OPTIMIZATION OF BIODIESEL PRODUCTION FROM YELLOW OLEANDER AND CASTOR OILS AND STUDIES OF THEIR FUEL PROPERTIES

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BY

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Declaration

I declare that the work in this dissertation entitled **"*Optimization of biodiesel production from Yellow oleander and Castor oils and studies of their fuel properties*"** has been carried out by me in the Department of Chemistry, A.B.U. Zaria. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

Ibrahim Abdulkadir Signature Date

Certification

This dissertation entitled "OPTIMIZATION OF BIODIESEL PRODUCTION FROM YELLOW OLEANDER AND CASTOR OILS AND STUDIES OF THEIR FUEL PROPERTIES" by Ibrahim ABDULKADIR meets the regulations governing the award of the degree of Master of Science in Analytical Chemistry of Ahmadu Bello University Zaria, and is approved for its contribution to knowledge and literary presentation.

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Acknowledgement

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Dedication

This research work is dedicated to my Mother, Mrs Mairo Abdulkadir.

Abstract

The optimization of biodiesel production from two non-edible oils and studies of their fuel and biodegradability properties was carried out. The two oil feedstocks (Yellow oleander and Castor oils) were extracted from their seeds using an oil expeller and their physicochemical properties such as iodine value, moisture content, saponification value, acid value, viscosity, specific gravity and refractive index were determined. Most of these properties were within the acceptable limit of American Standard Testing Method (ASTM). The methyl esters were optimized using methanol as solvent and by varying conditions like reaction temperature, reaction time, type and concentration of catalyst, molar ratio of methanol and oil. For maximum bio diesel production, the transesterification reaction showed that the concentration of alkali catalyst was 0.8 % sodium hydroxide, 0.33 %v/v alcohol/oil ratio, 1 hr reaction time, 60 ^{0}C temperature and excess alcohol 150 %v/v. Optimized parameters for production of biodiesel through base catalyzed transesterification gave maximum yield of 96 % and 98 % for yellow oleander and castor oil respectively. The Yellow Oleander Methyl Ester (YOME) and Castor Oil Methyl Ester (COME) and their diesel blends were comparatively analysed for fuel properties such as flash point, relative density, kinematic viscosity, calorific value, distillation, sulphur, phosphorous, water content, cetane number and acid number . The methyl ester of yellow oleander was found to have properties closer to ASTM D 6751 fuel specifications than that of castor oil. It is further observed from the results that the biodiesel from yellow oleander and castor oil are environmentally friendly, such that after spillage, it will take about 28 days for them to have biodegradability of 82.4 and 87.3 for YOME and COME respectively. This is an advantage over petro-diesel which was found to have biodegradability of 25.29 in 28 days.

Table of Contents

CONTENT	PAGE
Cover page	i
Title	ii
Declaration	iii
Certification	iv
Acknowledgement	v
Dedication	vi
Abstract	vii
Table of Contents	viii
List of Plates	xiv
List of Tables	xv
List of Figures	xvi
List of Appendices	xvii
List of Abbreviations and Symbols	xviii

CHAPTER ONE

1.0	**INTRODUCTION**	**1**
1.1	**Statement of Research Problem**	**6**
1.2	**Justification for Research**	**7**
1.3	**Aims and Objectives**	**8**

CHAPTER TWO

2.0 LITERATURE REVIEW 10

2.1 Biodiesel as an Alternative to Petroleum Diesel 10

2.2 Performance Characteristics of Biodiesel 11

2.3 Biodiesel Storage Stability 17

2.4 Biodiesel Production 19

2.5 Optimization of Transesterification Process 20

2.5.1 Catalyst type and concentration 20

2.5.2 Effect of free fatty acid and moisture 22

2.5.3 Effect of reaction time and temperature 24

2.5.4 Mixing intensity 25

2.5.5 Molar ratio of alcohol to oil and type of alcohol 25

2.5.6 Effect of using organic solvents 26

2.6 Transesterification under different Conditions 28

2.7 Biodiesel Properties 29

2.7.1 Flash point 30

2.7.2 Viscosity 31

2.7.3 Cloud and pour point 32

2.7.4 Specific gravity 33

2.7.5 Calorific value 33

2.7.6 Sulphur 34

2.7.7 Cetane number 35

2.7.8 Carbon residue 36

CHAPTER THREE

3.0 MATERIALS AND METHODS 37

3.1 Samples 37

3.2 Preparation of Solutions 37

3.2.1 Preparation of 1% v/v phosphoric acid solution 37

3.2.2 Preparation of 1 M sodium hydroxide solution `37

3.2.3 Preparation of 1M sulphuric acid solution 38

3.2.4 Preparation of 0.1M potassium hydroxide solution 38

3.2.5 Preparation of 0.8 % w/w sodium hydroxide solution 38

3.2.6 Preparation of 10 % potassium iodide solution 38

3.2.7 Preparation of 0.1N sodium thiosulphate solution 39

3.2.8 Preparation of 0.1M hydrochloric acid solution 39

3.3 Sample Collection and preparation 39

3.4 Extraction 40

3.5 Refining Process 40

3.5.1 De-waxing 40

3.5.2 Degumming 40

3.5.3 Neutralizing 41

3.6 Determination of Acid Value of the Oils 41

3.7 Determination of Percentage Free Fatty Acid Content 41

3.8 Transesterification 42

3.8.1 Acid esterification (Step I) 42

3.8.2 Alkaline transesterification (Step II) 42

3.9 Test Methods for Physico-Chemical Properties **46**

3.9.1 Kinematic viscosity 46

3.9.2 Density/API gravity measurement 46

3.9.3 Acid value 46

3.9.4 Iodine value 47

3.9.5 Peroxide value 48

3.9.6 Pour point 48

3.9.7 Cloud point 50

3.9.8 Sulphur content 50

3.9.9 Water content 51

3.9.10 Saponification value 51

3.9.11 Refractive index 52

3.9.12 Free and total glycerin 52

3.9.13 Flash point 53

3.9.14 Distillation characteristics 53

3.9.15 Cetane index 55

3.10 Biodegradation Study of the Biodiesels **55**

3.11Fuel Blends Preparation **56**

CHAPTER FOUR

4.0 RESULTS **58**

4.1 Result of Phytochemical Properties of Yellow Oleander and Castor oils **58**

4.2 Result of Process Optimization **59**

4.2.1 Result of acid esterification (Step I) 57

4.2.2 Result of transesterification (Step II) 65

4.3 Result of Characterization of Biodiesel Produced 71

4.4 Effect of Blending on fuel properties of the Biodiesels 73

4.5 Result of Distillation of Yellow Oleander and Castor oil methyl esters 79

4.6 Result of Biodegradability studies of Biodiesel 81

CHAPTER FIVE

5.0 DISCUSSION OF RESULTS 83

5.1 Percentage oil yield 83

5.2. Physiochemical Properties of Yellow oleander and Castor oil 83

5.3 Process Optimization 85

5.3.1 Acid esterification (Step I) 85

5.3.2 Transesterification (Step II) 85

5.4 Characterization of Biodiesel produced 86

5.5 Effect of Blending on Fuel properties of the Biodiesels 88

5.6 Distillation Characteristic of the Biodiesels produced 89

5.7 Biodegradability of the Biodiesels 89

CHAPTER 6

6.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS 91

6.**1 Summary 91**

6.2 Conclusion 92

6.3 Recommendations **93**

REFERENCES **94**

APPENDICES **102**

List of Plates

Plate I: Castor plant	3
Plate II: Thevetia plant	5
Plate III: Biodiesel production setup	43
Plate IV: Separation and washing of biodiesel derived from non-edible oil	45
Plate V: Cloud and pour point apparatus	49
Plate VI: Flash point apparatus	54

List of Tables

Table 2.1: Properties of biodiesel produced from several feed stocks 12

Table 3.1 Nomenclature and composition of various test fuels 57

Table 4.1: Result of phytochemical properties of yellow oleander and castor oils 59

Table 4.2: Characterization of biodiesel produced 72

Table 4.3: Distillation of biodiesel from yellow oleander and castor oil 80

List of Figures

Fig 4.1: Effect of temperature on yield of esterified oil at constant methanol/oil ratio 61

Fig 4.2: Effect of reaction time on yield of esterified oil at constant methanol/oil ratio 62

Fig 4.3: Effect of acid catalyst on yield of esterified oil at constant methanol/oil ratio 63

Fig 4.4 Effect of temperature on acid value at constant methanol/oil 64

Fig 4.5: Effect of temperature on biodiesel yield 66

Fig 4.6: Effect of methanol/oil ratio on methyl ester yield at constant temperature 67

Fig 4.7: Effect of percentage of excess alcohol on ester yield at constant temperature 68

Fig 4.8: Effect of reaction time on ester yield at constant temperature 69

Fig 4.9: Effect of concentration of alkali catalyst and methyl ester at constant temperature 70

Fig 4.10: Variation of TAN with increasing proportion of blend 74

Fig 4.11: Variation of viscosity with increasing proportion of blend 75

Fig 4.12: Variation of specific gravity with increasing proportion of blend 76

Fig 4.13: Variation of flash point with increasing proportion of blend 77

Fig 4.14: Variation of calorific value with increasing proportion of blend 78

Fig 4.15: Biodegradability of petro diesel and biodiesel from yellow oleander and castor oil after 28 days 82

List of Appendices

Appendix I: Effect of temperature (^{0}C) on yield of esterified oil at constant methanol/oil ratio 102

Appendix II: Effect of reaction time (hr) on yield of esterified oil at constant methanol/oil ratio 103

Appendix III: Effect of % of acid catalyst on yield of esterified oil at constant methanol/oil ratio 104

Appendix IV: Effect of temperature on acid value at constant methanol/oil ratio 105

Appendix V: Effect of temperature on biodiesel yield from yellow oleander and castor oil using NaOH catalyst 106

Appendix VI: Effect of methanol/oil ratio on metyl ester yield at constant temperature 107

Appendix VII: Effect of % of excess alcohol on ester yield at constant 108

Appendix VIII: Effect of reaction time on ester yield at constant temperature 109

Appendix IX: Effect of concentration of alkali catalyst on yield of methyl ester at constant temperature 110

Appendix X: Variation of TAN with increasing proportion of blend 111

Appendix XI: Variation of viscosity with increasing proportion of blend 112

Appendix XII: Variation of specific gravity with increasing proportion of blend 113

Appendix XIII: Variation of flash point with increasing proportion of blend 114

Appendix XIV: Variation of calorific value with increasing proportion of blend 115

Appendix XVI: Biodegradability of biodiesel from Yellow oleander and castor oil after 28 days 116

List of Abbreviations and Symbols

AOAC	American Oil Association of Chemist
AOCS	American Oil Chemist's Society
ASTM	American Standard Testing materials
B2	2% Biodiesel and 98% Diesel
B5	5% Biodiesel and 95% Diesel
B7	7% Biodiesel and 93% Diesel
B10	10% Biodiesel and 90% Diesel
B20	20% Biodiesel and 80% Diesel
B40	40% Biodiesel and 60% Diesel
B60	60% Biodiesel and 40% Diesel
B80	80% Biodiesel and 20% Diesel
B100	100% Biodiesel and 0% Diesel
CI	Compression Ignition
COME	Castor Oil Methyl Ester
CO	Carbon monoxide
CSO	Castor Seed Oil

FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC-MS	Gas Chromatography Mass spectroscopy
HC	Hydrocarbon
ISO	International Standard Organization
NAOME	Sodium methoxide
OPEC	Organization of Petroleum Exporting Countries
PAHs	Poly Aromatic hydrocarbons
PM	Particulate Matter
TAN	Total Acid Number
VOs	Vegetable Oils
YOME	Yellow Oleander Methyl Ester
YOSO	Yellow Oleander Seed Oil

CHAPTER ONE

1.0 INTRODUCTION

The world energy sector depends on the petroleum, coal and natural gas reservoirs to fulfill its energy requirements (Meher *et al.*, 2006). Nigeria is traditionally an energy-deficient country which exports above 70% of its crude oil production. The country is dependent upon import of petroleum products to sustain its growth. Diesel fuel plays an essential function in the industrial economy of Nigeria. The fuel is used in heavy trucks, city transport buses, electric generators, farm equipment etc. (Anjana, 2000). However, diesel engine also emits various forms of pollutants into the environment which can endanger human health and damage the ecological environment (Antolin *et a.l,* 2002). It is therefore essential that the world extend its interest towards new sources of energy. A relatively new alternative that is currently booming worldwide is fuel obtained from renewable resources or biofuel. Biofuels are well suited for decentralized development i.e can be utilised to meet the needs for social and economic progress, especially in rural communities where fossil fuels may be difficult or expensive to obtain (Nwafor and Nwafor, 2000; Ezeanyananso *et al.*, 2010).

Amongst the various alternative fuels which could match the combustion features of diesel oil and can be easily adapted for use in existing engine technologies with or without any major modifications is biodiesel. Biodiesel fuel produced from vegetable oils (both edible and non edible) or animal fats is one of the promising possible sources that can be substituted for conventional diesel fuel and produces favourable effects on the environment. Biodiesel is recommended for use as a substitute for petroleum diesel

mainly because it is a renewable, domestic resource with an environmentally friendly emission profile and is readily available and biodegradable (Zhang *et al.,* 2003).

The research and use of biodiesel fuel as an alternative started in the 1980's and the reason was the diesel crisis caused by the reduction of petroleum production by the Organization of Petroleum Exporting Countries (OPEC) and the resultant price hike. The biodiesel produced from locally available resources offer a great promise for future application in Nigeria as it can help in attaining much needed energy security and being environment friendly, will help to conform to stricter emission norms (Ezeanyananso, 2010).

Castor plant ***(****Ricininus communis****)***

Ricinus communis (Plate I) is a species that belongs to the Euphorbiaceae family and it is commonly known as castor oil plant, and Palma christi. Castor oil is possibly the plant oil industry's most underappreciated asset. It is one of the most versatile of plant oils, being used in over ten diverse industries.

Owing to its unique chemical composition and structure, castor oil can be used as the starting material for producing a wide range of end-products such as biodiesel, lubricants and greases, coatings, personal care and detergent, surfactants, oleo chemicals e.t.c. Compared to many other crops, castor crop requires relatively fewer inputs such as water, fertilizers and pesticides. The crop can also be grown on marginal land, thus providing an excellent opportunity for many regions of the world to utilize their land resources more productively (Dokwadanyi, 2011). The plant prefers well-drained moisture relative clay or sandy loan in full sun requires a rich soil and day time temperature above 20^{o}C for



Plate I: Castor plant

seedling to grow well. Castor is native to tropical Africa but it grows widely in Nigeria as weed it can be found in Borno, Sokoto, Jos, Zaria and so many other places in the country (Dokwadanyi, 2011). Though, it has been reported that the plants is not properly exploited, however a fiber for making ropes can be obtained from its stem. The growing

plant is said to repel flies and mosquitoes when grown in the garden and it is also said to rid it of moles and nibbling insect, while the leaves have insecticidal properties. (Abdulkareem *et al*, 2012).

Thevetia plant (*Thevetia peruviana)*

Thevetia peruviana (Plate II) is an ever – green ornamental dicotyledonous shrub that belongs to Apocyanaceae family (Dutta, 1964). It is commonly found in the tropics and sub – tropics but it is native to Africa, Central and South America. It grows to about 10 – 18 feet high, the leaves are spirally arranged, linear and about 13 – 15 cm in length. There are two varieties of the plant, one with yellow flowers, yellow oleander, and the other with purple flowers, nerium oleander. Both varieties flower and fruit all the year round providing a steady supply of seeds. Grown as hedges, they can produce between 400 – 800 fruits per annum depending on the rainfall pattern and plant age. The flowers are funnel-like with petals that are spirally twisted. The fruits are somewhat globular, with fleshy mesocarp and have a diameter of 4 – 5 cm. The fruits are usually green in colour and become black on ripening. Each fruit contains a nut which is longitudinally and transversely divided. The fruit contains between one to four seeds in its kernel, and the plants bears milky juice in all organs. In Nigeria, *Thevetia peruviana* has been grown for over fifty years as an ornamental plant in homes, schools and churches by missionaries



Plate II: Thevetia plant (yellow oleander)

and explorers (Ibiyemi *et al.,* 2002). All parts of the plant are toxic, due to the presence of glycosides. The toxicity of the glycoside is reflected in the accidental poisonings that occur among children that feed on the seed of the plants (Brewster 1986; Shaw and Pearn 1979). Some adults have reportedly died after consuming oleander leaves in herbal teas (Haynes *et al.,* 1985). According to Saravanapavanatha (1985), the kernel of about ten fruits may be fatal to an adult while kernel of one fruit may be fatal to children. Generally, small children and livestock are at higher risk of *Thevetia peruviana* poisoning Livestock poisoning after consuming thevetia has been reported by various workers. For instance Singh and Singh (2002) reported that leaf, stem and bark extracts of the plant killed fish. These extracts together with seed kernel extract also caused poisoning symptoms and death of albino rats (Oji and Okafor, 2000). Pahwa and Chartterjee (1990) reported 80 and 90% mortality of rats that were fed on 20 and 30% kernels of thevetia seed after ten days of feeding.

1.1 Statement of Research Problem

The use of vegetable oil for biodiesel production may result in increases in price of food or lead to food shortages (Ezeanyanaso *et al.,* 2010). Fortunately, non-edible vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative, with no competing food uses. Crude non-edible oils however have high free fatty acid (FFA) content, which affects biodiesel yield and capital cost. These oils can be pre-refined by reducing the free fatty acid content (FFA) using esterification and saponification processes. The fuel properties of biodiesel differ from those of petro-diesel fuels. This

implies that different engine performance and emissions will occur when biodiesel is used in diesel engines (Carraretto *et al.*, 2004).

Compared to petroleum-based diesel, the high cost of biodiesel is a major barrier to its commercialization; its cost is 150% more than that of petroleum-based diesel depending on feedstock used. Approximately 70-95% of the total biodiesel production cost arises from the cost of feedstock, solvent and refining process of the crude oil (Hass *et al*., 2006; Umer and Farooq, 2008).

Previous work on biodiesel has not quantified the biodegradability of Castor oil biodiesel. Furthermore, work is still ongoing by scientists on better methods of optimization of Biodiesel.

1.2 Justification for Research

Energy is the main driver of socio-economic growth of any nation. It plays a vital role in the overall frame work of development worldwide. Energy is an indispensable commodity and all aspect of human activities is hinged to it, It is also as a factor of production whose cost directly affects price of other goods and services (OPEC, 1994). Access to energy has been described as a key factor in industrial development and in providing vital services that improve the quality of life as well as the engine of economic progress (Singh and Sooch, 2004).

Diesel fuels produced from vegetable oils have practically no sulphur content, no green house gases emissions especially with CO_2, offer no storage difficulty, and they have excellent lubrication properties. Moreover, vegetable oils, yielding trees absorb more carbon dioxide from the atmosphere on burning (Erhan and Sharma, 2006). Hence,

diesel fuels essentially help to alleviate the increasing carbon dioxide content in the atmosphere. With this development, there has been a renewed focus on vegetable oils to make biodiesel fuels (Kim *et al*., 2004).

The substitution of diesel oil by renewable fuels produced within the country would generate higher foreign exchange savings, even for the major oil exporting countries like Nigeria. Therefore developing countries can use this kind of project not only to solve their environmental problems but also to improve their economy (Ezeanyananso *et al.*, 2010). There is need for the production of biodiesel using a cheaper reagent, which contributes to the reduction of capital, and manufacturing cost. Furthermore, more investigations are needed about the fuel properties of biodiesels, diesel fuels and their blends before using in a diesel engine (Hass *et al*., 2006).

1.3 Aims and Objectives

The aim of this research is to produce biodiesel from non-edible oils, optimize methods and compare physico-chemical properties of the biodiesels. Specific objectives are to:

I. extract the oil from yellow oleander and castor plant using an oil press machine;

II. prepare biodiesels by transesterification;

III. optimize the production process by varying reaction temperature, reaction time, concentration of catalyst and molar ratio of methanol/oil;

IV. blend the biodiesels with petro-diesel to improve their fuel properties;

III. determine the flash point, relative density, kinematic viscosity, cloud point, pour point, oxidative stability, calorific value, distillation, sulphur, water content,

cetane number, acid value and free fatty acid of diesel, biodiesel and different blends of these in accordance to appropriate ASTM standards and

IV. evaluate the biodegradability of the biodiesels and compare with petro-diesel.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Biodiesel as an Alternative to Petroleum Diesel

A review of some recent literature (Demirbas, 2003; Demirbas, 2005; Demirbas, 2007) show that vegetable oil derived fuel is one of alternative fuels which could match the combustion features of diesel oil at a relatively low price and which can be easily adapted for use in existing engine technologies. Biodiesel is a renewable fuel which is produced from vegetable oil or animal fat through a chemical process and can be used as either direct substitute, extender or as an additive to fossil diesel fuel in compression ignition engines. The most promising feature of biodiesel is that it can be utilized in existing design of diesel engine with no or very little modifications. It has a proven performance for air pollution reduction (Sinha *et al.,* 2008). Biodiesel is typically produced through the reaction of vegetable oils or animal fat with methanol or ethanol in the presence of catalyst to yield glycerol as major by product (biodiesel chemically called methyl or ethyl ester). However, the price of biodiesel is presently more as compared to petro-diesel. Higher cost of biodiesel is primarily due to the raw material cost (Demirbas, 2005).

Systematic efforts have been made by several researchers (Canakci and Van Gerpen, 1999; Agarwal and Das, 2001; Recep *et al*., 2001; Pilar *et al*., 2004; Erhan and Sharma, 2006) to use various vegetable oils as fuel in compression ignition engines. Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in

nature and can be produced locally and are environmental friendly as well (Demirbas, 2008).

Biodiesel is said to be carbon neutral, as biodiesel yielding plants absorb more carbon dioxide than that added to the atmosphere when used as fuel (Antolin *et al*., 2002; Lang *et al*., 2001; Sharma *et al*., 2008; Vicente *et al*., 2004). It is highly biodegradable in fresh water as well as in soil. The best part of biodiesel (90–98%) is mineralized in 21–28 days under aerobic or anaerobic conditions (Makareviciene and Janulis, 2003; Pasqualino *et al*., 2006; Zhang *et al*., 1998). Furthermore, the use of biodiesel in diesel engines reduces the emissions of hydrocarbons, carbon monoxide, particulate matter and sulphur dioxide. Only nitrogen oxides emission increases: this behavior is due to the oxygen content of biodiesel (Canakci *et al*., 2006; Dorado *et al*., 2003a; Dorado *et al*., 2003b; Labeckas and Slavinskas, 2006; Monyem *et al*., 2001; Turrio-Baldassarry, 2004; Usta, 2005).

2.2 Performance Characteristics of Biodiesel

Biodiesel prepared from a number of plant oils (edible as well as non-edible) and used successfully in existing diesel engines. Blending biodiesel in conventional diesel fuel is presently the most common form of biodiesel usages. The advantage of biodiesel blends is the simplicity of fuel preparation, which only requires mixing of the components Kumar *et al*. (2003)

Assessment of various physico-chemical properties of biodiesel derived from several feedstocks are shown in Table 2.1.

Table 2.1: Properties of biodiesel produced from several feed stocks

Feedstock	Cetane Number	Heating value (kJ/kg)	Viscosity (cSt)	Cloud point(^{o}C)	Pour point (^{o}C)	Flash point (^{o}C)
			*Methyl Alcohol			
Sunflower	46.6	39800	4.22(40^{o}C)	0	-4	-
Palm	62	33500	5.7(37.8^{o}C)	13	-	164
Cottonseed	51.2	-	6.8(21^{o}C)	-	-4	110
Jathropha	50	38450	5.65(40^{o}C)	-	-	170
Linseed	52	40374	3.59(40^{o}C)	-	-15	172
Tallow	-	-	-	12	9	96
Rapeseed	54.4	40449	6.7(40^{o}C)	-2	-9	84
Babasu	63	31800	3.6(37.8^{o}C)	4	-	127
Peanut	54	33600	4.9(37.8^{o}C)	5	-	176
Soybean	46.2	39800	4.08(40^{o}C)	2	-1	171
			**Ethyl Alcohol			
Palm	56.2	39070	4.5(37.8^{o}C)	8	6	19
Soybean	48.2	40000	4.41(40^{o}C)	1	-4	174

*Srivastava and Prasad, (2000)
**Kumar *et al*. (2003)

There have been numerous studies on use of biodiesel blends as a fuel in CI engines (Isigigur *et al*., 1994; Kusdiana and Saka, 2001). Scholl *et al*. (1993) conducted test on a 4-cylinder, 4-strokes, naturally aspirated, direct injection diesel engine with SME and found that HC, smoke and CO emissions were generally lower than those of the reference diesel fuel. NO_x was essentially unchanged. Choi *et al*. (1997) conducted tests on a single cylinder, caterpillar engine, using both single and multiple injection strategies with 20 and 40% biodiesel blended with diesel fuel. At high loads using single injection, particulate and CO emissions were decreased. A slight increase in NO_x was noticed as the biodiesel concentration increased. But in the case of multiple injections, a decrease in particulate emission was observed with little or no effect on NO_x. Desantes *et al*. (1999) compared diesel, rapeseed methyl ester and a rapeseed methyl ester-diesel mixture in a diesel engine. With rapeseed methyl ester, injection rate and spray behavior remained unchanged, however an increase in fuel droplet size was observed which was due to higher viscosity of rapeseed methyl ester. At higher air temperatures (i.e. beyond 700^oC), NO_x decreased slightly with a spectacular improvement in smoke and CO.

Wang *et al*. (2000) reported that higher nitrogen oxide is mainly due to shorter ignition delay when biodiesel is used. The shorter ignition delay, which advances the combustion timing, increase the peak pressure and temperature which enhances the NO_x. Agarrwal *et al*. (2001) converted linseed oil into biodiesel through base catalyzed route and carried out performance and emission studies on an unmodified diesel engine with different blends of biodiesel-diesel as a fuel. It was found that 20% blend of biodiesel with diesel gave best performance amongst all blends. A net advantage of blend of 2.5 percent in

peak thermal efficiency and there was substantial reduction in smoke opacity values were observed. The engine operating on optimum biodiesel blend showed substantially improved behavior in a long term endurance test. Al-widyan *et al*. (2002) investigated the performance and emission characteristics of ethyl ester of waste vegetable oil and found that the biodiesel/diesel blends burned more efficiently with less specific fuel consumption, and therefore, resulted in higher engine thermal efficiency. Furthermore, the blends produced less carbon monoxide and unburned hydrocarbons than petro-diesel fuel. The 100% biodiesel fuel and the blend of 75/25 biodiesel/diesel gave the best performance while the 50/50 blend consistently resulted in the lowest amounts of emissions. Selim *et al*. (2003) in their experiment investigated the performance and combustion noise of an indirect injection diesel engine running with *jojoba* methyl ester and its blends with diesel. Results showed that the biodiesel derived from jojoba is generally comparable and good replacement to gas oil in diesel engine at most engine operating conditions in terms of performance parameters and combustion noise produced.

Dorado *et al*. (2003a) studied exhaust emissions of a direct injection, diesel engine fueled with waste olive oil methyl ester at several steady state operating conditions. Results revealed that use of biodiesel resulted in lower emissions of CO, CO_2, NO and SO_2 but increased emissions of NO_2. The biodiesel also presented a slight increase in brake-specific fuel consumption and combustion efficiency remained constant using either biodiesel or diesel fuel. Also, Kumar *et al*. (2003) have reported increase in brake thermal efficiency and reduced smoke with the methyl ester of rice bran as compared to neat vegetable oil. The methyl ester showed higher diffusion combustion compared to standard diesel operation.

Neto da Silva *et al*. (2003) in their study observed that 5% of biodiesel in diesel resulted in increase in torque and power output, while 30% blend resulted in reduction of torque and power output. Similarly, the nitrogen oxide emissions were also lower at lower engine speeds for 5% blend while at higher % blends the nitrogen oxide emission was higher. Kalligeros *et al*. (2003) substituted marine diesel with biodiesel produced from sunflower oil and olive oil. The two types of biodiesel examined, performed in a similar way and results showed positive outcomes. They gave decreased particulate matter, carbon monoxide, hydrocarbons and nitrogen oxide emissions and a slight increase in the volumetric fuel consumption. Raheman and Phadatare (2004) studied the fuel properties of Karanja methyl ester (KME) and its blend with diesel from 20% to 80% by volume in running a diesel engine. It was found that the reduction in exhaust emissions such as CO, smoke density and NO_x was on an average of 80%, 50%, and 26% respectively. However, the brake power output increased on an average 6% up to biodiesel blend B40 and with a further increase in the biodiesel percentage in the blend reduced.

Nwafor and Nwafor (2000) investigated the potential of rubber seed methyl ester (RME) and its blend with diesel fuel. The fuel consumption trends showed an increase in fuel consumption proportional to the amount of RME added in the blend, high carbon dioxide emissions, low hydrocarbons and low fuel economy were observed at high engine load conditions with rapeseed methyl ester blend as compared to diesel fuels. Knocking problems were encountered at light loads due to longer ignition delays because of low cylinder temperature. On the other hand, brake thermal efficiency was reported to be higher as compared to diesel indicating that chemical energy of vegetable oil was more

effectively converted to mechanical work. The exhaust temperatures for both diesel fuel and RME were similar (Merve *et al*. 2005).

In a study of engine and winter road test performances of biodiesel produced from used cooking oil (Merve *et al*., 2005), the torque and brake power output obtained during application were 3-5% lesser than petro-diesel fuel. The engine exhaust gas temperature of the biodiesel was less than that of diesel fuel. It has also been observed that biodiesel containing 10-12% oxygen on weight basis causes reductions in engine torque and power due to its lower energy content (Usta *et al*. 2005). However, some studies have also reported that biodiesel can cause a slightly higher engine power than conventional diesel fuel (Kumar, 2007). This is because of complete combustion with the fuel oxygen in the fuel rich flame zone. The complete combustion also reduces exhaust emissions such as HC, smoke and CO. Two different aspects for NO_x emissions have also been reported. First, higher temperatures of combustion using biodiesel cause higher NO_x emissions. Higher exhaust temperatures from biodiesel fuelled engines may indicate higher NO_x. Secondly, there are lower NO_x emissions in biodiesel fuelled engines due to inbuilt oxygen content which shortens the ignition delay and reduces the amount of premixed fuel and peak burning temperature. In their own study, Usta *et al*. (2005) reported a slightly higher torque and power at both full load and partial loads despite lower heating value of biodiesel. It was found that 17.5% biodiesel addition gave the maximum power and thermal efficiency. The exhaust temperatures of the blend at full load were higher than those of diesel, while the differences were fairly small at partial loads.

Increased environmental concerns and tougher emission norms have led to the development of advanced engine technologies to reduce NO_x and particulate matter (PM)

emission. Ever increasing emission reduction demands present a continuing challenge to engine designers because of NO_x-PM trade-off associated with most of the emission reduction strategies. By using a B20 blend where the biodiesel portion contained 76% methyl oleate, the biodiesel NO_x effect was eliminated and a NO_x neutral blend was produced (Brown *et al*., 2000; Carraretto *et al*., 2004). Very low NO_x emissions from engines can be achieved with exhaust gas after treatment and optimized combustion processes (Eichlseder and Wimmer, 2003).

2.3 Biodiesel Storage Stability

The problems of fuel deterioration with biodiesel during storage are expected to be more severe than for the petro-diesel fuel. Although vegetable oil contains natural antioxidants, high degree of unsaturation makes them susceptible to gum formation (Thompson *et al*., 1998).

Oxidation produces hydroperoxides, aldehydes, ketones and acids that change the fuel's properties. Hydroperoxides are the initial products of oxidation at ordinary temperature. The formation of the hydroperoxide follows a well known peroxidation chain mechanism. They are very unstable and have a tendency to attack elastomers. As biodiesel oxidizes, it becomes more viscous. The hydroperoxide can induce polymerization of polymers and form insoluble gums and sediments (Canakci *et al*., 1999). Oxidation and formation of sediments and gum can cause fuel filter plugging.

Other fuel properties are also reported to be increasing with storage time Canacki *et al*. (1999) reported the increase of peroxide value, acid number and viscosity of oxidized biodiesel without anti-oxidants. Thompson *et al*. (1998) reported increase of peroxide

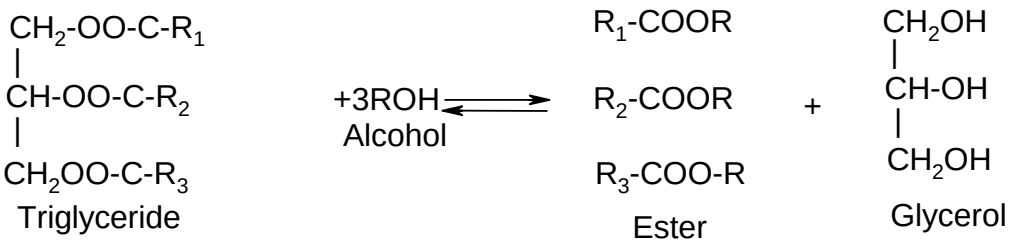
value, acid value, density, viscosity for stored rapeseed methyl and ethyl esters over a storage period of two years. Bondioli *et al*. (2003) investigated long term storage behavior of 11 biodiesel samples for a period of 1 year. The per-oxide value and kinematic viscosity of all the biodiesel samples were found to be increasing with storage time.

Since the physico-chemical properties of oxidized biodiesel change with storage period, it is expected that the performance and emission characteristics of oxidized biodiesel would be different from fresh biodiesel samples. Compared with unoxidized biodiesel, oxidized neat biodiesel produced 15 and 16% lower exhaust carbon monoxide and hydrocarbons respectively and reported decrease in smoke, hydrocarbon (HC) and CO emission levels with oxidized biodiesel as compared to base line diesel results (Monyem *et al*., 2001).

Appropriate additives for biodiesel are used to retard oxidative degradation and to guarantee a specific stability. Du Plessis *et al*. (1985) first evaluated the beneficial effects of the antioxidant *tert* -butylhydroquinone (TBHQ) on sunflower oil methyl and ethyl ester stability, it was found to retard oxidation of the biodiesel. Similar results on soybean oil methyl esters were observed by Dunn (2002) using TBHQ and α-tocopherol, even under accelerated conditions. Most recently, Siddharth and Sharma (2010), reported on the influence of numerous antioxidants on the oxidation stability of different types of biodiesel. Especially synthetic antioxidants like TBHQ, pyrogallol, *n*-propyl-gallate, 3-*tert* -butyl-4-hydroxyanisole (BHA), and 2,6-di-*tert* butyl-4-methyl-phenol (BHT) could significantly improve the stability of biodiesel, even at low antioxidant concentrations.

2.4 Biodiesel Production

The most common way to produce biodiesel is by transesterification. In this reaction, triglycerides, as the main components of vegetable oils, react with an alcohol to produce fatty acid mono-alkyl esters and glycerol as shown in equation 2.1(Ezeanyananso et al., 2010).



Equation 2.1: Transesterification of vegetable oil.

Methanol is the most common alcohol used because of its low price compared to other alcohols. In this case, the reaction is referred to as methanolysis. The stoichometry of methanolysis reaction requires 3 mol of methanol and 1 mol of triglyceride to give 3 mol of fatty acid methyl ester and 1 mol of glycerol. This reaction, in turn, consists of three consecutive reversible reactions with intermediate formation of diglycerides and monoglycerides. After the reaction is completed, the glycerol is separated by settling or centrifuging and the layer obtained is purified to be used in its traditional applications (the pharmaceutical, cosmetics and food industries) or in its recently developed applications (animal feed, carbon feedstock in fermentations, polymers, surfactants, intermediates and lubricants) (Claude, 1999). The biodiesel phase is also purified before being used as diesel fuel.

Generally, this reaction is catalyzed by a basic or an acid catalyst. However, the base catalysts (KOH or NaOH) are the most commonly used in biodiesel production, because the process proves faster and the reaction conditions are moderated (Freedman *et al*., 1984). Nonetheless, their utilisation in vegetable oil transesterification produces soaps by neutralising the free fatty acid in the oil and triglyceride saponification thereby forming soap. Soap formations are undesirable side-reactions, because they partially consume the catalyst, decrease the biodiesel yield and make the separation and purification steps more difficult (Vicente *et al*., 2004).

2.5 Optimization of Transesterification Process

The process of transesterification is affected by various factors depending upon the reaction condition used. The effects of these factors are described below.

2.5.1 Catalyst type and concentration

The Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective (Ma and Hanna, 1999). The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. Acid catalyzed transesterification was studied with waste vegetable oil. The reaction was conducted at four different catalyst concentrations, 0.5, 1.0, 1.5 and 2.25 M HCl in presence of 100% excess alcohol and the result was compared with 2.25M H_2SO_4 and the decrease in viscosity was observed.

H_2SO_4 has superior catalytic activity in the range of 1.5–2.25 M concentration (Mohamad and Ali, 2002).

In the process of alkaline methanolysis, mostly sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4 to 2% w/w of oil. Refined and crude oils with 1% either sodium hydroxide or potassium hydroxide catalyst resulted in successful conversion. Methanolysis of soybean oil with the catalyst 1% potassium hydroxide has given the best yields and viscosities of the esters (Tomasevic and Marinkovic, 2003). Methanolysis of beef tallow was studied with catalysts NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe (Ma *et al*., 1998). The catalysts NaOH and NaOMe reached their maximum activity at 0.3 and 0.5% w/w of the beef tallow, respectively. Sodium methoxide causes formation of several by-products mainly sodium salts, which are to be treated as waste.

Attempts have been made to use basic alkaline-earth metal compounds in the transesterification of rapeseed oil for production of fatty acid methyl esters. The reaction proceeds if methoxide ions are present in the reaction medium. The alkaline-earth metal hydroxides, alkoxides and oxides catalyzed reaction proceeds slowly as the reaction mixture constitutes a three-phase system oil–methanol-catalyst, which for diffusion reason inhibits the reaction (Gryglewicz, 1999). The catalytic activity of magnesium oxide, calcium hydroxide, calcium oxide, calcium methoxide, barium hydroxide, and for comparison, sodium hydroxide during the transesterification of rapeseed oil was investigated. Sodium hydroxide exhibited the highest catalytic activity in this process. The degree to which the substrates were reacted reached 85% after 30 min of the process and 95% after 1.5 h, which represented a close value to the equilibrium. Barium

hydroxide was slightly less active with a conversion of 75% after 30 min. Calcium methoxide was medially active. The degree to which the substrates were reacted was 55% after 30 min. eighty percents after 1 h and state of reaction equilibrium (93%) was reached after 2.5 h. The rate of reaction was slowest when catalyzed by CaO. Magnesium oxide and calcium hydroxide showed no catalytic activity in rapeseed oil methanolysis.

Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water require treatment, and free fatty acid and water interfere the reaction. Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems, which can overcome the problems mentioned above (Fuduka *et al*., 2001). In particular, the by-products, glycerol can be easily removed without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater than that of an alkaline one (Ezeanyananso *et al*, 2010).

2.5.2 Effect of free fatty acid and moisture

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base catalyzed reaction to completion; free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the oil the smaller is the conversion efficiency. Both excess as well as insufficient

amount of catalyst may cause soap formation (Ezeanyananso *et al.*, 2010). Ma *et al.* (1998) studied the transesterification of beef tallow catalyzed by NaOH in presence of free fatty acids and water. Without adding FFA and water, the apparent yield of beef tallow methyl esters (BTME) was highest. When 0.6 % of FFA was added, the apparent yield of BTME reached the lowest, less than 5 %, with any level of water added. The products were solid at room temperature, similar to the original beef tallow. When 0.9 % of water was added, without addition of FFA, the apparent yield was about 17 %. If the low qualities of beef tallow or vegetable oil with high FFA are used to make biodiesel fuel, they must be refined by saponification using NaOH solution to remove free fatty acids. Conversely, the acid catalyzed process can also be used for esterification of these free fatty acids (Ezeanyananso *et al.*, 2010). The starting materials used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all material should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes an increase in viscosity or formation of gels that interferes in the reaction as well as with separation of glycerol (Freedman *et al*., 1984). When the reaction conditions do not meet the above requirements, ester yields are significantly reduced. The methoxide and hydroxide of sodium or potassium should be maintained in anhydrous state. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide. Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, there are large amounts of low cost oils and fats that could be converted to biodiesel. The problem with processing these low cost oils and fats is that they often contain large amounts of free fatty acids that cannot be

converted to biodiesel using alkaline catalyst. Therefore, two-step esterification process is required for these feedstocks. Initially the FFA of these can be converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction (Canakci and Gerpen, 2001). Initial process development was performed with synthetic mixture containing 20 and 40% free fatty acid prepared by using palmitic acid. Process parameters such as molar ratio of alcohol to oil, type of alcohol, amount of acid catalyst, reaction time, and free fatty acid level were investigated to determine the best strategy for converting the free fatty acids to usable esters. The work showed that the acid level of the high free fatty acids feed stocks could be reduced to less than 1% with a two step pretreatment reaction. The reaction mixture is allowed to settle between steps so that the water containing phase could be removed. The two-step pretreatment reaction was demonstrated with actual feedstocks, including yellow grease with 12% free fatty acid and brown grease with 33% free fatty acids. After reducing the acid levels of these feedstocks to less than 1%, the transesterification reaction was completed with an alkaline catalyst to produce fuel grade biodiesel (Canakci and Gerpen, 2001).

2.4.3. Effect of reaction time and temperature

Ma *et al*. (1999) studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to mixing and dispersion of methanol into beef tallow. From one to 5 min, the reaction proceeds very fast. The production of beef tallow methyl esters reached the maximum value at about 15 min. Freedman *et al*. (1984) transesterified peanut, cotton-seed, sunflower and soybean oil under the condition of methanol oil molar ratio 6:1, 0.5 % sodium methoxide catalyst

and 60^0C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93–98%). Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of refined oil with methanol (6:1) and 1 % NaOH, the reaction was studied with three different temperatures (Freedman *et al*., 1984)). After 0.1 h, ester yields were 94, 87 and 64 % for 60, 45 and 32 ^{0}C, respectively. After 1 h, ester formation was identical for 60 and 45 ^{0}C runs and only slightly lower for the 32 ^{0}C run. Temperature clearly influenced the reaction rate and yield of esters (Ma and Hanna, 1999).

2.5.4 Mixing Intensity

As oils or fats are immiscible with sodium hydroxide - methanol solution, mixing is very important in the transesterification reaction. Once the two phases are mixed and the reaction is started, stirring is no longer needed. Initially the effect of mixing on transesterification of beef tallow was study by Ma *et al*. (Ma *et al*., 1999). No reaction was observed without mixing and when NaOH–MeOH was added to the melted beef tallow in the reactor while stirring, stirring speed was insignificant. Reaction time was the controlling factor in determining the yield of methyl esters. This suggested that the stirring speeds investigated exceeded the threshold requirement of mixing. (Ezeanyananso *et al.*, 2010).

2.5.5 Molar ratio of alcohol to oil and type of alcohol

Molar ratio of alcohol to triglyceride is one of the most important variables affecting the yield of ester. The stoichiometric ratio for transesterification requires three moles of

alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 should be used. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters (Tomasevic and Marinkovic, 2003). However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters. The transesterification of cynara oil with ethanol was studied at molar ratios between 3:1 and 15:1. The ester yield increased as the molar ratio increased up to a value of 12:1. The best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete. For a molar ratio of 15:1 the separation of glycerin is difficult and the apparent yield of esters decreased because a part of the glycerol remains in the biodiesel phase (Tomasevic and Marinkovic, 2003; Ezeanyananso *et al*., 2010).

2.5.6 Effect of using organic cosolvents

A 6:1 methanol–oil molar ratio for the methoxide base catalyzed methanolysis of soybean oil at 40^0C shows that formation of methyl esters proceeds approximately more slowly than butanolysis at 30^0C. This is interpreted to be the result of a two phase reaction in which methanolysis occurs only in the methanol phase. Low oil concentration in methanol causes the slow reaction rate; a slow dissolving rate of the oil in methanol causes an initiation period. Intermediate mono- and diglycerides preferentially remain in the methanol, and react further, thus explaining the deviation from second order kinetics. The same explanations apply for hydroxide ion catalyzed methanolysis (Ezeanyananso *et*

al., 2010). Using tetrahydrofuran, transesterification of soybean oil was carried out with methanol at different concentrations of sodium hydroxide. The ester contents after 1 min for 1.1, 1.3, 1.4 and 2.0% sodium hydroxide were 82.5, 85, 87 and 96.2%, respectively. Results indicated that the hydroxide concentration could be increased up to 1.3 wt%, resulting in 95% methyl ester after 15 min. (Boocock *et al*., 1998). Similarly for transesterification of coconut oil using THF/MeOH volume ratio 0.87 with 1% NaOH catalyst, the conversion was 99% in 1 min.

A single-phase process for the esterification of a mixture of fatty acids and triglycerides were investigated. The process comprises forming a single-phase solution of fatty acids and triglyceride in an alcohol selected from methanol and ethanol, the ratio of said alcohol to triglyceride being 15:1 – 35:1. The solution further comprises a cosolvent in an amount to form the single phase. In a first step, an acid catalyst for the esterification of fatty acid is added. After a period of time, the acid catalyst is neutralized and a base catalyst for the transesterification of triglycerides is added. After a further period of time, esters are separated from the solution (Boocock, 2001). Cosolvents like tetrahydrofuran, 1,4-dioxane and diethyl ether were also tested in order to conduct the reaction in a single phase. Although, there are other cosolvents, initial study was conducted with tetrahydrofuran. At the 6:1 methanol–oil molar ratio the addition of 1.25 volume of tetrahydrofuran per volume of methanol produces an oil dominant one phase system in which methanolysis speeds up dramatically and occurs as fast as butanolysis. In particular, THF is chosen because its boiling point of 67^0C is only two degrees higher than that of methanol. Therefore at the end of the reaction the unreacted methanol and THF can be co-distilled and recycled (Boocock *et al*., 1996).

An improved process was investigated for methanolysis and ethanolysis of fatty acid glycerides such as those found in naturally occurring fats and oils derived from plant and animals. The processes comprise solubilizing oil or fat in methanol or ethanol by addition of a cosolvent in order to form a one-phase reaction mixture, and adding an esterification catalyst. The processes proceed quickly, usually in less than 20 min, at ambient temperatures, atmospheric pressure and without agitation. The co-solvent increases the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactants. The lower alkyl fatty acid monoesters produced by the process can be used as biofuels and are suitable as diesel fuel replacements or additives (Boocock, 2001).

2.6 Transesterification under different conditions

Transesterification reaction of rapeseed oil in supercritical methanol was investigated without using the catalyst. An experiment has been carried out in the batch-type reaction vessel preheated at 350 and 400^0C and at a pressure of 45–65 MPa, and with a molar ratio of 1:42 of the rapeseed oil to methanol. It was consequently demonstrated that, in a preheating temperature of 350^0C, 450s of supercritical treatment of methanol was sufficient to convert the rapeseed oil to methyl esters and that, although the prepared methyl esters were basically the same as those of the common method with a basic catalyst, the yield of methyl esters by the former was found to be higher than that by the later. In addition, it was found that this new supercritical methanol process requires the shorter reaction time and simpler purification procedure because of the unused catalyst (Saka and Kusdiana, 2001; Ezeanyananso *et al.*, 2010).

Commercially available crude oils and fats contain considerable amounts of free fatty acids. These free fatty acids are known to react with the alkaline catalyst and form saponified products during transesterification reactions for biodiesel fuel production in the conventional commercial process. Purification of the products therefore becomes necessary after the reaction. In addition, it causes a longer production process and increases the production costs. For this aspect, supercritical methanol method without using any catalyst is evaluated in this work for the reaction of free fatty acids. As a result, complete conversion is achieved for saturated fatty acids to methyl esters at temperatures above 400^0C, whereas for unsaturated fatty acids, lower temperature of 350^0C is appropriate, and higher temperature resulted in a degradation of the products. Consequently, a conversion of free fatty acids to methyl esters is highest, over 95%, when treated at 350^0C. Fortunately, this temperature treatment is also most appropriate for transesterification of triglycerides. Thus, the overall conversion process of rapeseed oil to methyl esters is concluded to be adequate at 350^0C. This finding supports the superiority of supercritical methanol process on biodiesel fuel production, compared with the conventional method, in which the production process becomes much simpler and increases the total yield due to methyl esters produced from free fatty acids (Kusdiana and Saka, 2001; Ezeanyananso *et al.*, 2010).

2.7 Biodiesel properties

Austria was the first country in the world to define and approve the standards for rapeseed oil methyl esters as diesel fuel. As standardization is a prerequisite for successful market introduction and penetration of biodiesel, standards or guidelines for the quality of biodiesel have also been defined in other countries like Germany, Italy,

France, the Czech Republic and in the United states. The parameters, which define the quality of biodiesel, can be divided into two groups. One group contains general parameters, which are also used for mineral oil based fuel, and the other group especially describes the chemical composition and purity of fatty acid alkyl esters (Mittelbach *et al.*, 1996).

2.7.1 Flash point

The flash point of petroleum products is defined as the temperature to which the oil must be heated under prescribed conditions for sufficient vapour to be given off to form an inflammable mixture with air (Ezeanyananso *et al.*, 2010).

The importance of the flash point is limited, as it gives only an indication of the most readily ignitable proportion of inflammable vapours at atmospheric pressure and is carried out under rather artificial conditions. It does not indicate the general volatility of the fuel nor its ignition properties. Its chief importance is to indicate the safe storage temperature, perhaps the flash point of a fuel, particularly residual fuel which can be appreciably higher than the closed flash point, gives a better indication of the fire risk involved. Two values may be determined, the closed flash point, in which a flame is passed over the surface of the heated sample in an enclosed vessel; and the open flash point using the same apparatus but with the surface exposed to the atmosphere. The most widely used apparatus for distillate and residual fuels are the Pensky-martens (PM). The closed flash point, which is usually a few degrees lower than the open flash point is generally used for fuel oils. As would be expected, the flash point of typical gasoline and

kerosene is very low, being of the order of 40^{o}C gas oil 70^{o}C, marine diesel about 90 - 95^{o}C, medium residual fuel oil 105^{o}C and heavy fuel oil 115^{o}C (Clark, 1988).

Flash point is different from auto-ignition temperature of a diesel fuel, which is the temperature at which combustion will take place spontaneously with no external source of ignition. Products with low flash points, such as gasoline, have high auto-ignition temperatures and thus would be very poor fuels for diesel engines (Clark, 1988).

2.7.2 Viscosity

Viscosity is defined as the ease with which a fluid will flow (Institute of Petroleum UK (IP, 1983)**.** It is the ratio of the shear stress to the shear rate for a fluid. Diesel engine fuel injection pumps and injectors perform most effectively when the fuel has proper viscosity. If the fuel is not sufficiently viscous, the real spray will not penetrate across the combustion chamber and thus will not become properly mixed with air. On the other hand, if the fuel is too viscous, the fuel droplets will be too large; they will not break up and mix well with the air. The heavy viscous droplets may also strike the comparatively cool cylinder walls and fail to burn. Therefore, viscosity has a great influence on atomization and penetration of the fuel when it is injected. The smaller the engine, the less the degree of penetration necessary. Larger engines consequently will handle more viscous fuel than smaller engines. But if viscosity is too high, excessively high pressures can occur in the injection system and if too low, more frequent protection system maintenance may be required (Clark, 1988).

Two commonly used methods of measuring viscosity of diesel fuel are– Kinematic (ASTM D445) and Say bold Universal (ASTM D88). For all the methods, viscosity is

normally given for a temperature of 40^{o}C. The viscosities of most grade 2 diesel fuels are within the range of 2.0 to 4.3 centistokes (32.6 – 40.1 say bolt seconds) at 40^{o}C shown in ASTM D975 standard classification of diesel fuel oil. Viscosity of grade 1 diesel fuels falls within the range of 1.4 to 1.9 centistokes at 40^{o}C.

2.7.3 Cloud and pour points

The Institute of Petroleum defines the cloud point of an oil as the temperature at which a cloud or haze first appears when it is cooled under prescribed conditions (Clark, 1988). The pour point of oil is defined as 3^{o}C above that temperature at which the oil just fails to flow when cooled under prescribed conditions. IP method 219 is used to determine the cloud point and IP method 15, the pour point

In physical term all diesel fuels especially residual ones contain some paraffin wax in solution at normal ambient temperatures. As the temperature falls the wax comes out of solution in the form of long needle-like crystals the temperature at which it is first observed is the cloud point. As the temperature falls still further, the interlacing crystals prevent the flow of the remaining liquid portion of the fuel. This is the pour point. The cloud and pour points are of particular importance in relation to storage and handling in outdoor tanks and in ships bunkers. Cloud and pour points are also important in diesel-engine vehicles where small pipes below the chassis supply the engine. Such exposed pipes must be efficiently insulated to prevent fuel starvation during cold weather operation. With paraffinic distillate fuels, in cold weather, wax formation can cause blockage of small-bore engine fuel lines and filters, although this is not common in warm engine rooms. It has, however, proved troublesome abroad ship in some cold outside

compartments housing emergency diesel generators and diesel-driven bow and stern thrusters which are used only intermittently (Clark, 1988).

2.7.4 Specific gravity (Relative density)

Specific gravity is an index of its density or weight per unit volume. The specific gravity (SG) of a liquid fuel is the ratio of a given volume of the fuel at a stated temperature to the weight of an equal volume of fresh water, also at a stated temperatureIt is usual to quote specific gravities at either 15^oC or 60^oF for both liquids, i.e. $15^oC/15^oC$ or $60/60^oF$.

Density is the mass per unit volume of a substance expressed in units such as gram per cubic centimeter (g/cm^3) for solids, gram per milliliter (g/ml) for liquids and gram per litre (g/l) for gases. In practice however, there is little numerical difference between density and specific gravity, so that, for all practical purposes, they can be regarded as synonymous (Clark 1988).

2.7.5 Calorific value

The calorific value of a liquid fuel may be defined as the amount of heat produced as a result of its complete combustion. The gross calorific value of a fuel, at constant volume, is defined by the IP "as the number of heat units which would be liberated when unit weight of the fuel is burned in oxygen saturated with water vapour in a bomb calorimeter under standard conditions". Residual materials in the bomb calorimeter used in the laboratory test are considered as being gaseous (oxygen, carbondioxide, sulphur dioxide, nitrogen); liquid (water in equilibrium with its vapour and saturated with carbon dioxide); and solid (ash). Two values may be obtained from the "bomb test". These are the gross and net calorific values.

It is usual to quote the gross calorific value when discussing the heat of combustion of liquid hydrocarbon fuels. When combustion occurs in a diesel engine cylinder, boiler furnace or gas turbine combustion can, some of the useful heat is lost in the latent heat required to convert hydrogen to water vapour at the pressure prevailing in the machine. It is not recovered, as everything possible is done to prevent condensation in order to minimize the risk of corrosion. It is, therefore more meaningful to use net calorific values only. Both the gross and net calorific values of petroleum fuels are expressed in kJ/kg.

2.7.6 Sulphur

Depending on the crude oil source, refining processes and fuel grade diesel fuels contains varying amounts of sulphur. Sulphur tends to be more prevalent in the higher boiling reactions. Engine wear and formation of deposits can adversely be affected by presence of sulphur in the fuel, although the effect varies considerably and depends largely on operating conditions. High sulphur content can become a problem in diesel engine operation at low temperatures and during intermittent engine operation. Under these conditions, more moisture condensation can take place; sulphur in the fuel may react with the water to form sulphuric acid causing increased wear and corrosion of internal engine parts. Sulphur specifications are usually based on the bomb method (ASTM D129). Diesel fuels for automotive service (trucks, buses, tractors) normally have sulfur contents under 0.5% (weight) whereas heavier distillate and distillate residual fuel blends used in low and medium speed engines under sustained load, constant speed operation may contain up to 2.0% sulphur. Because of air pollution considerations, the trend is to lower sulfur contents (Clark, 1988).

2.7.7 Cetane number

Cetane number is the unit used in rating the ignition quality of diesel fuel. Cetane is n-hexadecane which has very high ignition quality (low ignition delay). It represents 100 on the cetane-number scale while 2,2,4,4,6,8,8–heptamethylnonane (HMN) has a cetane number of 15 and is the low quality reference fuel of the scale. Cetane number is given by the expression % cetane.

Although the ignition delay period is influenced by engine operating conditions, it depends primarily on the hydrocarbon composition of the fuel and to a lesser extent, on its volatility characteristic. A fuel which gives a long delay period is said to have poor ignition quality. This fuel property is expressed in terms of cetane number, the higher the number the better the ignition quality.

In the diesel combustion cycle, there is a delay between the start of fuel injection and the time that sufficient energy is released by burning to increase pressure in the cylinder above the obtained by compression of the air alone. This ignition delay period is an important factor in diesel engine combustion. If the delay period is too long, pressure may rise so rapidly when the accumulated fuel change finally starts to burn (that is knock or rough engine operation will occur) (Clark, 1988).

In general, high cetane fuels permit an engine to be started at low air temperatures, provide faster warm-up without misfiring or white smoke, and eliminate combustion roughness or diesel knock. However, there is a temperature for each engine below which starting cannot be achieved by using higher cetane fuel alone. High speed automotive diesels require short ignition delay periods and thus require higher cetane fuels than low

speed diesels. However, using fuels with a cetane number higher than that actually required by the engine does not materially improve engine performance. In fact, in some cases, if the cetane number is too high the ignition delay period may be too short to allow proper mixing of the fuel and air in the combustion space, leading to incomplete combustion and exhaust smoke. From the point of view of maximum fuel availability cetane number specified should be no higher than is actually required for satisfactory engine performance. The ASTM D613 engine test method is used for testing for cetane requirements (Clark, 1988).

2.7.8 Carbon residue

Carbon residue is the amount of material left after evaporation and chemical decomposition of the fuel have taken place at elevated temperature for a specified period of time. High carbon residue indicates that the fuel is not completely distilled or contain appreciable amount of aromatic compound. Carbon residue cannot be relied upon to predict the tendency of a fuel to form carbon deposits in an engine. Carbon residue should be low and for most automotive diesel fuels it is under 0.15% of the total weight by the Ransbotton method (ASTM D524) (Clark 1988).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Samples/ Materials used

Samples used for this study were seeds of yellow oleander (*Thevetia peruviana*) and castor plant (*Ricininus communis*).

All reagents used where of analar grade.

All solvents used were of analytical grade.

3.2 Preparation of Solutions

3.2.1 1% v/v phosphoric acid solution

This was prepared by transferring 1cm^3 from stock into a 100cm^3 volumetric flask with distilled water and then making up to the mark. The prepared solution was transferred into a clean, dry storage bottle and labeled.

3.2.2 Preparation of 1M sodium hydroxide solution

This was prepared by dissolving 40g of sodium hydroxide pellet in a 200 cm^3 beaker containing distilled water . The solution was then transferred into a 1000 cm^3 volumetric flask and then made to the mark with distilled water. This solution was standardized against 1M aqueous sulphuric acid. The prepared solution was transferred into a clean, dry storage bottle and labeled.

3.2.3 Preparation of 1M sulphuric acid solution

This was prepared by pipetting 56 cm^3 of 18 M concentrated acid in a fume cupboard and transferring into a 1000 cm^3 volumetric flask containing about 400 cm^3 distilled water. The dilution of sulfuric acid is exothermic so addition of the acid to distilled water was done slowly. The solution was then made up to mark with distilled water. The prepared solution was transferred into a clean, dry storage bottle and labeled.

3.2.4 Preparation of 0.1M potassium hydroxide solution

This was prepared by weighing 5.6g of potassium hydroxide pellets into a 1000 cm^3 beaker containing about 500 $cm^3$of distilled water, it was stirred until it dissolved and transferred quantitatively into a 1000 cm^3 volumetric flask. The solution was then diluted to mark. This solution was standardized against 1M aqueous sulphuric acid. The prepared solution was transferred into a clean, dry storage bottle and labelled.

3.2.5 Preparation of 0.8% w/w sodium hydroxide solution

This was prepared by weighing 0.8g of potassium hydroxide pellets and dissolving in 90.2g of distilled water in a 100 cm^3 beaker. The prepared solution was transferred into a clean, dry storage bottle and labeled.

3.2.6 Preparation of 10% potassium iodide solution

This was prepared by weighing 10g of potassium iodide pellets and dissolving in 60 cm^3 of distilled water in a 100 cm^3 beaker. The solution was transferred into a 100 cm^3 volumetric flask and made to the mark with distilled water. The prepared solution was transferred into a clean, dry storage bottle and labeled.

3.2.7 Preparation of 0.1N sodium thiosulphate solution

This was prepared by dissolving 24.818g of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_20$) into a 100 cm^3 beaker containing 60 cm^3 of freshly boiled water with continuous stirring. Sodium carbonate (0.2g) was added as a preservative to the solution. The solution was transferred into a 100 cm^3 volumetric flask and made up to mark with distilled water. The solution was kept for an hour and standardized against potassium dichromate using starch as an indicator. The prepared solution was transferred into a clean, dry storage bottle and labeled.

3.2.8 Preparation of 0.1M hydrochloric acid solution

This was prepared by pipetting 4.23 cm^3 of 36.5 % hydrochloric acid into a 500 cm^3 volumetric flask containing distilled water. The solution was made up to the mark. The prepared solution was transferred into a clean, dry storage bottle and labeled.

3.3 Sample Collection and Preparation

The plant seeds of *Thevetia peruviana* and *Ricininus communis* were handpicked from Ahmadu Bello University staff quarters (Area A), Zaria and National Research Institute for Chemical Technology (NARICT) farm, Zaria respectively in March, 2012.

The seeds collected were manually cleaned by removing foreign materials such as ticks, stains, leaves, other seeds, sand and dirt. The seeds were sun dried for 7days after collection to enhance the removal of the seed coat. The dried seeds were then mechanically dehauled to remove the seed coat. Removal of the seed coat was imperative because the seed coat contained little or no oil and more importantly its inclusion will

make extraction less efficient. The dehauled seeds were further dried at 50^0C for 72 hours to improve the efficiency of extraction.

3.4 Extraction

The oil from Castor and Thevetia seeds was extracted using an Oil expeller in the National Research Institute for Chemical Technology, Zaria. 10 kg of the seeds were used. The extracted oil was then drained out through a small gap between carefully positioned hardened steel bar in the barrel cage. The castor seed yielded 6.9 kg while the Thevetia seeds yielded 5.1kg of oil. The oil collected was then used for biodiesel production.

3.5 Refining Process

3.5.1 De-waxing

The extracted oils were subjected to de-waxing process to remove the wax; the oils were cooled to 5 ^{0}C, where the wax was converted into crystal form. Then, the wax was separated using a sieve and the de-waxed oils collected.

3.5.2 Degumming

Degumming converts the phosphatides in rubber seed oil to hydrated gums which are insoluble in oil and readily separated as sludge. In this process, 1litre of de-waxed oil was measured into a 2000 cm^3 beaker, heated to 60 ^{0}C, and then 1% v/v phosphoric acid was added and mixed thoroughly. The mixture was maintained at 60 ^{0}C for 1 hr, and 100 cm^3 hot water was added, and then mixed thoroughly. The mixture was transferred into a

separatory funnel where it separated into two layers. The heavy phase which contained phosphatides, pigments and other impurities was then separated and discarded.

3.5.3 Neutralizing

The oil obtained from the degumming process was mixed with 100 cm^3 of 1M NaOH, which mixed with the free fatty acids forming soap. The mixture was heated to 60 ^0C by continuous stirring for 1 hr to remove the free fatty acid.

3.6 Determination of Acid Value of the Oils

The oil sample (1.5g) was weighed in to a clean dried 250 cm^3 conical flask, and 50 cm^3 of propan-2-ol was added to ensure complete dissolution. Phenolphthalein indicator (5 drops) was added to the mixture and mixed thoroughly. The mixture was then titrated against 0.1M KOH to a faint pink colour end point. The acid value was calculated using equation 3.1.

$$\text{Acid value} = \frac{56.1 \text{ x V x C}}{\text{W}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .3.1$$

where V = Volume of KOH,

C = Molar concentration of KOH and

W = Weight of oil

3.7 Determination of Percentage Free Fatty Acid Content

The free fatty acid was determined by using equation 3.2.

$$\text{FFA (\%)} = \frac{\text{Acid Value}}{2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. 3.2$$

3.8 Transesterification

3.8.1 Acid esterification (Step I)

This step was to reduce the FFA value of the seed oil to about 2 % using acid catalyst. In this study, esterification method using sulphuric acid was used to reduce the FFA to less than 2 % before transesterification reaction.

The 200 g of seed oil was poured into the reactor (as shown in Plate III) and heated to about 60 ^{o}C. The sulphuric acid catalyst calculated as 4 % by weight of free fatty acid (FFA) for oil mixed with 600 cm^3 methanol and the mixture added to the pre-heated oil and stirred for 60 minutes at 60^{o}C and atmospheric pressure. On completion of this reaction, the product was transferred into a separatory funnel to remove excess alcohol and H_2SO_4. Due to the low density of the impurities, they moved to the top surface and were removed. The lower layer was separated for further processing (base catalyzed transesterification).

3.8.2 Alkaline Transesterification (Step II)

In the alkaline transesterification of vegetable oils, the esterified oil from step I reacts with an alcohol in the presence of a base, producing a mixture of fatty acids alkyl esters and glycerol. The stochiometric reaction required 1 mol of a triglyceride and 3 mol of the alcohol. After removing the impurities of the product of first step, the pretreated oil, was transesterified separately to mono-esters of fatty acids using alkaline (NaOH) catalyst. The experimental set-up for alkali catalyzed transesterification was the same as that was used for acid catalysed pretreatment reaction described in Step I.

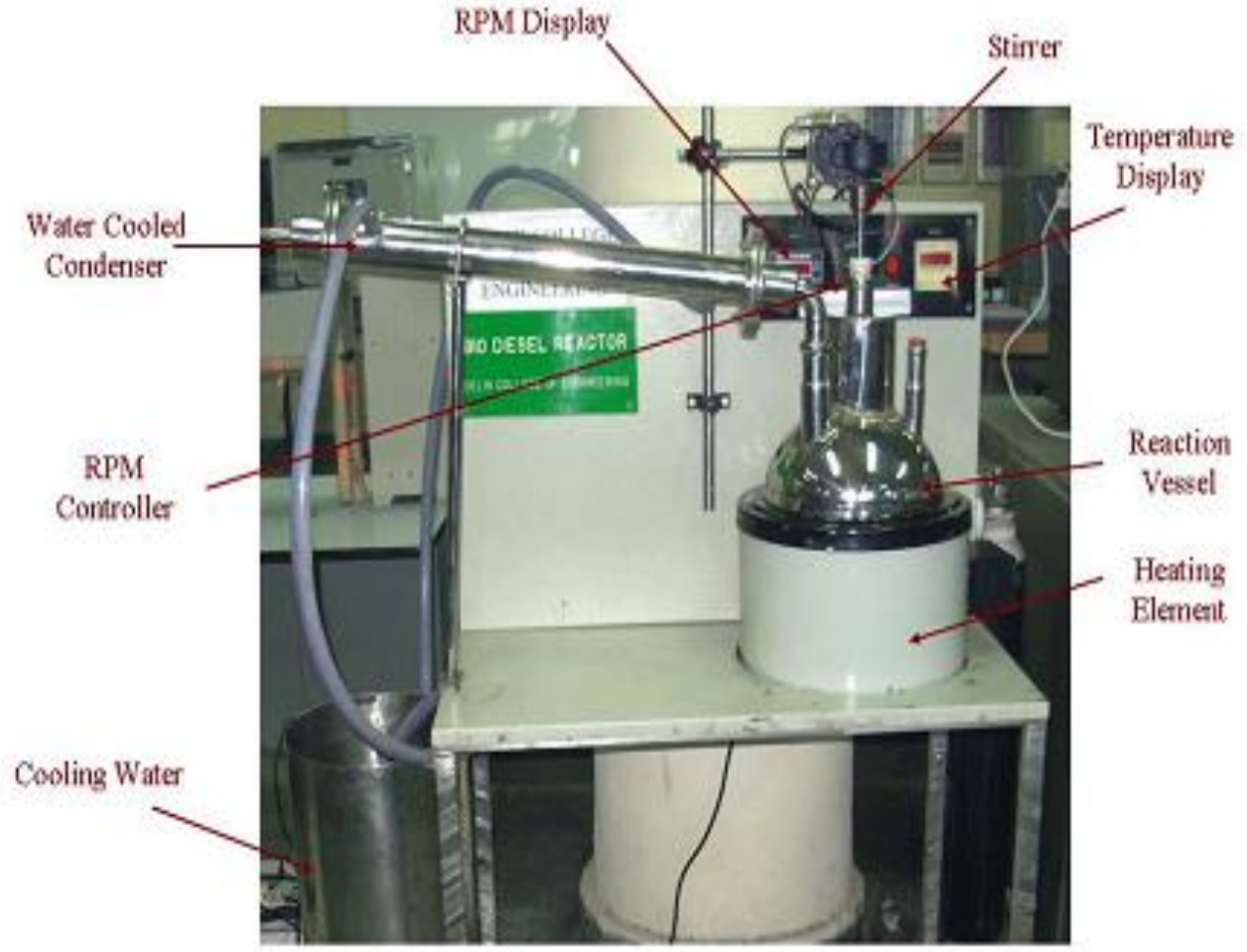


Plate III: Biodiesel Production Setup

Each sample (150 g) was preheated at 50 ^{0}C in the flask (and later increased to 75 ^{0}C at increases of 5^{0}C). Meanwhile, 0.8% w/w NaOH was dissolved in 3:1 molar ratio of alcohol to oil and is poured into the flask. The mixture is heated and stirred at 150rpm for 1h 45min. Between 0 – 60 min the product was drawn out at 5 min interval, after which they drawn out at 10min interval between 60 – 145mins. The products are allowed to separate into two layers as shown in Plate IV. The lower layer, which contained impurities and glycerol, was then drawn off. The ester remains in the upper layer.

The methyl esters were washed with hot distilled water (10% volume of ester) to remove the entrained impurities and glycerol. The excess methanol and water in ester phase was then removed by evaporation by heating the methyl ester to 100^{0}C. The biodiesel was weighed (for product yield calculation), and also the product was analysed by GC to determine its ester content (i.e. purity of product).

The reaction was investigated step by step. The optimal value of each parameter (value where the highest yield of methyl ester is obtained) in the process was determined while the rest of the parameters were kept constant. The optimal temperature was used to determine the concentration of catalyst while all other parameters are kept constant. The variables affecting transesterification such as catalyst concentration (0.25, 0.40, 0.60, 0.80, 1.00, 1.20 and 1.4% wt/wt of oil), alcohol/oil molar ratio (3:1, 6:1, 9:1 and 12:1), rate of agitation (150, 225, 300, 375 and 450 rpm) and reaction time (in that sequence) were studied over a wide range to get higher conversion under optimal reaction condition. After each optimal was attained, this value was adopted for optimization of the next parameter.

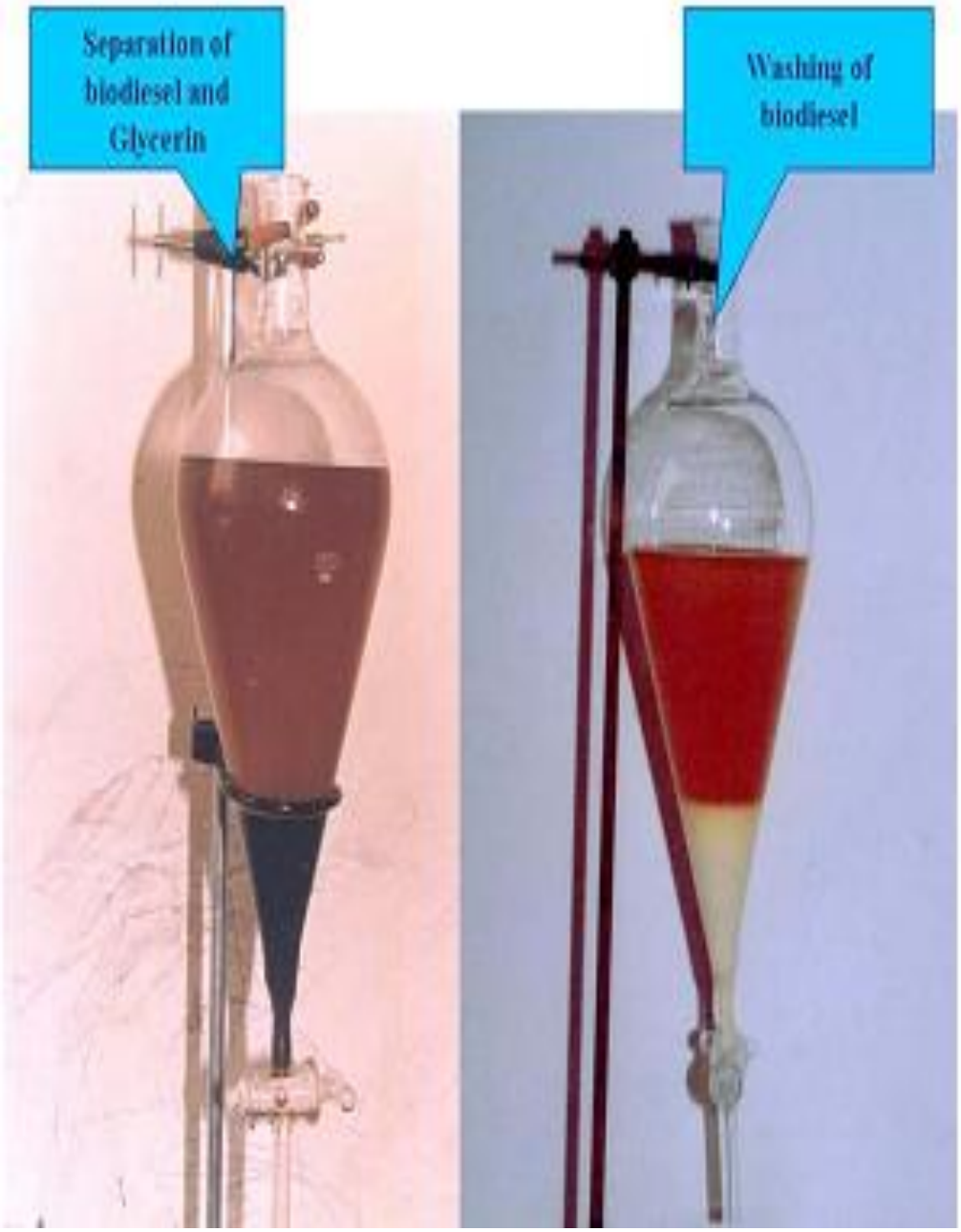


Plate IV: Separation and washing of biodiesel derived from non-edible oil

3.9 Test Methods for Physico-chemical properties

3.9.1 Kinematic viscosity

A viscometer was inserted into a water bath at the test temperature (30^0C) and left for 30minutes. The sample was added to the viscometer and allowed to remain in the bath as long as it reached the test temperature. The sample was allowed to flow freely and the time required for the meniscus to pass from the first to the second timing mark was taken using a stop watch. The procedure was repeated a number of times and the average value taken which was then multiplied with the viscometer calibration to give the kinematic viscosity.

3.9.2 Density/API gravity measurement

The density bottle was used in determining the specific gravity of the oil samples. A clean and dry bottle of 25 cm^3 capacity was weighed (W_0) and then filled with oil, stoppered inserted and reweighed to give (W_1). The oil was substituted with water after washing and drying the bottle and weighed to give (W_2). The specific gravity of oil was calculated using equation 3.3.

$$\text{Specific gravity} = \frac{W1 - Wo}{W2 - Wo} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.3$$

where $W_1 - W_o$ represent the mass of oils, and $W_2 - W_0$ stand mass for an equal volume of water.

3.9.3 Acid value

AOAC 940.28 (1990) /AOCS official method Ca5a-40 (1997) was used as reference. 1.5 g of the oil sample was weighed in a clean dried 250 cm^3 conical flask, and 50 cm^3 of

propan-2-ol was added to ensure complete dissolution. 5 drops of phenolphthalein indicator was added and mix thoroughly. The mixture was then titrated against 0.1 M KOH to a faint pink colour end point. The acid value was calculated using equation 3.4.

$$\text{Acid Value}\left(\frac{\text{mgKOH}}{\text{g}}\right) = \frac{56.1\ (\text{V x C})}{\text{W}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.4$$

where V = Volume of KOH,

C = Molar concentration of KOH and

W = Weight of oil

3.9.4 Iodine value (Wijs Method)

Oil sample (0.2 g) was weighed into a 250 cm^3 conical flask. 10 cm^3 of chloroform was then added to dissolve the oil by swirling. Wijs (20cm^3) solution was added and stoppered immediately and swirled. The mixture was allowed to stand in the dark for 30 minutes. 10% KI (15 cm^3) solution and 100 cm^3 of distilled water were added to the mixture. The mixture was swirled again and titrated against a solution of sodium thiosulphate using starch indicator, until the blue colour completely disappeared. The blank titration was also carried out without oil sample. Iodine Value was calculated using equation 3.5.

$$\text{Iodine Value } = \frac{(\text{B} - \text{S x N x } 12.69)}{\text{W}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

Where B = titre value for blank, S = Titre value for the sample,

N = Normality of $Na_2S_2O_3.5H_2O$ (sodium thiosulphate solution) and

W = Weight of the sample.

3.9.5 Peroxide value

AOAC Method 956.33, (1990) was used as reference. The sample (5g) was weighed into a 250 cm^3 conical flask. 30 cm^3 of acetic acid-chloroform solution was added. The mixture in the flask was swirled to obtain complete dissolution, 0.5 $cm^3$of saturated KI was added and the flask was shaken for few minutes. (30cm^3) of water was added and the resultant solution was titrated with 0.1 M sodium thiosulphate solution until yellow colour on iodine disappeared. 20 cm^3 of starch indicator was added and the titration continued until the blue colour of the solution disappeared. The blank determination was carried out at the same time but without sample.

$$\text{Peroxide Value} = \frac{1000T\,(V1 - V2)}{W} \quad \ldots \ldots \ldots \ldots \ldots \; 3.6$$

where W = mass (g) of oil,

V_1 = Volume (cm^3) of sodium thiosulphate solution used and

V_2 = Volume (cm^3) of sodium thiosulphate solution.

3.9.6 Pour point

Pour point test were performed according to the D97 ASTM (The American Society for Testing and Materials) standard method using the equipment shown in Plate V. The sample was poured into a test tube and heated without stirring in a water bath where the temperature was set at 48^0C. The sample was heated until it reached 46^0C. After heating, the sample was cooled to 25^0C. The sample was then placed in a metal cylinder in a methanol bath. The temperature of the methanol bath was set at -1.0^0C to $+2.0^0$C until the temperature of the sample reached 10.0^0C.



Plate V: Cloud and pour point apparatus (refrigerated)

The temperature of the methanol bath was reduced to -17^{0}C until the temperature of the sample reached -7.0^{0}C. The sample was taken out of the methanol bath at every reduction by 3^{0}C, to check the pour ability. The pour point of the sample was determined as the temperature when the sample in the test tube stopped pouring when taken out of the methanol bath. To the temperature recorded for each sample, 3^{0}C was added, to give the actual pour point value of the sample.

3.9.7 Cloud point

Cloud point analysis was performed according to the PORIM method using same equipment as pour point. The sample was filtered and heated at 130^{0}C for 5min. to remove all foreign particles and moisture in the sample. Afterwards, the sample was cooled in a water bath and stirred well to ensure temperature uniformity. The sample was stirred vigorously in a circular motion to prevent super-cooling and solidification of fat crystals at the side and at the bottom of the sample bottle. The sample bottle had to be taken out of the water bath from time to time to check if the sample had turned cloudy. The test was repeated with the temperature of the water bath set at 5^{0}C below the recorded cloud point. The result of repeated test was recorded and average value taken.

3.9.8 Sulphur content

Sulphur in the samples was determined by X-Ray spectrometry as per ASTM D-2622. 10 ml of test sample was placed in an X-ray beam and the peak intensity of the sulphur K *alfa line* at 5.373 A^0 was measured. The background intensity, measured at a recommended wavelength of 5.190 A^0 (5.437 A^0 for a Rh target tube) is subtracted from

the peak intensity. The net resultant counting rate was then compared to a previously prepared calibration curve to obtain the concentration of sulphur in sample.

3.9.9 Water content

Water content was determined Centrifugal method. In this method, 100cm^3 of biodiesel sample was centrifuged at a relative centrifugal force of 800 rcf for 10 minutes at 32°C in a centrifuge tube readable to 0.005cm^3 and measurable to 0.01cm^3 After centrifugation, the volume of water which has settled into the tip of the centrifuge tube was read to the nearest 0.005cm^3 and reported as the volumetric percent water by centrifuge.

3.9.10 Saponification value

The oil (1g) was weighed and transferred into a round bottomed flask. 20cm^3 of 0.5 N alcoholic KOH solution was added to the round bottomed flask. The above procedure without taking oil for blank titration was performed. Both round bottomed flasks were refluxed for 1 hour. After reflux, both the round bottomed flasks were allowed to cool. Both the samples were titrated using 0.5 N HCl with phenolphthalein indicator .The disappearance of pink indicated the end point. Saponification value was calculated using equation 3.7.

$$\text{Saponification Value} = \frac{(Tb - Ts) \times N \times 56.1}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.7$$

where Tb = Titre value of blank in cm^3,

Ts = Titre value of sample in cm^3,

N = Normality of KOH,

W = weight of oil and

56.1= Equivalent wt of KOH

3.9.11 Refractive index

This was determined with the aid of a refractometer. Precaution was made to make certain the prism of the refractometer was clean and completely dry. 5 drops of the sample were placed on the prism of the refractometer. The prism was closed and tightened firmly with a screw head. It was allowed to stand for 3 minutes so that the sample reaches the temperature of the instrument. The instrument and light was adjusted to obtain the most distinct reading possible and then the refractive index was determined. Several readings were taken and the average computed.

3.9.12 Free and total glycerin

A Shimadzu (Kyoto, Japan) gas chromatograph, GCMS-QP2010 PLUS, coupled with a flame ionization detector (FID) was used to analyze the fatty acid composition and ester content of the oils and biodiesel obtained from the transesterification reaction.

This was carried out according to the EN 14103 standard method. Separation was done with a DB-WAX capillary column (30 m × 0.25 mm, I.D. × 0.25 µm; J & W Scientific, Folsom, CA, USA). Helium was used as the carrier gas. Oven temperature at 120 °C was initially held for 1 min and then increased to 220 °C (held 15 min) at a rate of 4 °C/min. Injector and detector were set at 230 °C and 250 °C, respectively. A sample volume of 1.0 µL was injected using split mode (split ratio of 1:100). FAMEs were identified by comparing their relative and absolute retention times with those of authentic standards. Heptadecanoic acid (C17:0) was used as an internal standard. The FA composition was

reported as a relative percentage of the total peak area. The ester content was evaluated using equation 3.9.

$$\text{Ester}\ (\%) = \frac{\sum A - As}{As}\ \text{x}\ \frac{CsVs}{m}\ \text{x}\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .3.9$$

where $\sum A$ is the summation of the GC peak areas of methyl esters (C14:0–C24:1), A_s is the GC peak area of methyl heptadecanoate, C_s is the concentration of STD solution, V_s is volume of standard solution, and m is the amount of sample.

3.9.13 Flash point

Flash point of fuel is the minimum temperature at which it gives enough vapours to form a flammable mixture that ignite for a moment, when tiny flame is brought near to it. The flash point was determined by ASTM D-93 test method using the equipment as shown in plate VI. In this test method, the sample was heated in a test cup at a specific rate with continuous stirring.

3.9.14 Distillation characteristics

The distillation characteristics were studied using distillation apparatus (Model PMD 100) in accordance to the procedure in ASTM D 86. 100 cm^3 of the biodiesel was charged into the distillation flask. A thermometer provided with a snug-fitting cork was tightly fitted into the neck of the distillation flask. The flask was then fixed tightly into the condenser tube by raising and adjusting the flask support board of a calibrated distillation batch unit. Systematic observations and recordings of temperature readings at 5 cm^3, 10 cm^3, 20 cm^3, 30 cm^3, 40 cm^3, 50 cm^3, 60 cm^3, 70 cm^3, 80 cm^3, and 90 cm^3 respectively, and volumes of condensate were taken and recorded.



Plate VI Flash point apparatus

3.9.15 Cetane index

The ASTM-D4737 test method was used to calculate cetane index. Specific mass values obtained from Anton Paar DMA 4500 digital densimeter and distillation temperatures of 10%, 50% and 90% were used. The cetane index was calculated (CCI) using temperature values of 10%, 50% and 90% recovered (T10, T50 and T90) and of density at 15 °C (D) in an equation of four variables.

$$CCI = 45.2 + 0.0892T_{10N} + (0.131 + 0.901B)T_{50N} + (0.0523 - 0.420B)T_{90N} + 0.00049(T_{10N}^2 - T_{90N}^2) + 107B + 60B^2 \quad \text{.....3.10}$$

where $T_{10N} = T_{10} - 215$, $T_{50N} = T_{50} - 260$, $T_{90N} = T_{90} - 310$ and $B = [e^{-3.5(D-0.85)}] - 1$.

3.10 Biodegradation Study of the Biodiesels

The method employed for the biodegradability test was the respirometric method using E. colli bacteria. The innoculum was prepared by the method reported by Andriano, *et al.* (2008) and modified by Yarkasuwa *et al* (2013).

Preparation of innoculum:

To 500 cm^3 of de-ionized water, 0.5 g of organic matter rich soil, 1.0 cm^3 of aerated sewage mixed liquor, 25cm^3 of raw domestic sewage water, 25 mg/L of yeast extract and E. coli bacteria were added respectively. The mixture was then allowed to stand for 14 days. At day 14, the inoculum was filtered and was ready for use.

Procedure for biodegradation:

The determinations of the ethyl and methyl esters biodegradability were carried out in a corked conical flask system. To the corked conical flask, 50 cm^3 inoculums, 450 cm^3 of de-ionized water; and 5.0 cm^3 of biodiesel were added and mixed thoroughly. The conical flask was

connected via delivery tube to another well corked 50 cm^3 conical flask containing 10cm^3 of calcium hydroxide solution to trap the evolved CO_2. A similar but blank setup was used as a control. After inoculation, the flask were sealed and incubated with shaking in a dark cabinet. After every seven (7) days, the 10cm^3 of $Ca(OH)_2$ solution plus 30 cm^3 of rinsing water was removed for CO_2 measurement by titrating with 0.1 M HCl with phenolphthalein as indicator. Each time the reservoir was refilled with fresh $Ca(OH)_2$ solution. The CO_2 was determined at time zero and four other times to allow biodegradation plot for the test sample. The same periodic determination of % CO_2 was carried out for the blank set up. The percentage CO_2 evolved was obtained based on the following formula:

$$CO_2 \text{ evolution} = \frac{TF-CF}{C} \times 100 \quad \text{.....3.11}$$

where TF = volume of 0.1 M HCl required to titrate $Ca(OH)_2$ sample from the test flask,

CF = volume of 0.1 M HCl required to titrate $Ca(OH)_2$ from the control flask and

C = A constant which is equal to the amount of 0.1 M HCl required to titrate all the CO_2 evolved from metabolizing total carbon in the test sample by bacteria, for example 10 mg of carbon = 16.67 of 0.1 M HCl.

3.11 Fuel Blends Preparation

Different fuel blends were prepared from COME and YOME mixing them on volume basis in diesel. The nomenclature of various test fuels is given in Table 3.1.

Table 3.1 Nomenclature and composition of various test fuels

S/No	Biodiesel Blend	Blend Composition (%)	
		Methyl Ester (%)	Petro-diesel (%)
1.	B2	2	98
2.	B5	5	95
3.	B7	7	93
4.	B10	10	90
5.	B20	20	80
6.	B40	40	60
7.	B60	60	40
8.	B80	80	20
9.	B100	100	0

CHAPTER FOUR

4.0 RESULTS

4.1 Result of phytochemical Properties of Yellow oleander and Castor oils

Oil was extracted from yellow oleander and castor oils. The oils were characterized to determine their physiochemical properties such as density, pH, viscosity, acid value, iodine value, saponification value, acid value, free fatty acid, kinematic viscosity, specific gravity and refractive index. The result obtained on these properties were compared with that of American Oil Chemists' Society (AOCS) standard values and the results obtained presented in Table 4.1

Table 4.1 Result of phytochemical properties of castor and yellow oleander oils and comparison with AOCS standard values

Parameters	**Unit**	**Obtained Expt Value for yellow oleander oil**	**AOCS Standard Value for yellow oleander oil**	**Obtained Expt Value for castor oil**	**AOCS Standard Value for castor oil**
Percentage oil yield	%	69		51	
Iodine Value (IV)	gI_2/100g oil	94	84-96	86	83-88
Moisture content	%	0.52	0.488 Max	0.35	0.355 Max
Saponification Value (S.V)	mgKOH/g	193	186-194	180	176-184
Acid Value (AV)	mgKOH/g	18.46	1.0- 28.4	12.66	2.0 max
Free Fatty Acid (FFA)	mgKOH/g	9.23	< 1	6.33	< 1
Kinematic Viscosity (v) at 30 ^oC	mm^2/s	7.8	6.8-7.4	6.9	6.3-8.9
Specific Gravity (S.G) at 30^oC	-	0.925	0.912-0.916	0.9166	0.88-0.915
Refractive Index (R.I) at 30^oC	-	1.469	1.467-1.470	1.468	1.467-1.470

4.2 Result of Process Optimization

4.2.1 Result of acid esterification (Step I)

Sulphuric acid catalyst was utilized in the first step of optimization and the results are as presented in Figures 4.1 to 4.4.

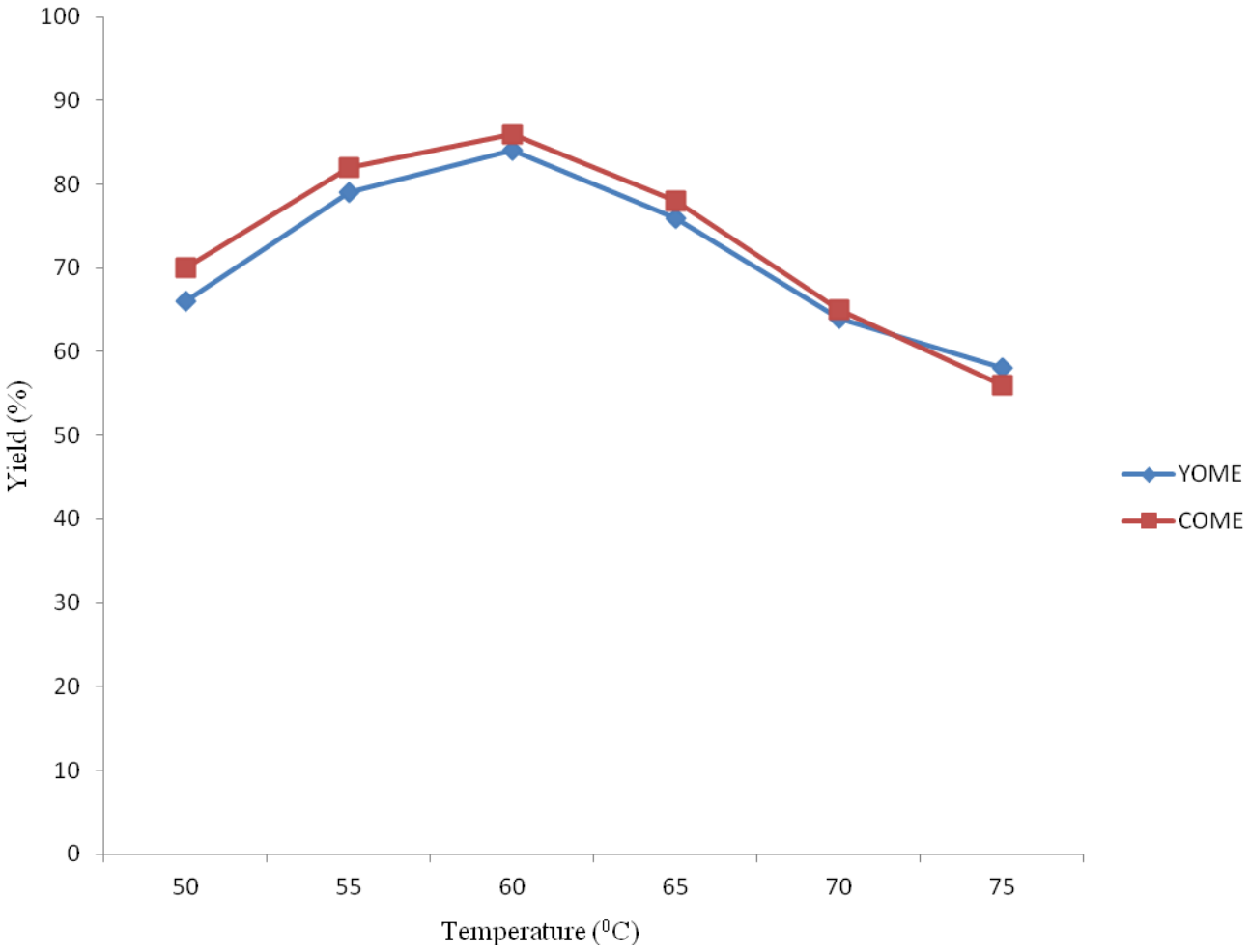


Fig 4.1: Effect of temperature on yield of esterified oil at constant methanol/oil ratio 0.33% v/v, acid catalyst = 4 %(H_2SO_4) and reaction time = 1 hr.

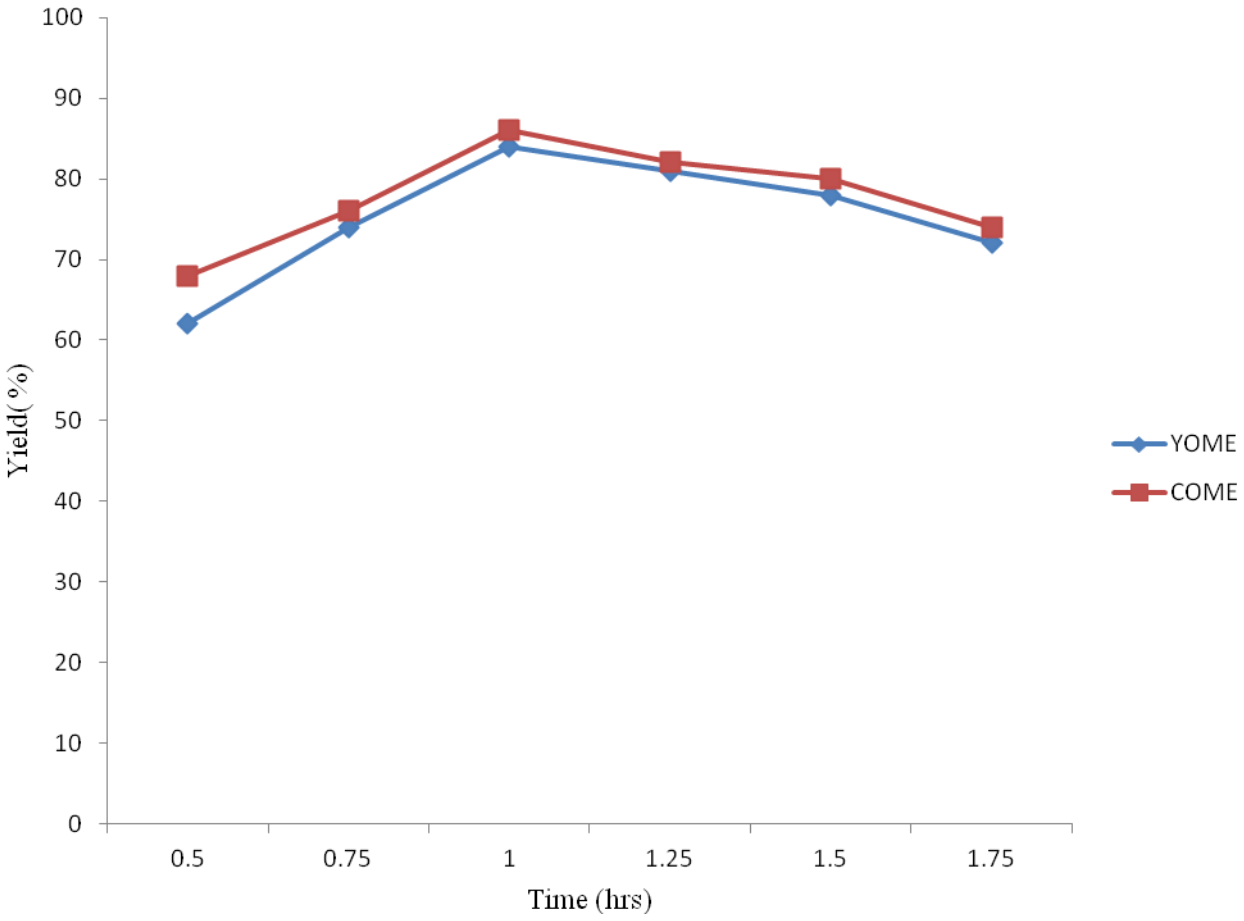


Fig 4.2 : Effect of reaction time on yield of esterified oil at constant methanol/oil ratio 3:1, temperature (60^0C) and acid catalyst =4%(H_2SO_4).

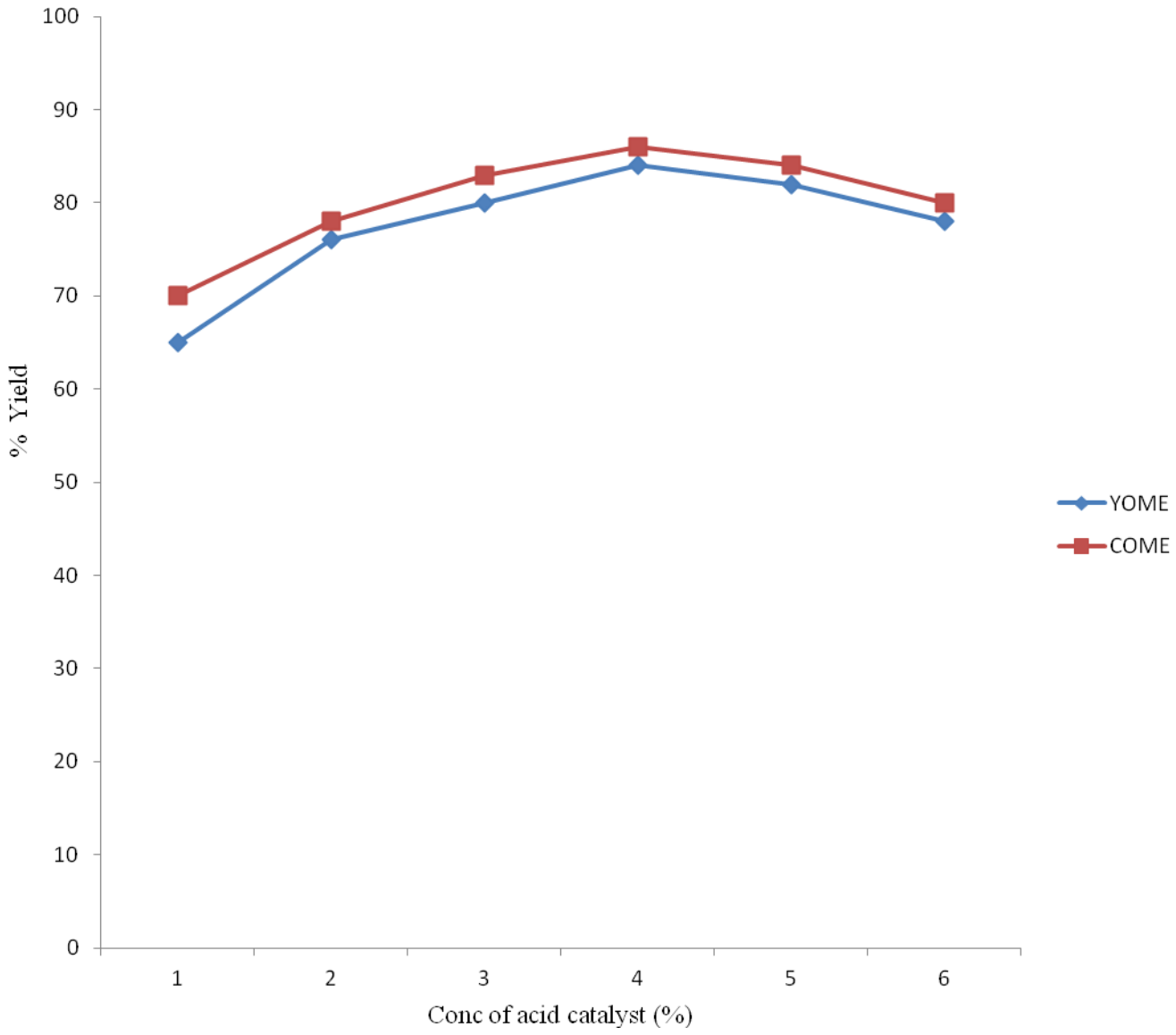


Fig 4.3: Effect of of acid catalyst on yield of esterified oil at constant methanol/oil ratio 0.33% v/v, temperature (60^0C) and reaction time = 1 hr

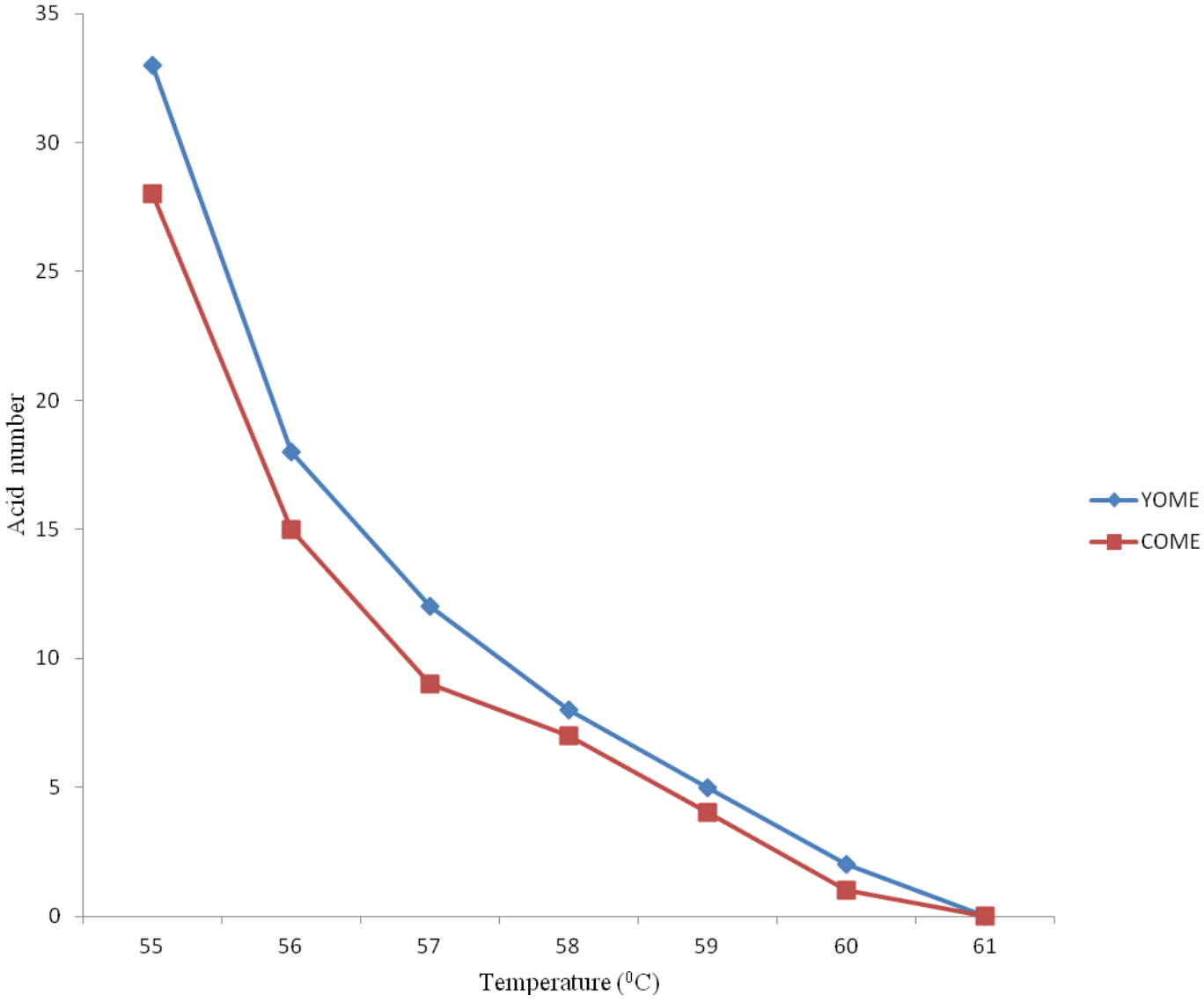


Fig 4.4 Effect of Temperature on acid value at constant methanol/oil ratio 0.33% v/v, reaction time = 1 hr and acid catalyst = 4% (H_2SO_4)

4.2.2 Result of Transesterification (Step II)

The optimized biodiesel from acid esterification was used for transesterification using sodium hydroxide catalyst. The result of this process is presented in Figures 4.5 to 4.9.

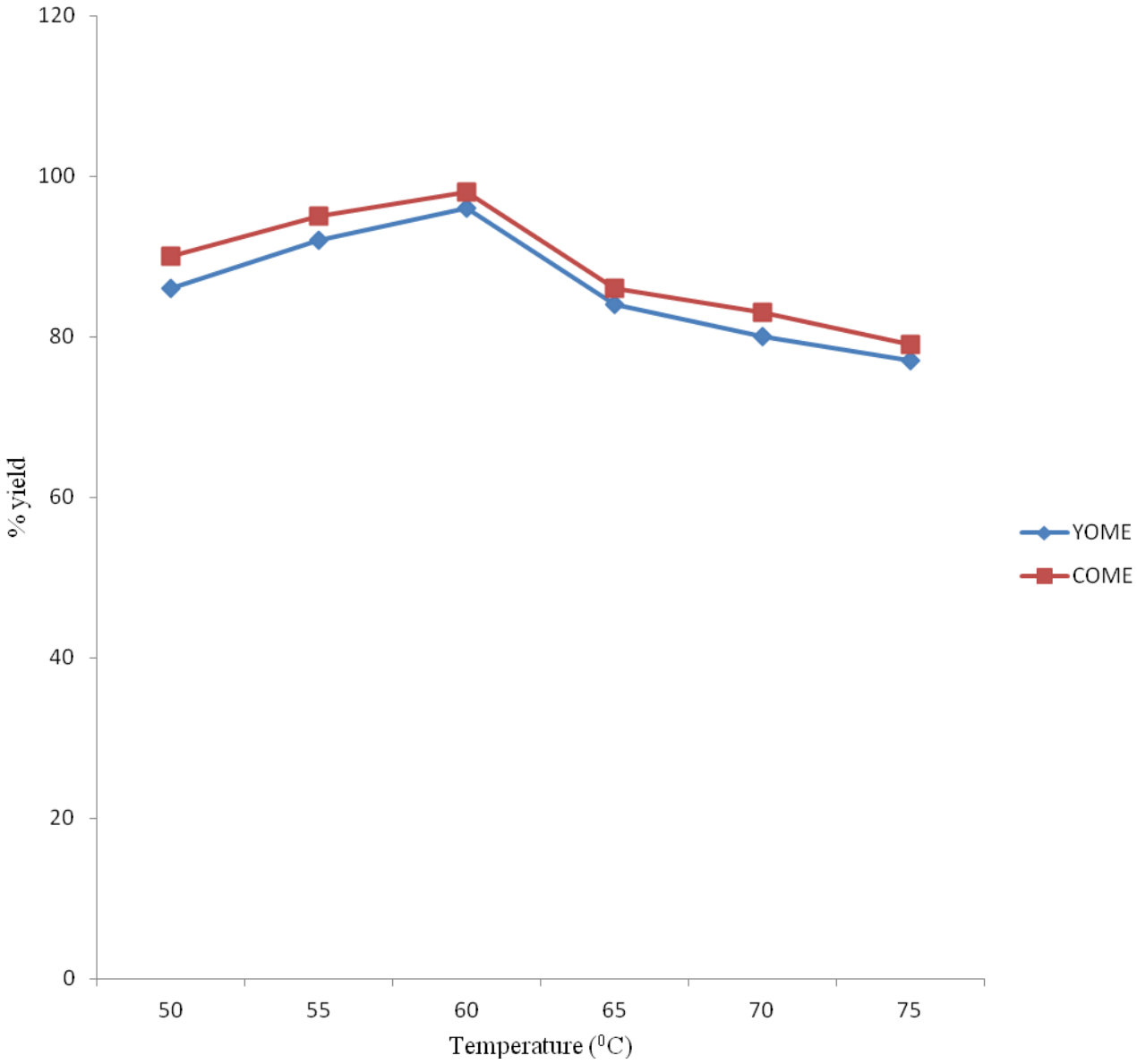


Fig 4.5: Effect of temperature on biodiesel yield from yellow oleander and castor oil using NaOH catalyst

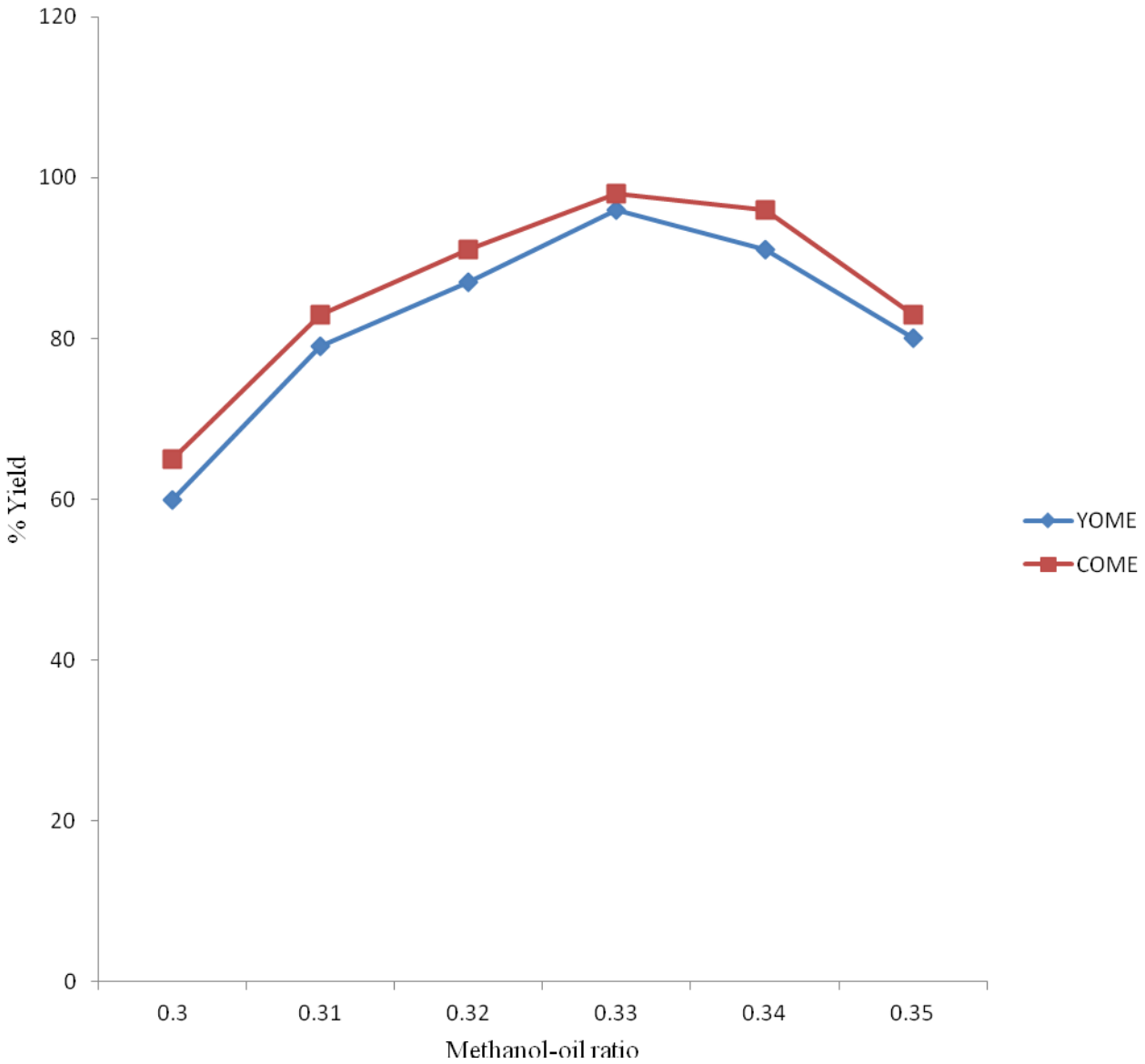


Fig 4.6: Effect of methanol/oil ratio on methyl ester yield at constant temperature (60^0C) Reaction time = 1 hr and alkali catalyst = 0.8 wt % sodium hydroxide, excess alcohol = 150 %.

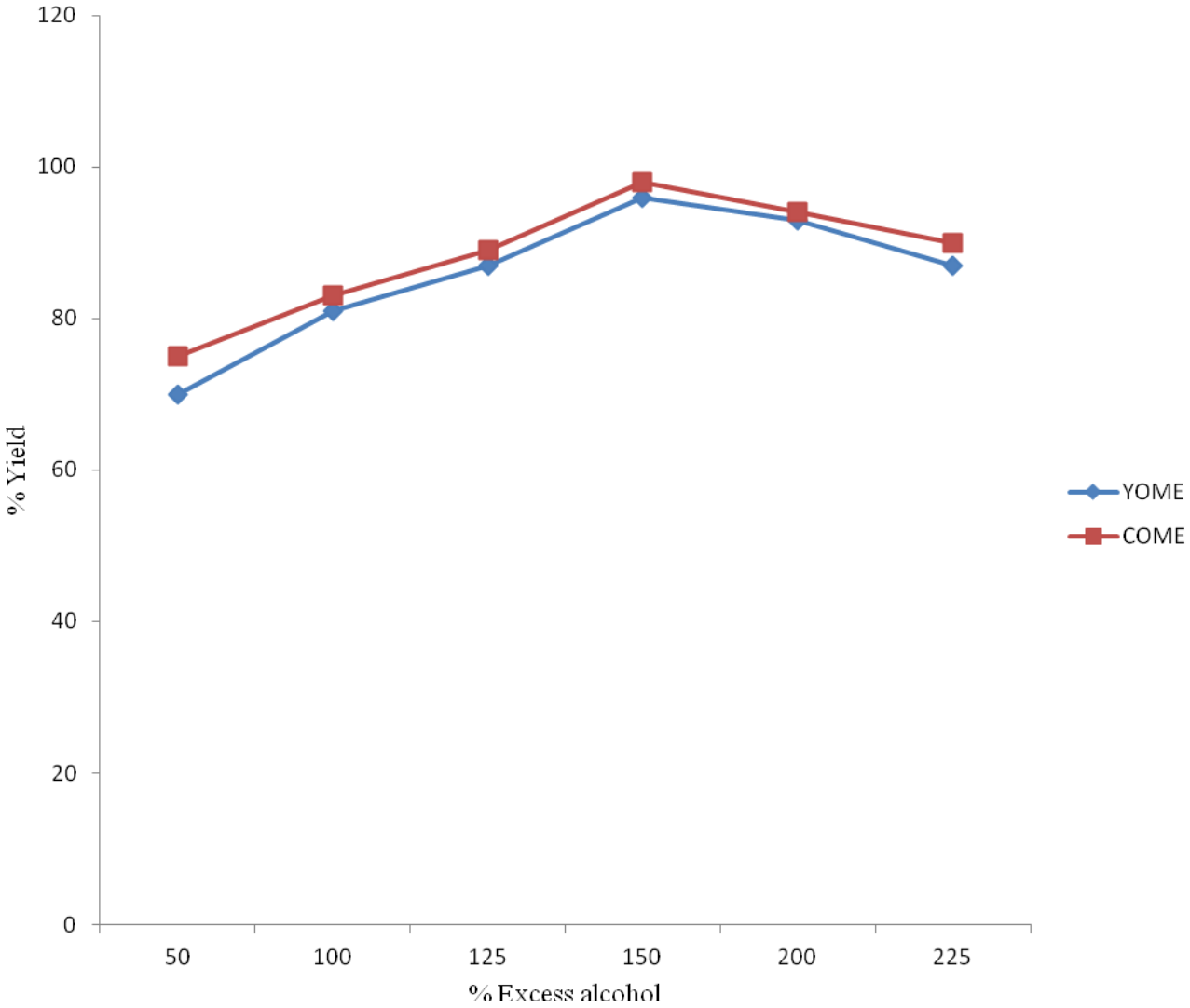


Fig 4.7: Effect of percentage excess alcohol on ester yield at constant temperature (60^0C), methanol/oil ratio 0.33% v/v, alkali catalyst = 0.8 wt % sodium hydroxide, and reaction time = 1 hr.

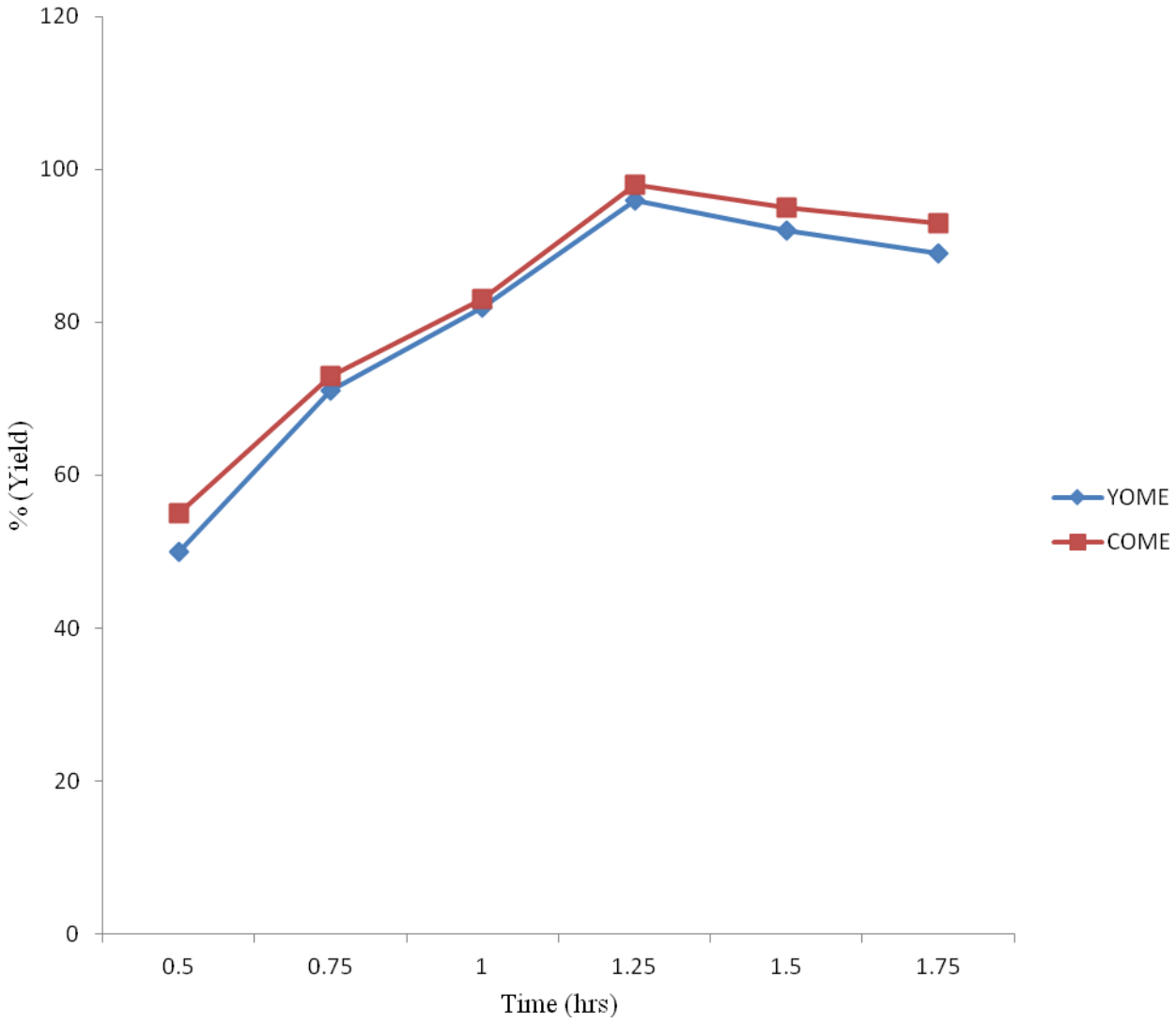


Fig 4.8: Effect of reaction time on ester yield at constant temperature (60^0C) methanol/oil ratio 0.33% v/v, alkali catalyst = 0.8 wt % sodium hydroxide, excess alcohol = 150 %.

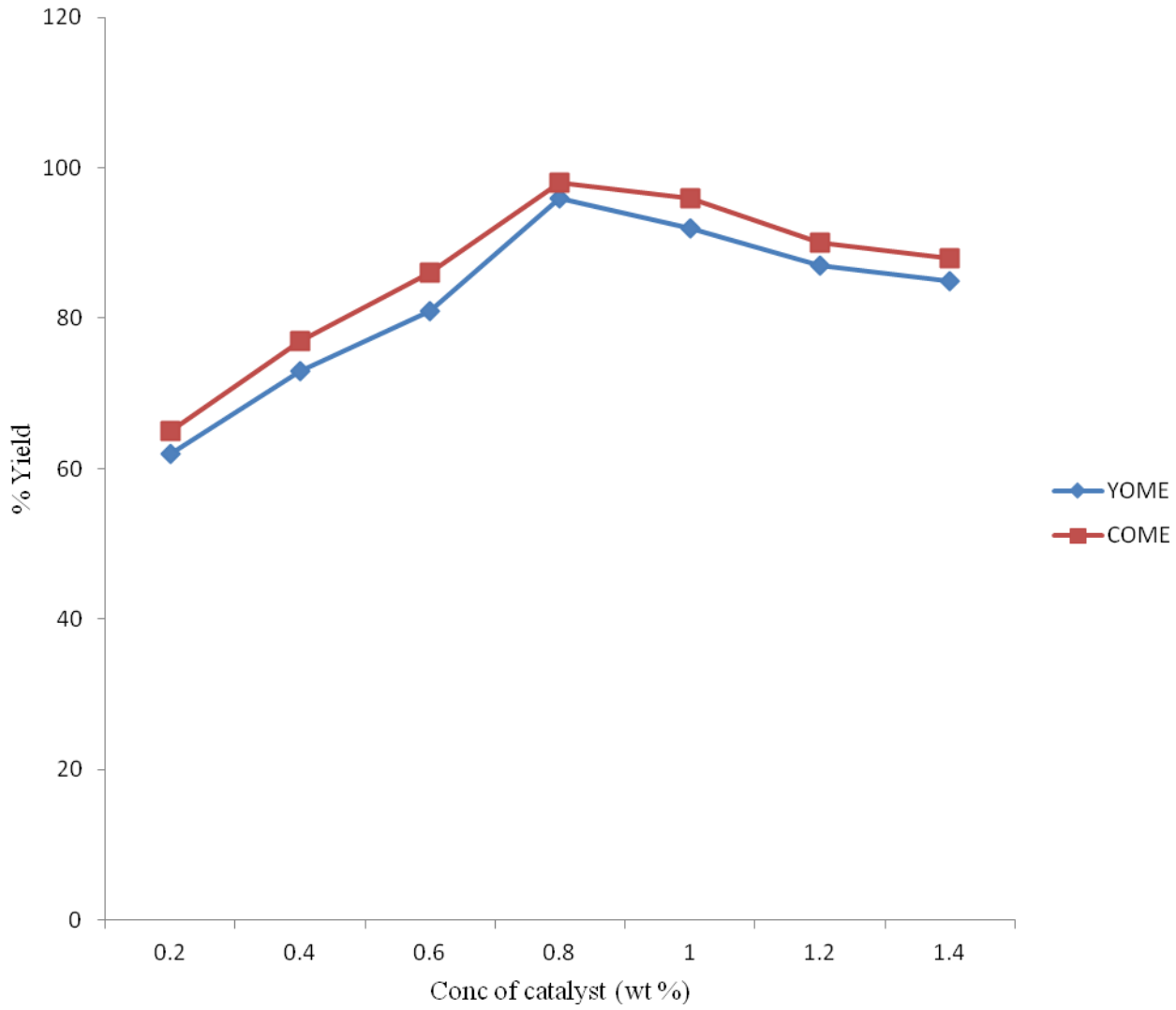


Fig 4.9: Effect of concentration of alkali catalyst and methyl ester at constant temperature (60^0C) methanol/oil ratio 0.33, excess alcohol = 150 % and reaction time = 1 hr.

4.3 Result of Characterization of Biodiesel Produced

The optimized biodiesels from yellow oleander (YOME) and castor oil (COME) were characterized. The characterized biodiesels were then compared with ASTM standard values for biodiesel and that of petrol diesel. The results obtained are as presented in Table 4.2.

Table 4.2: Characterization of biodiesel produced

Property	**Unit**	**ASTM Test Method**	**Expt. Value for YOME**	**Expt. Value for COME**	**ASTM Standard for Biodiesel (ASTM D 6751)**	**Petrol Diesel**	**ASTM Standard for Petrol diesel (ASTM D975)**
Kinematic Viscosity at 40^oC	mm^2/s	D 445	4.20	4.42	1.9-6.0	4.98	1.9-4.1
Flash Point	^0C	D 93	167	150.0	100-170	74	60-80
Cloud Point	^0C	D 2600	5	8	-3 to12	12	-15 to 5
Pour point	^0C		-3	-6	-15 to 10	-24	-35 to -15
Bottom Water & sediment	% vol	D 1796	Trace	0.07	0.05max	0.06	0.50 max
Total Sulphur	% wt	D 4294	0.03	0.05	0.05max	0.8	0.5max
Free Glycerine	% mass	D 6584	0.02	0.02	0.02 max	0.02	0.02 max
Total Glycerine	% mass	D 6584	0.24	0.21	0.24 max	0.21	0.24 max
Cetane Index	_	D 4737	56.88	51.42	47-55	49.2	40-55
Density/SG	kg/l	D 1298	0.870	0.86	0.86-0.89	0.89	0.95 max
Water by Distillation	% vol	D 95	Trace	0.06	_	0.70	0.50 max
Acid Number	mgKOH/g	D 6751-02	0.42	0.38	0.5	0.48	<0.8
Free Fatty Acid	mgKOH/g	D 6751-02	0.21	0.19	0.25	0.24	<0.4

4.4 Effect of Blending on fuel properties of the Biodiesels

The optimized biodiesel was blended with petrol diesel. Variations in the properties of the blends with varying blending ratio were investigated. The results are as presented from Figures 4.10 to 4.14.

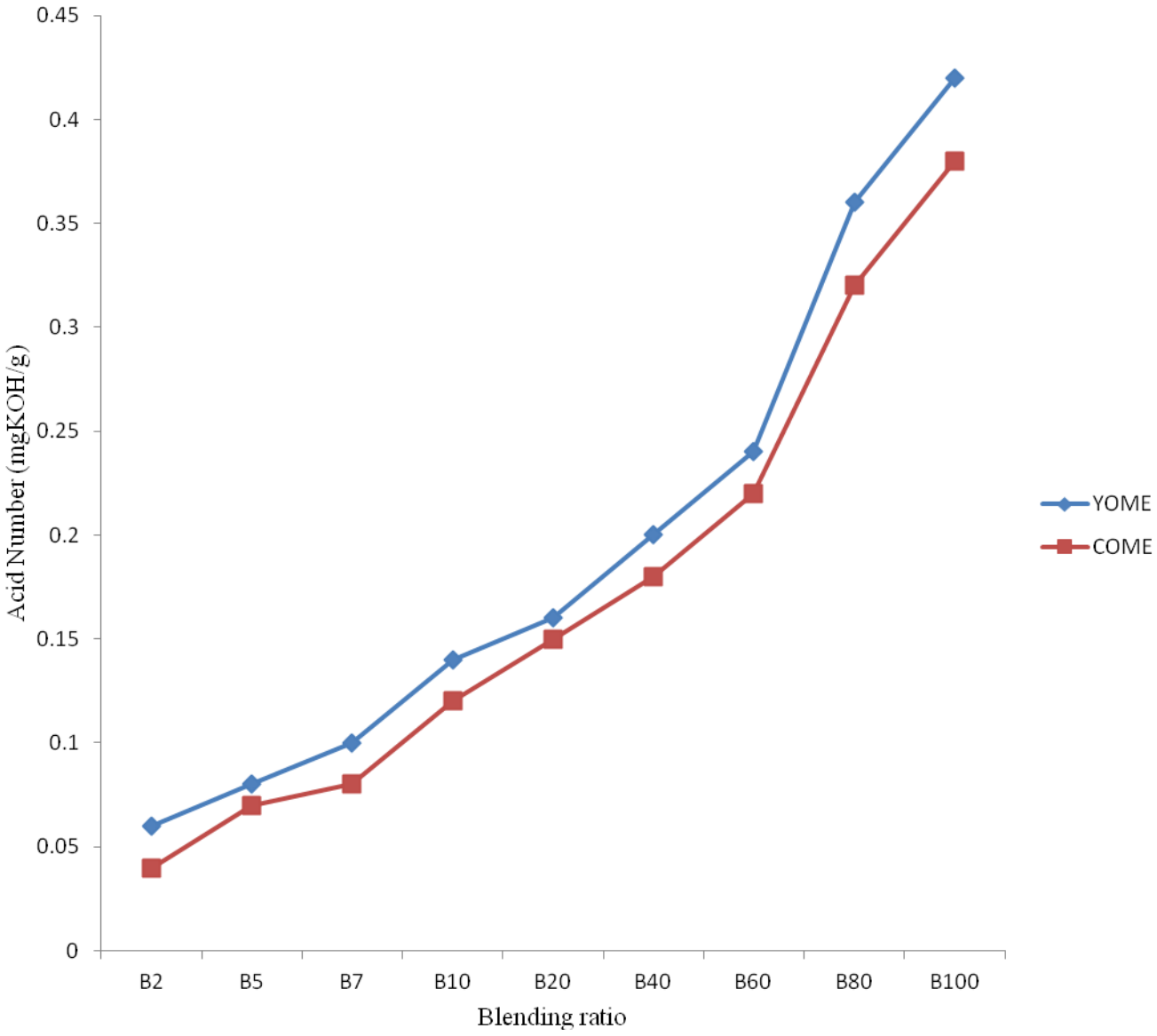


Fig 4.10: Variation of TAN with blending ratio

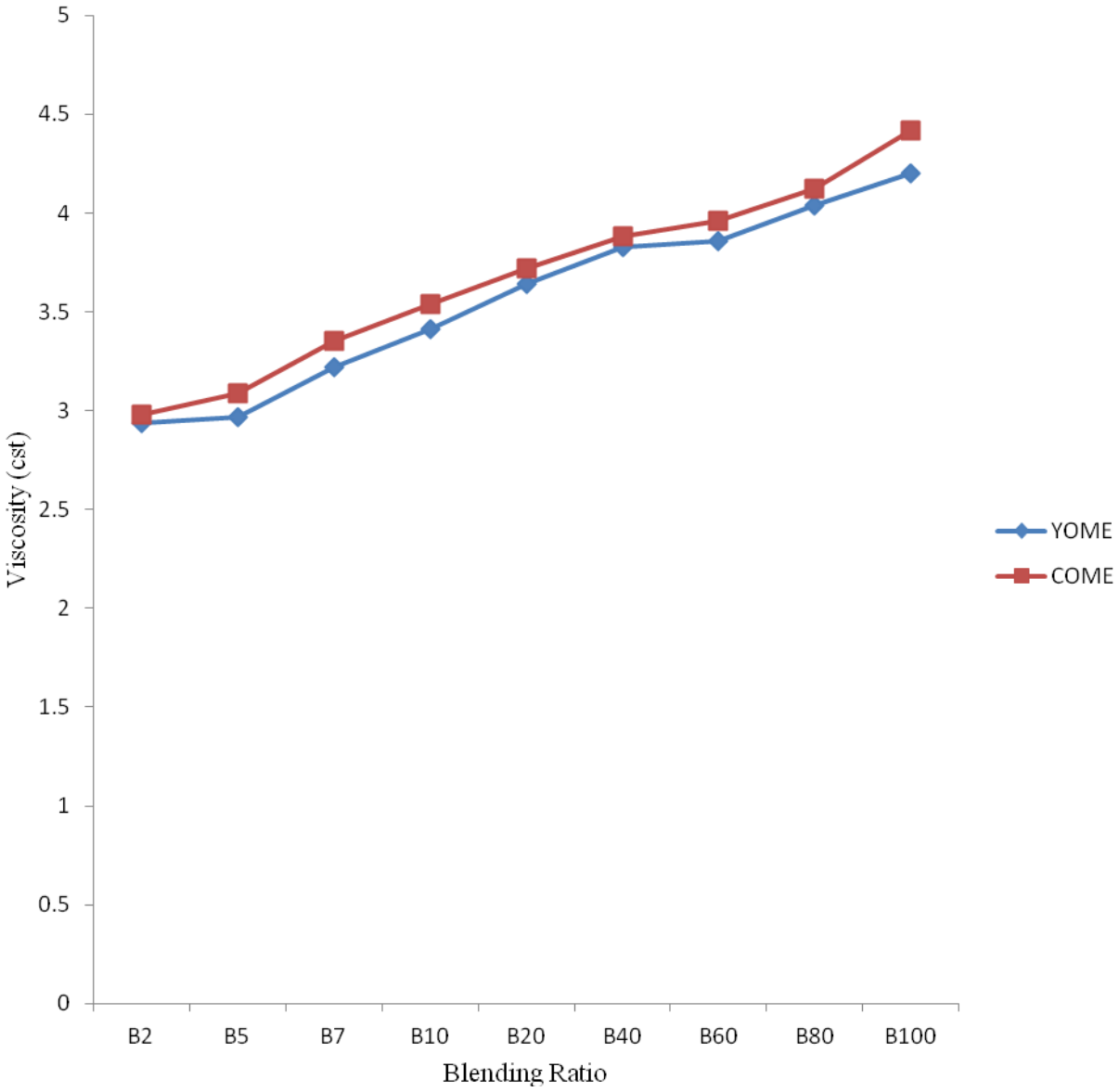


Fig 4.11: Variation of viscosity with in increasing proportion of blend

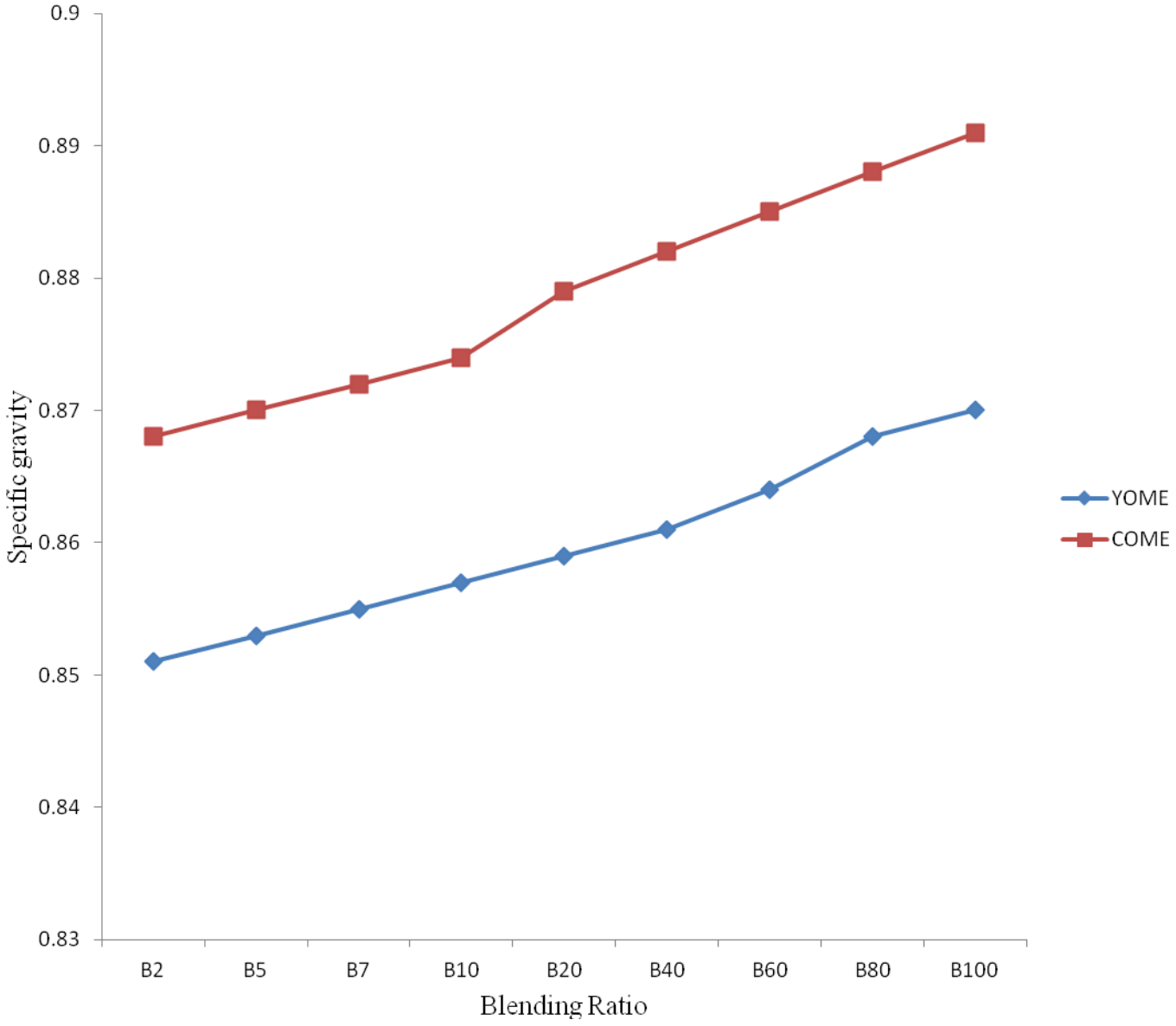


Fig 4.12: Variation of Specific Gravity with increasing proportion of blend

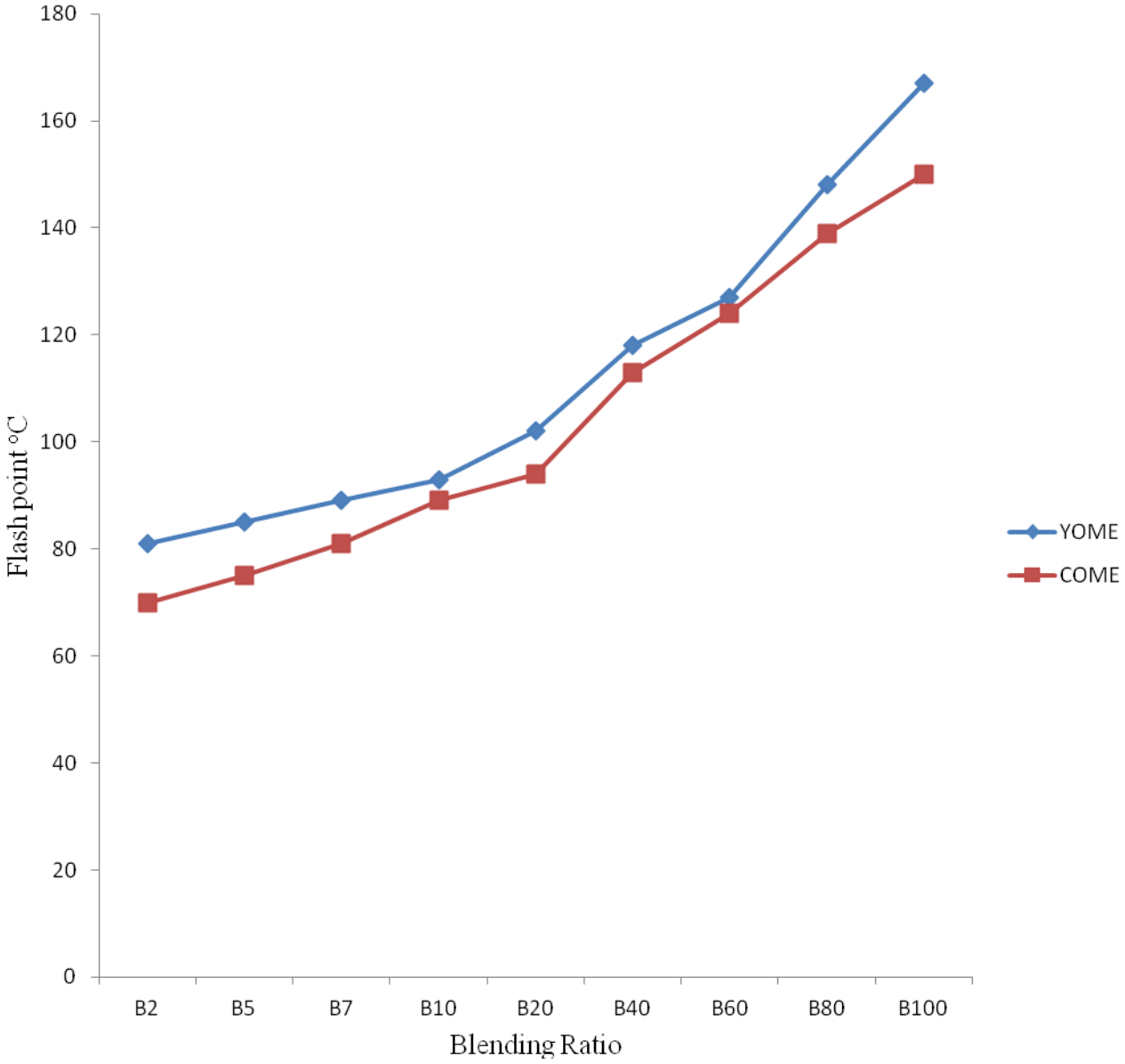


Fig 4.13: Variation of Flash point with increasing proportion of blend

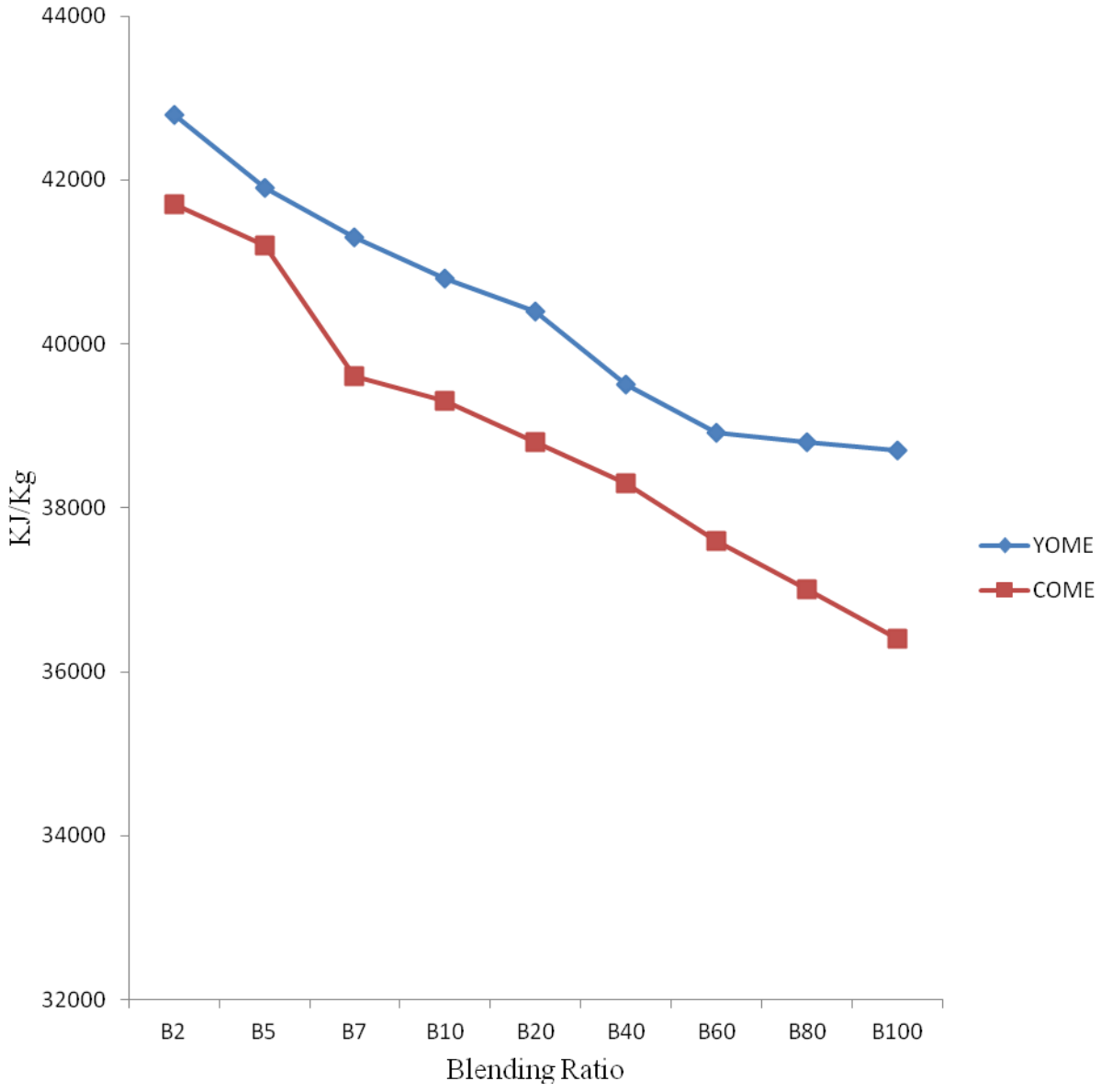


Fig 4.14: Variation of Calorific value with increasing proportion of blend.

4.5 Result of Distillation of Biodiesel from Yellow Oleander and Castor Oil

The distillation profile of biodiesel from Yellow oleander and Castor oil was obtained and compared with that of petroleum diesel. The result is presented in Table 4.3.

Table 4.3 Result of distillation of biodiesel from yellow Oleander and castor oil

Percentage recovery of distillates	**Temp (^{0}C)**		
	YOME	**DIESEL**	**COME**
IBP	174	155	222
5 %	234	162	298
10%	255	176	322
30%	260	204	319
50%	290	235	335
70 %	313	272	329
90 %	321	315	330
FBP	329	324	333
% total recovery	96.8	98.6	98

4.6 Result of Biodegradability studies of Biodiesel

Result of biodegradability studies of petro diesel and biodiesel from yellow oleander and castor oil after 28 days was experimentally determined and the result presented in Fig 4.15.

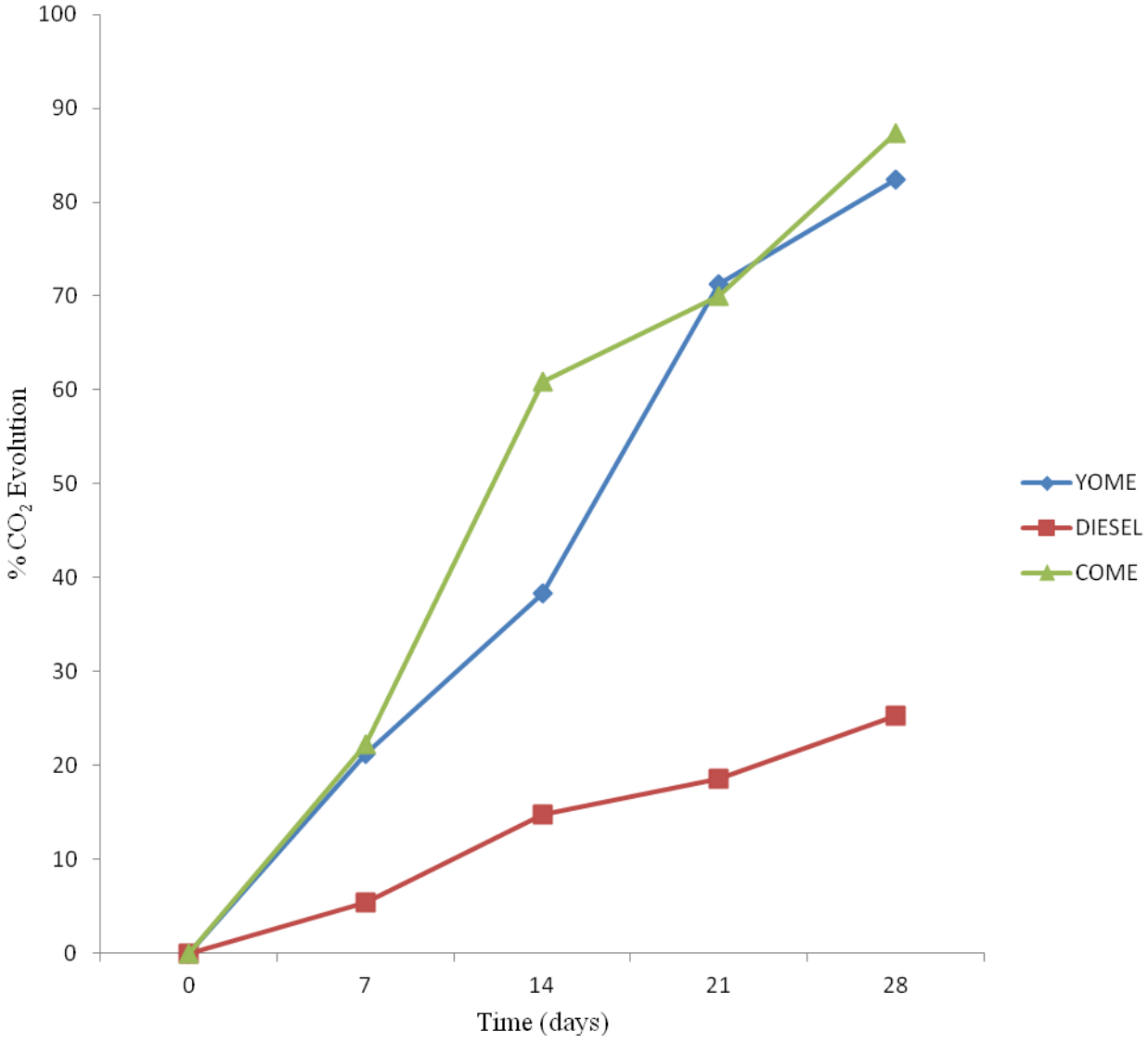


Fig 4.15: Biodegradability of petro diesel and biodiesel from Yellow oleander and castor oil after 28 days.

CHAPTER FIVE

5.0 DISCUSSION OF RESULTS

5.1 Percentage Oil Yield

The percentage oil yield of yellow oleander and castor oil seed was 69 and 51 percent of the dry mass as shown in Table 4.1. Based on the proposition by Edward and Dennis, 1994 and Foidl *et al.*, 1996, the oil yield is higher than that of other non- edible oils and can be used for the production of biodiesel. The oil yield is enough feedstock that can sustain large scale oleochemical industries not only for biodiesel production but also for the production of soap, nitrogeneous derivatives, surfactants and detergents (Azam *et al.*, 2005).

5.2 Physiochemical Properties of Yellow oleander and Castor oils

Iodine value obtained for both yellow oleander and castor oil were found to be 94gI_2/100g and 86gI_2/100g respectively and both values fall within the acceptable AOCS limit. The iodine value shows the level of unsaturation of the oil and also influences the oxidation and deposition formed in diesel engines. It is used in determining the drying property of the oil. The iodine value of yellow oleander oil (94gI_2/100g) was found to be higher than that of Castor oil (86gI_2/100g). This indicates that yellow oleander oil has a higher degree of unstauration than castor oil, although, both oils are classified as non-drying oils since their iodine value is below 115 gI_2/100g (AbdulKareem *et al.*, 2001).

The moisture content in both yellow oleander and Castor oil were found to be 0.52% and 0.35% respectively. Moisture in vegetable oil is a great impediment to the formation of esters due to increase in tendency of soap formation and thus will have to be minimal for transesterification to

occur. The result from this study shows that moisture content from both yellow oleander oil and Castor oil are within the range specified by AOCS.

The saponification value obtained for yellow oleander and Castor oil were found to be 193mgKOH/g and 180mgKOH/g respectively and are within the range specified by AOCS. The saponification value of oil is a measure of the tendency of the oil to form soap during the transesterification reaction. The saponification value of yellow oleander was found to be higher than that of Castor oil. This indicates that yellow oleander oil has a higher tendency of forming soap during transesterification reaction than castor oil.

The acid value obtained for both yellow oleander and Castor oil were found to be 18.46mgKOH/g and 12.66mgKOH/g respectively. The value for castor oil exceeds the AOCS limit of 2.0 mgKOH/g. Leung and Guo (2006) reported that oils with high acid value tend to deactivate catalyst used during transesterification. The acid value of yellow oleander (18.46mgKOH/g) was seen to be exceedingly higher than that of castor oil (12.66mgKOH/g) and this signifies that the ester yield of yellow oleander is expected to be less than that of Castor oil due to increased catalyst deactivation and soap formation.

Kinematic viscosity which is a measure of the flow capabilities of the oils was measured and found to be 7.8mm^2/s and 6.9mm^2/s for yellow oleander and Castor oil respectively. These are within the range specified by AOCS. However, castor oil with the lower viscosity has higher flow capability than yellow oleander and can easily undergo transesterification (Abdulkareem *et al*., 2012).

5.3 Process Optimization

5.3.1 Acid esterification (Step I)

Results of acid catalyzed esterification show that for maximum esterification, the concentration of acid catalyst was 4 %, alcohol/oil ratio = 0.33, reaction time = 1 hr and temperature = 60^0C

Acid esterification reduced the FFA for both yellow oleander and Castor oil from 9.23 and 6.33mmKOH/g to 0.21 and 0.19mmKOH/g respectively in 60 minutes at an operating temperature of 60^0C using 4 % sulphuric acid as catalyst. A low FFA tends to increase the process of transesterification (Fukuda *et al.,* 2001; Antolin *et al.,* 2002).

5.3.2 Transesterification (Step II)

In this study, all factors were kept constant except the temperature that was varied between 50^oC to 75^oC. Results obtained on the effect of temperature on the yield of biodiesel from yellow oleander and castor oil as the feed stock are presented in Fig 4.5. At the lower temperatures of 50 ^{o}C and 55 ^{o}C there was low collision of reacting molecules and thus, reduced biodiesel yield as seen in Table 4.5. The best yields were obtained for both the methyl ester of yellow oleander and castor oil at the temperature of 60^oC with the percentage methyl ester yield being 96% and 98% respectively. This was because at 60^oC, the molecules of the triglycerides of yellow oleander and castor oil have high kinetic energy. This lead to increase in the collision rate and therefore, improved the overall process by favouring the formation of methyl esters. The reason for this behaviour was due to the endothermic nature of the reaction. The higher reaction temperature favours endothermic reaction, thus increasing the rate of reaction as well as the ester concentration. Although at 65^oC, it was noticed that there was a drop in percentage methyl ester yield for both yellow oleander and Castor oil as shown with their corresponding values being 84% and 86% respectively. This was because at the reaction temperature (65^oC), there was

increased vaporization of the alcohol (methanol) used in the transesterification process due to the proximity of the reaction temperature (65^{o}C) to the boiling point of methanol (64.7^{o}C).

Keeping the temperature constant as illustrated in Fig 4.6, product yield increases until equilibrium so product yield was reduced beyond 0.33 methanol/oil ratio. This infers that the maximum yield was when the methanol-oil ratio is 0.33.

Fig 4.7 shows the effect of percentage excess alcohol on methyl ester yield for constant temperature, methanol/oil ratio and alkali catalyst and reaction time. In this case product yield was varied with percentage of excess alcohol but not with methanol/oil ratio. It shows that the maximum product yield was when the percent excess alcohol is 150% v/v.

Fig 4.8 shows that the time taken to produce the maximum yield of methyl ester was at 60 minutes while Fig 4.9 shows that the concentration of NaOH catalyst for optimum yield was 0.8wt%.

Based on the results obtained on the yield of biodiesel, it can be deduced that the optimum conditions for the production of methyl ester from crude yellow oleander and Castor oil through two stage transesterification are reaction temperature of 60^{o}C, oil to methanol molar ratio of 1:7, reaction time of 60 minutes and catalyst concentration of 0.8wt%.

5.4 Characterization of Biodiesel Produced

The biodiesel produced from Yellow oleander and Castor oil using the optimal conditions of 1:7 oil to methanol molar ratio, 0.8wt% catalyst concentration, 60 minutes reaction time and reaction temperature of 60^{0}C were analyzed for their fuel properties. Their properties were compared to the ASTM D 6751 biodiesel standard and the ASTM D 975 fossil diesel standard in order to confirm their suitability as fuel in diesel engines as shown in Table 4.2.

Kinematic viscosity is a measure of resistance to flow of a liquid due to internal friction of one part of the fluid moving over another. High viscosity affects the atomization of a fuel upon injection into the combustion chamber and thus leads to the formation of engine deposits (Allen et al, 1999). The kinematic viscosities of YOME and COME were determined to be 5.20 mm^2/s and 5.42 mm^2/s respectively and when compared to ASTM D 6571, it was seen that the viscosity of both biodiesels fall within range of the acceptable standard but higher than the experimental value for fossil diesel (4.98 mm^2/s).

The flash point obtained for YOME and COME were 167 ^0C and 150 ^0C respectively and they fall within the range of standard limit set by ASTM D 6751 (100-170 ^0C). The flash point is the lowest temperature at which an applied ignition source will cause the vapours of the fuel to ignite. The result for both biodiesels produced are considerably high and this leads to their safer handling and storage.

Cloud point and pour point have implications on the use of biodiesel in cold weather. The cloud point is the most common measure of the tendency of a fuel to crystallize and the cloud point of YOME and COME were determined as 5 ^0C and 8 ^0C respectively. This signifies that Castor oil has a high tendency of forming cloudy crystals easily in cold temperature than yellow oleander.

Biodiesel is also potentially subject to hydrolytic degradation caused by the presence of water. Fuel contaminated with water can cause engine corrosion and breakdown. From the results obtained, YOME has traces of bottom sediment and water while COME has 0.05 %vol and both values conforms to the ASTM D 6751 set standard whose maximum allowable limit is 0.05%vol. The sulphur content of both YOME and COME were 0.03%wt and 0.05%wt. This is within the ASTM D 6751 standard limit (0.05max). Sulphur in the atmosphere has negative impacts on human health and on the environment and biodiesel have traditionally been acknowledged as

sulphur-free which is of great advantage over fossil diesel and the results obtained confirms that fact. Also, the sulphur content of YOME was found to be lower than that of COME and this signifies that the former is more environmentally friendly than the latter.

The free and total glycerine determined for YOME and COME were (0.02wt% and 0.02wt%) and (0.24wt% and 0.21wt%) respectively. Both values are within the acceptable standard of ASTM D 6751. On comparison with each other, they were found to be approximately equal. . The free glycerine is a source of carbon deposits in the engine because of incomplete combustion. Elevated total glycerine values are indicators of incomplete esterification reactions and predictors of excessive carbon deposits in the engine. This can be as a result of incomplete washing of the ester after production

The cetane number of the methyl esters of yellow oleander and castor oil were found to be 56.88 and 51.42 respectively (Fig 4.12.10). Generally, the cetane number is a dimensionless descriptor of the ignition quality of a diesel fuel. As such, it is a prime indicator of diesel fuel quality. On comparison with standard, it was found that the cetane numbers were within the range stated by ASTM D 6751. On further comparison with fossil diesel, the cetane number of both YOME and COME was above that of fossil diesel. Thus results confirm the fact that biodiesels generally, have a higher cetane number than fossil diesels.

The result of the specific gravity of YOME and COME show that transesterification reduced the SG of the feed oil from 0.93 and 0.92 to 0.87 and 0.86 respectively. It also indicates that the SG of both YOME and COME was lower than that of fossil diesel.

5.5 Effect of Blending on Fuel properties of the Biodiesels

Fig 4.10 shows the variation of Total acid number (TAN) with blending ratio. TAN decreases with increasing proportion of petro-diesel in the blends.

Due to lack of oxidation and lower TAN, the viscosity of biodiesel blends with petro-diesel will also decrease with the increasing proportion of petro-diesel as shown in Fig 4.11.

Specific gravity and flash point decreases with increasing proportion of petro-diesel in the blends as shown in Fig 4.12 and 4.13 respectively. Finally, the energy content increases with increasing proportion of petro-diesel in the blends as shown in Fig 4.14.

5.6 Distillation Characteristics of the Biodiesel produced

Table 4.6 shows the distillation characteristic of YOME and COME. Boiling point is the temperature at which a liquid transition to a gas and it is also related to the flash point. For a pure substance the boiling point is a single temperature value. However, for a mixture of hydrocarbons as existing in biodiesel fuel, there is a range of boiling points for the different constituent chemical species. The data tested for in the methyl ester of yellow oleander and Castor oil includes the initial boiling point (IBP), boiling temperature corresponding to increments of the volume of fuel distilled (10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90%), final boiling point (FBP) and percentage total recovery.

5.7 Biodegradability of the Biodiesels

The biodegradability result obtained for YOME and COME after a period of four weeks is shown in Fig 4.15. It is found that the biodiesel from Yellow Oleander and castor oil is environmentally friendly, such that after spillage, it will take about 28 days for them to have a biodegradability of 82.4 and 87.3 for YOME and COME respectively. This is an advantage over petro-diesel which will have a biodegradability of 25.29 in 28 days. This also confirms the result from literature that biodiesel is more easily metabolized than diesel because the former is a natural product consisting of pure fatty acids that are hydrocarbon chains with two oxygen atoms

attached at one end, which are very biologically active, being recognized and attacked immediately by enzymes such as acetyl-CoA dehydrogenase.

CHAPTER 6

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary

The results obtain from this study show that optimum conditions for esterification are 4 %H_2SO_4, 0.33%v/v alcohol/oil ratio, 1 hr reaction time and temperature of 60^0C. For maximum bio diesel production, the transesterification reaction shows that the concentration of alkali catalyst is 0.8 % Sodium hydroxide, 0.33%v/v alcohol/oil ratio, 1 hr reaction time, 60^0C temperature and excess alcohol 150%v/v.

Based on the results of the experimental analysis, it can be concluded that oils from both feed stocks are suitable for the production of biodiesel. Also, temperature had a high effect on biodiesel yield and the yield increased with increasing temperature up to a point where the reacting temperature was proximal to the boiling point of the methanol. It can also be concluded that, though, castor oil had a higher methyl ester yield (98wt%) than yellow oleander (96wt%) at same optimal reaction conditions, the methyl ester of yellow oleander is a more suitable fuel for diesel engines than that of castor oil because the fuel properties obtained for the former were more compatible with the engines and in accordance with ASTM D 6751 than that of the latter.

Also from the results obtained, it can be seen that the biodiesel from the seeds of yellow oleander and castor plant is environmentally friendly, such that after spillage, it took about 28 days for them to have biodegradability of 82.4% and 87.3% for YOME and COME respectively. This is an advantage over petro-diesel which was found to have biodegradability of 25.29% in 28 days.

6.2 Conclusion

This study suggests that the yellow oleander and castor oils can be used as a source of triglycerides in manufacture of biodiesel by esterification and transesterification. The properties of the biodiesel produced showed theoretical compatibility with diesel engines in accordance with ASTM D 6751. Finally, the study shows that the biodiesel from the seeds of yellow oleander and castor plant is environmentally friendlier than petroleum diesel.

6.3 Recommendation

It is recommended that:

1. Studies on performance and exhaust emissions of a diesel engine fueled with YOME and COME using this optimization process be carried out and the results compared with results of petro diesel.
2. More intensive investigation are required for exploring different valuable by-products from glycerol and proper utilization of oil cake so as to make biodiesel production into an economically viable enterprise.

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APPENDICES

Appendix I: Effect of temperature (^{0}C) on yield of esterified oil at constant methanol/oil ratio 0.33, acid catalyst = 4 %(H_2SO_4) and reaction time = 1 hr.

Temperature (^{0}C)	Yield %	
	YOME	COME
50	66	70
55	79	82
60	84	86
65	76	78
70	64	65
75	58	56

Appendix II: Effect of reaction time (hr) on yield of esterified oil at constant methanol/oil ratio 0.33% v/v temperature (60^0C) and acid catalyst =4 %(H_2SO_4).

Time (hrs)	% Yield	
	YOME	COME
0.5	62	68
0.75	74	76
1	84	86
1.25	81	82
1.5	78	80
1.75	72	74

Appendix III: Effect of % of acid catalyst on yield of esterified at constant methanol/oil ratio 0.33% v/v, temperature (60^0C) and reaction time = 1 hr

Concentration of acid catalyst (H_2SO_4)	% Yield	
	YOME	COME
1	65	70
2	76	78
3	80	83
4	84	86
5	82	84
6	78	80

Appendix IV: Effect of Temperature on Acid value at constant methanol/oil ratio 0.33% v/v, Reaction time = 1 hr and acid catalyst = 4% (H_2SO_4)

Temperature	Acid number (mmKOH/g)	
	YOME	COME
55	17.86	12.02
56	12.09	9.23
57	8.56	7.06
58	5.24	4.68
59	1.42	1.24
60	0.42	0.38
61	0.31	0.26

Appendix V: Effect of Temperature on Biodiesel Yield from yellow oleander and Castor oil using NaOH catalyst.

Temperature (^{0}C)	% Yield	
	YOME	COME
50	86	90
55	92	95
60	96	98
65	84	86
70	80	83
75	77	79

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Appendix VI: Effect of methanol/oil ratio on metyl ester yield at constant temperature (60^0C) Reaction time = 1 hr and alkali catalyst = 0.8 wt % sodium hydroxide, excess alcohol = 150 %

Methanol-oil ratio	% Yield	
	YOME	COME
0.3	60	65
0.31	79	83
0.32	87	91
0.33	96	98
0.34	91	96
0.35	80	83

Appendix VII: Effect of % of excess alcohol on ester yield at constant temperature (60^0C) methanol/oil ratio 0.33% v/v, alkali catalyst = 0.8 wt % sodium hydroxide, and reaction time = 1 hr.

% Excess alcohol(ml)	% Yield	
	YOME	**COME**
50	70	75
100	81	83
125	87	89
150	96	98
200	93	94
225	87	90

Appendix VIII: Effect of reaction time on ester yield at constant temperature (60^0C) methanol/oil ratio 0.33% v/v, alkali catalyst = 0.8 wt % sodium hydroxide, excess alcohol = 150 %

Time (hour)	% Yield	
	YOME	COME
0.5	50	55
0.75	71	73
1	82	83
1.25	96	98
1.5	92	95
1.75	89	93

Appendix IX: Effect of concentration of alkali catalyst on yield of methyl ester at constant temperature (60^0C) methanol/oil ratio 0.33% v/v, excess alcohol = 150 % and Reaction time = 1 hr

Concentration of catalyst (Weight %)	% Yield	
	YOME	COME
0.20	62	65
0.40	73	77
0.60	81	86
0.80	96	98
1.0	92	96
1.2	87	90
1.4	85	88

Appendix X: Variation of TAN with blending ratio

Blending Ratio	TAN (mgKOH/g)	
	YOME	COME
B2	0.06	0.04
B5	0.08	0.07
B7	0.1	0.08
B10	0.14	0.12
B20	0.16	0.15
B40	0.2	0.18
B60	0.24	0.22
B80	0.36	0.32
B100	0.42	0.38

Appendix XI: Variation of viscosity with in increasing proportion of blend

Blending Ratio	Viscosity (cst)	
	YOME	COME
B2	2.94	2.98
B5	2.97	3.09
B7	3.22	3.35
B10	3.41	3.54
B20	3.64	3.72
B40	3.83	3.88
B60	3.86	3.96
B80	4.04	4.12
B100	4.20	4.42

Appendix XII: Variation of specific gravity with increasing proportion of blend

Blending Ratio	Specific gravity	
	YOME	COME
B2	0.851	0.868
B5	0.853	0.87
B7	0.855	0.872
B10	0.857	0.874
B20	0.859	0.879
B40	0.861	0.882
B60	0.864	0.885
B80	0.868	0.888
B100	0.87	0.891

Appendix XIII: Variation of flash point with increasing proportion of blend

Blending Ratio	Flash point (^{0}C)	
	YOME	COME
B2	81	70
B5	85	75
B7	89	81
B10	93	89
B20	102	94
B40	118	113
B60	127	124
B80	148	139
B100	167	150

Appendix XIV: Variation of calorific value with increasing proportion of blend

Blending Ratio	Calorific value (KJ/Kg)	
	YOME	COME
B2	42800	41700
B5	41900	41200
B7	41300	39600
B10	40800	39300
B20	40400	38800
B40	39500	38300
B60	38920	37600
B80	38800	37000
B100	38700	36400

Appendix XV: Biodegradability of biodiesel from Yellow oleander and castor oil after 28 days

s/no	Days	TF (cm^3)			% CO_2 EVOLUTION		
		YOME	COME	DIESEL	YOME	COME	DIESEL
1	0	0.0	0.0	0.00	0.00	0.00	0.00
2	7	50.1	50.3	13.23	21.2	22.3	5.34
3	14	52.9	56.7	14.02	38.3	60.9	14.82
4	21	58.4	59.7	14.98	71.2	70.0	18.56
5	28	60.25	61.1	15.46	82.4	87.3	25.29