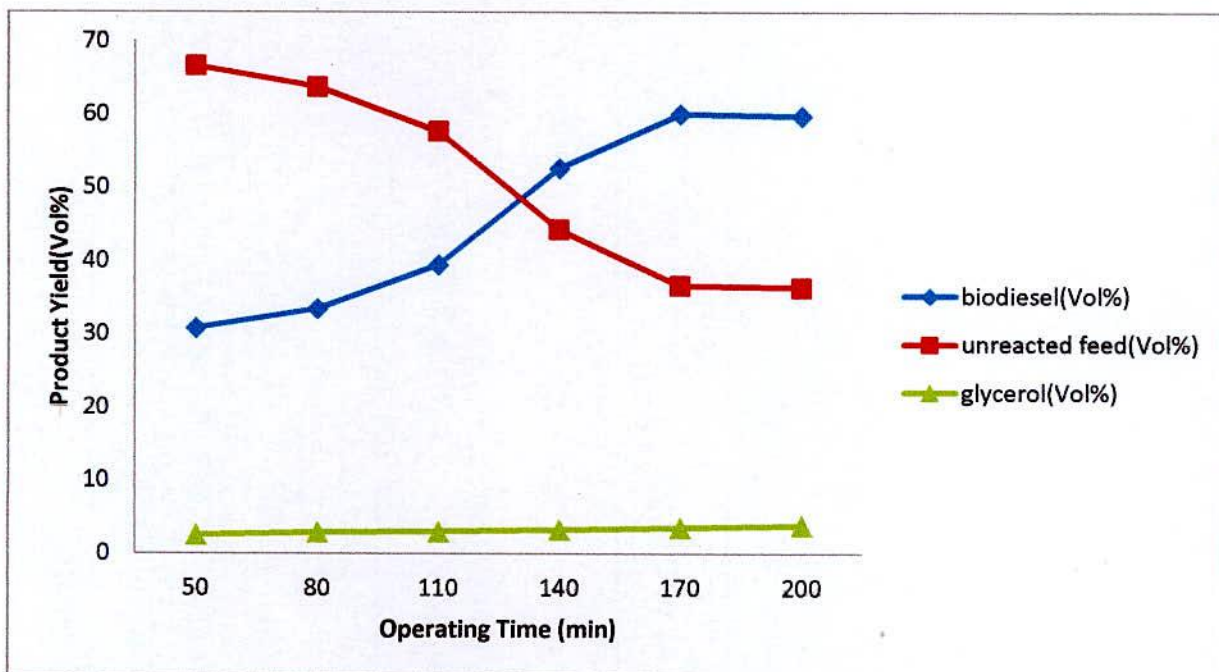
Figure 5.12: Effect of Operating Time on product yields using $H_2SO_4$ as catalyst with molar ratio= 1.02: 6.60
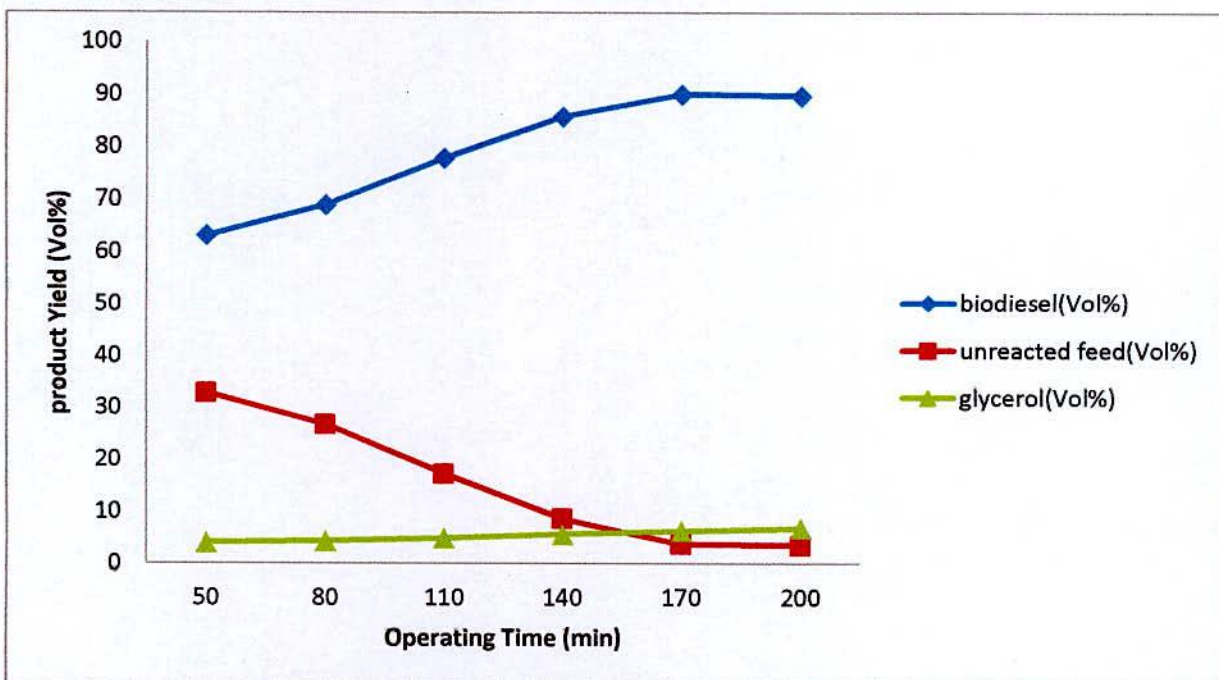


Figure 5.13: Effect of Operating Time on product yields using NaOH as catalyst with molar ratio= 1.02: 6.60

## 5.2 Comparison of biodiesel with biodiesel standards and petro-diesel standards:

Table 5.11: Meaning of symbol

| Symbol | Meaning of symbol |
|--------|-------------------|
| B20 | 20% biodiesel and 80% petro-diesel |
| B30 | 30% biodiesel and 70% petro-diesel |
| B70 | 70% biodiesel and 30% petro-diesel |
| B100 | 100% biodiesel |

Table 5.12: Meaning of symbol

| Symbol | Meaning of symbol |
|--------|-------------------|
| Biodiesel-1 | Biodiesel found from 1st experiment |
| Biodiesel-2 | Biodiesel found from 2st experiment |
| Biodiesel-3 | Biodiesel found from 3rd experiment |
| Biodiesel-4 | Biodiesel found from 4th experiment |
| Biodiesel-5 | Biodiesel found from 5th experiment |
| Biodiesel Standard | Standard value of Biodiesel as per D 6751 |
| Petro- Diesel Standard | standards Value of Petro-Diesel |

The properties of biodiesel were tested in laboratory of Petromax Refinery Ltd. at Mongla. The important properties of Biodiesel (methyl esters) are compared with biodiesel standards and petro-diesel standards. This biodiesel was blended with petro-diesel with different volumetric proportion. The results are presented in Table 5.13 to 5.17.

Table 5.13: Properties of Biodiesel-1

| Specification | B20 | B30 | B70 | B100 | Biodiesel standard | Petro-Diesel standard |
|---|---|---|---|---|---|---|
| Density(g/ml) @ 30°C | 0.832 | 0.845 | 0.891 | 0.920 | 0.88 | 0.820 Min 0.870 Max |
| Density(g/ml) @ 15°C | 0.837 | 0.856 | 0.895 | 0.925 | 0.90 | 0.820 Min 0.870 Max |
| Viscosity @ 40°C (mm²/s) | 1.92 | 3.05 | 7.45 | 8.68 | 1.9-6.0 | 1.3-4.1 |
| Pour Point (°C) | -19 | -14.5 | -9.5 | -14.70 | -15 to 10 | -35 to -15 |
| Cloud Point (°C) | -7.8 | -7.3 | -3.20 | -8 | -3 to 12 | -15 to 5 |
| Flash Point (°C) | 69.5 | 76 | 134 | 141 | 130 to 170 | 52 to 80 |
| Cetane Index | 46 | 47.2 | 57 | 62.5 | 47 to 65 | 40 to 55 |
| Copper strip corrosion | 1a | 1a | 1a | 1a | 1 Max | 1 Max |
| Carbon residue | 0.16 | 0.18 | 0.22 | 0.28 | 0.2 | 0.2 Max |
| Calorific Value (MJ/kg) | 41.20 | 40.08 | 36.50 | 35.20 | 39.76 | 43.40 |

Table 5.14: Properties of Biodiesel-2

| Specification | B20 | B30 | B70 | B100 | Biodiesel standard | Petro-Diesel standard |
|---|---|---|---|---|---|---|
| Density(g/ml) @ 30°C | 0.838 | 0.857 | 0.887 | 0.923 | 0.88 | 0.820 Min 0.870 Max |
| Density(g/ml) @ 15°C | 0.84 | 0.860 | 0.897 | 0.93 | 0.90 | 0.820 Min 0.870 Max |
| Viscosity @ 40°C (mm²/s) | 2.09 | 3.56 | 7.8 | 9.00 | 1.9-6.0 | 1.3-4.1 |
| Pour Point (°C) | -20.0 | -15.4 | -11.3 | -15.22 | -15 to 10 | -35 to -15 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Cloud Point (°C) | -8.34 | -7.85 | -3.43 | -8.65 | -3 to 12 | -15 to 5 |
| Flash Point (°C) | 70.8 | 77.2 | 136 | 156 | 130 to 170 | 52 to 80 |
| Cetane Index | 45.50 | 46.8 | 60.5 | 63.8 | 47 to 65 | 40 to 55 |
| Copper strip corrosion | 1a | 1a | 1a | 1a | 1 Max | 1 Max |
| Carbon residue | 0.18 | 0.19 | 0.24 | 0.31 | 0.2 | 0.2 Max |
| Calorific Value (MJ/kg) | 40.85 | 39.62 | 37.25 | 35.39 | 39.76 | 43.40 |

Table 5.15: Properties of Biodiesel-3

| Specification | B20 | B30 | B70 | B100 | Biodiesel standard | Petro-Diesel standard |
|---|---|---|---|---|---|---|
| Density(g/ml) @ 30°C | 0.827 | 0.843 | 0.874 | 0.905 | 0.88 | 0.820 Min 0.870 Max |
| Density(g/ml) @ 15°C | 0.838 | 0.857 | 0.88 | 0.915 | 0.90 | 0.820 Min 0.870 Max |
| Viscosity @ 40°C (mm²/s) | 2.8 | 3.66 | 7.05 | 8.75 | 1.9-6.0 | 1.3-4.1 |
| Pour Point (°C) | -18 | -11.4 | -7.6 | -14 | -15 to 10 | -35 to -15 |
| Cloud Point (°C) | -7.4 | -6.8 | -4 | -7.8 | -3 to 12 | -15 to 5 |
| Flash Point (°C) | 66.4 | 70 | 128 | 137 | 130 to 170 | 52 to 80 |
| Cetane Index | 45.8 | 47.0 | 58 | 61 | 47 to 65 | 40 to 55 |
| Copper strip corrosion | 1a | 1a | 1a | 1a | 1 Max | 1 Max |
| Carbon residue | 0.11 | 0.18 | 0.20 | 0.27 | 0.2 | 0.2 Max |
| Calorific Value (MJ/kg) | 40.6 | 40.10 | 38.30 | 35.34 | 39.76 | 43.40 |

Table 5.16: Properties of Biodiesel-4

| Specification | B20 | B30 | B70 | B100 | Biodiesel standard | Petro-Diesel standard |
|---|---|---|---|---|---|---|
| Density(g/ml ) @ 30°C | 0.826 | 0.842 | 0.873 | 0.887 | 0.88 | 0.820 Min 0.870 Max |
| Density(g/ml ) @ 15°C | 0.830 | 0.848 | 0.884 | 0.905 | 0.90 | 0.820 Min 0.870 Max |
| Viscosity @ 40°C (mm²/s) | 1.75 | 2.15 | 5.00 | 7.30 | 1.9-6.0 | 1.3-4.1 |
| Pour Point (°C) | -17 | -12.5 | -8.5 | -13 | -15 to 10 | -35 to -15 |
| Cloud Point (°C) | -7.9 | -5 | -2.5 | -6.5 | -3 to 12 | -15 to 5 |
| Flash Point (°C) | 65 | 71 | 126 | 144 | 130 to 170 | 52 to 80 |
| Cetane Index | 46.0 | 48.7 | 57 | 64.5 | 47 to 65 | 40 to 55 |
| Copper strip corrosion | 1a | 1a | 1a | 1a | 1 Max | 1 Max |
| Carbon residue | 0.15 | 0.17 | 0.20 | 0.24 | 0.2 | 0.2 Max |
| Calorific Value (MJ/kg) | 40.25 | 39.70 | 36.80 | 35.25 | 39.76 | 43.40 |

Table 5.17: Properties of Biodiesel-5

| Specification | B20 | B30 | B70 | B100 | Biodiesel standard | Petro-Diesel standard |
|---|---|---|---|---|---|---|
| Density(g/ml ) @ 30°C | 0.830 | 0.845 | 0.881 | 0.893 | 0.88 | 0.820 Min 0.870 Max |
| Density(g/ml ) @ 15°C | 0.834 | 0.845 | 0.885 | 0.902 | 0.90 | 0.820 Min 0.870 Max |
| Viscosity @ 40°C (mm²/s) | 1.82 | 2.38 | 5.86 | 7.50 | 1.9-6.0 | 1.3-4.1 |
| Pour Point (°C) | -20 | -13 | -9 | -14 | -15 to 10 | -35 to -15 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Cloud Point (°C) | -8 | -6 | -3 | -7 | -3 to 12 | -15 to 5 |
| Flash Point (°C) | 68 | 74 | 131 | 142 | 130 to 170 | 52 to 80 |
| Cetane Index | 44.8 | 47.5 | 56 | 60 | 47 to 65 | 40 to 55 |
| Copper strip corrosion | 1a | 1a | 1a | 1a | 1 Max | 1 Max |
| Carbon residue | 0.14 | 0.16 | 0.19 | 0.25 | 0.2 | 0.2 Max |
| Calorific Value (MJ/kg) | 40.19 | 39.90 | 37.19 | 34.89 | 39.76 | 43.40 |

## 5.3 Discussion

### 5.3.1 Product Analysis

Two types of products were obtained from transesterification of castor oil: Biodiesel and Glycerol. The product distributions obtained from transesterification of castor oil for temperature range of 45°C to 70°C at every 5°C are presented in Table 4.3 through 4.12 and Table 5.1 through 5.10.

### 5.3.2 Effect of Temperature and Catalyst on Product Yield of Castor oil

The effect of temperature on products yield obtained from castor oil is shown in Tables 5.1 to 5.10. The tests were performed at temperature range of 45°C to 70°C and data were collected at every 5°C interval. Five samples were tested. The results of these are plotted in Figure 5.1 to 5.5 ($H_2SO_4$ was used as catalyst) and Figure 5.6 to 5.10 (NaOH was used as catalyst). In both the cases two types of products which are biodiesel and glycerol were obtained.

It is observed that with the increase in temperature the biodiesel production rate increases until it reaches a maximum and then decreases. All the curves from Figure 5.1 to 5.5 show the similar nature. In first step, the result of which is shown in Figure 5.1 to 5.5. The maximum biodiesel yield of about 58%, 59%, 59%, 60% and 60% (by volume) can be obtained from the esterification of castor oil with $H_2SO_4$ catalyst at 65°C. The yield then decreases to 57.75%, 58.75%, 58.67%, 59.73%, and 59.73% (by volume) at a temperature of 70°C. In second step, the result of which is shown in Figure 5.6 to 5.10. The maximum biodiesel yield of about 85%, 87.67%, 87.87%, 90% and 90% (by volume) can be obtained from the transesterification of castor oil with NaOH catalyst.

### 5.3.3 Effect of Operating Time on Product Yield of Castor oil

The effect of operating time on the product yield is shown in Figure 5.12 for $H_2SO_4$ catalyst and in Figure 5.13 for NaOH catalyst for transesterification of castor oil. From Figure 5.12 to 5.13, it is observed that at low temperature ($<50°C$) reaction rate was very slow, more operating time was required to complete the conversion of castor oil to biodiesel and glycerol. At high temperature ($>50°C$) reaction rate was very fast, less operating time was required to complete the conversion of castor oil to biodiesel and glycerol.

### 5.4  Analysis of Biodiesel Properties

The tabular values shown in Table 5.13 to 5.17 are plotted on graphs. These are shown in Figure 5.14 to 5.20 and are discussed below:

### 5.4.1 Density

Density is the mass per unit volume. It was determined by digital density meter (Anton paar) according to ASTM D4052 test methods. Castor oil density was 0.944 g/ml at 30°C. Oil that is denser contains more energy. Biodiesel density is 0.893g/ml (at 30°C). Type of Biodiesel VS Density is shown graphically in Figure 5.14.
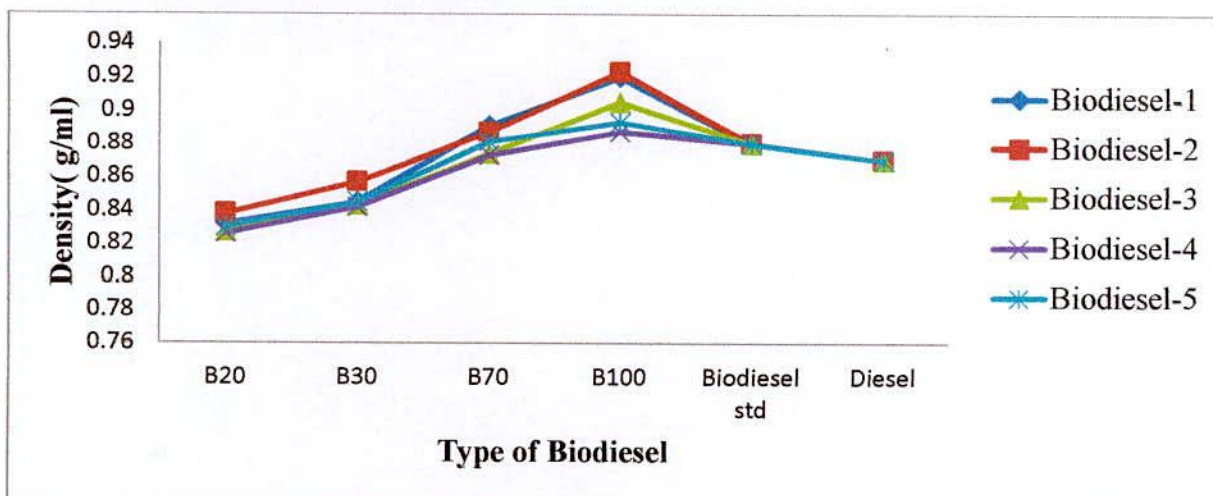


Figure 5.14: Type of Biodiesel VS Density and comparison with standard biodiesel

## 5.4.2 Kinematic Viscosity

It refers to the thickness of oil and is determined by measuring amount of time taken for a given measure of oil to pass through an orifice of a specified size. It affects injector lubrication and fuel atomization. Fuels with lower viscosity may not provide sufficient lubrication for injection pump resulting in wear and high viscosity tends to form larger droplet which can cause poor combustion and increased exhaust smoke and emission. It was determined using Glass Capillary Kinematic Viscometer according to ASTM D445 test methods. Castor oil has viscosity 20 times more than that of biodiesel. Its value is 154.678mm$^2$/s at 40°C and after Transesterification it is 7.5mm$^2$/s. Type of Biodiesel VS Viscosity is shown graphically in Figure 5.15.
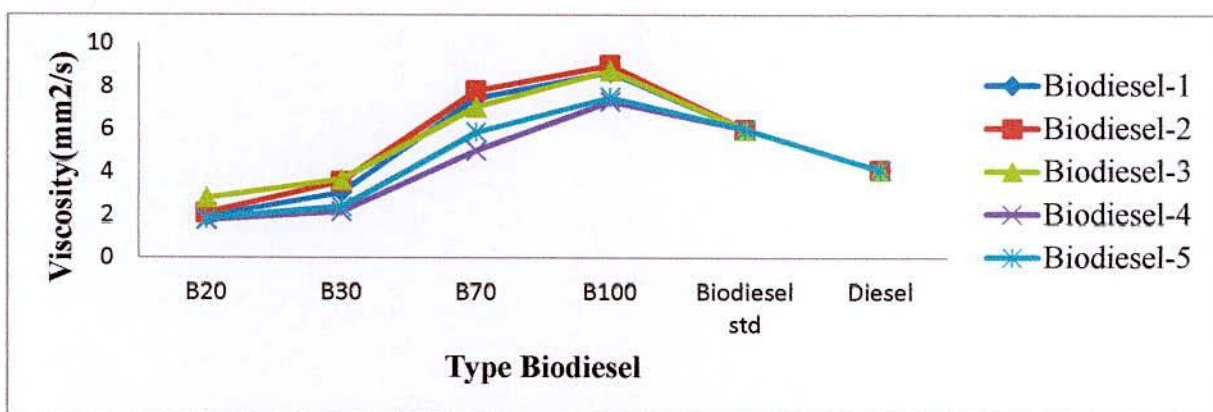
Figure 5.15: Type of Biodiesel VS Viscosity and comparison with standard biodiesel

## 5.4.3 Flash Point

It is the minimum temperature at which fuel will ignite (flash) on application of ignition source. It varies inversely with fuel's volatility. It was determined by Pensky Martens Closed Cup Tester (PMCC) according to ASTM D93 test methods. Castor Oil has its value 230°C and after Transesterification it is 142°C. Type of Biodiesel VS Flash point is shown graphically in Figure 5.16.
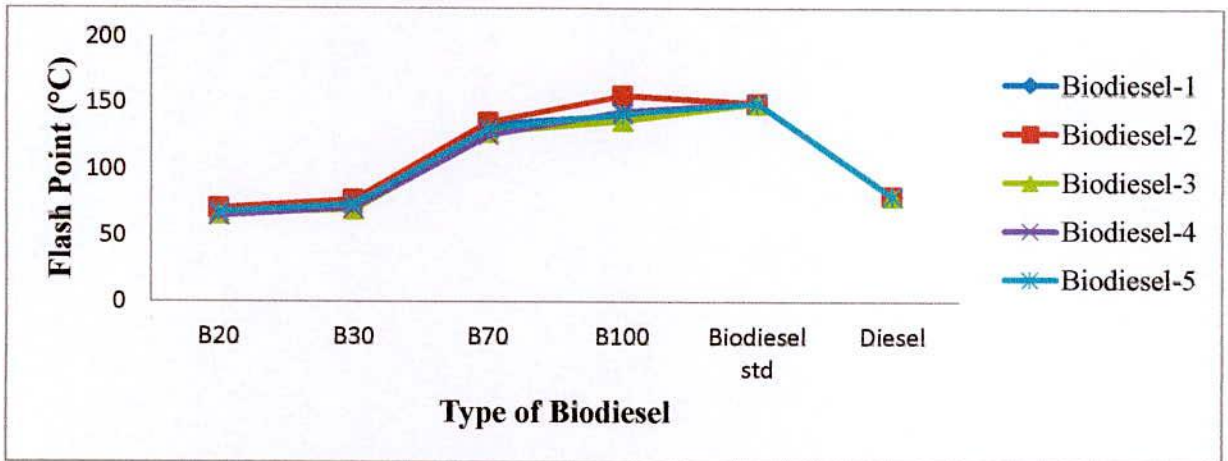
Figure 5.16: Type of Biodiesel VS Flash point and comparison with standard biodiesel

## 5.4.4 Cetane Index

It is the relative measure of interval between beginning of injection and auto-ignition of fuel. Higher number gives shorter delay interval and greater combustibility and lower number will result in difficult starting, noise and exhaust smoke. It was determined according to ASTM D976 test methods. Its value for biodiesel is 45 to 65. Type of Biodiesel VS Cetane Index is shown graphically in Figure 5.17.
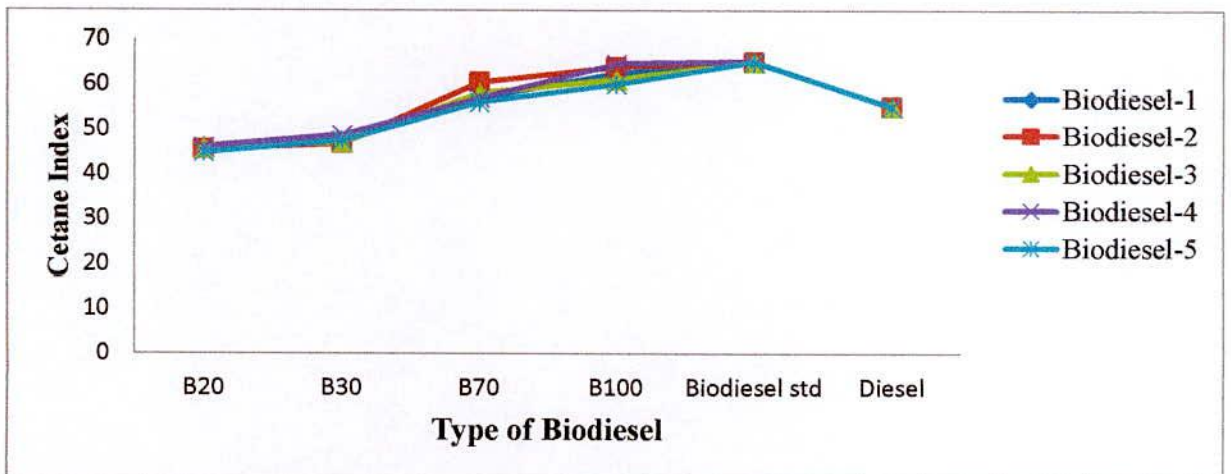


Figure 5.17: Type of Biodiesel VS Cetane Index and comparison with standard biodiesel

## 5.4.5 Pour Point

The pour point of a liquid is the temperature at which it becomes semi solid and loses its flow characteristics. Pour Point is the temperature at which diesel fuel becomes so thick that it will

no longer pour from a container. At this temperature the fuel is essentially unable to pump. Pour point is measured at intervals of 3°C. It was determined by pour point apparatus according to ASTM D97 test method. After Transesterification, the pour point of biodiesel is -14°C. Type of Biodiesel VS Pour Point is shown graphically in Figure 5.18.
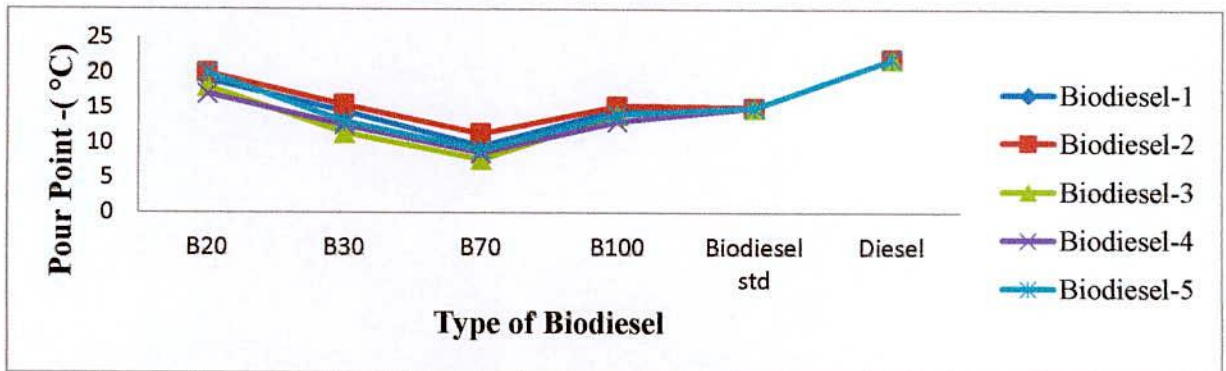


Figure 5.18: Type of Biodiesel VS Pour Point and comparison with standard biodiesel

### 5.4.6  Cloud-Point

The cloud point is the temperature at which wax crystals begin to form in a petroleum product as it is cooled. Cloud point indicates the tendency of the oil to plug filters or small orifices at cold operating temperatures. Cloud point is measured at intervals of 2°C. It was determined by Cloud point apparatus according to ASTM D2500 test methods.  After Transesterification, the cloud point of biodiesel is -7°C. Type of Biodiesel VS Cloud-Point is shown graphically in Figure 5.19.
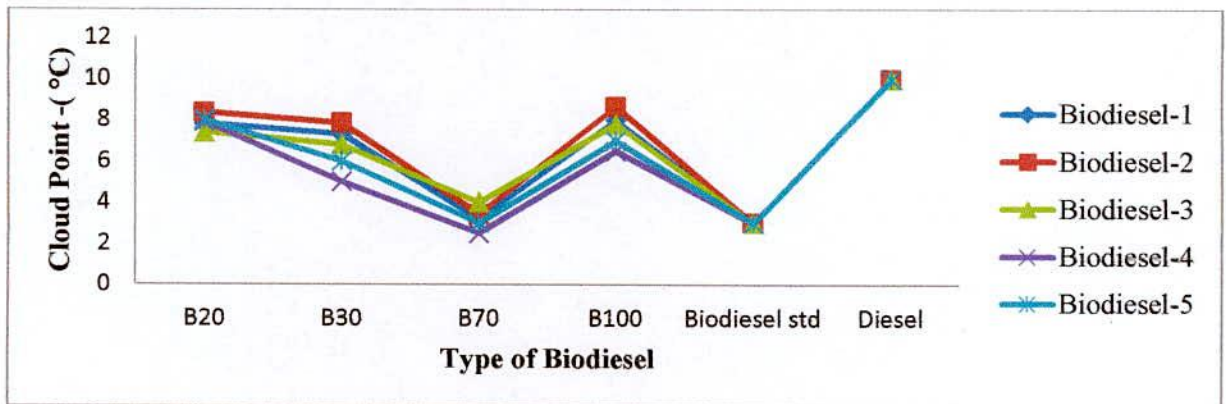


Fig 5.19: Type of Biodiesel VS Cloud-Point and comparison with standard biodiesel

### 5.4.7 Calorific Value

The calorific value of a fuel is the quantity of heat produced by its combustion at constant pressure and under "normal" ("standard") conditions (i.e. to $0^oC$ and under a pressure of 1.013 bar).The Calorific Value of diesel is 43.40 MJ/kg. After Transesterification, the Calorific Value of biodiesel is 34.89 MJ/kg. Type of Biodiesel VS Calorific Value is shown graphically in Figure 5.20.
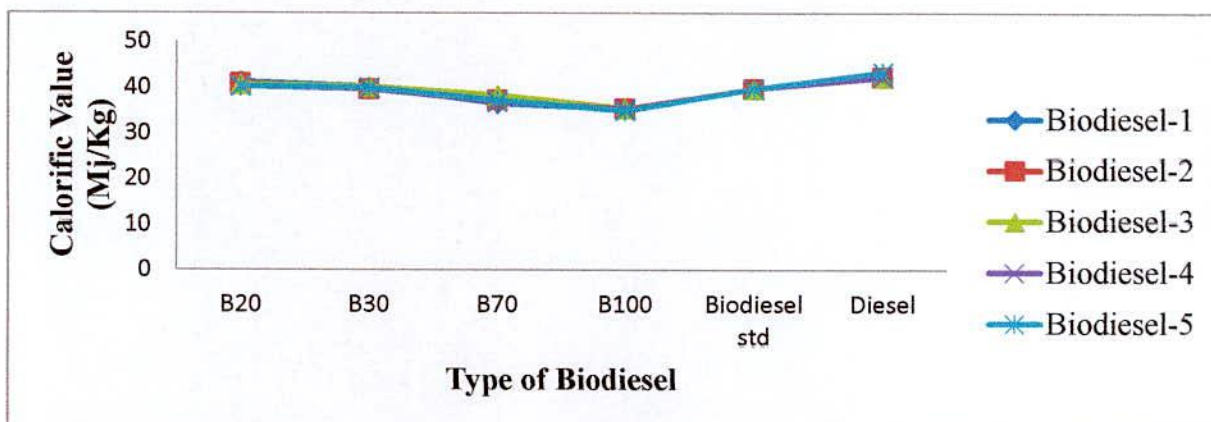


Figure 5.20: Type of Biodiesel VS Calorific Value and comparison with standard biodiesel

### 5.4.8 Compositional Group Fourier Transform Infra-Red (FTIR) Spectroscopy

The test carried out at CARS, University of Dhaka. The FTIR results are shown in Table 5.18 to 5.19.

### Chemical Composition Group Analysis

The absorption frequency spectra representing the functional group composition analysis of the Biodiesel are presented in Figure 5.21 for B100 (B5) and Figure 5.22 for B70. Figure 5.21 to 5.22 are summarized in figure 5.23.

The strong absorbance peaks of C-H vibrations are between 2850-2960 cm$^{-1}$ and 1325-1600 cm$^{-1}$ which indicate the presence of alkanes. The absorbance peaks is between 1690-1740 cm$^{-1}$ and 1170-1300 represent the C-O stretching vibration, indicates the presence of primary, secondary and tertiary alcohols, phenol, esters and ethers.

The strong absorbance peaks between 3000-3650 $cm^{-1}$ represent the O-H stretching vibration; indicate the presence of alcohol, phenol, carboxylic acid. The absorbance peaks 3500-3700 cm⁻1 symbolize the N-H vibration which specifies the alkynes and amines.

From the FTIR analysis it is revealed that the biodiesel obtained from Castor Oil mostly the hydrocarbon compounds.

Table 5.18: The FTIR Functional Groups and the Indicated Compound of Biodiesel.

| Absorbance Range (cm-1) | Functional Group | Class of Compound | B100 (B5) |
|---|---|---|---|
| 3500 - 3700 | N-H | Amines | 3653 |
| 3200-3650 | O-H | Alcohol, phenol, | 3381 |
| 3000 - 3200 | O-H | Carboxylic Acid | 3007 |
| 2850-2960 | C-H | Alkanes and Alkyl group | 2856, 2926 |
| 1690-1740 | C-O | Aldehyde | 1737 |
| 1450-1600 | C-C | Alkanes | 1454 |
| 1325-1425 | C-H | Alkanes | 1361 |
| 1170-1300 | C-O | Primary, secondary and tertiary alcohols, phenol, esters and ethers | 1173, 1248 |
| 1000-1150 | C-H | Alkanes | 1038, 1099 |
| 875-950 | HC≡CH | Alkynes | 920 |
| 600-950 | | Aromatic compound | 723, 862 |

Comment;
B-5

Date/Time; 2/14/2017 2:02:40 PM
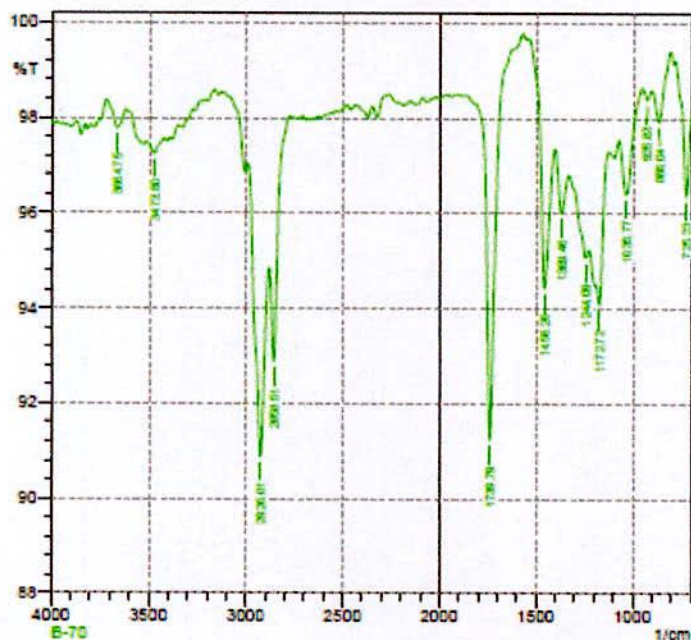No. of Scans;
Resolution:
Apodization;

Sample: B100 (B5)

Figure 5.21: FTIR spectra of Biodiesel (B100) derived from castor oil.

Table 5.19: The FTIR Functional Groups and the Indicated Compound of Biodiesel (B70).

| Absorbance Range (cm⁻1) | Functional Group | Class of Compound | B70 |
|---|---|---|---|
| 3500 - 3700 | N-H | Amines | 3665 |
| 3200-3650 | O-H | Alcohol, phenol, | 3473 |
| 3000 - 3200 | O-H | Carboxylic Acid | - |
| 2850-2960 | C-H | Alkanes and Alkyl group | 2858, 2926 |
| 1690-1740 | C-O | Aldehyde | 1739 |

| 1450-1600 | C-C | Alkanes | 1456 |
|---|---|---|---|
| 1325-1425 | C-H | Alkanes | 1369 |
| 1170-1300 | C-O | Primary, secondary and tertiary alcohols, phenol, esters and ethers | 1172, 1244 |
| 1000-1150 | C-H | Alkanes | 1036 |
| 875-950 | HC≡CH | Alkynes | 925 |
| 600-950 | | Aromatic compound | 725, 866 |



Sample: B70

Figure 5.22: FTIR spectra of Biodiesel (B70) derived from castor oil.

Sample: Combined Graph of B100 and B70.

Figure 5.23: Combined FTIR spectra of Biodiesel derived from castor oil.

### 5.4.9 P^H Value

$P^H$ was tested by digital $P^H$ meter. $P^H$ of B100 was found nil.

### 5.4.10 Moisture content

Moisture content was determined by Aquamax KF Coulometric in Laboratory of Pertomax Refinery Limited. Moisture content of B100 was found 16277.41 ppm.

## 5.5 Cost Analysis for Present Project

### 5.5.1 Capital cost

Capital costs are fixed, one-time expenses incurred on the purchase of land, buildings, construction, and equipment used in the production of goods or in the rendering of services. Put simply, it is the total cost needed to bring a project to a commercially operable status. Whether a particular cost is capital or not depend on many factors such as accounting, tax laws, and materiality.

The cost analysis is based on the following assumptions:

Equipment expected life = 5 years

4 run per day and 300 working days per year.

The details of capital cost are shown in Table 5.18:

Table 5.20: Components of Capital Cost

| Name of material | Amount taken | Unit Price Tk. | Total Cost (Tk.) |
|---|---|---|---|
| Reactor | 1 pc | 5580 | 5580 |
| Heater Coil | 1 pc | 1200 | 1200 |
| Electric Motor (0.5hp) | 1pc | 3700 | 3700 |
| Temperature controller | 1 pc | 1434 | 1434 |
| Thermocouple | 1 pc | 200 | 200 |
| Magnetic contactor | 1 pc | 850 | 850 |
| Steel box | 1 pc | 1000 | 1000 |
| MS angle | 13 kg | 50 | 650 |
| Measuring Cylinder | 2 pc | 780 | 780 |
| Washing vessel | 1 pc | 5000 | 5000 |
| Pressure safety valve | 1pc | 2000 | 2000 |
| Pressure Gage | 1 pc | 900 | 900 |
| Level Gage | 2 set | 1187.5 | 2375 |
| Ball Valve | 7 pcs | 400 | 2800 |
| Total Capital cost for 5 yrs | | | 28469 |
| Total capital cost per yr = Tk. 5693.8 | | | |

## 5.5.2 Operating cost

Operating costs are the expenses which are related to the operation of a business, or to the operation of a device, component, and piece of equipment or facility.

The cost analysis for the present project is based on one single run

Castor oil = 3L @ Tk.50 =Tk.150

Methanol = 0.75L @ Tk.250 = Tk.187.5

Sulfuric acid = 0.05L @ Tk.55 = Tk. 2.75

NaOH =16g @ Tk.80 = Tk. 1.28

Total Electricity required for transesterification of 3 L castor oil = 1.5 kWh

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Cost for electricity = Tk. 4.5 /kWh.

Charge for electricity = $4.5 \times 1.5$ = Tk.6.75

Labour = 3 hr@ Tk. 50 = Tk.150

Miscellaneous = Tk. 10

Total operating cost per batch =Tk.508

Total annual operating cost = $300 \times 4 \times 508$ = Tk.609600

Total Cost = Total Annual capital cost + Total Annual operation cost

$$= Tk. (5693.8 + 609600) = Tk.615293.8$$

## 5.5.3 Payback Period

Payback period is the time in which the initial cash outflow of an investment is expected to be recovered from the cash inflows generated by the investment. It is one of the simplest investment appraisal techniques.

$$\text{Payback Period} = \frac{\text{Initial Investment}}{\text{Cash Inflow per Period}}$$

Calculation:

Operation time: 3 hrs per batch and 4 batches per day

Yield of biodiesel per batches =3.38 L

Annual product yield of biodiesel = 3.38 L/run × 4 runs /day ×300 days/ yr

$$=4056 \text{ L/yr}$$

Price of biodiesel = Tk.60/ L

Total annual value of product = Tk. (4056 × 60) =Tk.243360

Payback period = (615293.8) ÷ (243360) = 2.53 yrs

Based on present calculation, the payback period is feasible. If the feed materials are in large scale then Payback period could be decrease. On the other hand the important environment issues are the vital factor to consider operating cost.

# CHAPTER VI

## CONCLUSIONS AND RECOMMENDATIONS

Biodiesel was produced from non-edible castor oil by two-step method. Crude castor oil was transesterified using $H_2SO_4$ and NaOH as catalyst and methanol to form biodiesel .The conversion was 90% at 65°C. The fuel properties like Density, Viscosity, Flash point, Pour point, Cloud point, Cetane Index, Copper strip corrosion, Carbon residue, Calorific value of the transesterified product (biodiesel) was compared with accepted biodiesel standards i.e ASTM D6751.

The viscosity of biodiesel is nearer to that of petro-diesel. The properties of the B100 combustible and its B20, B30 and B70 mixtures are comparable to those of petroleum diesel and acceptable within what is specified for biodiesel in the ASTM D 6751 standard.

The properties of B70 are match with Biodiesel standard. We can use B70 in diesel engine.

Biodiesel is more lubricating than that of petro-diesel, so it increases the life of engines, biodegradable, non-toxic. High flash point and hence safe to transport and store, Oxygenated fuel and hence clean burning.

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