



NORTH-WEST UNIVERSITY
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Biodiesel production from sunflower oil using microwave assisted
transesterification

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B.Sc. (Hons)

Dissertation submitted in partial fulfilment for the requirements for Master of Science
in Engineering Science in Chemical Engineering at the North-West University
(Potchefstroom Campus)

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April 2013

ABSTRACT

Biofuels are becoming more attractive worldwide because of the high energy demands and the fossil fuel resources that are being depleted. Biodiesel is one of the most attractive alternative energy sources to petroleum diesel fuel and it is renewable, non toxic, biodegradable, has low sulphur content and has a high flash point. Biodiesel can be generated from domestic natural resources such as coconuts, rapeseeds, soybeans, sunflower, and waste cooking oil through a commonly used method called transesterification. Transesterification is a reaction whereby oil (e.g. sunflower oil) or fats react with alcohol (e.g. methanol) with or without the presence of a catalyst (e.g. potassium hydroxide) to form fatty acid alkyl esters (biodiesel) and glycerol. The high-energy input for biodiesel production remains a concern for the competitive production of bio-based transportation fuels. However, microwave radiation is a method that can be used in the production of biodiesel to reduce the reaction time as well as to improve product yields. Sunflower oil is one of the biodiesel feedstocks that are used in South Africa and is widely used in cooking and for frying purposes.

This study aims to use microwave irradiation to reduce the energy input for biodiesel production. The effect of various reaction variables, including reaction time (10 – 60 seconds), microwave power (300 – 900 watts), catalyst (potassium hydroxide) loading (0.5 – 1.5 wt%) and methanol to oil molar ratio (1:3 – 1:9) on the yield of fatty acid methyl ester (biodiesel) was investigated. The quality of biodiesel produced was analysed by Gas Chromatography (GC), Fourier Transform Infrared Spectroscopy (FTIR) and viscometry. The FTIR results confirmed the presence of functional groups of the FAME produced during transesterification.

The results showed that transesterification can proceed much faster under microwave irradiation than when using traditional heating methods. The interaction between the alcohol and oil molecules is significantly improved, leading to shorter reaction times (seconds instead of hours) and improved diesel yields. The highest biodiesel yield obtained was 98% at 1:6 oil-to-methanol molar ratio for both 1 wt% and 1.5 wt% potassium hydroxide (KOH) at a reduced reaction time (30 seconds). The chemical composition of FAME (biodiesel) obtained from different conditions

contained palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) and 70% linoleic acid (C18:2). The physical properties (cetane number, viscosity, density and FAME content) of biodiesel produced met the SANS 1935 specification. The energy consumption was reduced from 1.2 kWh with the traditional transesterification to 0.0067 kWh with the microwave transesterification.

Microwave irradiation was shown to be effective in significantly lowering the energy consumption for production of biodiesel with good quality for small scale producers.

Key words: Biodiesel, sunflower oil, microwave irradiation, yield, reaction time, catalyst load

UITTREKSEL

Biobrandstowwe word wêreldwys meer aantreklik as gevolg van hoer energievereistes en die uitputting van fossielbrandstofhulpbronne. Biodiesel is een van die mees aantreklike alternatiewe energiebronne teenoor petroleumdiesel en dit is hernubaar, nie giftig, bio-afbreekbaar, het 'n lae swaelinhoud en het 'n hoë flitspunt. Biodiesel kan gegeneer word deur plaaslike natuurlike hulpbronne soos kokosneute, canola-sade, sojabone, sonneblomme, en die kook van afval deur middel van 'n algemene metode wat transesterifikasie genoem word. Transesterifikasie is 'n reaksie waardeur olie (soos sonneblomolie) of vette met alkohol (soos metanol) reageer met of sonder die teenwoordigheid van 'n katalisator (bv. kaliumhidroksies) om vetsuuralkielesters (biodiesel) en gliserol te vorm. Die hoë energie-inset vir biodieselproduksie bly 'n bron van kommer vir die kompeterende produksie van bio-gebaseerde vervoerbrandstowwe. Mikrogolfbestraling is egter 'n metode wat gebruik kan word in die produksie van biodiesel om die reaksietyd te verminder en om produkopbrengste te verbeter. Sonneblomolie is een van die biodieselvoedingsbronne wat in Suid-Afrika gebruik word en word algemeen gebruik in die kook en braai van kos.

Hierdie studie het ten doel om mikrogolfbestraling te gebruik om die energie-inset vir biodieselproduksie te verminder. Die effek van verskeie reaksieveranderlikes, waaronder reaksietyd (10 – 60 sekondes), mikrogolfkrag (300 – 900 watt), katalisator (kaliumhidroksies) lading (0.5 – 1.5 wt%) en metanol tot olie molêre verhouding (1:3 – 1:9) op die opbrengs van die vetsuurmetielester (biodiesel) is ondersoek. Die kwaliteit van die biodiesel wat geproduseer is, is geanaliseer deur gaschromatografie (GC), Fourier Transform-infrarooispektroskopie (FTIR) en viskositeitsmeting.

Die resultate het getoon dat die transesterifikasie baie vinniger onder mikrogolfbetraling ontwikkel as wanneer tradisionele verhittingsmetodes gebruik word. Die interaksie tussen die alkohol en die oliemolekules het beduidend verbeter, wat korter reaksietye daargestel het (sekondes in plaas van ure) en dieselopbrengste verbeter het. Die hoogste biodieselopbrengs wat behaal is, was 98% by 'n 1:6 olie-tot-metanol molêre verhouding vir beide 1 wt% en 1.5 wt% kaliumhidroksied (KOH) teen 'n verlaagde reaksietyd (30 sekondes). Die chemiese

samestelling van VSME (biodiesel) wat uit verskillende toestande verkry is het palmitiensuur (C16:0), steariensuur (C18:0), oleïensuur (C18:1) en 70% linoleïensuur (C18:2) bevat. Die fisiese eienskappe (setaangetal, viskositeit, digtheid en VSME-inhoud) van die biodiesel wat geproduseer is het aan die SANS 1935-spesifikasie voldoen. Die energieverbruik van 1.2 kWh met die tradisionele transesterifikasie is verminder tot 0.0067 kWh met die mikrogolftransesterifikasie. Die FTIR-resultate het die teenwoordigheid van funksionele groepe van die VSME bevestig wat gedurende transesterifikasie geproduseer is.

Daar is aangetoon dat mikrogolfbestraling doeltreffend werk om die energieverbruik beduidend te verminder vir die produksie van biodiesel van goeie gehalte vir kleinskaalse produsente.

Slutelwoorde: Biodiesel, sonneblomolie, mikrogolfbestraling, opbrengs, reaksietyd, katalisatorlading

DECLARATION

I, Nokuthula E. Magida, hereby declare that the dissertation entitled “Biodiesel production from sunflower oil using microwave assisted transesterification” which I submitted to the North West University in partial fulfilment for the requirements set for Master of Science in Engineering Science in Chemical Engineering, is my own work.

Student signature

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April 2013

ACKNOWLEDGEMENTS

“I can do ALL things through Christ who gives me the strength”- Philippians

I would like to firstly thank God for his mercy, because without Him I would not have completed this study and I love you almighty Father.

To my supervisor, Prof. Sanette Marx, thank you very much for your leadership, guidance and understanding. My gratitude is also extended to Dr. Idan Chiyanzu and Corneels Schabort for their support.

I would also like to thank my parents Lunga H. and Nothozamile E. Magida for their prayers, encouragement and love, not forgetting my one and only son Khwezi, who has been patiently waiting for his mother.

Finally, thank you very much to Coega Development Corporation (CDC) for the student financial support, National Research Foundation (NRF) and South African National Energy Research Institute (SANERI) for the research financial support.

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NOMENCLATURES

Abbreviations	Description
GHG	Greenhouse gas
U.S.	United State
%	Percentage
kg	kilogram
ha	Hectare
H ₂ SO ₄	Sulphuric acid
H ₃ PO ₄	Phosphoric acid
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
NaOCH ₃	Sodium methoxide
wt	Weight
g	Gram
mg	milligram
°C	Degrees Celsius
mm ²	millimetre squared
L	Litre
mL	millilitre
K	Kelvin
s	Seconds

min	Minutes
Vol.	Volume
FAME	Fatty acid methyl ester
HC	Hydrocarbon
C	Carbon
CO	Carbon monoxide
CO ₂	Carbon dioxide
NO _x	Nitrogen oxide
SO _x	Sulphur oxide
H ₂	Hydrogen gas
He	Helium
B100	Pure biodiesel
B20	20% biodiesel in 80% diesel
FFA	Free fatty acid
e.g.	Example
<	Greater than sign
>	Less than sign
W	Watts
mol.	Moles
TMSH	Trimethylsulfonium hydroxide solution
kHz	kilohertz

MHz	Megahertz
GHz	Gigahertz
GC	Gas Chromatography
FID	Flame ionisation detector
FTIR	Fourier Transform Infrared Spectroscopy
DCM	Dichloromethane
IS	Internal standard
kPa	kilopascal
cP	centi Poise
µL	microlitre
cm	centimetre
Unk	Unknown
dod	Dodecane
MW	Molecular weight
MeOH	Methanol
SANS	South African National Standard

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1. Introduction

In this chapter an over view of the study is given. The background as well as the motivation of this study is discussed in Section 1.1. The aim and objectives are set out in Section 1.2 and the scope of this study is provided in Section 1.3.

1.1. Background

Traditional fossil fuel resources are being depleted because they are non-renewable energy resources; there is steady increase in its consumption, and increased industrialisation. To date, fossil fuels account for more than 80% of the energy consumed in the world of which 58% alone is consumed by the transport sector (Batidzirai *et al.*, 2012). The depletion of fossil fuel resources also led to an increase in crude oil prices (Zabeti *et al.*, 2009). During the past 27 years, higher standards of living, increased transportation and use of plastics and other petrochemicals, had resulted from the steady increase of petroleum consumption. According to BP's annual Statistical Review of World Energy (2008), the world proven oil reserves were estimated at 1.7×10^{11} tons with a reserve-to-production ratio of 42 years (Balat and Balat, 2010). The contribution of fossil fuels to greenhouse gas (GHG) emissions during its production and use is a major concern and leads to many negative effects including climate change, receding of glaciers, rise in sea levels and loss of biodiversity (Gullison *et al.*, 2007). Therefore, progress has been made to obtain alternative, renewable, sustainable efficient and cost-effective energy resources with less or no emissions.

Renewable energy resources are becoming increasingly important as alternative fuels to fossil fuels. This is because they are non-toxic, renewable and biodegradable. Biofuels, alternatives to fossil fuels, are any solid, liquid or gaseous fuels that are derived from biomass and are known to contribute to reduction in greenhouse gas emissions (Lee *et al.*, 2008).

Bioethanol and biodiesel are the most common types of transport biofuels. Bioethanol, which is an alcohol, is more prominent, since it accounted for approximately 84% of the total biofuels produced in 2008 (Mandil and Shihab-Eldin, 2010). Currently, the U.S. and Brazil, accounted for approximately 81% of total biofuel production and approximately 91% of global bioethanol production (Mandil and Shihab-Eldin, 2010). Bioethanol is produced from fermented sugar and starch-containing plant feedstock such as sugarcane and maize, respectively (Fortman *et al.*, 2008). Bioethanol can also be produced from lignocellulosic materials derived from plant matter such as wood, switch grass and crop residues.

Biodiesel is an ester based renewable and biodegradable form of fuel which consists of mono-alkyl esters of fatty acids derived from vegetable oils (such as canola, soybean and sunflower oil) and animal fats (Zabeti *et al.*, 2009). Biodiesel is mainly produced from rapeseed oil in Brazil, and amounted to approximately 2.4 billion litres in 2010 (Sousa *et al.*, 2012). Biodiesel is divided into three types based on the feedstock from which they are made. First generation biodiesel, which is produced from food-grade feedstocks such as sunflower oil, second generation biodiesel, which is produced from non-edible feedstocks such as waste vegetable oil and third generation biodiesel, which is produced from algae.

Biodiesel has a potential as an alternative fuel due to advantages such as high flash point, high cetane number, low viscosity, high lubricity and biodegradability. Biodiesel is also environmentally friendly because it produces less carbon dioxide than petroleum diesel when burned in an engine (Zabeti *et al.*, 2009). On the other hand, some disadvantages are low oxidation stability and oxidation products that may be harmful to vehicle components. The low oxidation stability and oxidation products can also cause dilution of engine lubricant oil, but the dilution of engine lubricant oil can be prevented by strictly monitoring the storage conditions and changing the oil frequently (Nolte, 2007).

Soybeans and sunflowers are the main oilseeds produced in South Africa, and canola, which is only grown in the winter rainfall production region, is used as a rotation crop. Soybeans produce a low oil yield per hectare (~328 kg/ha) but are

produced on large enough scale to be considered for biodiesel production. Canola oil yield (~440 kg/ha) is lower than that of sunflower, but a low canola price makes it a potential crop for biodiesel production, even though it would only be able to contribute to a small part of the necessary feedstock (Nolte, 2007).

Sunflower (*Helianthus annuus*), an annual vertical broadleaf plant, is one of the leading oilseed crops cultivated mainly in the provinces of Mpumalanga, Gauteng, North West, Limpopo and Free State in South Africa (DAFF, 2010). Sunflower oil, extracted from sunflower seeds is mainly used for human consumption, but it is also considered as an important feedstock for biodiesel production because sunflower produces higher yields of oil/ha (~513 kg/ha) than other oil crops (Nolte, 2007) and sunflowers can be grown both in spring and summer (Rashid *et al.*, 2008).

Four processes are used in the production of biodiesel. These are dilution/blending, micro-emulsification, pyrolysis, and transesterification. Among all these techniques, transesterification seems to be the best choice, as the physical characteristics of fatty acid esters are very close to those of diesel fuel and the process is relatively simple. Transesterification has been widely used to decrease the high viscosity of triglycerides (Meher *et al.*, 2006). Transesterification is a catalysed chemical reaction of an oil (or fat) and alcohol to produce fatty acid alkyl esters (biodiesel) and glycerol (Zhang *et al.*, 2010).

The dilution technique does not require any chemical process. In this technique, the problem posed by high viscosity of vegetable oils can be minimised by blending them with conventional diesel fuel (Balat and Balat, 2010).

Micro-emulsification is the formation of microemulsions (co-solvency), which is a potential solution for solving the problem of high vegetable oil viscosity. To solve the problem of the high viscosity of vegetable oils, microemulsions with immiscible liquids, such as methanol, ethanol and ionic or non-ionic amphiphiles have been studied (Balat and Balat, 2010).

Pyrolysis is used to optimise high-value fuel products from biomass by thermal and catalytic means. The conversion of vegetable oils and animal fats by pyrolysis

reaction shows a promising option for the production of biodiesel (Balat and Balat, 2010).

With the ever-increasing concerns about the use of fossil fuels for transportation both in South Africa and the world, there is a definite need to replace these with biofuels and other alternatives. The focus of this study is to see if microwave irradiation can be used to lower the cost of biodiesel production while still producing biodiesel that conforms to the SANS standard.

1.2. Aims and Objectives

The main aim of this study is to use microwave irradiation to reduce the energy input for biodiesel production.

The influence of the following parameters on biodiesel yield and composition during microwave assisted transesterification of sunflower oil was assessed:

- Reagent loading (alcohol: oil ratio)
- Catalyst loading (wt% catalyst)
- Power use (irradiation intensity)
- Reaction time

1.3. Scope of the dissertation

- **Chapter 1** provides an introduction on biofuels, specifically biodiesel as well as the motivation for and the objectives of the study.
- **In Chapter 2** sunflower oil and its composition as well as biodiesel and its production processes are discussed. Literature about microwave assisted transesterification as well as parameters that influence biodiesel production are also discussed.
- **In Chapter 3** the details of experimental method used in this study as well as analytical techniques employed are given.

- **In Chapter 4** the results of this study and a discussion of the influence of reaction time, microwave power, oil/alcohol ratio and catalyst loading on biodiesel yield and composition are provided. The biodiesel produced using microwave assisted transesterification is also tested against the South African standard (SANS 1935). Lastly, the energy input of microwave assisted transesterification compared to conventional transesterification is evaluated.
- **Chapter 5** provides the conclusions and recommendations based on the findings of this study.

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2. Literature Study

In this chapter, sunflower oil and its composition is discussed as well as biodiesel and its production processes. A description of sunflower oil is given in section 2.1 while biodiesel description, its properties, emissions and production processes are given in Section 2.2. The technologies used to produce biodiesel are discussed in section 2.3 and parameters that influence biodiesel production are discussed in section 2.4.

2.1. Sunflower seed

Sunflower (*Helianthus annuus*) is one of the most important oil-producing crops grown worldwide that contain a fatty acid composition that have high nutritional value to humans (Grompone, 2005). The demand for sunflowers, a vegetable oil plant, has increased drastically since the 1970s and is expected to further increase due to the world population growth and the increasing demands, especially in biodiesel production. The annual production of sunflower seeds was globally estimated at 404 million ton in 2008/2009, while South Africa produced between 170 000 and 1100 000 ton in the same year (DAFF, 2010). Sunflowers are planted more widely in the drier western areas (Lichtenburg and Koonstad) of the Highveld region than in the wetter eastern areas (Middelburg) (Durand, 2006). The area in which sunflowers were planted constituted approximately 70% of the total area for all oilseeds crops in 2007 (see Figure 2.1) (Marvey, 2009). Sunflower plants have been reported to require less irrigation than maize (Durand, 2006). Therefore, in seasons where rain is late, farmers plant sunflower as an alternative crop just to get a yield from a field.

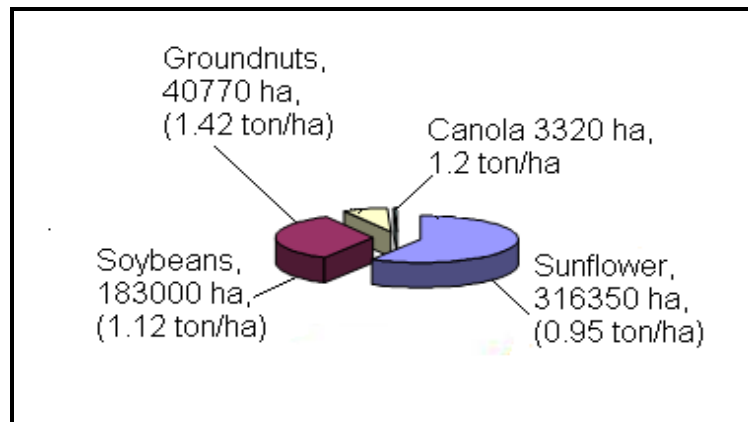


Figure 2.1: Oilseed production in South Africa showing area planted (ha) and yield in 2007 (Marvey, 2009).

The sunflower seed is 4-sided and flat, approximately 0.6 cm long and 0.3 cm wide. The seed comprises a pericarp (hull), a seed coat and kernel that is also known as embryo. The kernels contain nearly all the oil in the seeds. Additionally, they also contain protein and carbohydrates. The average oil content of the kernel is 50-70% and the average protein content of the seed is 20-30% (Grompone, 2005). Figure 2.2 shows the composition of sunflower kernel.

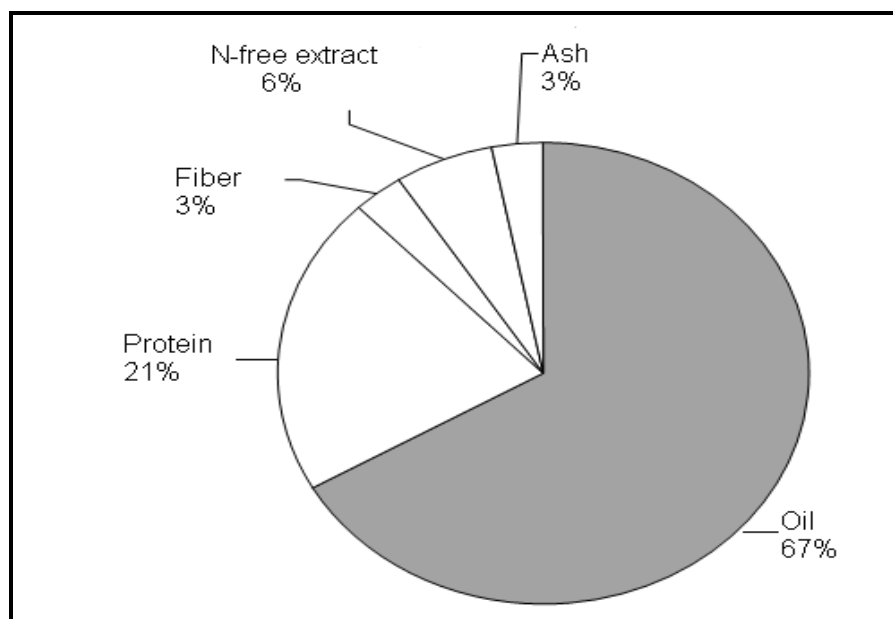


Figure 2.2: Composition of sunflower kernel (Grompone, 2005).

The way in which sunflower oil is extracted, is by pressing the sunflower seeds and collecting the oil. Native Americans used to obtain the oil by boiling the seeds and skimming the oil from the top of the boiling pot. From every 100kg of sunflower seed, it is estimated that approximately 40kg of oil, 30kg of high-protein meal and 20-25kg of by-products are produced (FAO, 2010). The schematic flow diagram describing the steps of obtaining sunflower oil from the plant is shown in Figure 2.3.



Figure 2.3: Schematic flow diagram of sunflower oil from the plant.

2.1.1. Sunflower oil composition

Sunflower oil consists of mainly two unsaturated fatty acids (oleic acid and linoleic acid) and two types of saturated fatty acids (palmitic acid and stearic acid). The quality of the oil is associated with the percentage composition of the fatty acids in the oil. Generally, 90% is oleic acid (C18:1) and linoleic acid (C18:2) in reciprocal proportions (Murphy, 1994), although Lide (1991) states that sunflower oil consists of 25.1% oleic acid and 66.2% linoleic acid. Palmitic acid (C16:0) and stearic (C18:0) acid make up 7-10% of the oil composition. Ma *et al.*, (1997) found that minor constituents of arachidic (C20:0), behenic (C22:0) and lignoceric acid (C24:0) may be present in sunflower oil. Table 2.1 shows the chemical composition of sunflower oil (FAO, 2010).

Table 2.1 Average fatty acid composition of sunflower oil (FAO, 2010).

Common name	Formula	Weight %
Palmitic acid	C 16:0	4-9
Stearic acid	C 18:0	1-7
Oleic acid	C 18:1	14-40
Linoleic acid	C 18:2	48-70

2.1.2. Sunflower oil as a potential biodiesel feedstock

Sunflower seeds have a great potential to become biodiesel due to their comparable properties to diesel, including calorific values and cetane number. The results of recent studies indicated that sunflower seeds can be grown for biodiesel production purposes only and the seeds provided the highest yields among the varieties tested (Chigeza *et al.*, 2012). New hybrids of sunflowers with different compositions of fatty acids, growth characteristics and oil content, have been cultivated (Zheljazkov *et al.*, 2008). In South Africa, genetic improvements to the sunflower seed yield, oil quality and oil contents in different cultivars have been conducted for the past four decades (Chigeza *et al.*, 2012).

2.2. Biodiesel

Biodiesel is a biofuel that consists of mono-alkyl esters of fatty acids derived from vegetable oils and animal fats by transesterification. It is a renewable and biodegradable form of energy and has potential as an alternative fuel (Zabeti *et al.*, 2009). The properties of biodiesel are given in Table 2.2.

Table 2.2 Allowed quantities in diesel and biodiesel (SANS 1935, 2004; SANS 342, 2006).

Property	Diesel	Biodiesel
Standard	SANS 342	SANS 1935
Composition	HC ^a (C10–C21)	FAME ^b (C14–C22)
Ester content (% mass fraction)	-	>96.5
Kinematic viscosity (mm ² /s) at 40°C	2.0–4.5	3.5–5.0
Density at 15°C (kg/m ³)	820-845	860-900
Cetane number	>47	>51.0
Flash point (°C)	>55	>120
Water (% mass fraction)	-	<0.05

^a Hydrocarbons.

^b Fatty acid methyl esters.

The major challenges associated with the use of biodiesel as a fuel are its high viscosity, low energy content, high cloud point and pour point, high nitrogen oxide emission, lower engine speed and power, injector coking, engine compatibility, high price, and high engine wear (Demirbas, 2008). The high cost of biodiesel production, which is 1.5 times higher than that of petroleum diesel, is an obstacle in the use of biodiesel (Lin *et al.*, 2012). Biodiesel can be blended with diesel to reduce the particulate emissions from the engine as well as the cost impact of biodiesel.

Biodiesel can be either used in its pure form (B100) or can be blended with conventional diesel (e.g. B20) (Szybist *et al.*, 2007). Biodiesel can also be used as an additive because it is a very effective lubricity enhancer (Nolte, 2007). A further use of biodiesel is in conventional compression-ignition engines without the need for

engine modification (Dube *et al.*, 2007). Biodiesel contains electronegative elemental oxygen, therefore it is slightly more polar than diesel fuel, and as a result the viscosity of biodiesel is higher than that of diesel fuel. The heating value of biodiesel is lower than diesel fuel due to the presence of elemental oxygen (Balat and Balat, 2010).

2.3. Technologies for biodiesel production

Among the available biodiesel production technologies; dilution/blending, micro-emulsification and pyrolysis; transesterification seems to be the best choice, as the physical characteristics of fatty acid esters are very close to those of diesel fuel and the process is relatively simple.

2.3.1. Transesterification process

Transesterification is a widely used process to produce biodiesel (Meher *et al.*, 2006). Transesterification is a chemical reaction of oil with alcohol to produce esters and glycerol (see Figure 2.4) (Abdullah *et al.*, 2007). The reaction can proceed either with or without a catalyst. A 3:1 molar ratio of alcohol to triglyceride is required to complete the reaction stoichiometrically (Stavarache *et al.*, 2005). Since the reaction is reversible, an additional amount of alcohol is required to shift the equilibrium to the product's side (Vyas *et al.*, 2010). Alcohols that are primarily used in the transesterification reaction are primary and secondary monohydric aliphatic alcohols, having 1-8 carbon atoms (Banerjee and Chakraborty, 2009; Demirbas, 2009). The alcohols that are used in transesterification are generally short chain alcohols, such as methanol, ethanol, propanol, and butanol (Lucia *et al.*, 2006). The alcohols most often used are methanol and ethanol, but methanol find frequent commercial application because of its low cost and its physical and chemical advantages (polar and short chain alcohol) (Banerjee and Chakraborty, 2009; Balat and Balat, 2010).

3



Figure 2.4: Transesterification reaction of triglycerides with alcohol (Abdullah *et al.*, 2007).

Catalysts that can be used in transesterification reactions are divided into two categories, namely homogeneous (single phase) and heterogeneous (solid) catalysts. Homogeneous catalysts are more often used due to their superior performance in transesterification reactions. Acid or base (alkaline) catalysts can be used, depending on the nature of the oil used for the biodiesel production. Moreover, the choice between acid or alkaline catalyst may depend on the free fatty acids (FFA) content in the raw oil. Acid-catalysed transesterification is only effective when the oil has a high amount of free fatty acids and the process is very long. Alkaline-catalysed transesterification is most often used because it is much faster than acid-catalysed transesterification (Hoque *et al.*, 2011).

2.3.1.1. Alkali-catalysed transesterification

Alkali-catalysed transesterification have been used widely for accelerating the chemical reaction in producing biodiesel and for achieving higher reaction yields within a short time (Shahbazi *et al.*, 2012). Bases that are used in the transesterification reaction are alkaline metal alkoxides, hydroxides and sodium or potassium carbonates. Conventional industrial processes favour homogeneous basic catalysts, such as alkaline hydroxides (sodium hydroxide, potassium hydroxide and sodium methoxide) due to its higher reaction rates and requirement of lower reaction temperature (between 25°C and 70°C) and pressure (atmospheric). Furthermore, small amounts of catalyst required for the reaction and little or no darkening of the oil compared to the acid-catalysed reaction is found (Singh and Padhi, 2009). Amongst

all bases, KOH is more often used than NaOH, because the reactive electron in the case of Na⁺ is situated on the s³ orbital and the OH⁻ is more tightly bound to the Na⁺ and less available for the reaction. In the case of K⁺, the reactive electron is on the s⁴ orbital, thus in this instance the OH⁻ is more mobile and therefore much more reactive (Stavarache *et al.*, 2006).

Despite the many named advantages, base-catalysed reactions produce water from the reaction between hydroxide and alcohol, even though water-free oil and alcohol are used. The presence of water leads to the hydrolysis of esters and then causes a saponification reaction to occur (Yee *et al.*, 2011) (see Figure 2.5).

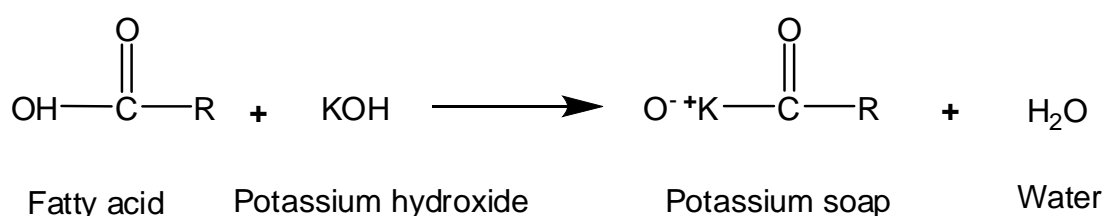


Figure 2.5: Saponification reaction (Van Gerpen, 2005).

The yield of fatty acid methyl esters (FAME) may be decreased by the formation of soap, which can also lead to difficulty in downstream separation processes and thus an increase in the cost of the operation (Kansedo *et al.*, 2009). Additionally, the soap binds with the catalyst, meaning more catalyst has to be added to complete the transesterification process (Van Gerpen, 2005).

A three-step mechanism for alkali-catalysed transesterification of vegetable oils (Schuchardt *et al.*, 1998) is provided in Figure 2.6. A base speeds up the reaction by removing a proton from the alcohol, thus making it more reactive (Demirbas, 2008). At the carbonyl group of the triglyceride, the nucleophilic attack of the alkoxide produces a tetrahedral intermediate (step 1). From this step, the alkyl ester and the corresponding anion of the diglyceride are generated (step 2). The latter deprotonates the catalyst, thus regenerating the active species (step 3). This active species is now able to react with a second molecule of the alcohol, starting another catalytic cycle (Balat and Balat, 2010). The same mechanism is used for the

conversion of diglycerides and monoglycerides to a mixture of alkyl esters and glycerol (Schuchardt *et al.*, 1998).

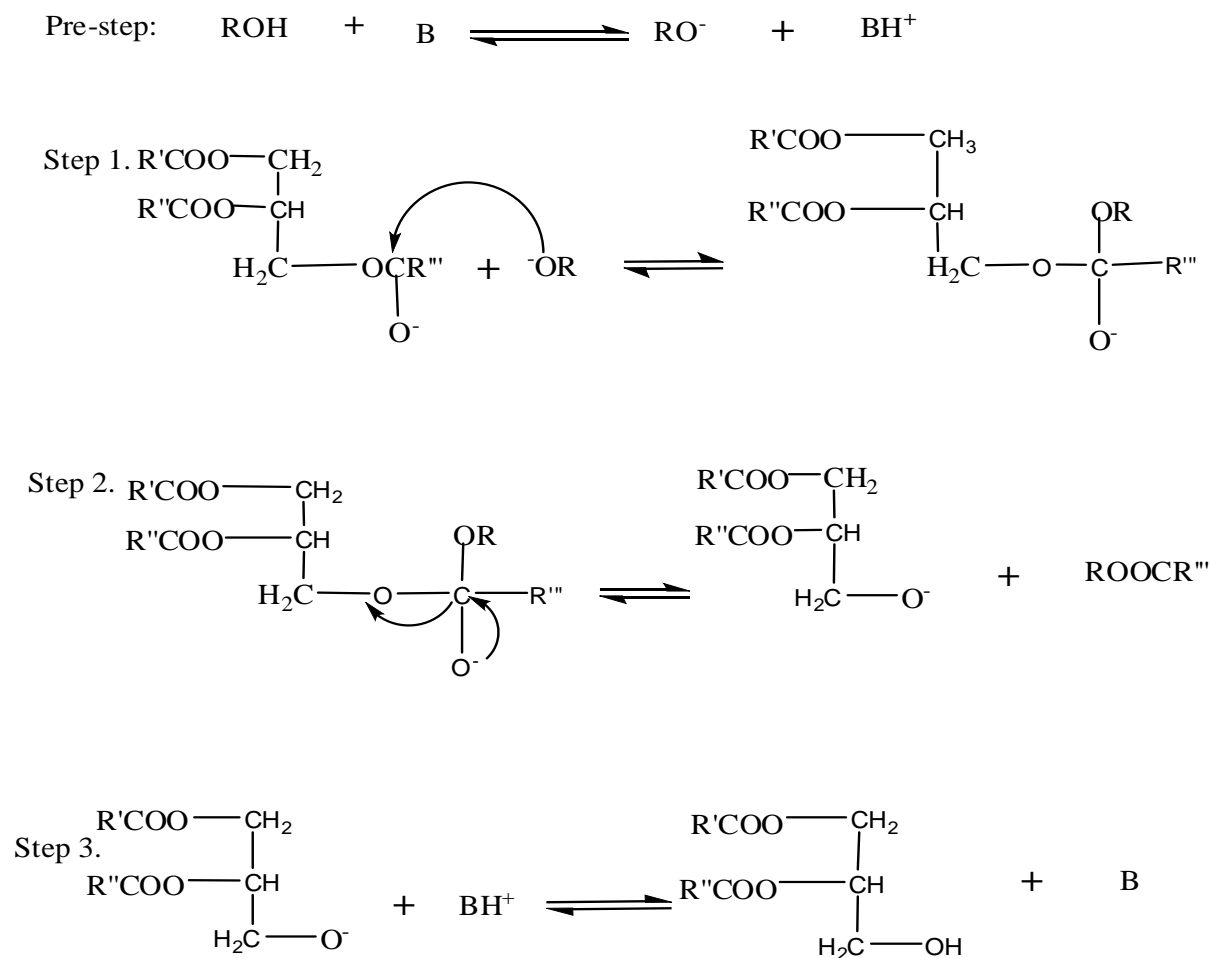


Figure 2.6: Mechanism of base-catalysed transesterification reaction B (base) (Schuchardt *et al.*, 1998).

2.3.1.2. Microwave assisted transesterification

The production of biodiesel has previously been happening by using conventional heating systems. However, these systems are inefficient and usually require longer reaction times. Microwave irradiation is an alternative stimulant that can be used for the synthesis of biodiesel (Nezihe and Aysegul, 2007). Microwave-assisted transesterification was first mentioned in 1986 when Gedye and Guigere carried out two experiments, one with conventional heating and the other with microwave irradiation (Lidstrom *et al.*, 2001). The obtained data from both experiments was

compared and a significant reduction of reaction time was noted with the microwave experiment. This resulted in an increased application of the microwave technique (Da Ros *et al.*, 2012). The word microwaves refer to electromagnetic waves that have frequencies between 300 MHz and 300 GHz.

Microwaves activate a small degree of variance in polar molecules and ions, such as alcohol, with the continuously altering magnetic field. When molecular dipoles and charged ions interact with the altering electrical field, they have a rapid rotation, and heat is generated due to molecular friction (Nezihe and Aysegul, 2007). Microwave irradiation is increasingly becoming popular for heating since it is cheap, clean and it is a convenient technology. The use of microwave irradiation often reduces the reaction and separation time while product yields are improved (Vyas *et al.*, 2010). Other advantages of using microwave transesterification include; low oil/alcohol ratio, ease of operation, a drastic reduction of by-products, with the addition of reduced energy consumption.

A 93.7% (for 1 wt% KOH) and 92.2% (for 1 wt% NaOH) yield of biodiesel have been reported at 40°C after being heated for one minute in the microwave (Nezihe and Aysegul, 2007). The efficiency of using microwave irradiation was again shown when Barnard *et al.* (2007) obtained a 98% conversion to biodiesel after five minutes of microwave assisted transesterification with methanol at an oil-to-alcohol ratio of 1:6 and with NaOH as a catalyst. Refaat and Sheltawy (2008) reported a 100% biodiesel yield through the microwave irradiation application after two minutes, compared to one hour with the conventional transesterification. The separation step was completed within thirty minutes compared to eight hours of the conventional technique. Liao and Chung (2011) also reported a conversion of 99% at a 1:6 oil-to-methanol ratio, 1 wt% NaOH catalyst loading and 3 mL/minute flow rate using a continuous microwave system set at 80 W. A conversion of 97% was obtained at two minutes, 1 wt% KOH and 1:7.5 oil to methanol ratio using microwave irradiation compared to 98% that was obtained after one hour using the conventional transesterification method (El Sherbiny *et al.*, 2010). Lin *et al.* (2012) reported a 99% biodiesel yield at after minutes, at a 1:6 oil to methanol ratio, with a 0.75 wt%

CH₃ONa catalyst loading using a microwave system set at 750 W, and 97% using conventional heating at 90 minutes. The total energy consumption was 3.05 and 0.14 kWh for the conventional and microwave heating systems, respectively (Lin *et al.*, 2012).

2.4. Parameters that influence biodiesel production

While there are many factors affecting transesterification reactions, the most important variables that influence biodiesel production and its quality are: reaction time, temperature, type of catalyst and its concentration and molar ratio of alcohol to oil. Although transesterification reactions are well-established techniques, it is important that parameters are always optimised to avoid either incomplete reactions or lower yields.

2.4.1. Effect of reaction time

In the transesterification reaction, reaction time is the key to the yield and quality of biodiesel obtained. In the base catalysed transesterification of vegetable oil, a reaction time of one hour is the norm. Felizardo *et al.* (2006) for example reported that after one hour of reaction, at a methanol/oil molar ratio of 4:8 and using a catalyst concentration of 0.6% (by wt of oil) the highest yield of methyl ester was obtained using cooking oil as a feedstock. Zheng *et al.* (2006) carried out an acid-catalysed transesterification of waste frying oil, using excess methanol and noticed that the reaction was complete after four hours. They were using the following conditions; 70°C with oil: methanol: acid molar ratio in the range of 1: 245: 3:8 and at 80°C with oil: methanol: acid molar ratio in the range of 1:9–1: 245: 3:8. The reaction time does not increase the conversion but favours the backward reaction (hydrolysis of esters), which results in a reduction of product yield (Banerjee and Chakraborty, 2009). Therefore, the shorter reaction time is preferred as it will also save the energy that is used to produce biodiesel.

2.4.2. Effect of reaction temperature

The rate of transesterification is strongly affected by the reaction temperature. However, the reaction can be carried out at room temperature if enough time is provided (Srivastava and Prasad, 2000). The reaction temperature is always kept

close to the boiling point of methanol, if methanol is used as the alcohol at atmospheric pressure. According to Cvenegros and Cvenegrosova (2004), the reaction temperature can be maintained at 65°C in the transesterification of used frying oils using a NaOH/methanol solution. Srivastava and Prasad (2000) reported a maximum yield of fatty acid methyl esters at temperatures ranging between 60 and 80°C at an alcohol to oil molar ratio of 6:1.

2.4.3. Effect of catalyst concentration

The transesterification reaction can be catalysed by alkali, acid or enzyme catalysts. Enzymes-catalysed methods use lipase as catalyst and do not produce side reactions, but lipases are very expensive for industrial scale production. Acid-catalysed methods use acids such as H₂SO₄ and H₃PO₄ and are useful when a high amount of free acids (<3%) are present in the vegetable oil, but the reaction time is very long (48–96 h), and a high molar ratio of alcohol to oil (20:1) is needed. The base-catalysed method (e.g. KOH and NaOH) produces some soap which acts as phase transfer catalyst, thus helping the mixing of the reactants. Base-catalysed processes are strongly affected by the mixing of the reactants and/or by efficient heating that produces tiny droplets, thus increasing the reaction area. Today, mixing/heating is the process of choice used in industrial application in over 85 biodiesel plants worldwide (Stavarache *et al.*, 2005).

In the transesterification of waste cooking oil, Meng *et al.* (2008) reported 1wt% NaOH as the optimum catalyst concentration. Similarly, Yuan *et al.* (2008) obtained the highest conversion at 1wt% catalyst (alkaline) concentration in the transesterification of waste rapeseed oil. The alkaline catalyst concentration in the range of 0.5–1% by weight yield 94–99% conversion of vegetable oil into esters (Banerjee and Chakraborty, 2009).

2.4.4. Effect of alcohol to oil ratio

The alcohol-to-oil molar ratio is another important parameter which has a tremendous influence on the yield of esters. For a transesterification reaction to be completed stoichiometrically, a 3:1 alcohol/oil molar ratio is required (Vyas *et al.*, 2011). The transesterification reaction being a reversible one, the yield of biodiesel

through the forward reaction is favoured at excess of alcohol or by separation of one of the products from the reaction mixture. Vyas *et al.* (2011) obtained a 95% conversion when using Jatropha oil and an ultrasonic bath (30 kHz) as a heating source. The optimum molar ratio of alcohol to oil, 6:1, is used in most of the industrial processes of biodiesel synthesis. The oils with high free fatty acid content (e.g. waste cooking oil), use a high molar ratio (15:1) under acid catalysis (Banerjee and Chakraborty, 2009). Alcohols that favour the reaction in the forward direction are primary and secondary monohydric aliphatic alcohols having 1–8 carbon atoms.

2.5. Concluding remarks

The demand for sunflower oil for the production of biodiesel is clearly increasing due to negative environmental effects of fossil diesel and the decreasing petroleum resources. Current studies have shown that sunflower oil containing a suitable type of triglyceride oil is suitable as a feedstock for biodiesel production. Since vegetable oils cannot be directly utilised in engines due to their high viscosity, poor cold flow properties and low volatility, there is a need to modify the viscosity to meet conventional diesel standards. One of the ways to improve the characteristics of triglycerides is by catalysed transesterification with methanol in the presence of an alkaline catalyst.

Microwave irradiation is an alternative method of heating that can be used to speed up the reaction rate. In future, microwave heating system can be employed using KOH as a catalyst, since it is more reactive than NaOH, and methanol as an alcohol because of its low cost, physical and chemical advantages (polar and short chain alcohol). Microwave irradiation can be used with the following optimum conditions; 1:6 molar ratio of oil to methanol and 1wt% KOH catalyst loading.

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3. Experimental

In this chapter, the details of the experimental methods used in the production of biodiesel using microwave assisted transesterification are given. The materials and chemicals used in this study are listed in Section 3.1. The experimental procedure is described in Section 3.2 while the descriptions of analytic equipments as well as the method used for analyses are provided in section 3.3.

3.1. Materials and chemicals

A list of materials and chemicals that were used in this study are given in Table 3.1.

Table 3.1 Material and chemicals used in the study.

Component	Supplier	CAS-no	Purpose
Sunflower oil	Shoprite	-	Oil for biodiesel production
Potassium hydroxide (KOH)	Sigma-Aldrich	1310-58-3	Catalyst
Methanol	Sigma-Aldrich	67-56-1	Reagent for biodiesel production
Cyclohexane	Sigma-Aldrich	110-82-7	FTIR (Eraspec) analysis
Dichloromethane	Sigma-Aldrich	75-09-2	Solvent for GC analysis
Dodecane	Sigma-Aldrich	112-40-3	Internal standard for GC analysis
Methyl nonanoate	Sigma-Aldrich	1731-84-6	Internal standard for GC analysis
Trimethylsulfonium hydroxide solution (TMSH)	Sigma-Aldrich	17287-03-5	Sample derivative

3.2. Experimental procedure

The experimental procedure followed in the production of biodiesel in this study is visually illustrated in Figure 3.1.

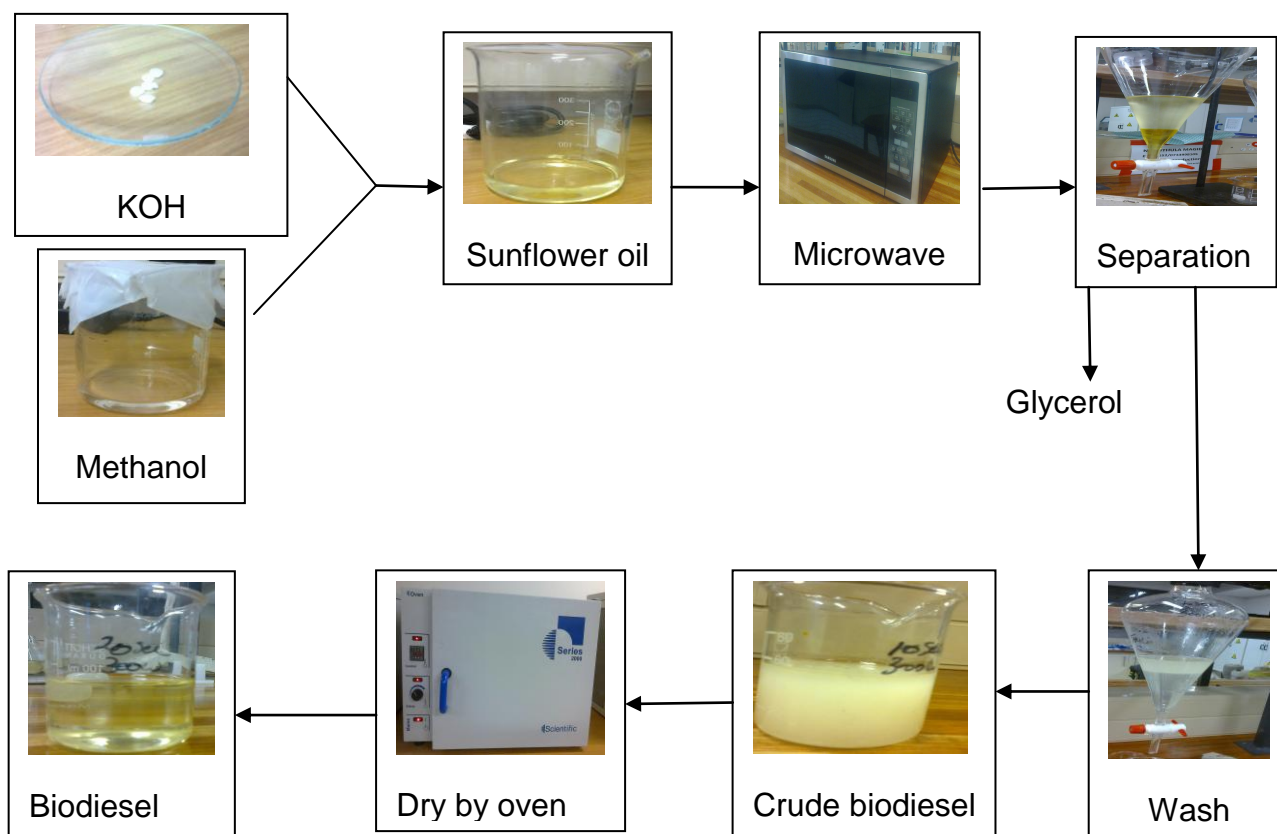


Figure 3.1: Experimental procedure for biodiesel production.

3.2.1. Microwave-assisted transesterification (modified from Rashid *et al.*, 2008)

Transesterification reactions were carried out at different oil-to-methanol ratios (1:3, 1:6 and 1:9), different microwave powers (300 W, 450 W, 600 W and 900 W) and different reaction times (10, 20, 30, 40, 50 and 60s) in the presence of potassium hydroxide (KOH) catalyst (0.5 wt%, 1 wt% and 1.5 wt%). The KOH catalyst was dissolved in methanol and the mixture was added to the oil. The reaction mixture was then heated by a microwave oven with a power range from 100-900 W (shown in Figure 3.2) for the desired reaction time. The reaction was stopped with 0.5 mol/L

hydrochloric acid (1 mL) immediately after taking it out of the microwave. About 216 experiments were conducted by changing one variable and keeping the others constant, and each experiment used 50g of oil as starting material.



Figure 3.2: Household microwave oven.

3.2.2. Separation/purification of biodiesel from the reaction mixture

The reaction mixture was cooled at room temperature and then poured into a separating funnel to separate biodiesel from glycerol for two hours (Figure 3.3). After two hours, the glycerol phase was withdrawn at the bottom of the funnel and the crude biodiesel layer was washed three times with 50ml hot water (80°C), to remove any traces of catalyst and glycerol. The washed biodiesel was then dried overnight at 105°C using a conventional oven.

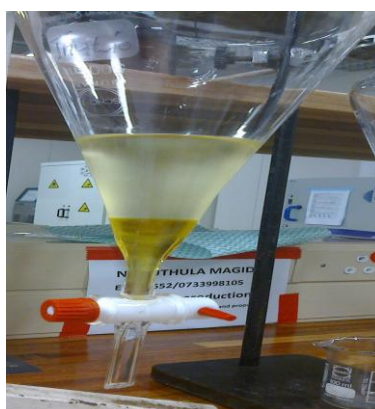


Figure 3.3: Biodiesel and glycerol separation.

3.3. Analyses

The produced biodiesel was analysed by using Gas Chromatography (GC), a Fourier Transform Infrared Spectroscopy (FTIR) and Viscometry to determine the yield as well as the quality of the biodiesel.

3.3.1. Gas Chromatography (GC) analysis

Gas chromatography (Agilent 7890A) was used to determine the composition of fatty acid methyl esters (FAME). The instrument is equipped with an Agilent 5975C auto-injector, HP-88 (100 m) column and a flame ionization detector (FID) (see Figure 3.4).



Figure 3.4: Gas chromatography.

The method information in which the gas chromatography operated was: Helium was the carrier, linear viscosity of 35 cm/s, a split ratio of 1/150, an injection of 1.0 μL , an inlet temperature of 250°C and a pressure of 381.98 kPa, an oven programming of 100°C for 5 min, FID detector at 350°C, H₂ flow rate of 40mL/min, an air flow rate of 400mL/min, a make-up He flow rate of 1.0mL/min and dichloromethane was a solvent for the needle. The calibration curves of fatty acid composition are given in Appendix B.1.

3.3.1.1. Sample preparation

(a) Biodiesel analysis: A 100 μL of biodiesel sample was transferred into a sample vial and the mass was recorded. An internal standard (methyl nonanoate) (20 μL) was added to the biodiesel sample and the mass of the mixture was recorded.

$$m_{\text{IS}} = m_{\text{combined}} - m_{\text{biodiesel}}$$

The mixture of biodiesel and IS was diluted to approximately one mL using dichloromethane (DCM). The mixture was vortexed and analysed by GC.

(b) Sunflower oil analysis: A 100 μL of sunflower oil was mixed with Trimethylsulfonium hydroxide solution (TMSH) (100 μL). After vortexing the mixture, 10 μL of dodecane was added and then the mixture was analysed by GC.

3.3.2. Fourier Transform Infrared Spectroscopy (FTIR) analysis

(a) The Fourier transform infrared spectroscopy (Eraspec, South Africa) (shown in Figure 3.5) was used to determine the biodiesel properties, amongst others the cetane number and density. The Eraspec was cleaned with a cyclohexane before and after analysing the samples. Each sample was sucked using the yellow pump attached to the machine, scanned seven times and the results were displayed on the screen.



Figure 3.5: Fourier transform infrared spectroscopy (Eraspec).

(b) The Fourier transform infrared spectroscopy (FTIR) IRAffinity-1 (Shimadzu, South Africa) (shown in Figure 3.6) was used to investigate the functional groups of biodiesel. Each biodiesel sample was dropped on top of an ATR unit, which was fitted on top of the sample holder. The samples were then scanned ten times and the wavelength ranged from 600 cm^{-1} to 4000 cm^{-1} . The ATR was cleaned with propanol after every sample analysis. All spectra were referenced against the background spectrum (the ATR without biodiesel). IR resolution software was used to analyse the spectra produced.



Figure 3.6: Fourier transform infrared spectroscopy (mid IRAffinity-1).

3.3.3. Viscometry analysis

A U-tube viscometer (shown in Figure 3.7) was used to determine the biodiesel viscosity and to confirm the biodiesel yield. The U-tube was filled to a marked point C with a biodiesel sample. The sample was pumped up to a marked point A and the pump was removed. The time the sample travelled from point A to point B was measured. The kinematic viscosity of biodiesel in mm^2s^{-1} was calculated by dividing the measured dynamic viscosity with the measured density (Viswanath *et al.*, 2007; Sparks *et al.*, 2009). The U-tube calibration curve and the formula used to calculate the viscosity are given in Appendix A.4.

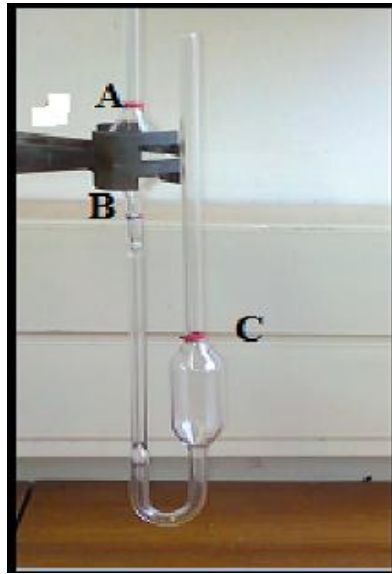


Figure 3.7: U-tube viscometer used in this study.

3.3.3.1. Sample preparation

The Sunflower oil and the FAME (biodiesel) mixtures were used to make up solutions of different concentrations starting from 0% up to 100% at 40°C (Eleftheriades and von Blottnitz, 2012). The time the mixture takes to flow from a marked point A to a marked point B was measured. The calibration curve was plotted with the viscosity on the Y-axis and percentage conversion on the X-axis (see Appendix A.3). The biodiesel yield of a known viscosity was measure from the calibration curve.

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4. Results and Discussion

4.1. Chemical composition of sunflower oil and its corresponding fatty acid methyl ester (FAME)

In this study sunflower oil is the feedstock used to produce biodiesel using microwave irradiation as a heating system. The fatty acid composition of the sunflower oil used was determined by using Gas Chromatography (GC) and are within the expected range (see Table 4.1) (FAO, 2010).

Table 4.1 Fatty acid composition of sunflower oil.

Name	Formula	Weight %	Expected range
Palmitic acid	C16:0	8.07	(4-9)
Stearic acid	C18:0	0.65	(1-7)
Oleic acid	C18:1	20.85	(14-40)
Linoleic acid	C18:2	70.43	(48-74)

The fatty acids obtained were palmitic acid, stearic acid, oleic acid and linoleic acid. The results showed large amounts of unsaturated fatty acids, with linoleic acid being the most abundant, comprising approximately 70% of the sunflower oil.

The produced fatty acid methyl ester (biodiesel) was also analysed using GC and the FAME composition corresponded to the composition of fatty acids in the sunflower oil used in the transesterification reaction. The chemical structure of the FAME at 1 wt% KOH, a 1:9 molar ratio, a 900 W and 30 s of reaction time composed of 6.4 wt% palmitic acid, 5.0 wt% stearic acid, 20.7 wt% oleic acid and 66.9 wt% linoleic acid. This is comparable to the results obtained by Ramadhas *et al.* (2005). The chemical compositions of biodiesel at different conditions are given in Appendix C and gas chromatograms that show the chemical compositions are given in Appendix B.2.

4.2. Biodiesel production by microwave assisted transesterification

Biodiesel was produced from sunflower oil using microwave assisted transesterification at different power settings (300, 450, 600 and 900 W), reaction times (10, 20, 30, 40, 50 and 60 s), catalyst concentrations (0.5, 1 and 1.5 wt %) and oil-to-methanol ratios (1:3, 1:6 and 1:9).

4.2.1. Effect of reaction time

Reaction time is one of the important transesterification parameters that need to be optimised when producing fatty acid methyl esters. A shorter reaction time leads to less production of esters and an increased production of diglycerides and monoglycerides (Zhang *et al.*, 2010). This study was carried out at different reaction times (10-60 s) and microwave power settings (300, 450, 600 and 900 W), while other parameters were kept constant (0.5 wt% KOH and 1:6 oil-to-methanol ratio). Other experiments were conducted at a 1:3 and 1:9 oil/methanol ratio for 1 wt%, 0.5 wt% and 1.5 wt% were both used at a 1:3, 1:6 and 1:9 oil-to-methanol ratio (results are shown in Appendix E.1). The influence of reaction time on biodiesel yield at different power settings is given in Figure 4.1 and the fatty acid composition of biodiesel at 450 W is given in Table 4.2.

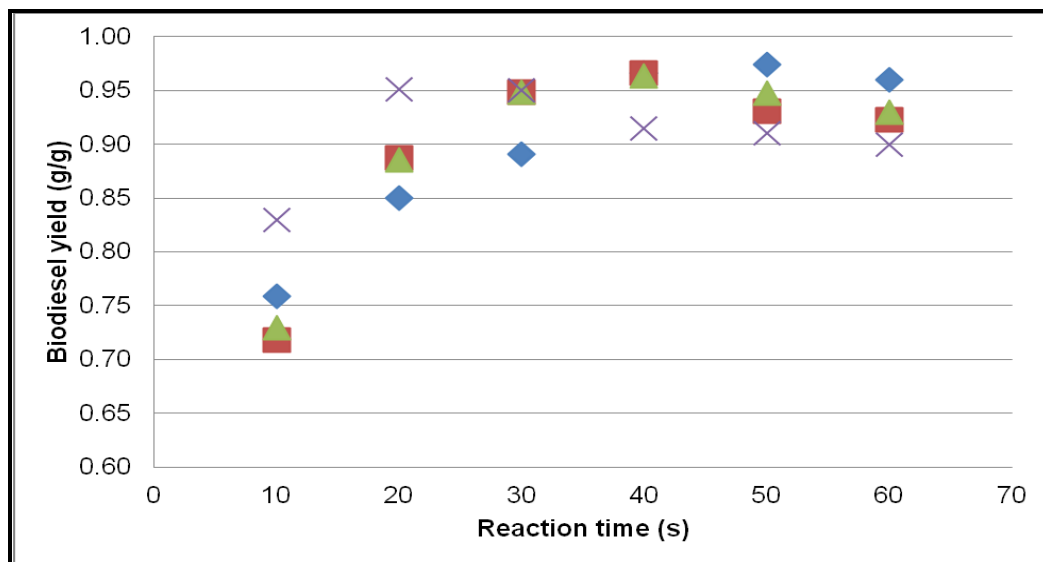


Figure 4.1: Effect of reaction time on biodiesel yield at 0.5 wt% KOH, 1:6 oil/methanol molar ratio (♦300 W ■450 W ▲600 W ✕900 W).

Within 10-40 s, the FAME yield rapidly increased with increasing transesterification time. The highest biodiesel yield (97%) was obtained at 40 and 50 s for 450 W and 300 W, respectively. After 40 s, the yield decreased gradually, meaning that the FAMES reached the equilibrium point and the formation of soap was observed due to a longer reaction time. Saponification was observed at higher reaction times (50 and 60 s), except at 300 W. The saponification led to difficulty in the washing step, which resulted in reduced biodiesel yields (92% at 60 s and 450 W). Therefore, from the results in Figure 4.1, 40 s seems to be the optimum reaction time for biodiesel production under microwave irradiation except 900 W which shows the maximum yield at 20 s.

However, at 900 W the highest biodiesel yield (95%) was obtained at a very shorter time of 20 s and this is because power is related to temperature, the higher the power the higher the temperature. Therefore, the maximum point was reached within a short reaction time with 900 W because the longer reaction time caused soap formation with a resulting loss of FAMES.

Table 4.2 Fatty acid composition of biodiesel (0.5 wt% KOH, 1:6 oil/methanol molar ratio and 450 W).

Reaction time (s)	Wt% C16:0	Wt% C18:0	Wt% C18:2
10	6.6	27.2	65.9
20	6.2	27.4	64.9
30	6.3	27.7	64.8
40	6.6	25.3	67.9
50	6.7	25.5	66.8
60	6.7	25.9	66.6

The results in Figure 4.1 may be attributed to an incomplete transesterification reaction between methanol and oil in the shorter time (10 to 40 s); the longer the reaction time meant a higher reaction temperature, resulting in a greater solubility of the reactants. The results obtained are higher than those previously reported by Azcan and Danisman (2008). They obtained yields of 92.2%, 92.7% and 92.0% respectively for reaction times of 1, 3 and 5 minutes, during the transesterification of rapeseed with 1.0% NaOH, an oil-to-methanol molar ratio of 1:6 and at a microwave power of 1200 W. There was no significant difference in the profile of the FAME yield with change in microwave power.

A comparative study of the effect of reaction time on biodiesel yield was also performed using U-tube viscometer. Viscometry is an alternative analytic method that was used to confirm the biodiesel yield as calculated from GC analyses (Sousa *et al.*, 2012). Analysing transesterification products by viscometry, is a cheap method to quickly assess the conversion of the transesterification reaction, compared to GC, because the latter requires specific standards, columns and expensive gases. The experiments were done with 1 wt% KOH, a 1:9 oil/methanol molar ratio and a power of 450 W and the results are shown in Figure 4.2. The results in Figure 4.3 were obtained using the same conditions.

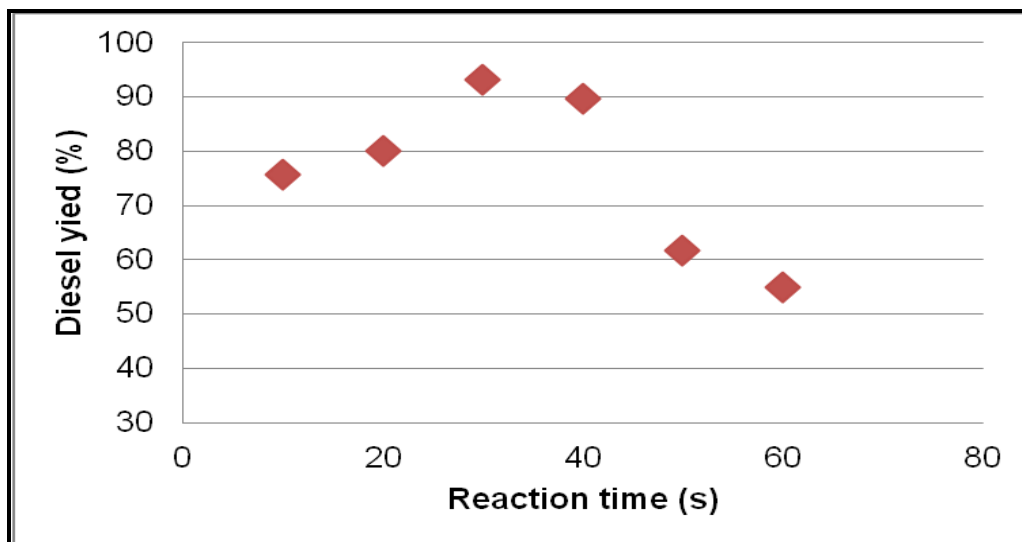


Figure 4.2: Effect of reaction time on percentage FAME in reaction mixture (1 wt% KOH, 1:9 molar ratio and 450 W).

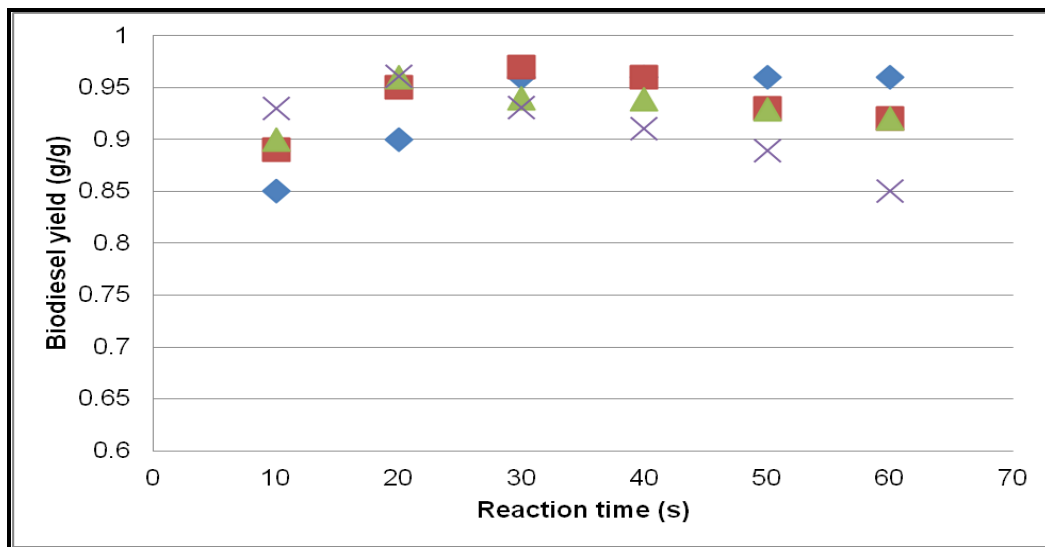


Figure 4.3: Effect of reaction time on biodiesel yield at 1 wt% KOH, 1:9 oil/methanol ratio (♦300 W ■450 W ▲600 W ×900 W).

The highest biodiesel yield was obtained at 30 s and this was comparable to the results obtained from the Gas Chromatography. With the GC results, a highest yield of 97% was obtained while 93% was obtained using viscometry. These results were similar for the two analytical methods used and the error was only 4%. The other results at 10, 20, 40, 50 and 60 s were totally different for the two methods, because the lowest biodiesel yield that was obtained at 60 s is 55% with viscometry and 92% with GC, giving an error of 37%. However, the results obtained at 40 s also gave a better agreement between the two methods as 95% was obtained with the GC and 90% with the viscometry. Therefore, the results show that the viscometry can be used as a fast and cheap analytical method to determine the biodiesel yield. The fatty acid methyl ester composition is shown in Table 4.3.

Table 4.3 Fatty acid composition of biodiesel (1 wt% KOH, 1:9 oil/methanol molar ratio and 450 W).

Reaction time (s)	Wt% C16:0	Wt% C18:0	Wt% C18:1	Wt% C18:1
10	6.2	1.4	20.9	71.5
20	6.2	0.5	19.9	73.4
30	6.2	1.0	19.7	73.1
40	6.3	0.4	19.8	73.5
50	6.2	0.7	21.3	71.8
60	6.4	0.8	21.3	71.4

4.2.2. Effect of microwave power

Microwave irradiation has been reported to reduce the reaction time (Manco *et al.*, 2012) by rapid heating that leads to a localised high temperature and pressure. These drive reactions at enhanced mass transfer rates. The power use is related to temperature, because the more power applied, the higher the temperature obtained. Low power usage leads to incomplete transesterification of oil to FAME and very high power usage leads to alcohol evaporation and therefore results in soap formation and loss of FAME. In this study, the effect of microwave power on the yield was carried out at different powers (300, 450, 600 and 900 W) and three methanol-to-oil molar ratios (1:3, 1:6, and 1:9), while other parameters were kept constant. The influence of microwave power on biodiesel yield at different conditions is provided in Appendix E.2. The influence of microwave power on biodiesel yield at 30 s and different oil/methanol ratio is shown in Figure 4.4.

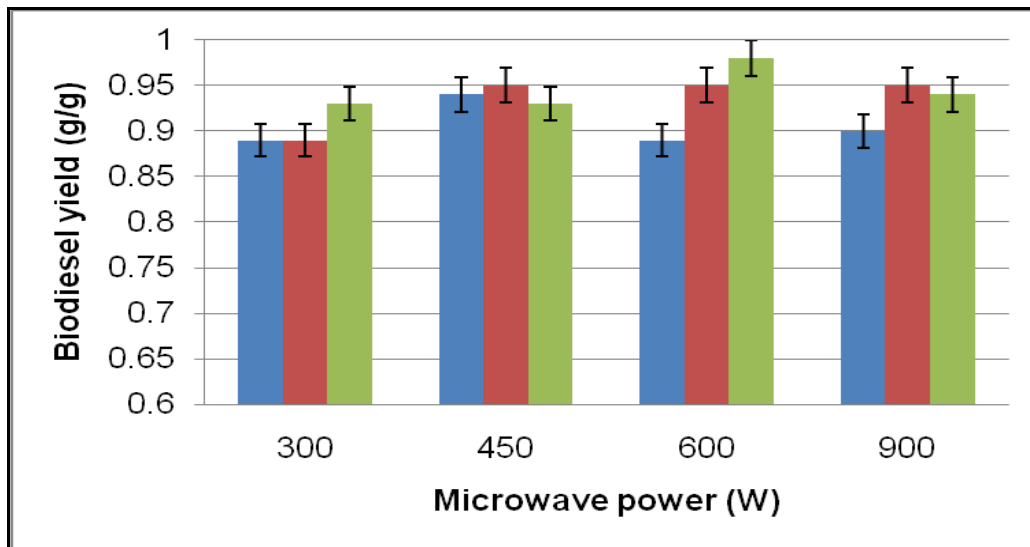


Figure 4.4: Effect of microwave irradiation on biodiesel yield at 30 s and 0.5 wt% KOH (■1:3 ■1:6 ■1:9).

The oil-to-methanol molar ratio did not show any trends with increasing power. The highest biodiesel yield (98%) was obtained at 600 W for a 1:9 molar ratio. This might be due to high temperatures (that are obtained by high microwave power) which can improve the efficiency of transesterification and enhance the conversion rate (Hasio *et al.*, 2011). At 900 W, a decrease in biodiesel yield was observed, because at a very high microwave power it has been reported that there is a reduction in the biodiesel yield and an increase in the soap formation from triglycerides (Mathiyazhagan and Ganapathi, 2011) due to methanol evaporation. Therefore, a microwave power of 600 W at a 1:9 oil-to-methanol molar ratio gave the optimum FAME yield at a catalyst concentration of 0.5 wt%.

4.2.3. Effect of oil/alcohol molar ratio

The oil-to-alcohol molar ratio is one of the critical parameters that affect the transesterification reaction. The increased amount of methanol results in an increased yield of FAMEs (Mathiyazhagan and Ganapathi, 2011). Although other alcohols such as ethanol can be used in the transesterification process, methanol was selected in this study for two reasons. Firstly, methanol is a good microwave radiation absorption material as its dipole quickly re-orientates during microwave irradiation. This property is an advantage in transesterification reactions (Yuan *et al.*, 2009). Secondly, methanol is relatively cheap compared to other types of alcohols. A high methanol-to-oil ratio of 3:1 is initially required to complete the reaction stoichiometrically (Sylvia *et al.*, 2011). This study investigated the influence of different oil/methanol ratios (1:3, 1:6 and 1:9) on biodiesel yield at different microwave powers (300, 450, 600 and 900 W) while keeping other variables constant. The results that shows the influence of an oil/methanol ratio on biodiesel yield at a 0.5 wt% KOH are given in Figure 4.5.

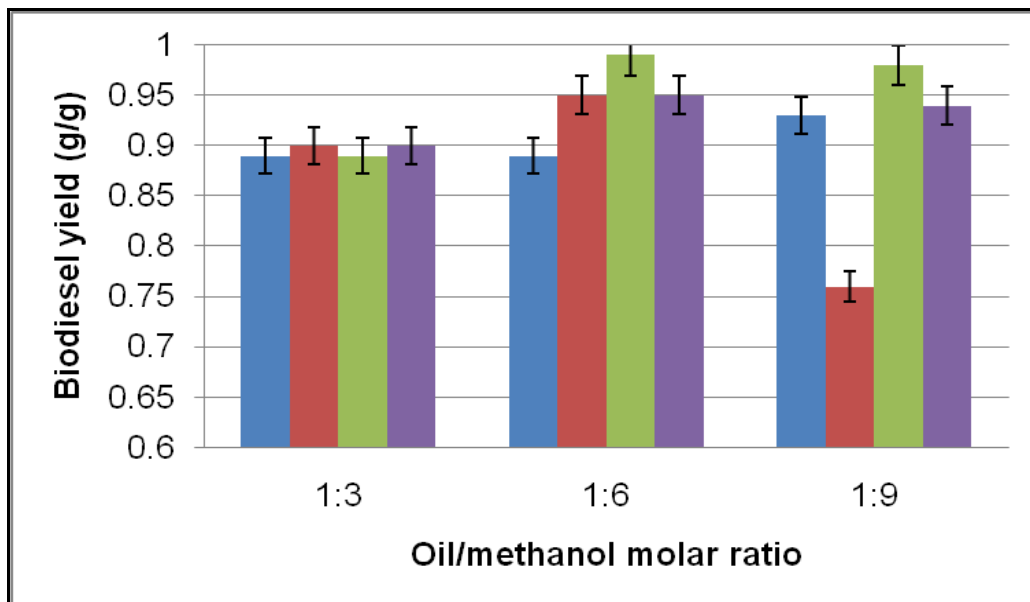


Figure 4.5: Effect of oil/alcohol ratio on biodiesel yield at 0.5 wt%, 30 s (■300 W ■450 W ■600 W ■900 W).

The biodiesel yield increased with an increasing methanol/oil ratio from 1:3 to 1:6, but decreased at 1:9. The biodiesel yields were found to be highest at a 1:6 oil-to-methanol ratio and were 95%, 98% and 95% for 450 W, 600 W and 900 W, respectively. It is important to note that 300 W only gave the highest FAME yield (95%) at an oil/methanol ratio of 1:9. The other microwave powers (450-900 W) gave the highest yield at a 1:6 molar ratio. This is because low microwave power results in a slow conversion of FAMEs. Two factors may account for the decrease in FAME yield at an oil/methanol molar ratio of 1:9. Firstly, the excess amounts of methanol in the reaction mixture would increase the solubility of glycerol, thus initiating a reverse reaction that reduces the FAMEs formed (Hsiao *et al.*, 2011). Secondly, the excess methanol at a 1:9 molar ratio reduces the concentration of the catalyst and reactants, thus decreasing the conversion rate (Zhang *et al.*, 2010). These results show high biodiesel yield at an optimum molar ratio of 6:1 alcohol/oil as stated in the literature (Mathiyazhagan and Ganapathi, 2011).

Although a stoichiometric ratio of 1:3 oil:methanol is required to complete the transesterification of oil to biodiesel, an excess amount of methanol was required to shift the equilibrium to the product's side. However, a further increase of the methanol amount results in the decreased conversion of FAMEs, therefore methanol should be added up to a specific concentration. A decrease in the FAME conversion was observed at a molar ratio of 1:9 at 450 W, 600 W and 900 W. The decrease in biodiesel yield at a molar ratio of 1:9 might be due to the excess amount of alcohol added, since this is associated with the deactivation of the catalyst, hence reducing its effectiveness. In conclusion, 1:6 molar ratio was the best oil/methanol ratio since it gave the highest biodiesel yield. The biodiesel yields (95%, 98% and 95%) obtained at a 1:6 molar ratio are higher than those that were obtained by Encinar *et al.* (2011) using a microwave flow system, which were 75.6%, 94.1% and 95.5% for 1:3, 1:6 and 1:9 molar ratio, respectively. Other results that show the effect of the oil/methanol molar ratio on biodiesel yield at 1 wt% and 1.5 wt% are given in Appendix E.3.

4.2.4. Effect of catalyst loading

Catalyst loading is one of the important parameters that affect the transesterification of oil to biodiesel. The catalyst speeds up the transesterification reaction by lowering the activation energy and reacts with methanol, making it more reactive for the triglycerides. The increase of catalyst loading in the transesterification of triglycerides has been reported to increase the biodiesel yield (Encinar *et al.*, 2011). However, the catalyst should be added up to a certain concentration, because high catalyst concentration results in the reaction of triglycerides with the catalyst, producing soap. In this study, the influence of different catalyst loadings (0.5 wt%, 1 wt% and 1.5 wt%) was investigated with a change in microwave power (300 W, 450 W, 600 W and 900 W) while keeping the other parameters constant. The influence of the catalyst (KOH) loading on biodiesel yield at a 1:6 oil/methanol molar ratio in combination with a microwave power (300W, 450W, 600W and 900W) and reaction time of 30 s is shown in Figure 4.6.

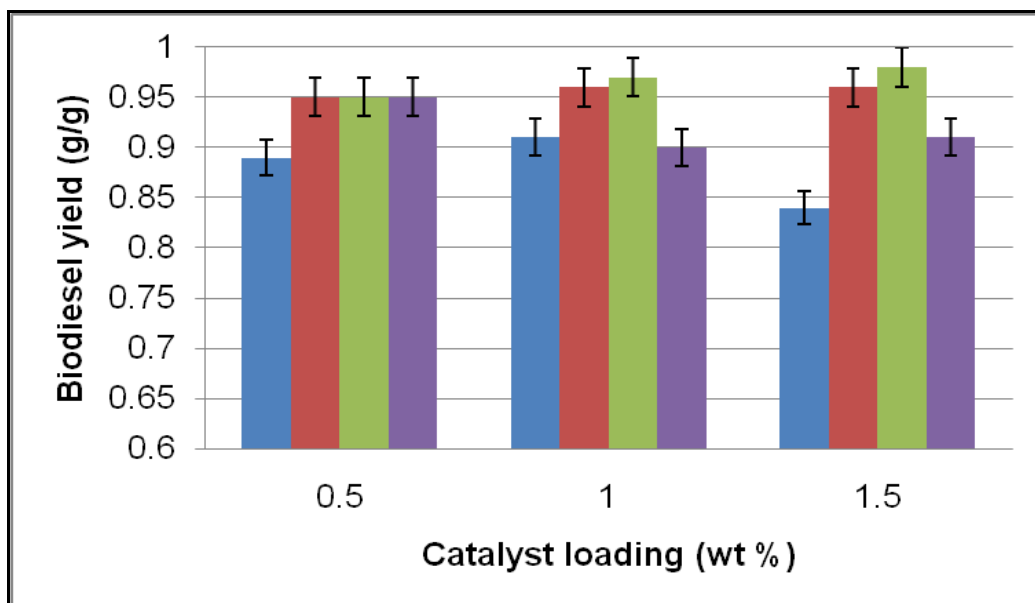


Figure 4.6: Effect of catalyst loading at 1:6 oil/methanol molar ratio, 30 s (■300 W ■450 W ■600 W ■900 W).

An increased biodiesel yield was observed as the amount of catalyst was increased from 0.5 wt% to 1.0 wt% at 300, 450 and 600 W. The highest yield (98%) was obtained at 1.5 wt% with 600 W and this is very comparable to the results obtained by Encinar *et al.* (2011) who also found the highest yield (97%) at 1.5 wt% KOH. Changing the catalyst concentration at 450 W did not have much of an influence on the yield because a 95% yield was obtained at 0.5 wt% and 96% for both 1 and 1.5 wt%. Azcan and Danisman (2008) obtained the same results, which shows the increase of biodiesel yield with an increasing catalyst loading, however, not much of an increase was indicated from 1 wt% to 1.5 wt%. Generally, the results show that lower concentrations of the catalyst may not effectively advance the transesterification reaction, while higher catalyst concentrations do not have a significant influence on biodiesel yield. The disadvantages of using high basic catalyst concentrations are their corrosive nature and tendency to form soap, which then hinders the transesterification process (Leadbeater *et al.*, 2008). The results that show the effect of catalyst loading on biodiesel yield at a 1:3 and 1:9 oil/methanol molar ratio are given in Appendix E.4.

The best biodiesel yield obtained in this study at different reaction conditions are given in Table 4.4. When comparing all the catalyst loadings, 1 wt% are preferred because it produces higher biodiesel yield of 98% and 97% for all three molar ratios at 450 W. The same yield of 98% biodiesel could only be obtained at 0.5 and 1.5 wt% catalyst loadings with a higher energy input (600 W).

Table 4.4 Summary of optimal biodiesel yields at different condition.

Catalyst loading (wt%)	Molar ratio	Reaction time (s)	Power (W)	Optimum yield (%)
0.5	1:3	30	450	94
	1:6	50	300	97
	1:9	30	600	98
1	1:3	30	450	97
	1:6	40	450	98
	1:9	30	450	97
1.5	1:3	30	450	95
	1:6	30	600	98
	1:9	30	450	97

Overall, 450 W is the best microwave power to use since it gives the highest biodiesel yield. In addition, 450 W would be recommended to be used at a reaction time of 30 s and at a 1:6 oil/methanol ratio. These conditions give better results (98% conversion) compared to 83% at a 1:6 molar ratio and 30 s, reported by Lertsathapornsuka *et al.* (2008). The best catalyst concentration for the reactions was found to be 1.0 wt%.

4.3. Energy consumption

The reaction time is approximately two hours and the separation time approximately twenty four hours with the traditional transesterification method. This is consuming a lot of energy, using approximately 1.2 kWh to obtain a 95% conversion (Leung *et al.*, 2010). A 98% conversion was obtained with the microwave transesterification method with an energy consumption of only 0.0067 kWh. Microwave assisted transesterification thus reduced the energy consumption by a factor of 179. This proves that the use of a batch microwave as a heating system for biodiesel production reduces the energy input and increases biodiesel yields even more than the continuous microwave that has been used in the literature (Azcan and Danisman, 2008; Encinar *et al.*, 2011). The batch microwave reaches higher temperature quicker (in seconds) compared to the continuous microwave system (minutes) which is connected to pumps that transfer the reactants into the condenser in the microwave and transfer the mixture to the separating funnel. Therefore, with batch microwave heating, high biodiesel yields are obtained in a short reaction time that in turn reduces the energy consumption.

4.4. Physicochemical properties of biodiesel

Some of the properties of biodiesel obtained from the optimal conditions were measured. The properties that determine the quality of biodiesel include density, cetane number, viscosity and FAME content. The physical properties of biodiesel produced in this study were compared with the SANS 1935 standard and are given in Table 4.5.

Table 4.5 Biodiesel properties obtained using microwave heating under optimised conditions. ^a

Properties	Reaction time (s)						SANS 1935
	10	20	30	40	50	60	
Density (g/ml)	0.89	0.88	0.88	0.88	0.89	0.89	0.86- 0.90
Cetane no. (vol. %)	79	56	56	56	55	59	>51
Viscosity at 40°C (mm²/s)	6.9	6.2	5.3	4.6	5.2	5.0	3.5-5.0
FAME content (%)	99	100	98.9	98.9	98.8	98.9	>96.5

^a Biodiesel properties obtained at 1 wt%, 1:9 oil/methanol molar ratio and 450 W.

The biodiesel obtained at a 1 wt% KOH, a 1:9 oil/methanol molar ratio, 450 W and a 10 s reaction time had physical properties that are comparable to the SANS specifications. Only the biodiesel produced at 40 s (4.6 mm²s⁻¹) and 60 s (5.0 mm²s⁻¹) showed viscosities that are within the expected limit of the standard (3.0-5.0 mm²s⁻¹). The viscosities of produced biodiesel at 10, 20, 30 and 50 s were outside of the limits set by the SANS standard. However, the densities (0.88 – 0.89g/ml) of all biodiesel produced in this study were found to be within the limits of the SANS standards (0.86 – 0.90g/ml). The cetane number and FAME number were within the acceptable limits of 51 vol% minimum and 96.5 % minimum, respectively.

4.5. Qualitative analysis of biodiesel

A Fourier transform infrared spectroscopy (FTIR) is a qualitative method that identifies the functional groups and bands that are corresponding to bending or stretching vibration in the oil and biodiesel samples (Ahmad *et al.*, 2011). Changes of the carbonyl functional group to the metoxycarbonyl group indicate that the transesterification reaction had occurred and that fatty acid methyl ester (FAME) has been formed (Sebayang *et al.*, 2010). In this study, the formation and loss of functional groups between sunflower oil and fatty acid methyl ester (FAME) were identified using FTIR. The FTIR spectra that show the comparison between sunflower oil and the corresponding FAME are given in Figure 4.7.

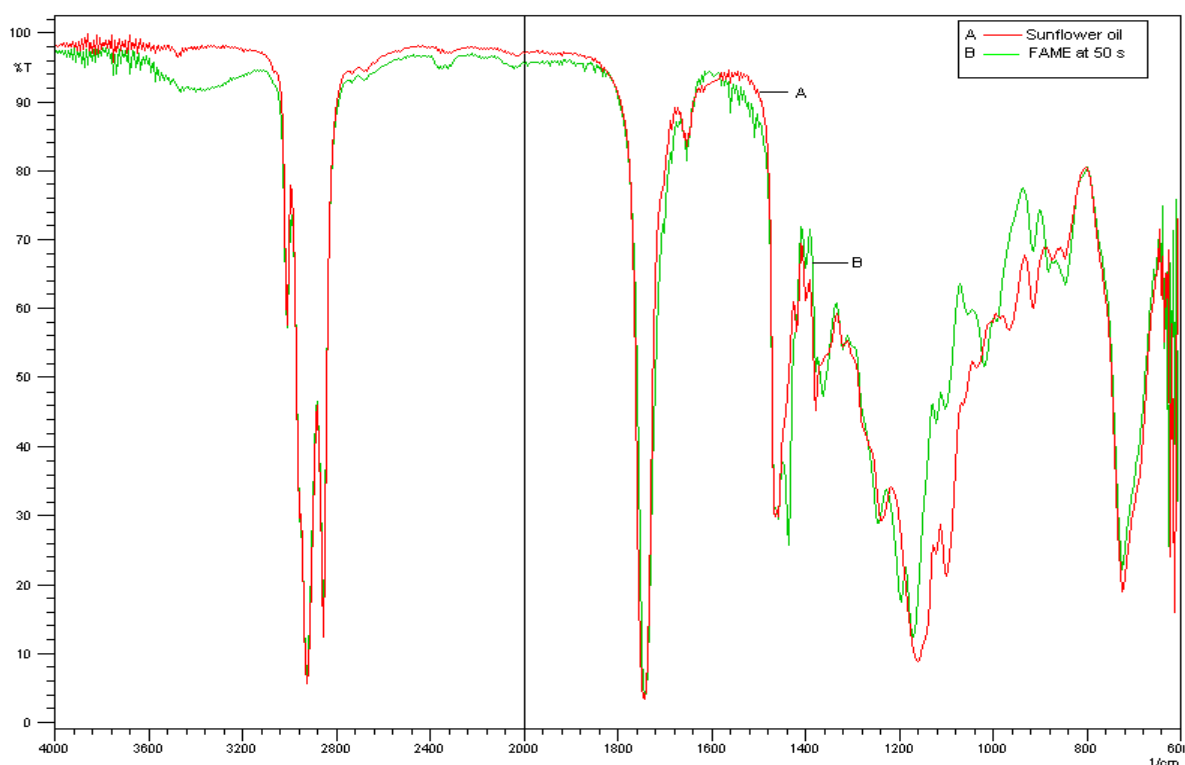


Figure 4.7: Comparison of sunflower oil spectrum to that of the corresponding fatty acid methyl ester (FAME) produced at 1 wt% KOH, 1:9 oil/methanol molar ratio, 450W, 50 s.

The sunflower oil absorption peak was identified at 1098.7 cm^{-1} , and this indicated the C-CH₂-O vibration. The FAME spectrum shows a peak at 1198.4 cm^{-1} , which can be attributed to the O-CH₃ initial methyl group stretch and one peak at 1437.1 cm^{-1} comes from the -CH₃ asymmetric bending vibration. Based on the appearance of the FAME peaks, the transesterification of the oil had occurred, thereby forming the methyl molecule as a product. The FAME peaks that were identified at 1198.4 cm^{-1} and 1437.1 cm^{-1} are very comparable to the ones obtained by Sebayang *et al.* (2010) using waste cooking oil. The band that occurred between 3103.5 cm^{-1} and 3644.6 cm^{-1} shows the overtone of the ester functional group. The summary of the comparison of the biodiesel functional groups between 10-60 s, 1 wt%, a 1:9 oil/methanol ratio and 450 W is given in Table 4.6.

Table 4.6 Functional groups of FAME from sunflower oil (1 wt%, 1:9 molar ratio, and 450 W).

Reaction time (s)	O-CH ₃ stretch	-CH ₃ bend vibration	=C-H stretch
10	n/a	1437.1	3473.7
20	1194.9	1433.5	3338.3
30	1198.4	1437.1	3438.1
40	1198.4	1437.1	3366.9
50	1198.4	1437.1	3103.5
60	1198.4	1437.1	3416.8

n/a - Not available

The most important peaks appeared at 1198.4 cm^{-1} , which shows the initial formation of the methyl group (O-CH₃), and at 1437.1 cm^{-1} , indicating the asymmetric bending vibration of CH₃ and a C-H stretching vibration of *cis*-double bond (=CH) between 3103.5 cm^{-1} and 3644.6 cm^{-1} (Vlachos *et al.*, 2006). The FAME spectra for

biodiesel produced at 10, 20, 30, 40 and 60 s are provided in Appendix F. The important peaks for biodiesel were identified for all the different reaction times, except for 10 s which did not show any peak at 1198.4 cm^{-1} .

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5. Conclusion and Recommendations

5.1. Conclusion

- The produced biodiesel contained approximately 6.16 wt% C16:0, 0.86 wt% C18:0, 20.7 wt% C18:1 and 72.3 wt% C18:2.
- A highest biodiesel content of 98% was obtained at 1 wt% and a 1:6 oil/methanol molar ratio for all power settings (300-900 W) and the lowest content (97%) was obtained at 0.5 wt%.
- The produced biodiesel is of good quality, because it met the SANS standard specification that allows a minimum percentage of 96.5% (SANS 1935, 2004).
- The reaction time under microwave irradiation was reduced from hours (used in the conventional transesterification method) to seconds.
- The catalyst loading of 1 wt% at a 1:6 oil-to-methanol molar ratio was found as the best reaction conditions for the microwave transesterification of triglyceride to biodiesel and the energy consumption was reduced by a factor of 179 from 1.2 kWh to 0.0067 kWh.
- The main conclusion from this study is that the microwave irradiation heating system reduces the reaction time and therefore reduces the energy consumption.

5.2. Recommendations

Based on the findings and analyses in this study, the following recommendations can be made:

- Comparison of the effect of microwave heating system on biodiesel production from pure vegetable oils and waste vegetable oils.
- Economic evaluation on microwave irradiation method compared to traditional heating method.
- Kinetic studies on biodiesel production using microwave irradiation.
- Thermodynamic studies on biodiesel produced using microwave irradiation.
- Finally, it is mainly recommended to use different types of alcohols and catalysts when producing biodiesel by microwave irradiation.

APPENDIX A- Calculations**Appendix A.1. Molecular weight of Oil**

$$X_{16:0} + X_{18:0} + X_{18:1} + X_{18:2} + X_{unk} = 1 \quad (1)$$

$$\text{Therefore: } X_{16:0} = 1 - X_{18:0} - X_{18:1} - X_{18:2} - X_{unk} \quad (2)$$

Mass fraction is given in terms of areas relative to the internal standard (dodecane);

$$X_{16:0} = 1/ K_{16:0} (A_{16:0}/ A_{dod}); \quad X_{18:0} = 1/ K_{18:0} (A_{18:0}/ A_{dod}); \quad X_{18:1} = 1/ K_{18:1} (A_{18:1}/ A_{dod});$$

$$X_{18:2} = 1/ K_{18:2} (A_{18:2}/ A_{dod}) \quad (3)$$

According to the calibration curves: $K_{16:0} = 1.2685$; $K_{18:0} = 1.2495$; $K_{18:1} = 1.185$;
 $K_{18:2} = 1.1952$; $K_{unk} = 1$

Therefore

$$X_{18:0} = 1/ (1 + X_{16:0}/ X_{18:0} + X_{18:1}/ X_{18:0} + X_{18:2}/ X_{18:0} + X_{unk}/ X_{18:0})$$

Replacing mass fractions with equations in (3) and substituting with values of areas, $X_{16:0}$ was obtained:

$X_{18:0} = 0.02$; $X_{18:1} = 0.31$; $X_{18:2} = 0.38$; $X_{unk} = 0.00$ (can be neglected because it does not contribute to the total mass) and from (2) $X_{16:0} = 0.29$

Mass fractions together with molecular weight of each component were used to calculate an average molecular weight of fatty acids triglyceride.

$$\begin{aligned} MW_{oil} &= 0.29MW_{16:0} + 0.02MW_{18:0} + 0.31MW_{18:1} + 0.38MW_{18:2} \\ &= 273.3 \text{ g/mol} \end{aligned}$$

Therefore sunflower oil molecular weight was calculated in the following manner:

$$MW_{oil} = 3MW_{FA} + MW_{Glycerol} - 3MW_{water} = 857.9 \text{ g/mol}$$

Table A.1 Data used for determination of sunflower oil molecular weight.

Name	Formulas	Areas	Mass fraction	Molecular weight g.mol ⁻¹
Palmitic	C16:0	3019.58081	0.29	256.42
Stearic	C18:0	358.74162	0.02	284.48
Oleic	C18:1	5626.95916	0.31	282.46
Linoleic	C18:2	6.81E+03	0.38	280.45
Unknowns	/	2070.22079	0.00	/
Glycerol				92.09
Water				18.02

Appendix A.2. Molar ratio of oil to methanol and catalyst loading

For 50 g of oil, number of moles was calculated using:

$$n = \text{mass of oil} / MW_{oil} = 50 / 857.9 = 0.058 \text{ mol}$$

With $n_{oil} / n_{meOH} = 1 / 9$ hence number of moles for methanol is $n_{meOH} = 9 * n_{oil}$

Therefore mass of $MeOH = 9 * n_{oil} \times MW_{MeOH} = 16.7 \text{ g}$

With molecular weight of $MeOH$ as 32.04 g/mol

Mass of $KOH = 1.5\%$ of mass oil = 0.75 g

Appendix A.3. Determination of diesel layer with the use of viscometer tube

The mass ratio of (methyl oleate and sunflower) sample mixture to isopropanol was 1/3. The total mass of the oil and ester mixture was 5g. The mass fraction in the sample mixture in terms of the methyl oleate was varied from 0%, 25%, 50%, 75% and 100% while the isopropanol amount was kept constant. The time it takes to flow

from a marked point through the capillary was recorded. A calibration standard was plotted (see Figure A.1).

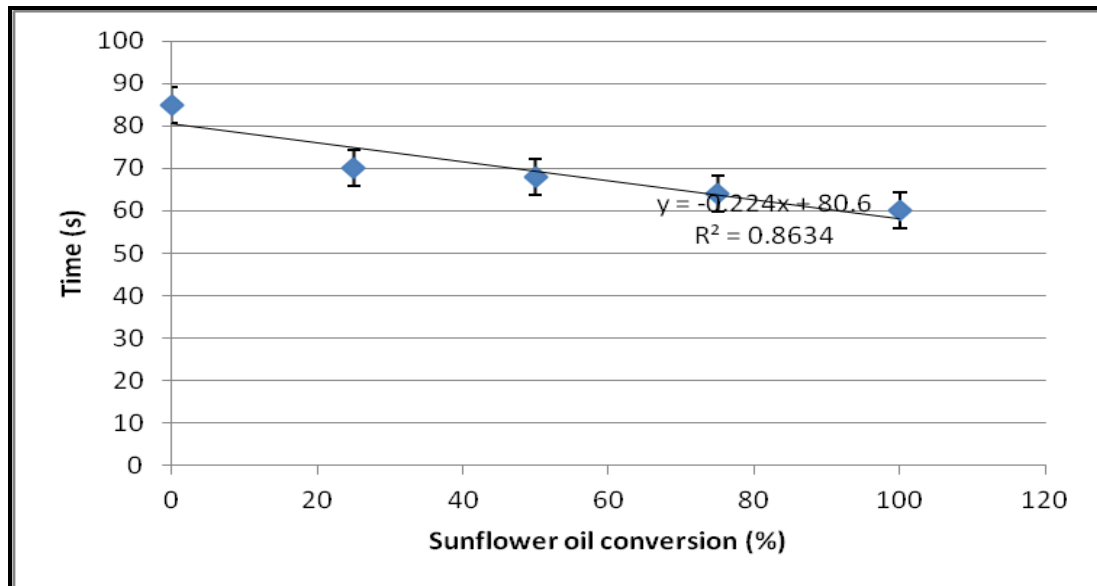


Figure A.1: Calibration curve of U-tube viscometer used to determine sunflower oil conversion.

From Figure A.1; total diesel yield was calculated with the equation of a straight line:

$y = mx + c$ where y is the measured time, x is the weight fraction of diesel.

Therefore, for all the diesel samples, the weight was calculated as: $x = (t/m - c/m)$

For average time of $t = 63$ s (sample of 1 wt%, 1:6, 450W and 40 s) using U-tube conversion is:

$$x = (63 / -0.224) - (80.6 / -0.224) = 78.6$$

Then *total diesel layer* = (*diesel layer*) $x = 48.6 * 78.6 / 100 = 45.3$ g

The total diesel yield will be then:

$$\text{Yield (\%)} = (\text{Actual diesel mass} / \text{mass raw oil}) * 100 = (45.3 / 50) * 100 = 93.1\%$$

Calculations were done on excel using the method given above for total diesel yield. Table A.2 gives total diesel yield with the influence of changing reaction time at 450W and 1:9 molar ratio.

Table A.2 Biodiesel yield determined from U-tube calibration.

Reaction time (s)	Total biodiesel yield (%)
10	75.7
20	80.0
30	93.1
40	89.7
50	61.8
60	55.0

Appendix A.4. Calculations of the kinematic viscosity from the dynamic viscosity.

The U-tube calibration curve was plotted using glycerol (99%) and distilled water as standards. The calibration curve was used to calculate biodiesel viscosity and is given in Figure A.2.

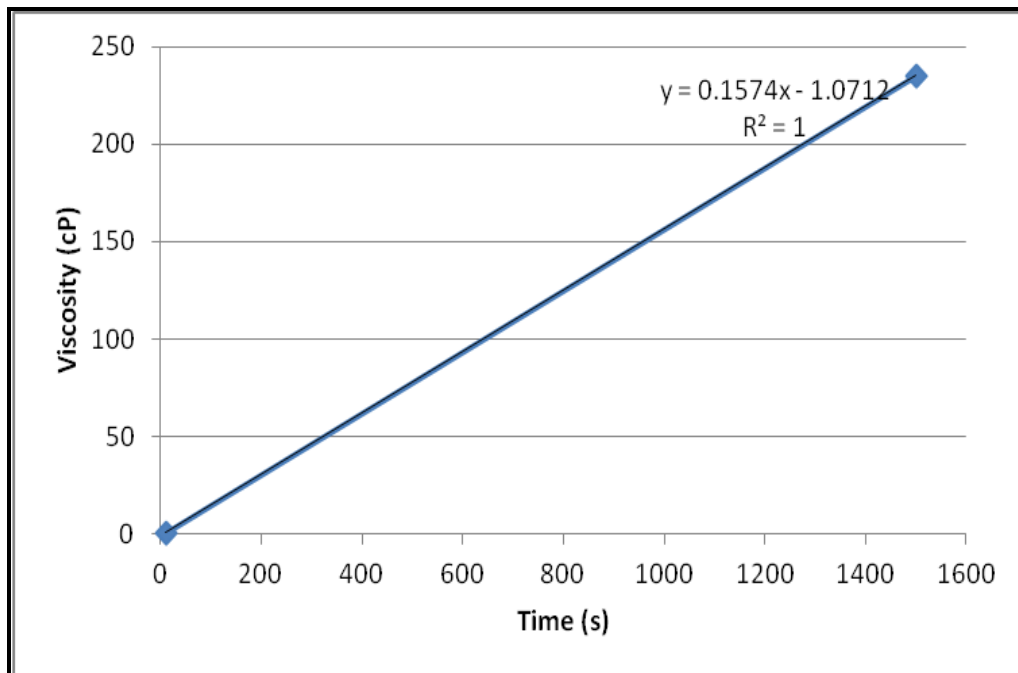


Figure A.2: U-tube calibration curve.

The dynamic viscosity was calculated by multiplying the measured resistance time with the constant (Sparcks *et al.*, 2009):

$$\eta = Kt$$

Where η is the dynamic viscosity (cP), K is the constant and t is the resistance time (s). The kinematic viscosity (mm^2s^{-1}) was calculated by dividing the dynamic viscosity with density (g/ml) (see Table A.3).

$$\nu = \eta / \rho$$

Table A.3. Data used to calculate kinematic viscosity of biodiesel.

Reaction time (s)	Flow time (s)	Dynamic viscosity (Cp)	Density (g/ml)	Kinematic viscosity (mm ² /s)
10	39	6.1	0.8902	6.9
20	35	5.5	0.8844	6.2
30	30	4.7	0.8849	5.3
40	26	4.1	0.8834	4.6
50	29	4.6	0.8860	5.2
60	28	4.4	0.8900	5.0

Appendix A.5. Determination of diesel composition

Diesel composition was determined using the following equations:

$m_{16:0} = K_{16:0}(A_{16:0}/A_{dod})m_{dod}$; $m_{18:0} = K_{18:0}(A_{18:0}/A_{dod})m_{dod}$; $m_{18:1} = K_{18:1}(A_{18:1}/A_{dod})m_{dod}$;
 $m_{18:2} = K_{18:2}(A_{18:2}/A_{dod})m_{dod}$; $m_{unk} = K_{unk}(A_{unk}/A_{dod})m_{dod}$ where m_i is the mass of component in the GC sample.

$$\text{Actual FAME mass (g)} = m_{16:0} + m_{18:0} + m_{18:1} + m_{18:2} + m_{unk}$$

The calibration curves were calibrated in terms of the mass of n-dodecane in the mass of the sample.

In these calculations, the following constants were used:

$$K_{16:0} = ; K_{18:0} = ; K_{18:1} = ; K_{18:2} = ; \text{ and } K_{unk} = 1$$

Therefore weight % of each composition was determined in the diesel layer:

$$WT\% = (m_i / \text{actual FAME mass}) 100$$

$$\text{Total WT\% of components} = WT\% (C_{16:0} + C_{18:0} + C_{18:1} + C_{18:2})$$

The mass of diesel layer (g) was calculated from the following equation:

$$\text{Mass of diesel layer (g)} = (\text{mass of product} * \text{WT\% of components}) / 100$$

Then finally, the yield of diesel (g/g) was calculated from the following equation:

$$\text{Yield (g/g)} = \text{mass of diesel layer (g)} / \text{initial mass of oil (g)}$$

APPENDIX B- FAME calibration curves and fatty acid composition

Appendix B.1. Calibration curves of fatty acid methyl esters

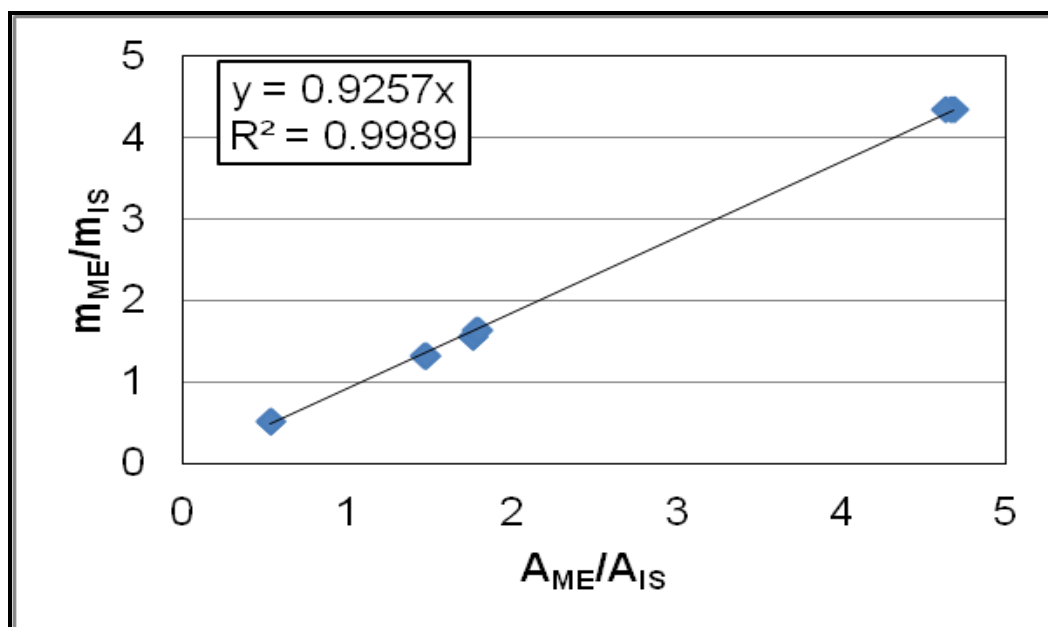


Figure B.1: Calibration curve of C16:0.

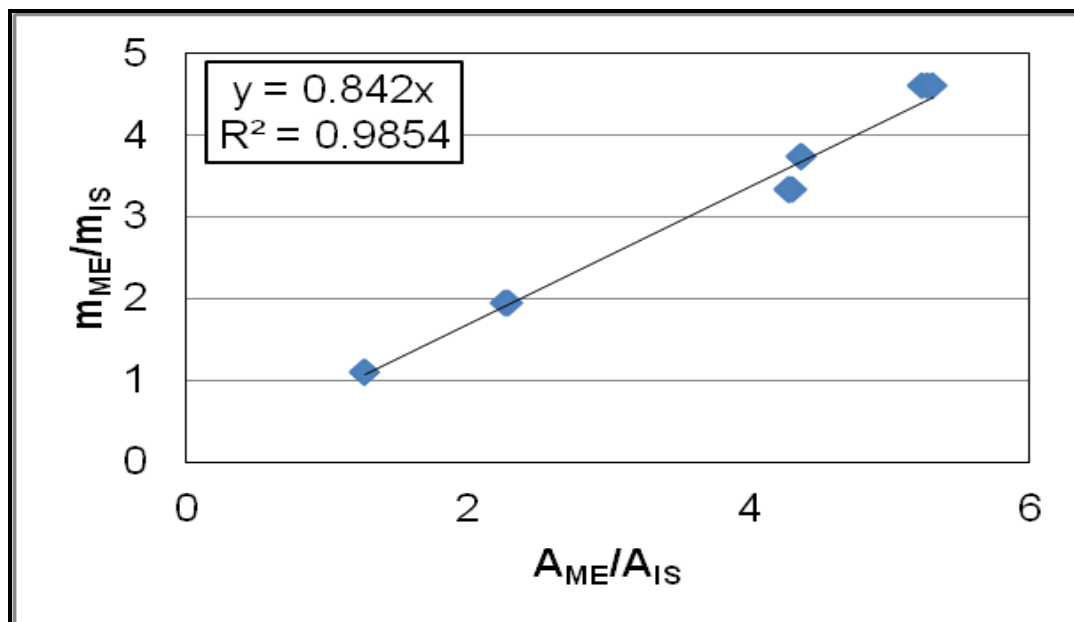


Figure B.2: Calibration curve of C18:0.

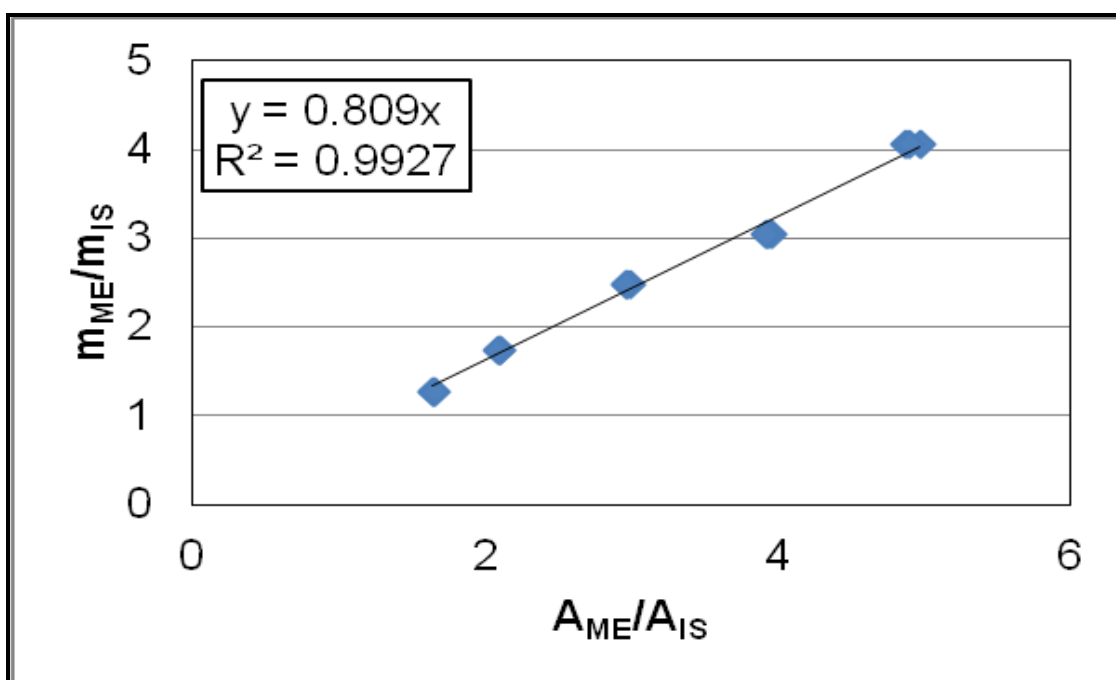


Figure B.3: Calibration curve of C18:1.

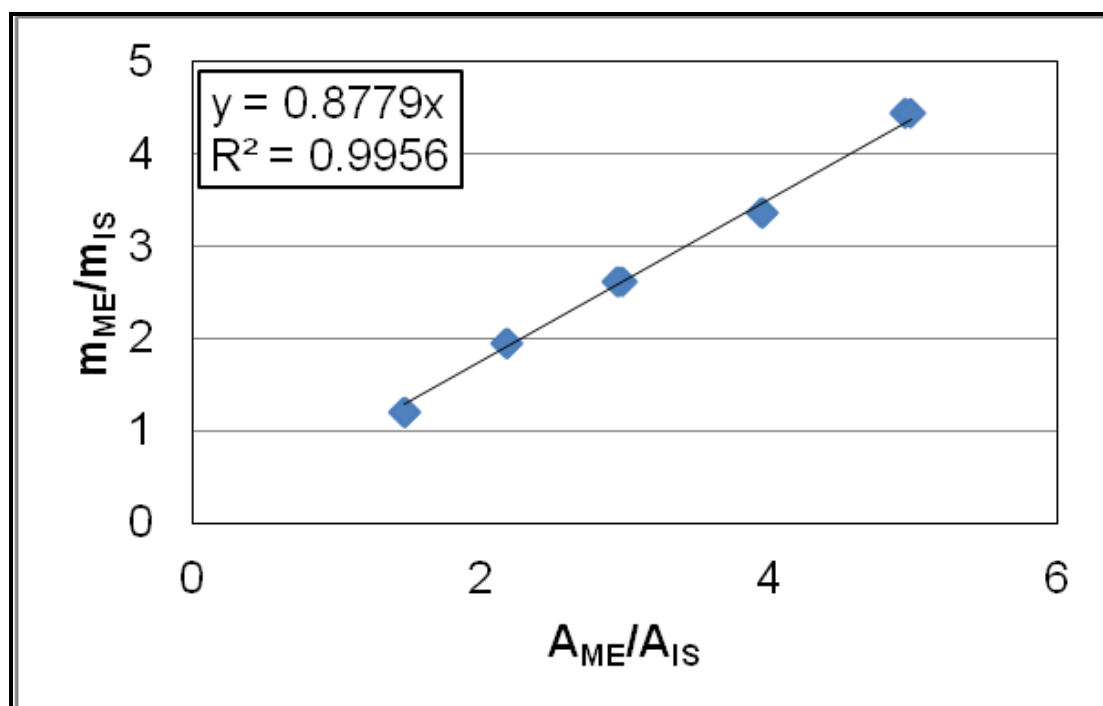


Figure B.4: Calibration curve of C18:2.

Appendix B.2. Fatty acid composition in Biodiesel

The diesel composition (Appendix A.4) was determined from the chromatograms that are shown in Figure B.5-13).

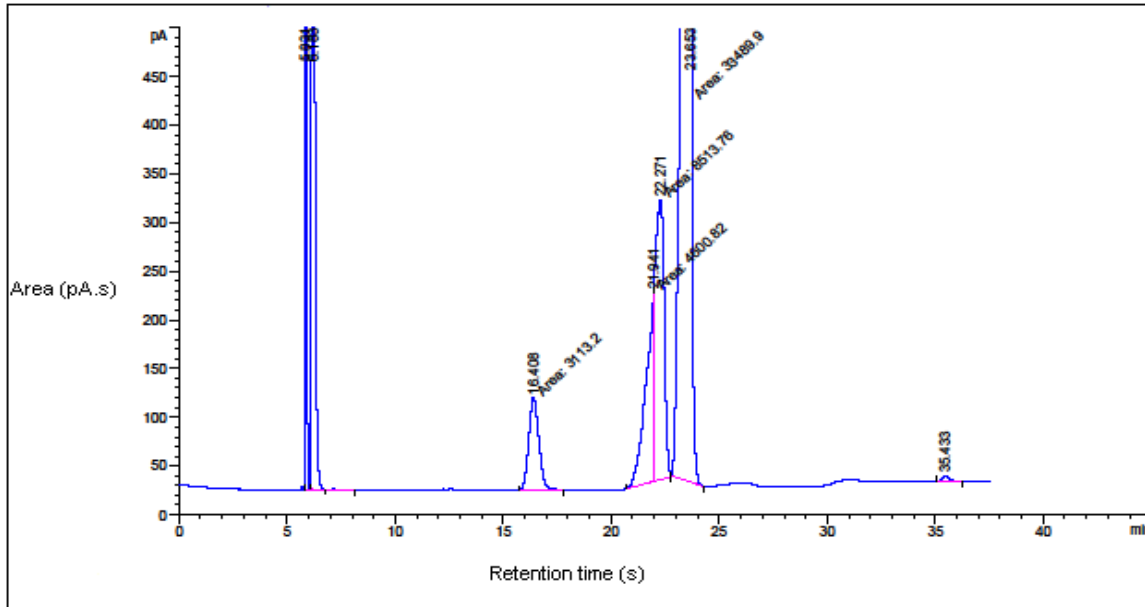


Figure B.5: Chromatogram at 0.5 wt%, 1:3 oil/methanol molar ratio, 450 W and 30 s.

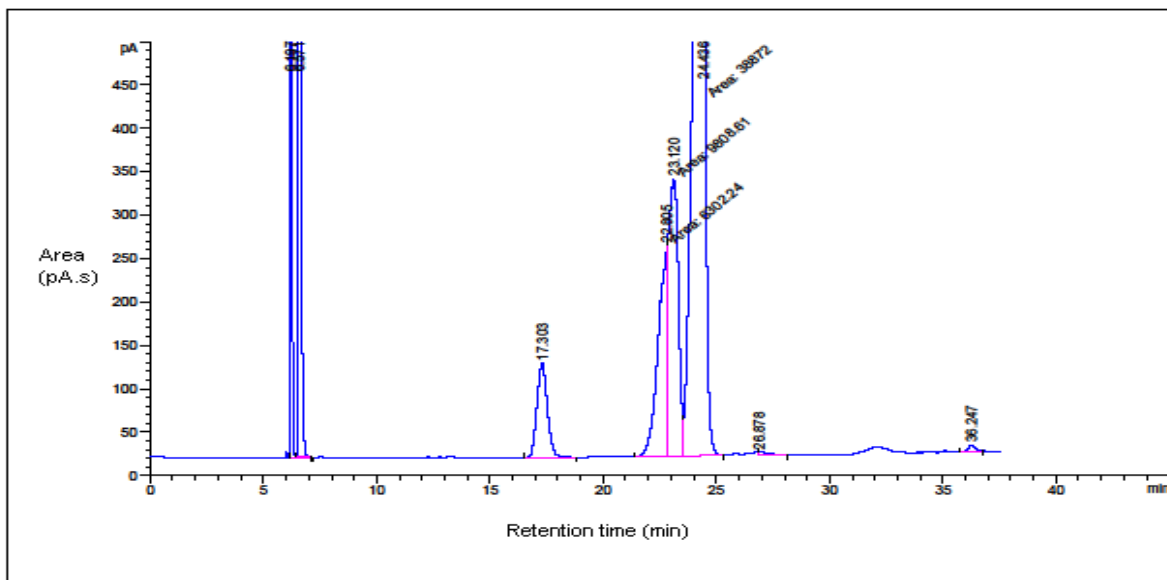


Figure B.6: Chromatogram at 0.5 wt%, 1:6 oil/methanol molar ratio, 300 W and 50 s.

Appendix B – FAME calibration curves and fatty acid composition

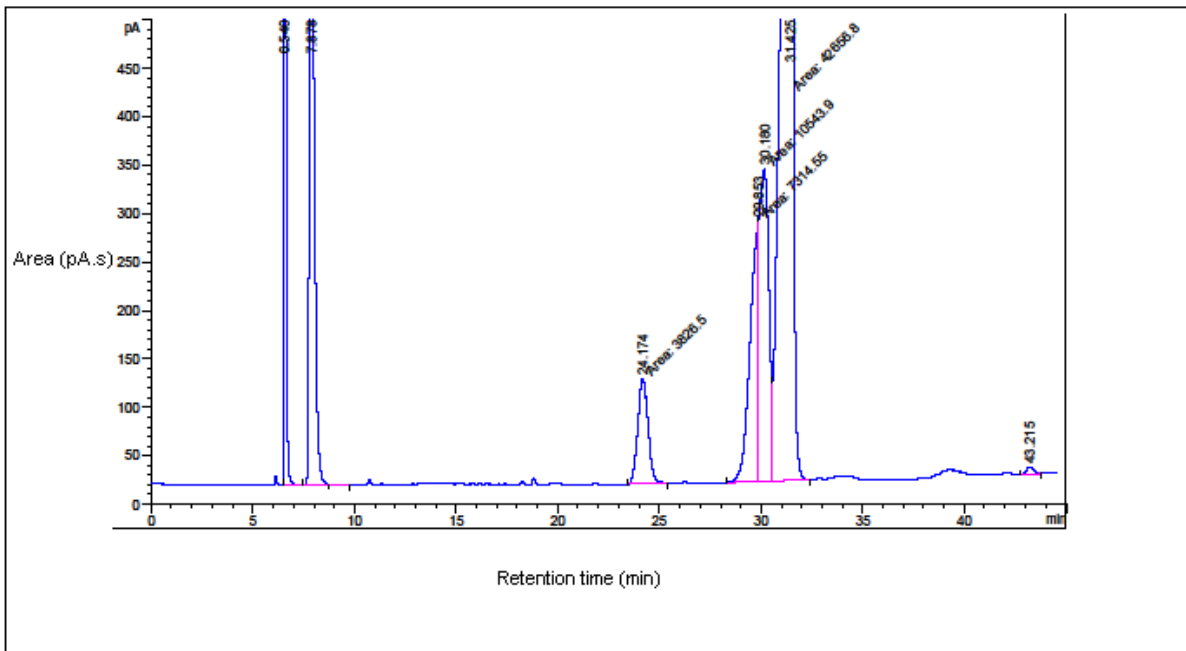


Figure B.7: Chromatogram at 0.5 wt%, 1:9 oil/methanol molar ratio, 600 W and 30 s.

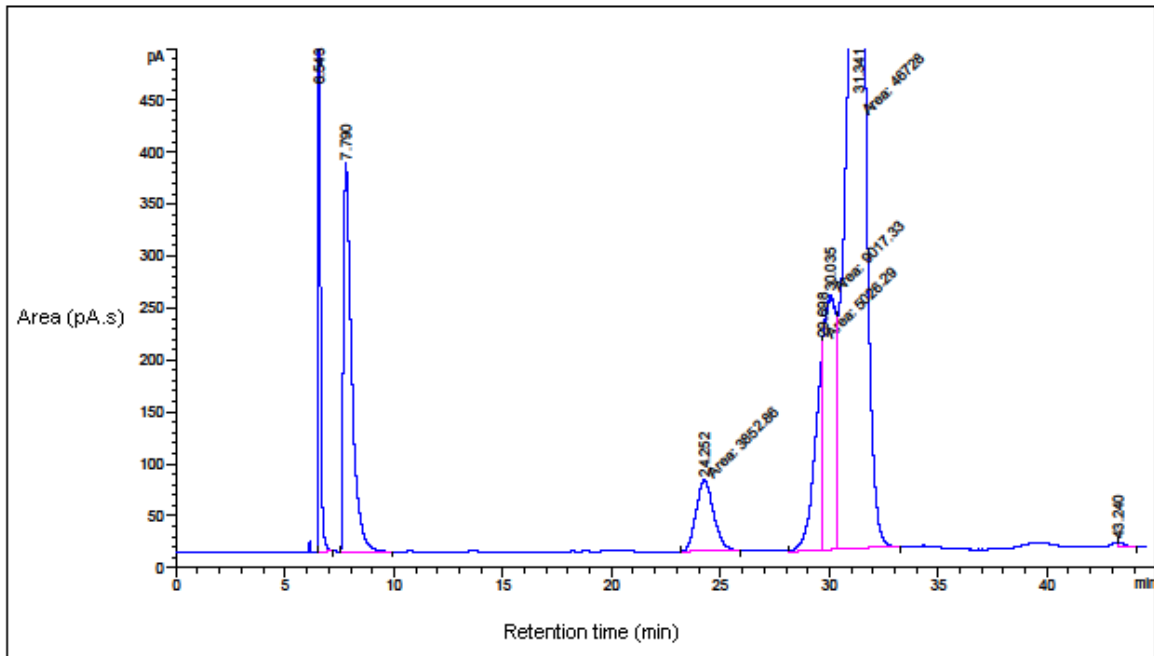


Figure B.8: Chromatogram at 1 wt%, 1:3 oil/methanol molar ratio, 450 W and 30 s.

Appendix B – FAME calibration curves and fatty acid composition

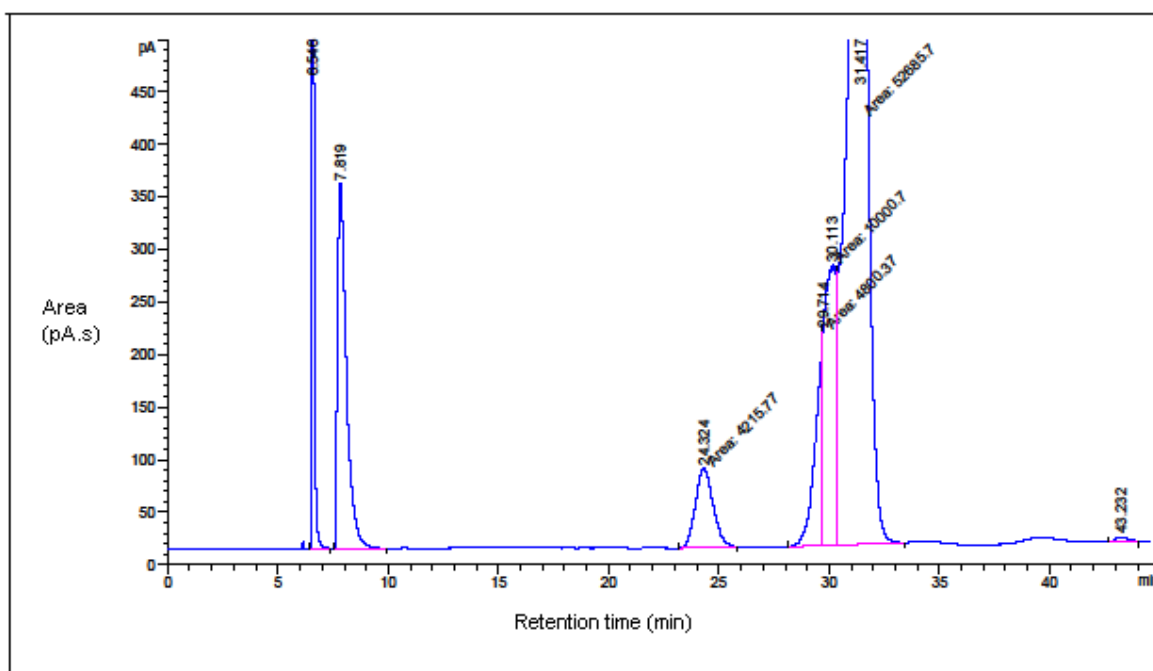


Figure B.9: Chromatogram at 1 wt%, 1:6 oil/methanol molar ratio, 450 W and 40 s.

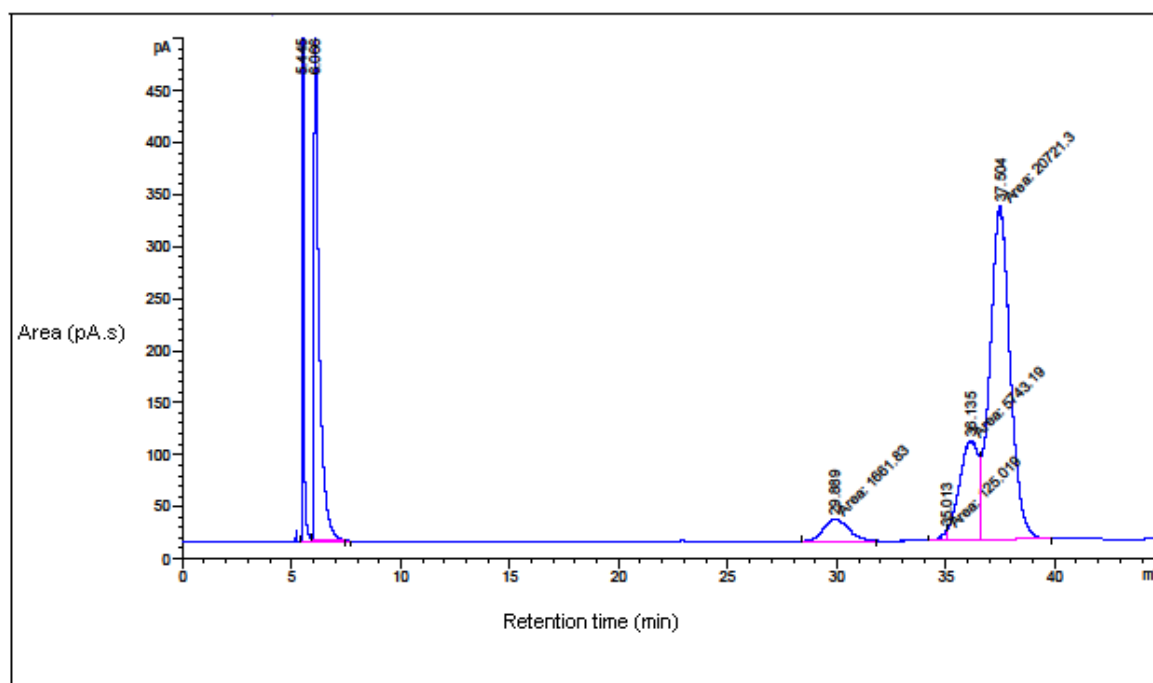


Figure B.10: Chromatogram at 1 wt%, 1:9 oil/methanol molar ratio, 450 W and 30 s.

Appendix B – FAME calibration curves and fatty acid composition

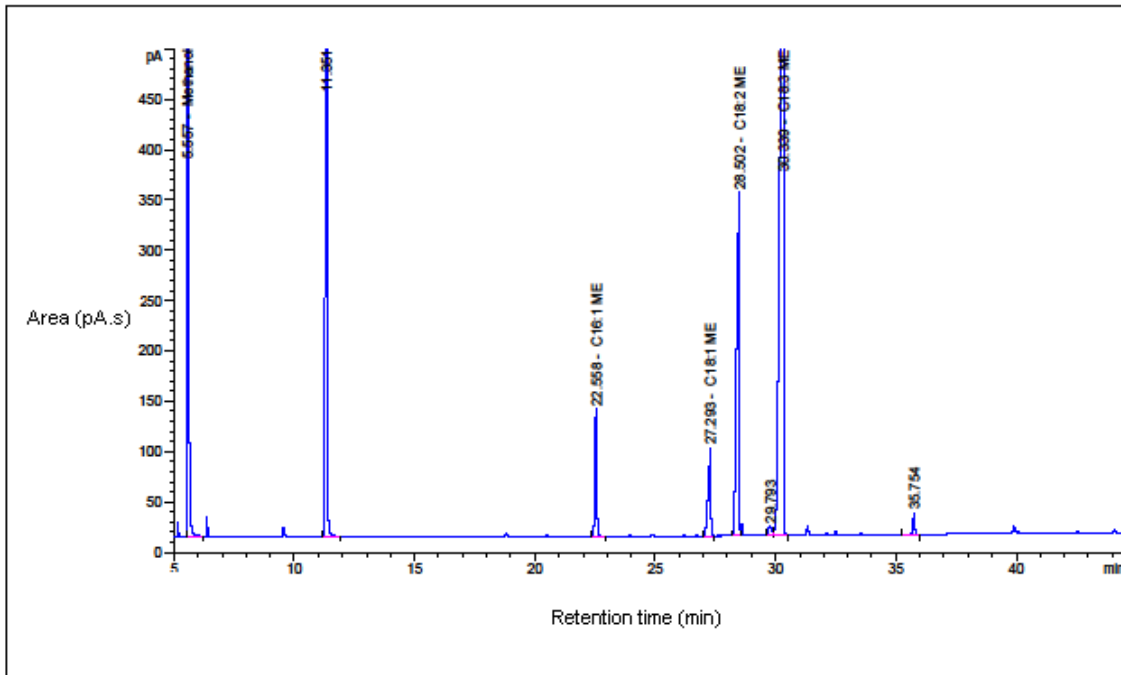


Figure B.11: Chromatogram at 1.5 wt%, 1:3 oil/methanol molar ratio, 450 W and 30 S.

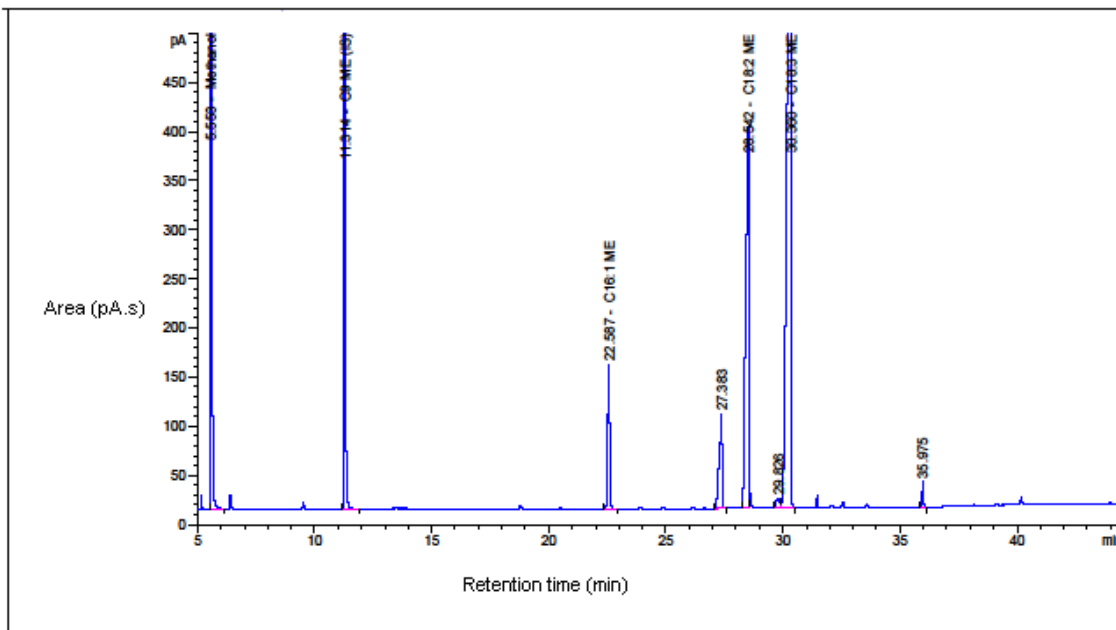


Figure B.12: Chromatogram at 1.5 wt%, 1:6 oil/methanol molar ratio, 600 W and 30 S.

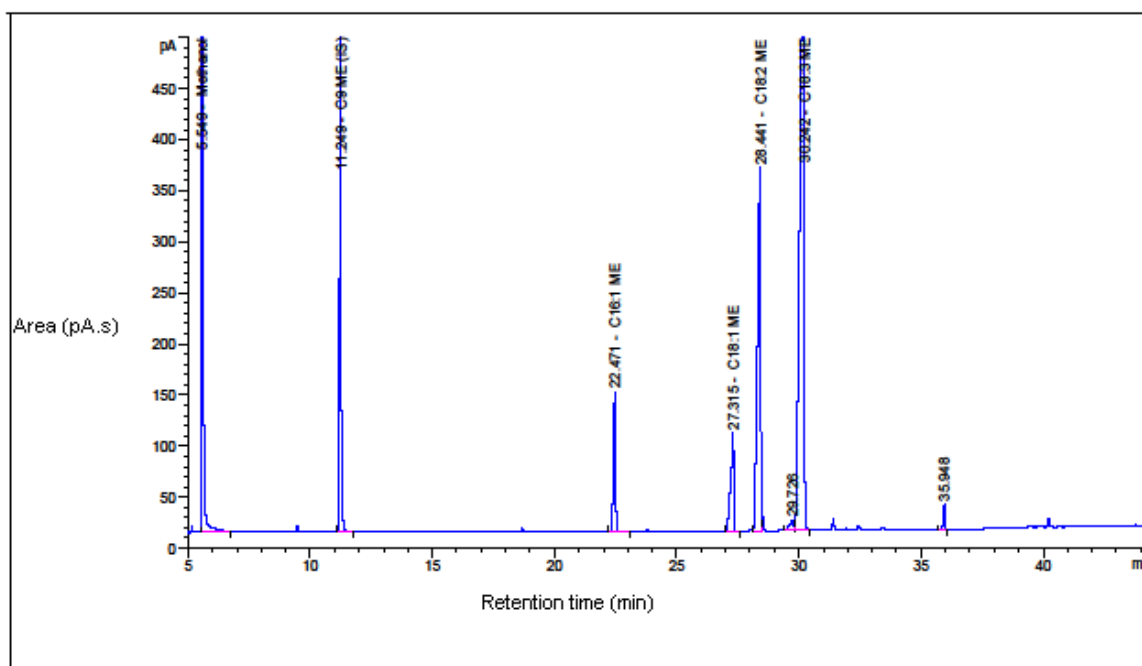


Figure B.13: Chromatogram at 1.5 wt%, 1:9 oil/methanol molar ratio, 450 W and 30

s.

APPENDIX C - Chemical composition of biodiesel (FAME)

Appendix C. gives the chemical composition of FAME (biodiesel) at different conditions (0.5-1.5 wt%).

Table C.1 Chemical composition of biodiesel (0.5 wt% KOH, 3:1 alcohol/oil ratio, 600 W).

Reaction time (s)	wt% C16:0	wt% C18:1	wt% C18:2	Total wt%	Wt% Unknown
10	6.845	25.226	67.738	99.808	0.192
20	6.817	25.961	67.020	99.797	0.203
30	6.803	25.564	67.486	99.853	0.147
40	6.704	25.994	67.086	99.784	0.216
50	6.708	26.147	67.145	100.000	0.000
60	6.731	26.264	67.005	100.000	0.000

Table C.2 Chemical composition of biodiesel (1 wt% KOH, 6:1 alcohol/oil ratio, 300 W).

Reaction time (s)	wt% C16:0	wt% C18:0	wt% C18:1	wt% C18:2	Total wt%	wt% Unknown
10	6.410	0.507	20.296	72.786	98.990	1.010
20	6.281	0.796	19.660	73.262	98.995	1.005
30	6.215	0.678	20.218	72.889	98.993	1.007
40	6.223	0.606	19.788	73.384	98.991	1.009
50	6.275	0.629	19.941	73.155	98.980	1.020
60	6.089	0.817	19.853	73.241	98.981	1.019

Table C.3 Chemical composition of biodiesel (1.5 wt% KOH, 9:1 alcohol/oil ratio, 450 W).

Reaction time (s)	wt% C16:0	wt% C18:0	wt% C18:1	wt% C18:2	Total wt%	wt% Unknown
10	6.454	5.217	22.034	65.285	98.990	1.010
20	6.474	5.229	22.081	65.211	98.995	1.005
30	6.451	5.219	22.046	65.277	98.993	1.007
40	6.463	5.232	22.026	65.269	98.991	1.009
50	6.481	5.276	21.999	65.224	98.980	1.020
60	6.435	5.228	21.975	65.344	98.981	1.019

Appendix D- Experimental data

Appendix D.1 gives the experimental data of the biodiesel yield calculated according to the equations in Appendix A.4.

Table D.1 Biodiesel yield at 0.5 wt %, 1:3 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
1	300	10	30	85
2	300	20	35	85
3	300	30	38	89
4	300	40	40	84
5	300	50	45	82
6	300	60	50	80
7	450	10	34	88
8	450	20	40	89
9	450	30	43	94
10	450	40	50	92
11	450	50	60	87
12	450	60	64	86
13	600	10	38	88
14	600	20	48	91
15	600	30	53	89
16	600	40	65	89
17	600	50	70	85
18	600	60	75	78
19	900	10	40	94
20	900	20	55	93
21	900	30	68	90
22	900	40	78	89
23	900	50	87	88
24	900	60	95	80

Table D.2 Biodiesel yield at 0.5 wt %, 1:6 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
25	300	10	40	77
26	300	20	45	85
27	300	30	48	90
28	300	40	54	97
29	300	50	55	98
30	300	60	57	97
31	450	10	45	72
32	450	20	54	90
33	450	30	58	96
34	450	40	60	97
35	450	50	65	94
36	450	60	66	93
37	600	10	46	73
38	600	20	55	93
39	600	30	58	99
40	600	40	64	99
41	600	50	70	95
42	600	60	72	94
43	900	10	48	83
44	900	20	60	98
45	900	30	68	95
46	900	40	75	93
47	900	50	90	91
48	900	60	93	90

Table D.3 Biodiesel yield at 0.5 wt %, 1:9 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
49	300	10	42	93
50	300	20	45	94
51	300	30	47	93
52	300	40	50	94
53	300	50	54	94
54	300	60	55	95
55	450	10	44	84
56	450	20	48	92
57	450	30	50	93
58	450	40	58	97
59	450	50	62	96
60	450	60	64	95
61	600	10	44	92
62	600	20	57	98
63	600	30	60	98
64	600	40	64	97
65	600	50	66	95
66	600	60	70	87
67	900	10	45	82
68	900	20	58	98
69	900	30	65	95
70	900	40	72	95
71	900	50	75	85
72	900	60	85	84

Table D.4 Biodiesel yield at 1 wt %, 1:3 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
73	300	10	34	94
74	300	20	37	97
75	300	30	40	98
76	300	40	50	95
77	300	50	53	92
78	300	60	56	91
79	450	10	95	96
80	450	20	93	97
81	450	30	98	97
82	450	40	95	94
83	450	50	92	92
84	450	60	95	91
85	600	10	42	95
86	600	20	58	96
87	600	30	60	95
88	600	40	62	94
89	600	50	72	89
90	600	60	74	88
91	900	10	40	96
92	900	20	53	95
93	900	30	66	90
94	900	40	80	92
95	900	50	85	92
96	900	60	95	90

Table D.5 Biodiesel yield at 1 wt %, 1:6 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
97	300	10	38	83
98	300	20	41	90
99	300	30	44	91
100	300	40	48	94
101	300	50	50	93
102	300	60	53	92
103	450	10	40	88
104	450	20	42	93
105	450	30	43	96
106	450	40	52	98
107	450	50	54	89
108	450	60	57	86
109	600	10	42	92
110	600	20	46	96
111	600	30	49	97
112	600	40	58	93
113	600	50	65	93
114	600	60	80	80
115	900	10	45	93
116	900	20	50	98
117	900	30	65	92
118	900	40	75	85
119	900	50	80	78
120	900	60	97	74

Table D.6 Biodiesel yield at 1 wt %, 1:9 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
121	300	10	38	85
122	300	20	40	90
123	300	30	43	96
124	300	40	50	96
125	300	50	52	96
126	300	60	54	96
127	450	10	40	89
128	450	20	45	95
129	450	30	47	97
130	450	40	52	96
131	450	50	57	93
132	450	60	60	92
133	600	10	42	90
134	600	20	50	97
135	600	30	52	95
136	600	40	55	95
137	600	50	62	94
138	600	60	65	93
139	900	10	45	93
140	900	20	52	97
141	900	30	55	94
142	900	40	60	92
143	900	50	70	90
144	900	60	80	85

Table D.7 Biodiesel yield at 1.5 wt %, 1:3 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
145	300	10	36	90
146	300	20	38	92
147	300	30	40	94
148	300	40	47	90
149	300	50	55	82
150	300	60	57	79
151	450	10	38	89
152	450	20	43	90
153	450	30	47	96
154	450	40	60	80
155	450	50	70	75
156	450	60	72	73
157	600	10	40	94
158	600	20	50	96
159	600	30	55	88
160	600	40	65	78
161	600	50	80	74
162	600	60	85	70
163	900	10	42	96
164	900	20	50	96
165	900	30	65	90
166	900	40	80	77
167	900	50	90	74
168	900	60	100	70

Table D.8 Biodiesel yield at 1.5 wt %, 1:6 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
169	300	10	40	76
170	300	20	42	80
171	300	30	44	85
172	300	40	60	96
173	300	50	65	96
174	300	60	70	95
175	450	10	40	80
176	450	20	55	86
177	450	30	60	97
178	450	40	65	95
179	450	50	70	91
180	450	60	75	90
181	600	10	40	85
182	600	20	60	91
183	600	30	62	99
184	600	40	65	95
185	600	50	80	85
186	600	60	85	83
187	900	10	40	91
188	900	20	60	95
189	900	30	65	92
190	900	40	85	88
191	900	50	95	83
192	900	60	105	80

Table D.9 Biodiesel yield at 1.5 wt %, 1:9 oil/methanol molar ratio.

Exp.	Power (W)	Time (s)	Temperature (°C)	Wt% yield
193	300	10	40	93
194	300	20	42	94
195	300	30	45	95
196	300	40	50	97
197	300	50	52	97
198	300	60	55	95
199	450	10	40	94
200	450	20	45	96
201	450	30	50	98
202	450	40	55	96
203	450	50	60	93
204	450	60	62	89
205	600	10	43	95
206	600	20	50	96
207	600	30	53	97
208	600	40	58	92
209	600	50	65	83
210	600	60	70	81
211	900	10	43	95
212	900	20	50	96
213	900	30	55	93
214	900	40	64	89
215	900	50	75	85
216	900	60	85	73

Appendix E- Parameter influence on biodiesel yield

Appendix E.1. Effect of reaction time on biodiesel yield

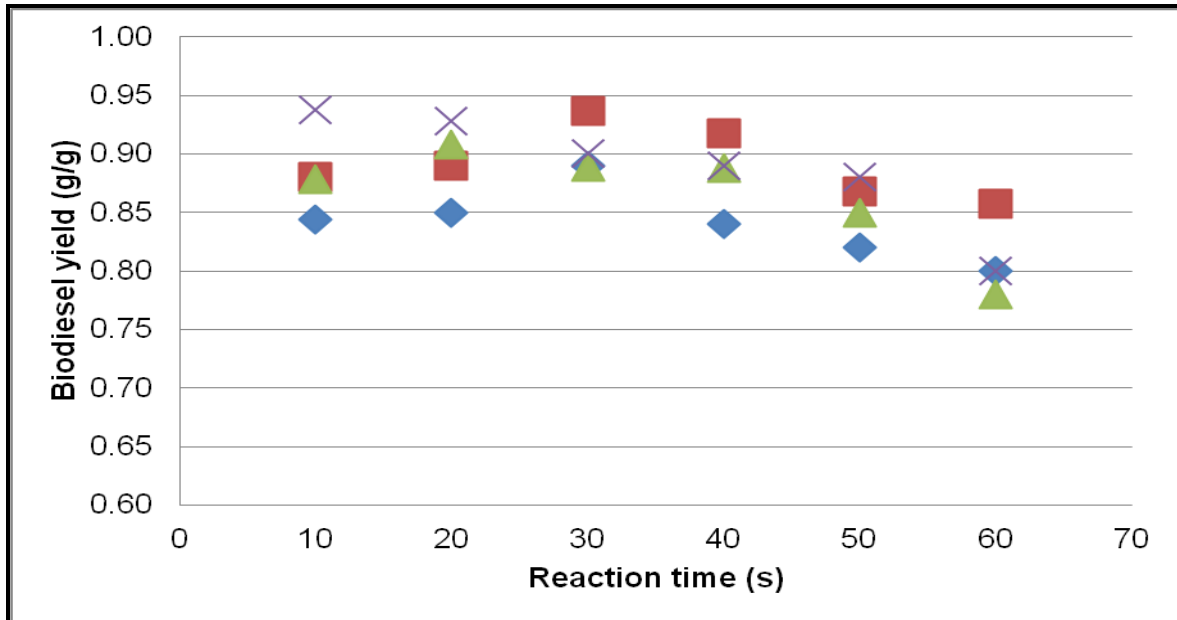


Figure E.1: Effect of reaction time on biodiesel yield at 0.5 wt% KOH, 1:3 oil/methanol molar ratio (♦300 W ■450 W ▲600 W ✕900 W).

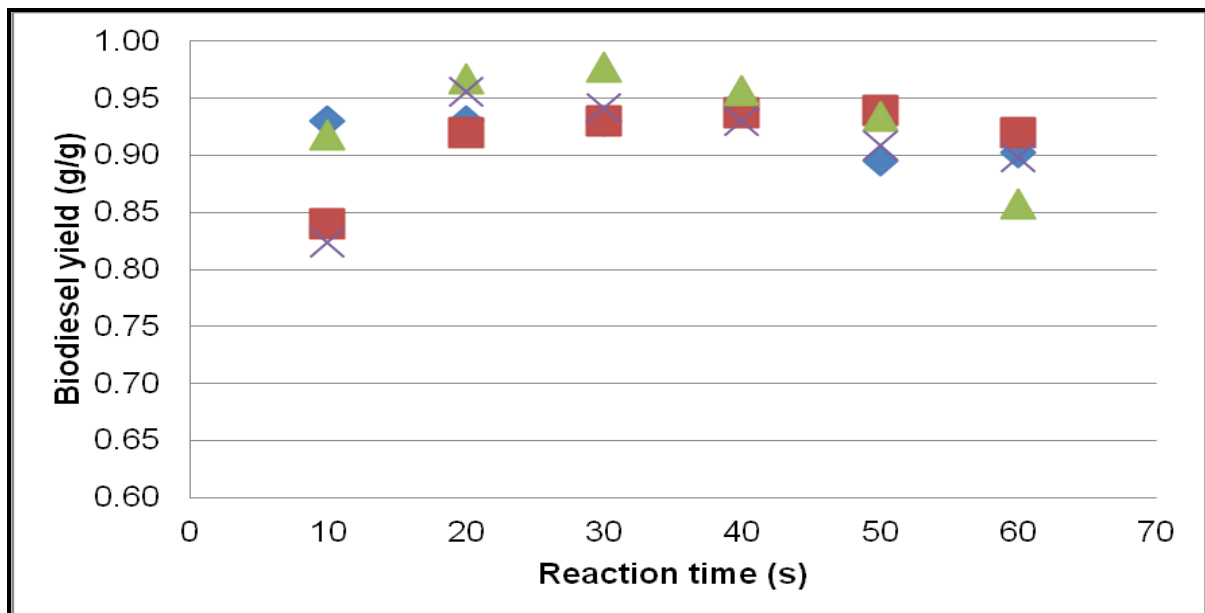


Figure E.2: Effect of reaction time on biodiesel yield at 0.5 wt% KOH, 1:9 oil/methanol ratio (♦300 W ■450 W ▲600 W ✕900 W).

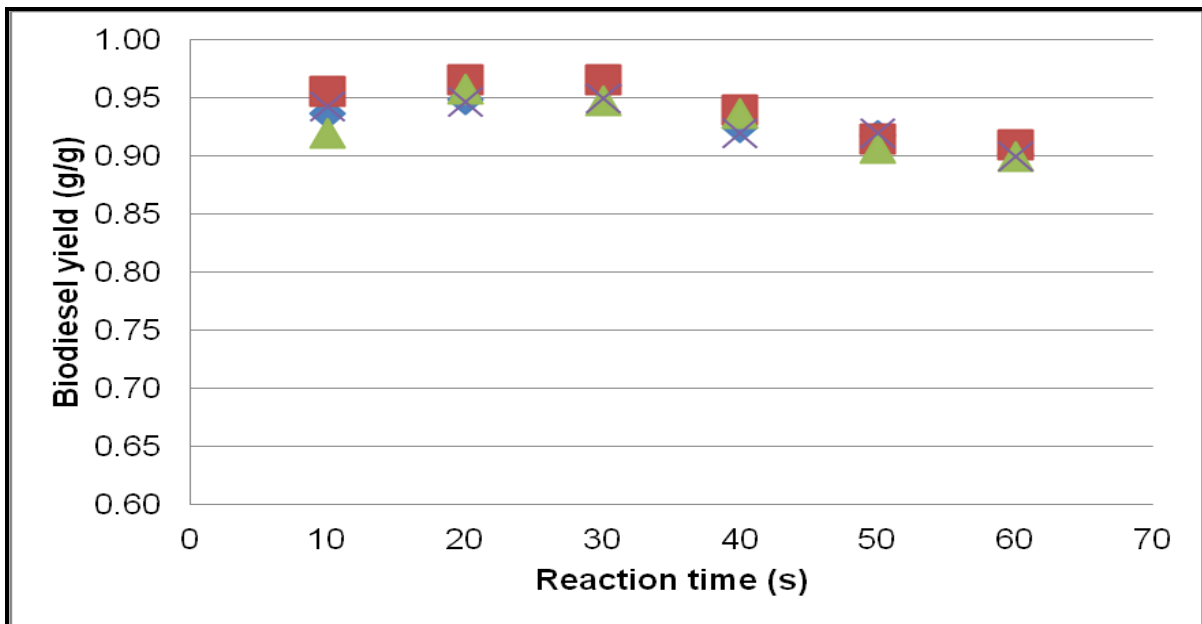


Figure E.3: Effect of reaction time on biodiesel yield at 1 wt% KOH, 1:3 oil/methanol ratio (♦300 W ■450 W ▲600 W ✕900 W).

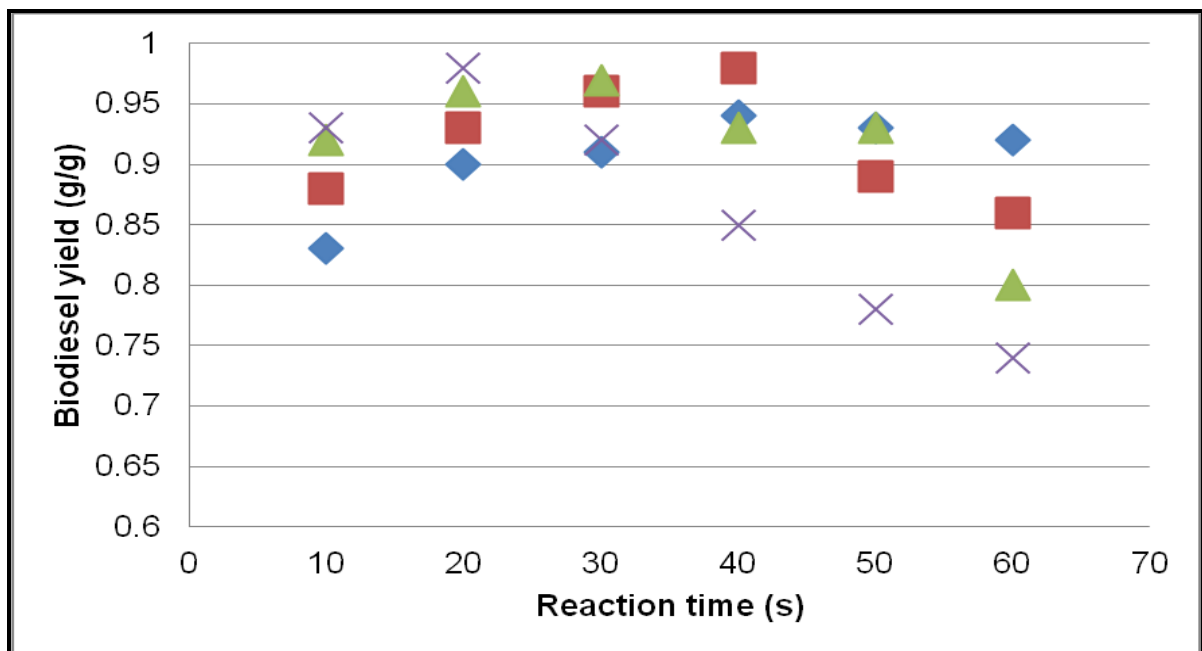


Figure E.4: Effect of reaction time on biodiesel yield at 1 wt% KOH, 1:6 oil/methanol ratio (♦300 W ■450 W ▲600 W ✕900 W).

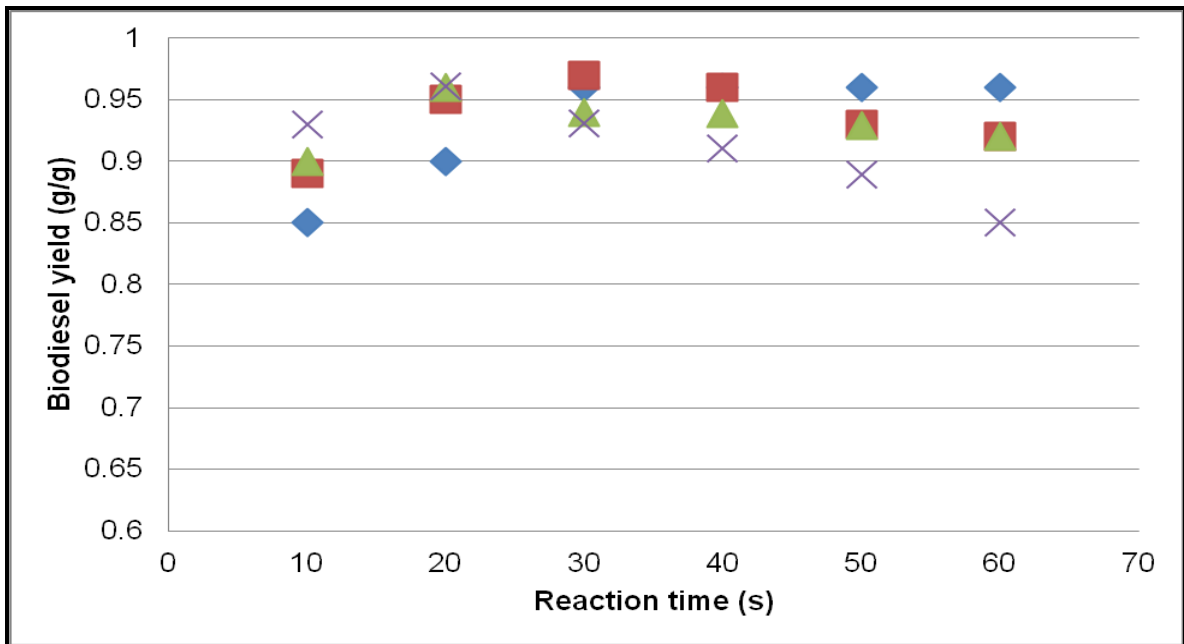


Figure E.5: Effect of reaction time on biodiesel yield at 1 wt% KOH, 1:9 oil/methanol ratio (♦300 W ■450 W ▲600 W ✕900 W).

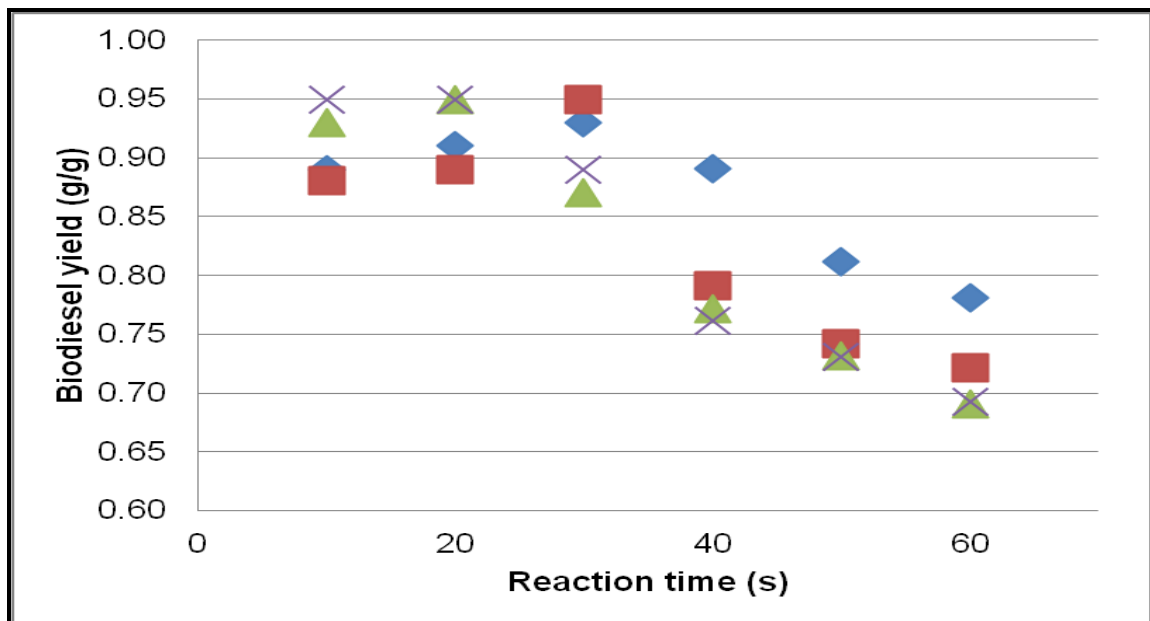


Figure E.6: Effect of reaction time on biodiesel yield at 1.5 wt% KOH, 1:3 oil/methanol ratio (♦300 W ■450 W ▲600 W ✕900 W).

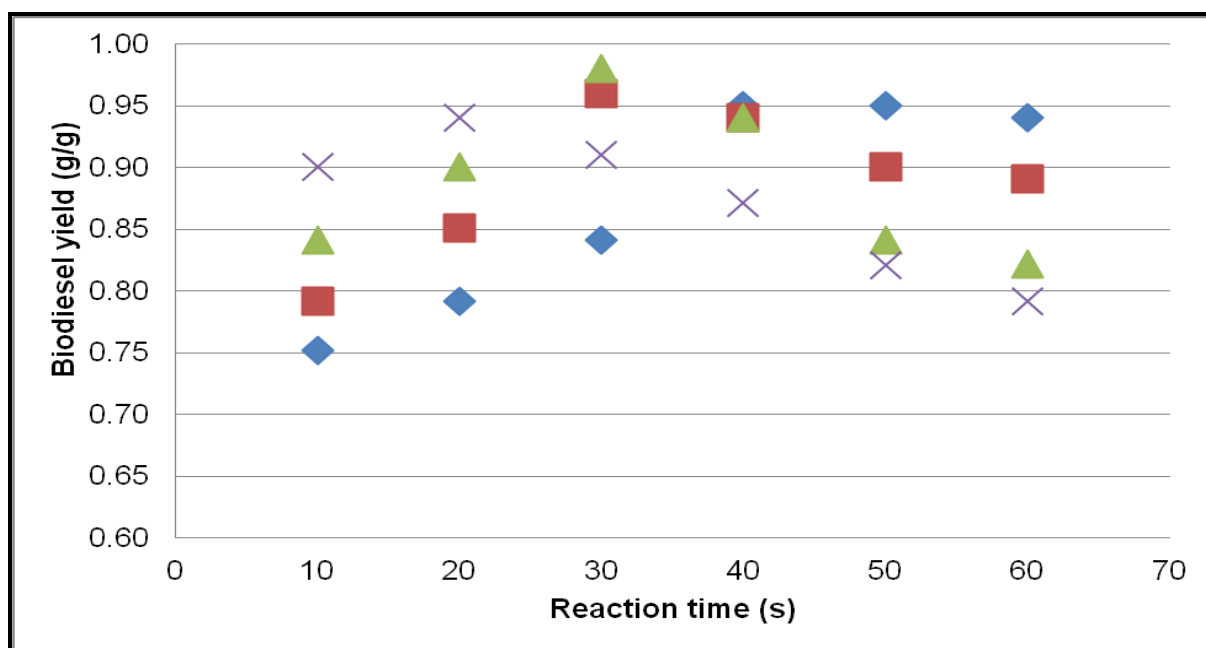


Figure E.7: Effect of reaction time on biodiesel yield at 1.5 wt% KOH, 1:6 oil/methanol ratio (♦300 W ■450 W ▲600 W ✕900 W).

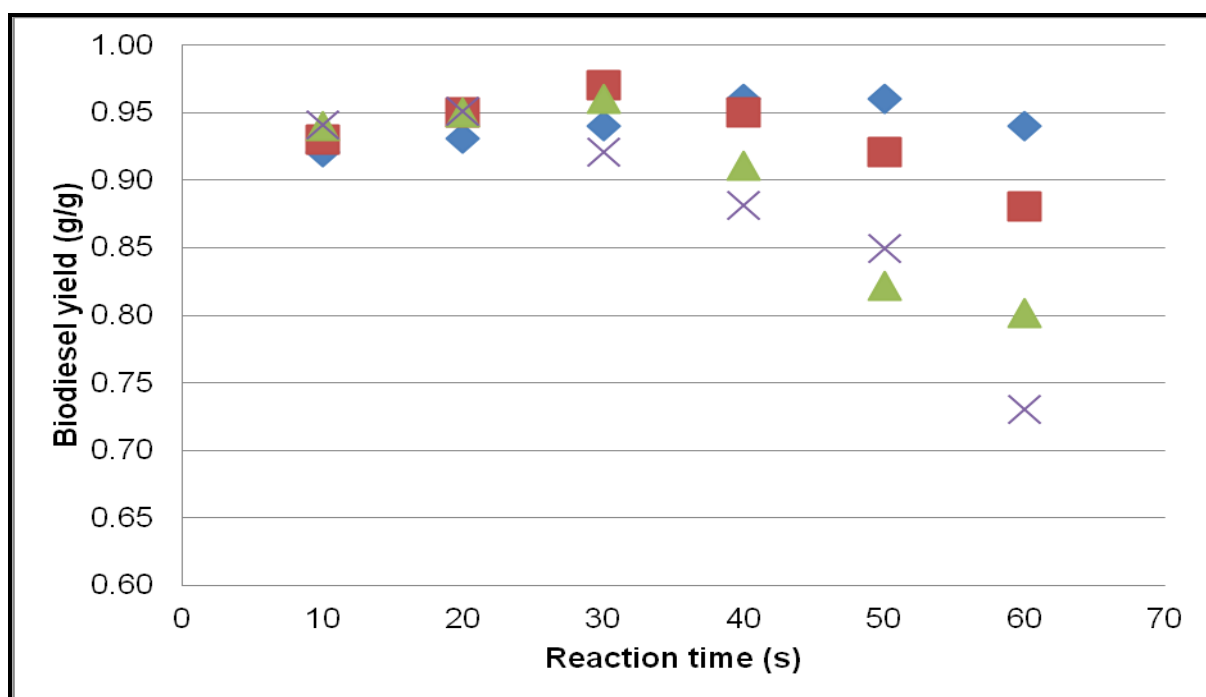


Figure E.8: Effect of reaction time on biodiesel yield at 1.5 wt% KOH, 1:9 oil/methanol ratio (♦300 W ■450 W ▲600 W ✕900 W).

Appendix E.2 . Effect of microwave intensity on biodiesel yield

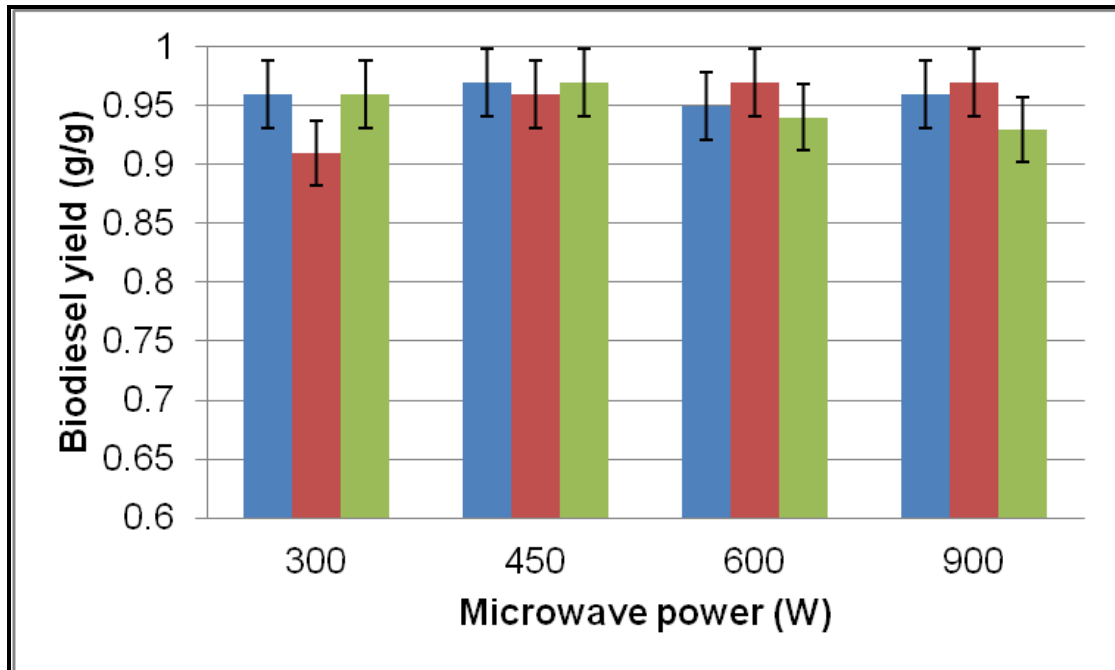


Figure E.9: Effect of microwave power on biodiesel yield at 1 wt% KOH, 30 s (■1:3 ■1:6 ■1:9).

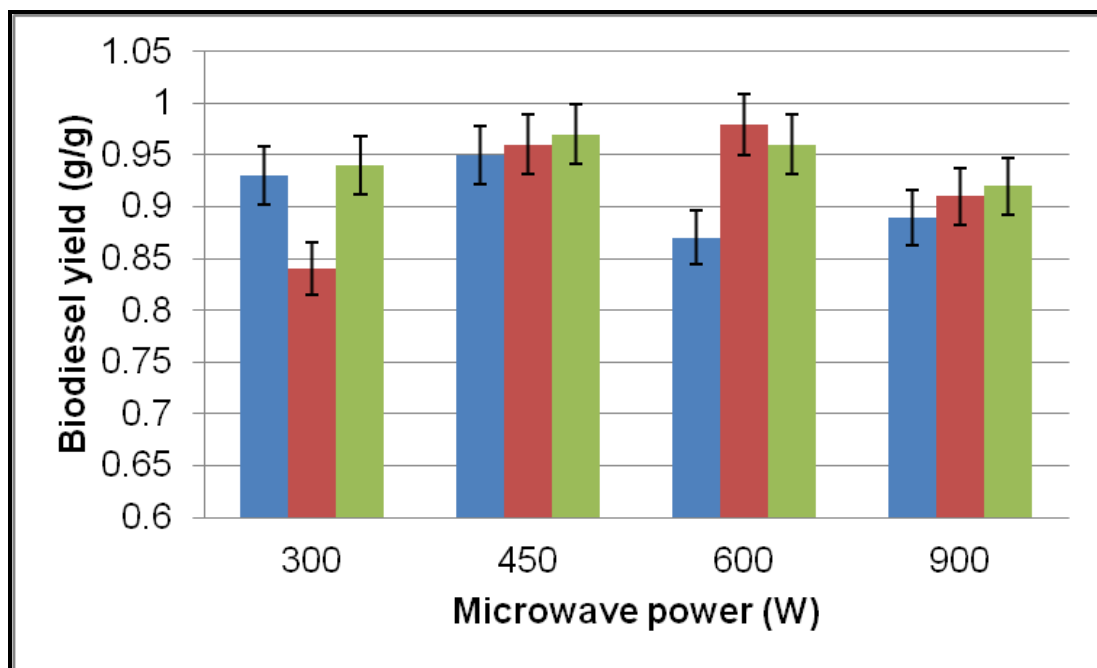


Figure E.10: Effect of microwave power on biodiesel yield at 1.5 wt% KOH, 30 s (■1:3 ■1:6 ■1:9).

Appendix E.3. Effect of oil/alcohol molar ratio on biodiesel yield

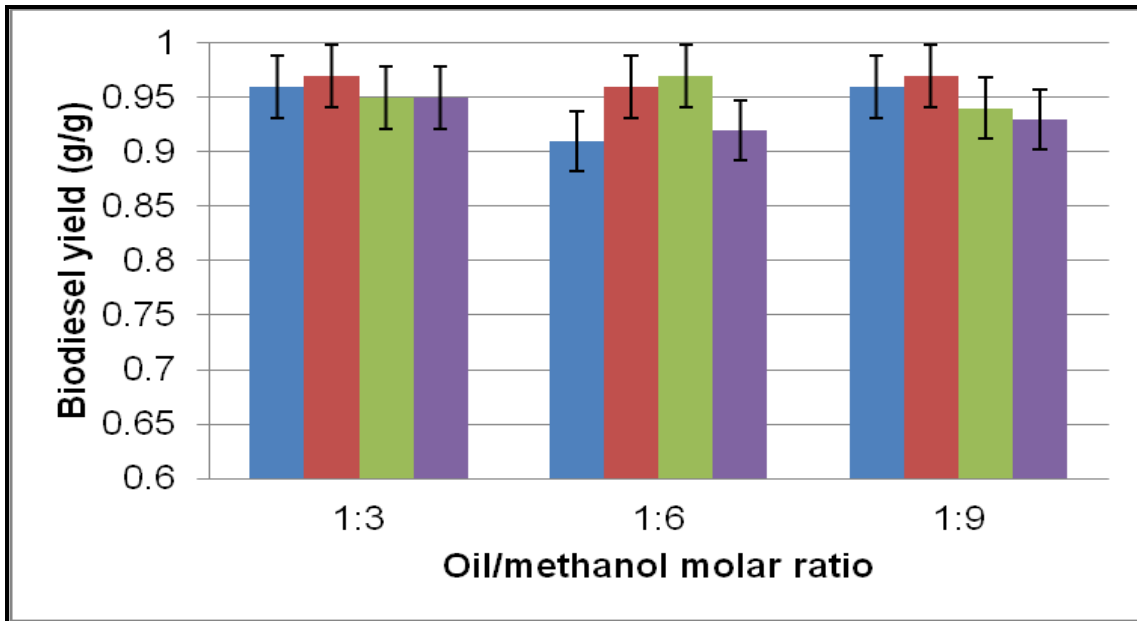


Figure E.11: Effect of oil/alcohol ratio on biodiesel yield at 1 wt%, 30 s (■ 300 W ■ 450 W ■ 600 W ■ 900 W).

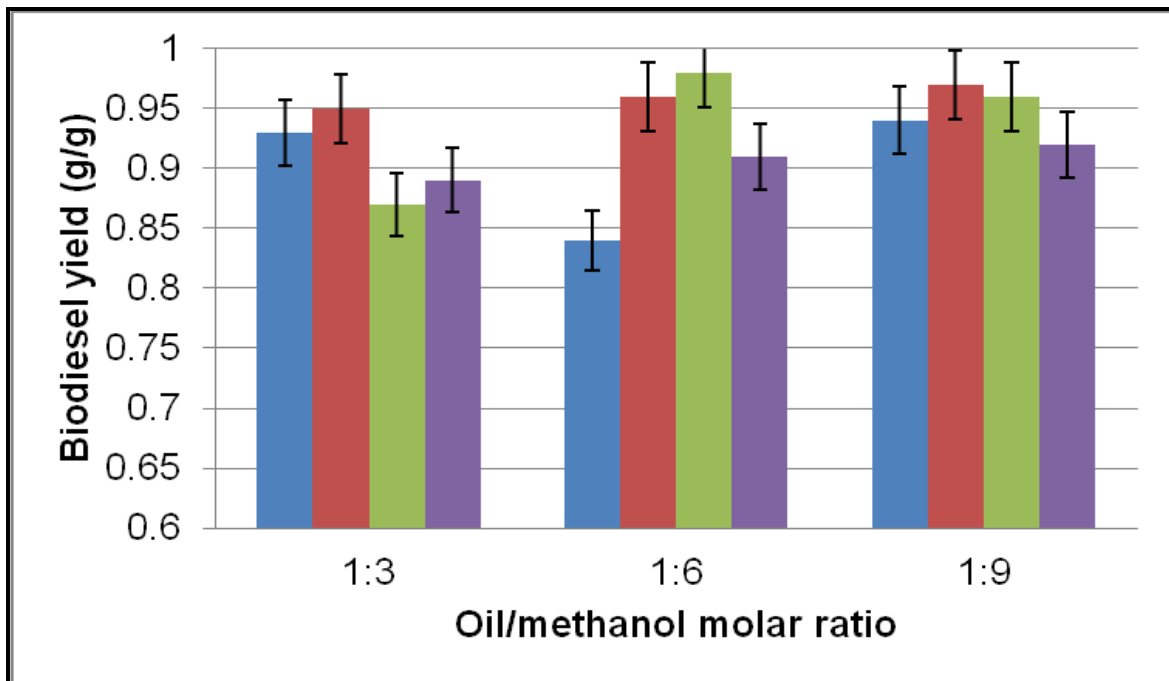


Figure E.12: Effect of oil/alcohol ratio on biodiesel yield at 1.5 wt%, 30 s (■ 300 W ■ 450 W ■ 600 W ■ 900 W).

Appendix E.4. Effect of catalyst loading on biodiesel yield

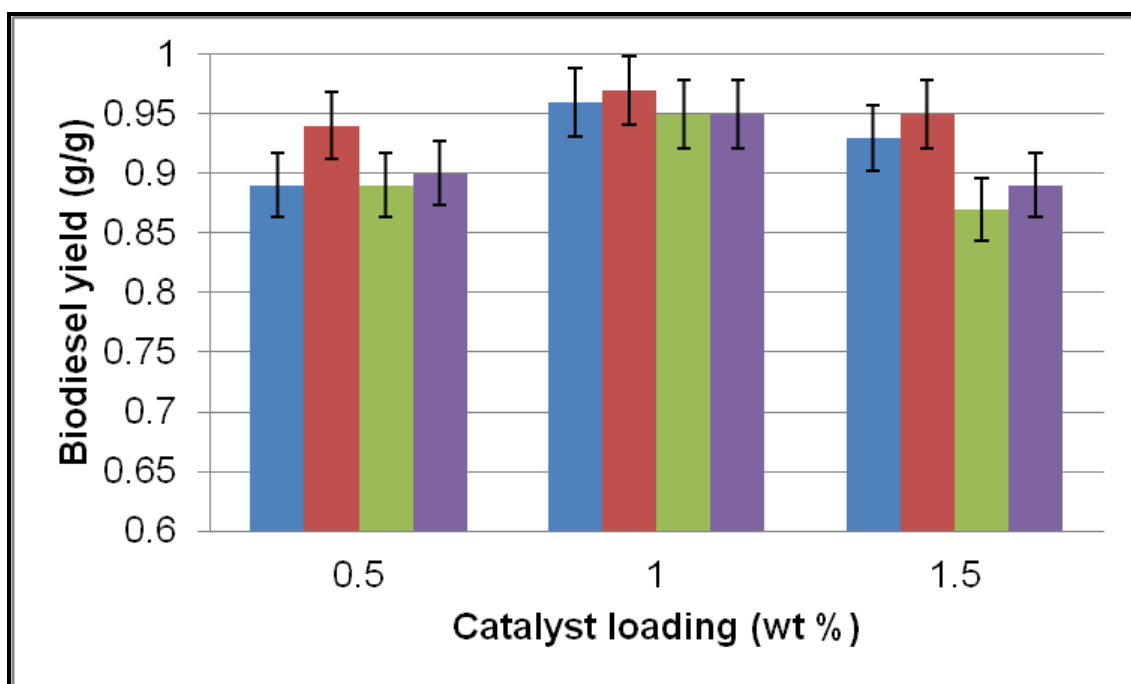


Figure E.13: The effect of a catalyst loading at a 1:3 molar ratio, 30 s (■ 300 W ■ 450 W ■ 600 W ■ 900 W).

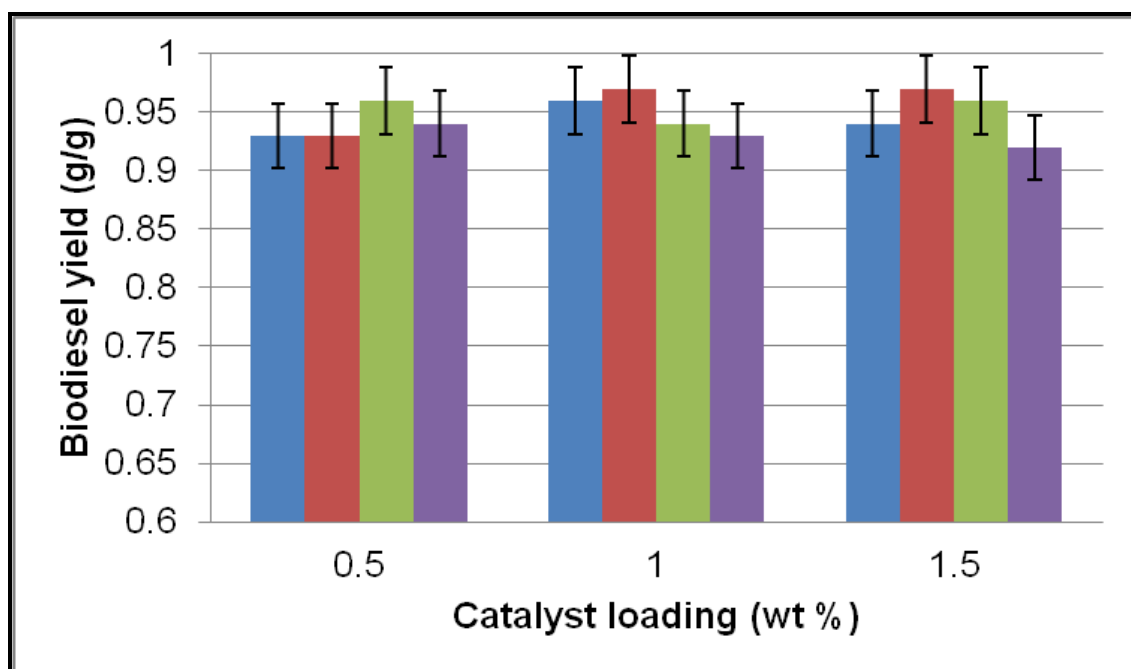


Figure E.14: The effect of a catalyst loading at a 1:9 molar ratio, 30 s (■ 300 W ■ 450 W ■ 600 W ■ 900 W).

Appendix F- FTIR spectra

Appendix F provides the comparison between FTIR spectra of sunflower oil and biodiesel produced in this study.

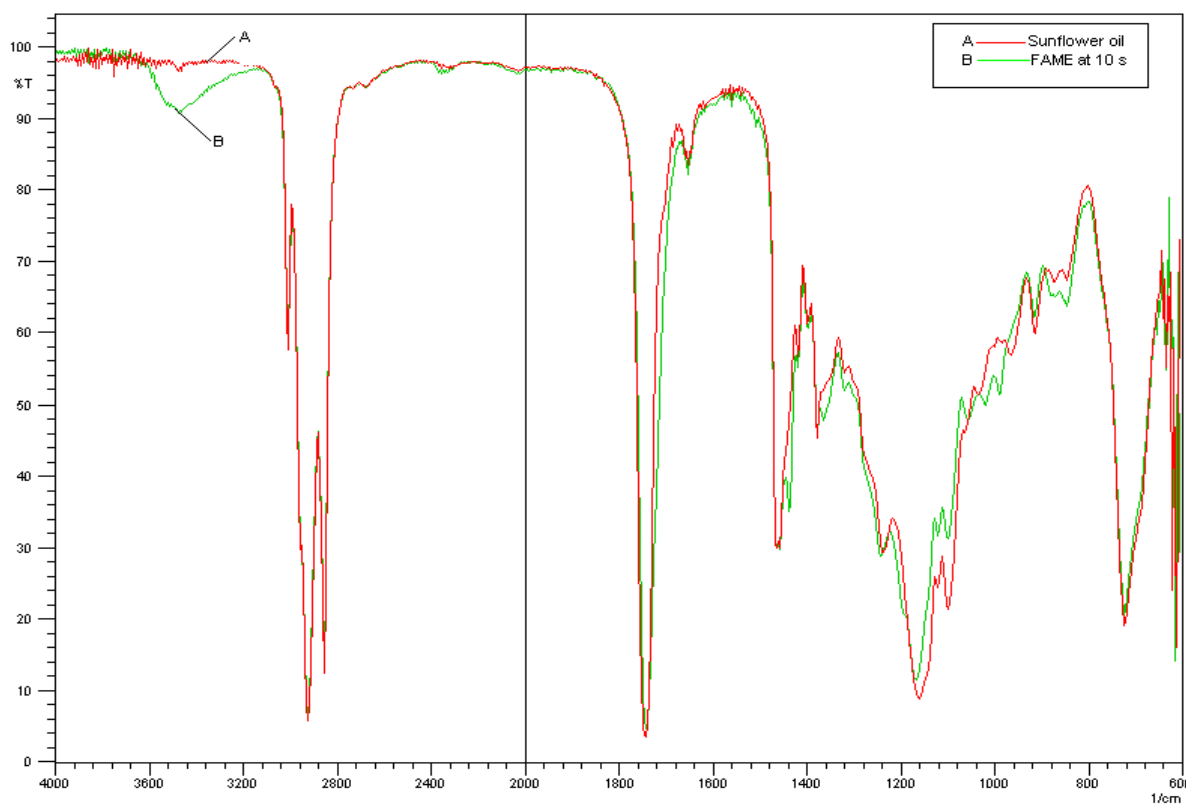


Figure F.1: Comparison of sunflower oil spectrum to that of the corresponding fatty acid methyl ester (FAME) produced at 1 wt% KOH, 1:9 oil/methanol molar ratio, 450 W, 10 s.

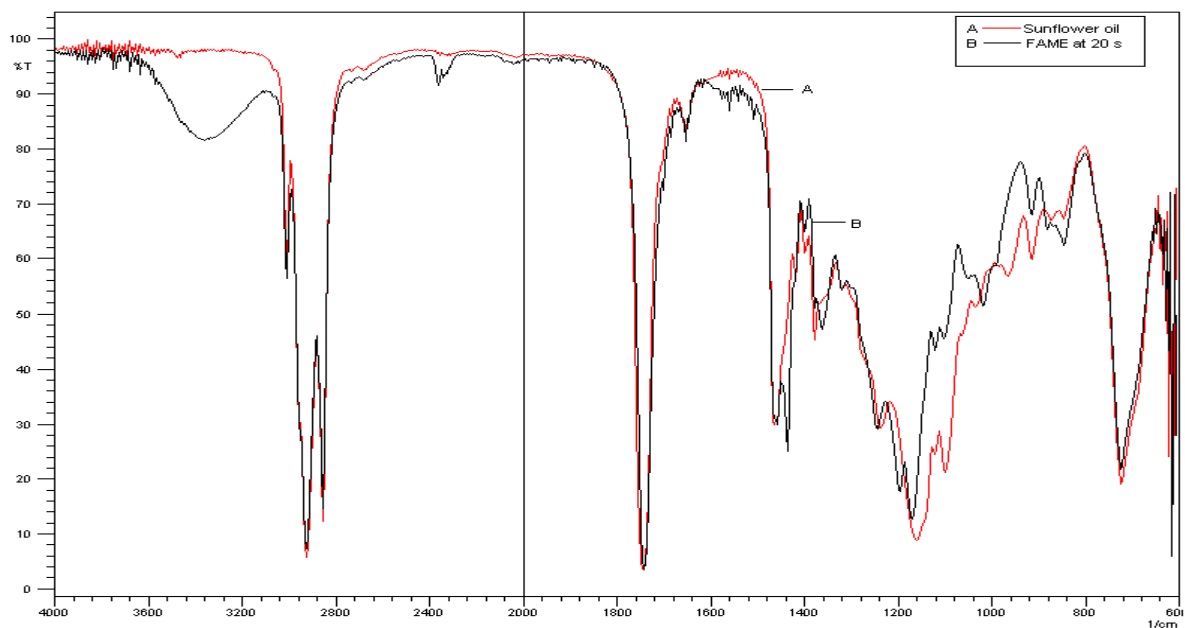


Figure F.2: Comparison of sunflower oil spectrum to that of the corresponding fatty acid methyl ester (FAME) produced at 1 wt% KOH, 1:9 oil/methanol molar ratio, 450 W, 20 s.

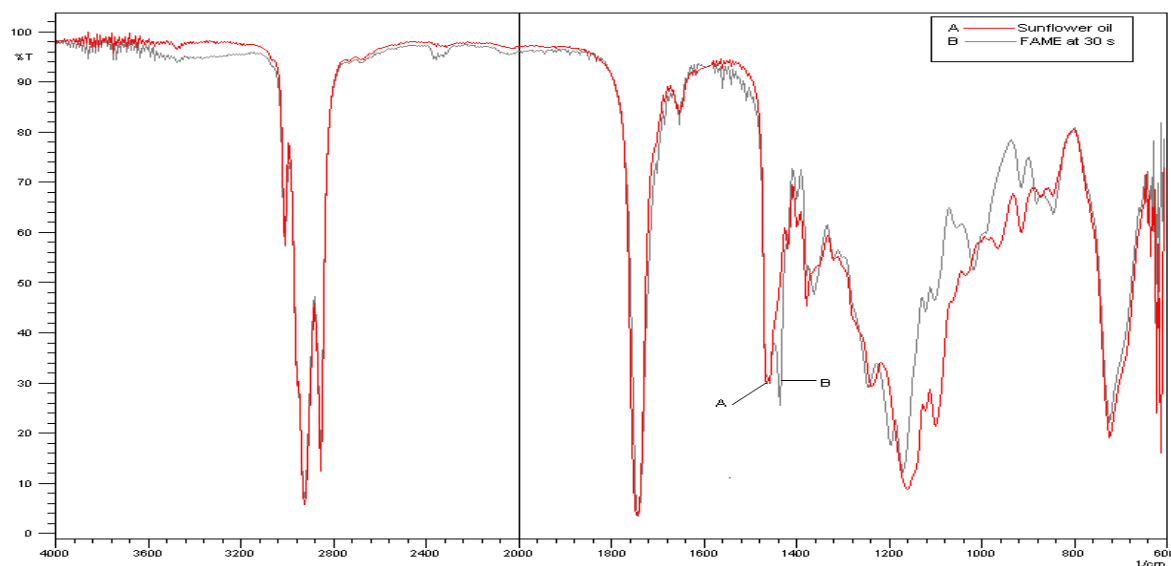


Figure F.3: Comparison of sunflower oil spectrum to that of the corresponding fatty acid methyl ester (FAME) produced at 1 wt% KOH, 1:9 oil/methanol molar ratio, 450 W, 30 s.

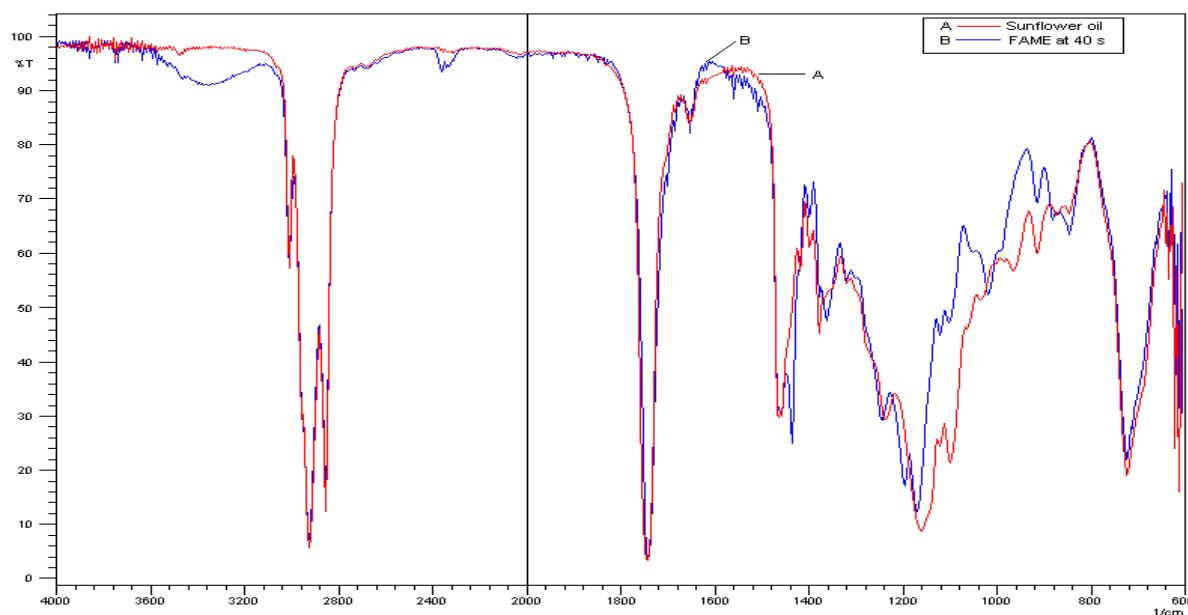


Figure F.4: Comparison of sunflower oil spectrum to that of the corresponding fatty acid methyl ester (FAME) produced at 1 wt% KOH, 1:9 oil/methanol molar ratio, 450 W, 40 s.

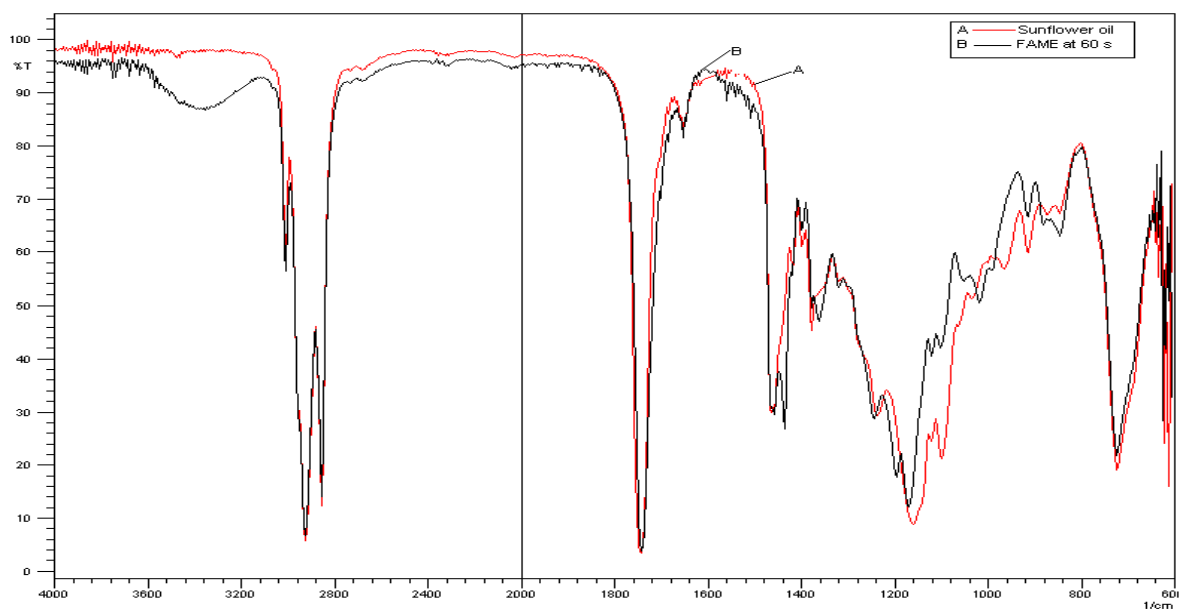


Figure F.5: Comparison of sunflower oil spectrum to that of the corresponding fatty acid methyl ester (FAME) produced at 1 wt% KOH, a 1:9 oil/methanol molar ratio, 450 W, 60 s.

References

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