

Continuous microwave-assisted biodiesel production

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ABSTRACT

The impetus of this study focuses on the production of fuel-substitute i.e. biofuels. This arises from its similar properties with petroleum diesel and being environmentally benign. In particular, biodiesel is defined as composed of mono-alkyl esters with long fatty acids chains.

The primary aim of the study was to investigate the effect of surface area of the reactor vessel when producing biodiesel using continuous microwave-assisted transesterification. The effects of energy input on FAME yields and biodiesel properties were determined.

Three different tubular reactor coils with same volume (100 ml) and different surface area (0.082, 0.057, and 0.045 m²) were used in this study. The experiments were carried out in one of these reactors, with a constant 6:1 methanol-to-oil molar ratio, and constant 1wt% KOH catalyst, varying residence time (40, 50, and 60 s) and 400, 500, 600 W microwave powers.

According to results, the highest FAME yield was obtained at 50 s residence time, 400 W microwave power with an energy input of 67.96 J/g at reactor surface (0.082 m²). A further increase of power usage led to a decrease in FAME yields. Produced biodiesel was analysed using gas chromatography (GC), Fourier transformer infrared spectrometer (FTIR) eraspec, Eraflash, and Viscometer.

Biodiesel was tested according to SANS 1935 standard specification. The properties of produced biodiesel met the SANS 1935 standard specification. Viscosity and oxidation stability did not meet the requirements. It was noticed that when oxidation stability values are low, the viscosity decreases. An antioxidant plays a pivotal role to stabilise biodiesel.

Keywords: Biodiesel, surface area, continuous microwave, energy input, properties

DECLARATION

I Nomsa Cynthia Nodede declare that the thesis I submitted in the fulfillment of Master of Science in Chemical Engineering has never been submitted in any university.

.....

Nomsa Cynthia Nodede

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**“Fear not, for I am with you; be not dismayed, for I am your God; I will strengthen you,
I will help you, I will uphold you with my righteous right hand.”**

Isaiah 41:10

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LIST OF ABBREVIATIONS

Abbreviation	Description
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
CH ₃ ONa	Sodium methoxide
GHG	Greenhouse gas
SANS	South African National Standards
%	Percent
WHO	World Health Organization
°C	Degrees Celsius
Kg	Kilogram
Cm	Centimetre
mm ² /s	Millimetre squared per second
mg	Milligram
h	Hours
g	Gram
cSt	Centistokes
K	Kelvin
FAME	Fatty acid methyl ester
FFA	Free fatty acid
GHz	Gigahertz
W	Watt
wt%	Weight percentage
<	Greater than sign
>	Less than sign
ml/min	Millilitre per minute
GC	Gas Chromatograph
FTIR	Fourier Transformer Infrared spectrometer
FID	Flame ionization detector
ACE	Associated Chemical Enterprise
TMSH	Trimethylsulphonium hydroxide
DCM	Dichloromethane
IS	Internal standard

H ₂	Hydrogen gas
He	Helium
m	Metre
cm/s	Centimetre per second
μl	Microliter
kpa	Kilopascal
s	Seconds
min	Minutes
RPM	Rounds per minute
kJ/g	Kilo Joule per gram
g/g	Grams per gram
MeOH	Methanol
IP	Induction period

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CHAPTER 1

1. INTRODUCTION

Chapter 1 is divided into four sections. The background and motivation of the study are discussed in section 1.1. Section 1.2 contains the problem statement, and the aim and objects are listed in section 1.3. The project scope is provided in section 1.4.

1.1 Background and motivation

At present, the world is experiencing an energy crisis (Tippayawong & Sittisun, 2012) and it has become a more crucial issue because of an increase in energy demand and supply. Energy is a common necessity for every sector in the country. This results in increasing energy demands along with the growth in human population and industrialisation (Choedkiatsakul *et al.*, 2015; Talebian-Kiakalaieh *et al.*, 2013).

Energy is commonly produced from sources such as petroleum, natural gas, and coal, which are fossil fuels. The increase in energy consumption has rapidly led to the depletion of non-renewable energy sources. Every country is experiencing a rise in fossil-based fuels and potential shortages in the near future that have led to a major concern about energy security (Juan *et al.*, 2011). South Africa produces its fuel needs from gas, local crude oil, coal, and imported oil Figure 1-1. In 2002, a white paper was released stating that by 2013 South Africa will produce approximately 5% energy from renewable energy sources.

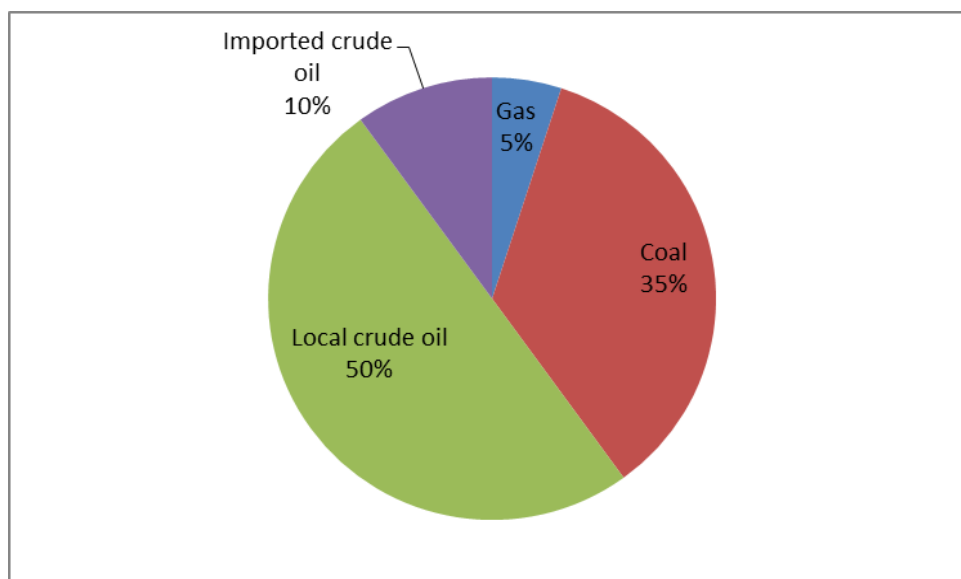


Figure 1-1: South Africa's production of fuel needs (Government Communications, 2013)

Renewable energy research has received increasing attention in recent years (Gude *et al.*, 2013) due to the depletion of fossil fuel resources and the need to reduce greenhouse gas emissions. Apart from this, the fuel consumption is expected to increase by 60% in the next 25 years. As a result, there is an increased attention in biofuels, such as biodiesel, which can be used as an alternative fuel in diesel engines (Rahimi *et al.*, 2014).

Biodiesel has drawn an interest as an alternative for petroleum diesel fuel, because it is produced from renewable resources. However, the cost of biodiesel is a major challenge for its commercialisation, because 1L of biodiesel costs approximately 1.5 times more than petroleum diesel (Chen *et al.*, 2012). The high costs of biodiesel production are due to its feedstock (Demirbas, 2005), which accounts for approximately 60 to 80% of biodiesel costs (Koh & Ghazi, 2011).

To reduce feedstock costs, biodiesel can be produced using non-edible oils such as jatropha, karanja and waste cooking oil, but they have high FFA, so they need pre-treatment. Another way to reduce the cost of biodiesel is to increase biodiesel yields. FAME yields increase with increasing reaction temperature, lowering reaction time, catalyst amount, and the alcohol-to-oil molar ratio (Koh & Ghazi, 2011).

Traditionally, transesterification reactions are carried out in conventional heating processes, which require large amounts of energy, needs long reaction times (up to 90 minutes) and the reaction mixture needs preheating (Refaat *et al.*, 2008). Microwave-assisted technology has

been used as an alternative to conventional heating for biodiesel production. The use of microwave-assisted transesterification leads to decreased reaction times, low oil-to-methanol ratios, increased reaction rates, reduced separation time and improved product yield (Vyas *et al.*, 2010; Hernando *et al.*, 2007).

1.2 Problem statement

Microwave irradiation is an alternative method that can be used for biodiesel production. The heat transferred through microwave reactions is more effective than the conventional, and therefore the diesel reactions can be completed in a shorter reaction time with reduced energy input. The surface area for heat transfer to the reactor, that has not been previously investigated, will be studied.

1.3 Aim and objectives

1.3.1 Research aim

The main aim of the study is to investigate the effect of surface area of the reactor vessel when producing biodiesel using microwave-assisted transesterification.

1.3.2 Specific objectives

The specific objectives of the study to meet the aim of the study are:

- Determine the effect of microwave power input on biodiesel yield
- Determine the effect of energy input on biodiesel yields
- Evaluate the effect of operating parameters on the properties of the biodiesel such as viscosity, cetane number and ester content.

1.4 Project scope

Chapter 1: Introduction

A brief background and motivation of the study, problem statement, and aim and objectives are presented.

Chapter 2: Literature review

A relevant review on biodiesel production methods, factors affecting the production of biodiesel and properties of biodiesel as studied by other researchers is presented in this chapter.

Chapter 3: Experimental

A description of experimental materials used, experimental procedure for continuous transesterification process and analytic methods used is presented.

Chapter 4: Results and discussion

In this chapter, results on the influence of microwave power, energy input, reactor surface area on FAME yield and diesel properties are discussed.

Chapter 5: Conclusion and recommendations

The overall conclusion from the study and recommendations for future work are presented in this chapter.

1.5 References

- Chen, K.S., Lin, Y.C., Hsu, K.H. & Wang, H.K. 2012. Improving biodiesel yields from waste cooking oil by using sodium methoxide and a microwave heating system. *Energy*, 38:151-156.
- Choedkiatsakul, I., Ngaosuwan, K., Assabumrungrat, S., Tabasso, S. & Cravotto, G. 2015. Integrated flow reactor that combines high-shear mixing and microwave irradiation for biodiesel production. *Biomass and Bioenergy*, 77:186-191.
- Demirbas, A. 2005. Biodiesel production from vegetables oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, 31:466-487.
- Government Communications. 2013. Energy. (In: Tibane, E. & Vermeulen, A. eds. South Africa Yearbook 2013/14. 2015. Government communications.).
- Gude, V.G., Patil, P., Martinez-Guerra, E., Deng, S. & Nirmalakhandan, N. 2013. Microwave energy potential for biodiesel production. *Sustainable Chemical Processes*, 1(5):1-31.
- Hernando, J., Leton, P., Matia, M.P., Novella, J.L. & Alvarez-Builla, J. 2007. Biodiesel and FAME synthesis assisted by microwaves: Homogeneous batch and flow processes. *Fuel*, 86:1641-1644.
- Juan, J.C., Kartika, D.A., Wu, T.Y. & Hin, T.Y. 2011. Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: An overview. *Bioresource Technology*, 102:452-460.
- Koh, M.Y. & Ghazi, T.I.M. 2011. A review of biodiesel production from jatropha curcas L. oil. *Renewable and Sustainable Energy Reviews*, 15:2240-2251.
- Rahimi, M., Aghel, B., Alitabar, M., Sepahvand, A. & Ghasempour, H.R. 2014. Optimization of biodiesel production from soybean oil in a microractor. *Energy Conversion and Management*, 79:599-605.
- Refaat, A.A., El Sheltaway, S.T. & Sadek, K.U. 2008. Optimum reaction time, performance and exhaust emissions of biodiesel produced by microwave irradiation. *International Journal of Environmental Science and Technology*, 5(3):315-322.

Talebian-Kiakalaieh, A., Amin, S. Aishah N. & Mazaheri, H. 2013. A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, 104:683-710.

Tippayawong, N. & Sittisun, P. 2012. Continuous-flow transesterification of crude jatropha oil with microwave irradiation. *Scientia Iranica*, 19(5):1324-1328.

Vyas, A.P., Verma, J.L. & Subrahmanyam, N. 2010. A review on FAME production processes. *Fuel*, 89:1-9.

CHAPTER 2

2. LITERATURE REVIEW

A literature review is given on biodiesel production using microwave-assisted technology. There is a brief review on global energy in section 2.1 and renewable energy fuels are discussed in section 2.2. A description of biofuels is provided in section 2.3. In section 2.4, biodiesel properties and advantages and disadvantages of biodiesel are discussed. Methods of biodiesel production and operating parameters that affect FAME yields are discussed in section 2.5, and section 2.6 respectively.

2.1 Global energy

The world's major energy resources are derived from fossil fuels, renewable resources and nuclear resources. Since 1850, the global use of fossil fuels has increased to dominate the energy supply (Bilgen *et al.*, 2015); approximately three quarters of the world's energy is produced from fossil fuels (Ozbugday & Erbas, 2015). Energy has become a crucial factor for humanity to continue economic growth and maintain high standards of living (Atabani *et al.*, 2012).

The main reason for the search for an alternative to fossil fuels is the increased demand of fossil fuels in all sectors of human life, transportation, power generation, industrial processes, and residential consumption (Talebian-Kiakalaieh *et al.*, 2013). The world will need 50 % more energy in 2030 than today (Arun *et al.*, 2015; Atabani *et al.*, 2012).

2.2 Renewable energy fuels

The world is experiencing an increase in greenhouse gas (GHG) emissions and a depletion in crude oil reserves and these all result in an increase in transportation fuel prices (Fazal *et al.*, 2011). The consumption of energy is increasing due to two reasons, i.e. a change in life styles and significant population growth (Fattah *et al.*, 2013; Mazur, 2011). The use of renewable energy resources is of great importance to prevent global warming caused by greenhouse gas emission from fossil fuels (Ozbugday & Erbas, 2015). Major contributors of environmental pollution are motor vehicles, which emit approximately 70% of carbon monoxide and 19% of carbon dioxide globally (Deenanath *et al.*, 2012). An energy source is referred to as green energy when its production has no effect on the environment. Examples of sources of green energy are biomass, solar, wind, geothermal, hydropower and marine

energies (Demirbas, 2007; Elnugoumi *et al.*, 2012). Biofuels are hailed as an environmentally-sustainable solution to the global energy crisis, and a way to counterbalance global increases in carbon dioxide (Deenanath *et al.*, 2012).

2.3 Biofuels

Biofuels are renewable energy resources that have drawn interest as a substitute to fossil fuels. Biofuels are categorised as liquid, solid and gaseous fuels, derived from biomass (Kajikawa & Takeda, 2008; Uriarte, 2010). Biofuels are being developed as a substitute to petroleum derived transportation fuels for reasons such as energy cost, energy security and global warming associated with fossil fuels (World Health Organization, 2006). In most developed and developing countries, biofuels have been proven as a means of reducing dependence on oil imports, lowering GHG emissions and meeting the goals of rural development. The production of biofuels worldwide showed an increase of 4.4 to 50.1 billion litres from 1980 to 2005, with dramatic increases predicted for the future (Singh & Singh, 2010).

2.3.1 Types of biofuels

Biofuels are categorised into first-generation, second-generation and third-generation biofuels, and are distinguished by the feedstock used to produce fuel as shown Figure 2-1 (Lee & Lavole, 2013). For biodiesel production, first-generation biodiesel is produced from food grade feedstock such as sunflower oil and canola. Second-generation biodiesel is produced from waste cooking oil, and third-generation biodiesel is produced from algae (Ahmad *et al.*, 2011; Dragone *et al.*, 2010).

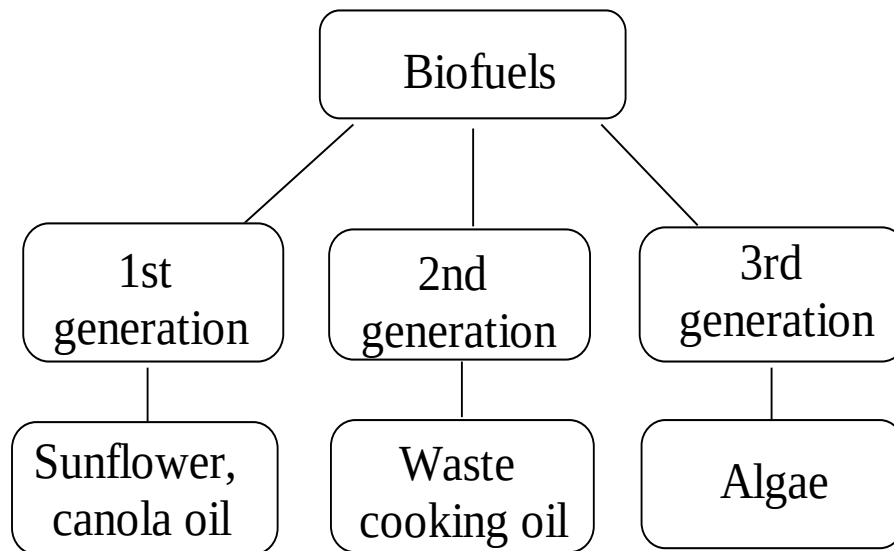


Figure 2-1: Types of biofuels (Dragone et al., 2010)

2.4 Biodiesel as a fuel

Biodiesel has developed an attraction in research nowadays due to the depletion of petroleum reserves and increasing environmental concerns in developed and developing countries (Leung *et al.*, 2010). Biodiesel is used as an alternative to petroleum diesel fuel. Biodiesel is a mixture of mono-alkyl esters of long fatty acid chains, derived from vegetable oils and animal fats (Lokman *et al.*, 2014). Biodiesel is produced by reacting vegetable oils or animal fat with alcohol in the presence or absence of a catalyst (Gerpen, 2009; Leung *et al.*, 2010). There are advantages and disadvantages of using biodiesel as a substitute to petroleum diesel.

2.4.1 Advantages of biodiesel production

Biodiesel has some advantages over petroleum diesel. Biodiesel is produced from renewable sources, such as vegetable oils and animal fats. The production of biodiesel reduces greenhouse gas emissions (Demirbas, 2009; Motasemi & Ani, 2012). Biodiesel can be used in diesel engines with little modifications or no modifications at all. Biodiesel has a high flash point, which makes it safer than petroleum diesel fuel at high temperatures (Nolte, 2007; Sarin, 2012).

2.4.2 Disadvantages of biodiesel production

Biodiesel production has disadvantages over petroleum diesel. The production of biodiesel from first-generation feedstock can lead to food shortages. Biodiesel is more expensive than petroleum diesel fuel, due to its high feedstock costs and that makes it not feasible enough to replace petroleum fuel. The production of biodiesel is highly dependent on the nature and availability of feedstock. Biodiesel has a higher freezing point than diesel fuel, and that can be inconvenient in cold climates (Demirbas, 2009; Motasemi & Ani, 2012; Nolte, 2007).

2.4.3 Properties of biodiesel according to South African standards (SANS 1935)

Biodiesel to be used commercially in South Africa needs to conform to the SANS: 1935 standard for biodiesel see (Table 2-1).

Table 2-1: Biodiesel properties according to South African standards (SANS 1935:2004)

Property	Requirements	Test method
Methyl ester content, % mass fraction	>96,5	EN14103
Density at 15°C, kg/cm	860-900	ISO 3675
Kinematic viscosity at 40°C, mm²/s	3,5 – 5,0	ISO 3104
Flash point °C	>120	ISO 3679
Sulphur content, mg/kg	<10	ISO 20846
Cetane number	>51	ISO 5165
Water content, % mass fraction	<0,05	ISO 12937
Oxidation stability at 110 °C, h	>6	EN 14112
Acid value, mg KOH/g	<0,5	EN 14104
Free glycerol, % mass fraction	<0,02	EN 14105
Total glycerol, % mass fraction	<0.25	EN 14105

As observed from Table 2-1, biodiesel has many similar chemical and physical properties to petroleum diesel fuel, but a higher viscosity and cloud point are some of the major problems associated with the use of biodiesel in diesel engines. These properties affect the fuel droplet size during injection (Bajpai & Tyagi, 2006).

2.5 Methods for biodiesel production

Despite the fact that crude vegetable oils can be used to run diesel engines, its high viscosity, low volatility and reactivity of unsaturated hydrocarbon chains make the use thereof in modern engines problematic. Many efforts have been made to improve vegetable properties to meet diesel fuel standards. Pyrolysis, dilution, microemulsion and transesterification are the techniques commonly used to overcome the problems mentioned above.

2.5.1 Pyrolysis

Pyrolysis is a process where the conversion of oil occurs over a catalyst in the absence of air or oxygen. Vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids have been used to produce biodiesel through pyrolysis (Pragya *et al.*, 2013). Biodiesel produced from pyrolysis has similar properties to petroleum diesel. Produced fuels have a high cetane number, low viscosity, acceptable amounts of sulphur, water and sediment contents, and copper corrosion (Atabani *et al.*, 2012; Pragya *et al.*, 2013).

2.5.2 Dilution

Vegetable oils can be diluted with diesel to lower the viscosity and improve the engine performance, and there are no chemicals needed for this process. Investigations were carried out with 25% sunflower oil and 75% diesel, which were blended as diesel fuel (Atabani *et al.*, 2012). The results showed that the blend had a viscosity of 4.8 cSt at 313 K, while the maximum specified ASTM value is 4.0 cSt at 313 K. The use of oil and diesel blends is not possible in modern direct injection engines (Atabani *et al.*, 2012; Demirbas, 2009).

2.5.3 Micro-emulsion

Short-chain alcohols such as ethanol and methanol and ionic or non-ionic amphiphiles have been used to solve the problem of the high viscosity of vegetable oils (Balat & Balat, 2010; Pragya *et al.*, 2013; Yusuf *et al.*, 2011). Although viscosity is lowered by micro-emulsions of vegetable oils, irregular sticking of injector needles and heavy carbon deposits due to incomplete combustion of oil have been found (Demirbas, 2009).

2.5.4 Transesterification

Transesterification is the reaction of fats or oils with alcohol in the presence of a catalyst to form esters and glycerol as presented in Figure 2-2. The catalyst is used in this reaction to improve the reaction rate and yield. Transesterification consists of three consecutive reversible reactions. Firstly, triglycerides are converted to diglycerides followed by the conversion of diglycerides to monoglycerides and then monoglycerides are converted to glycerol (Singh & Singh, 2010). Typically, one mole of triglycerides is reacted with three moles of alcohol, but the amount of alcohol can be increased to increase the yield of alkyl esters by enhancing the forward reaction (Balat & Balat, 2010; Koh & Ghazi, 2011). Primary and secondary monohybrid aliphatic alcohols having 1-8 carbon atoms are usually used for this reaction (Singh & Singh, 2010).

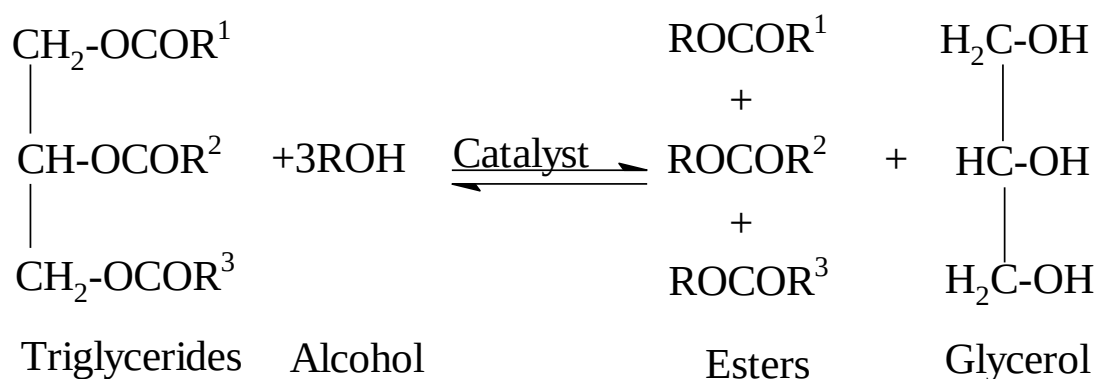


Figure 2-2: Transesterification of triglycerides with alcohol (Demirbas, 2009; Kapilan & Baykov, 2014)

Transesterification is most often used to lower the viscosity of vegetable oils, because of its low cost, simplicity and the physical characteristics of the biodiesel produced. Biodiesel is the main product of this reaction and glycerol is the by-product that can be used as a feedstock in the cosmetic industry. Transesterification reactions can be carried out using different types of catalysts (Bankovil-llic *et al.*, 2012).

2.5.4.1 Alkali-catalysed transesterification

Transesterification reactions can be also carried out using alkali catalysts. Sodium hydroxide (NaOH), sodium methoxide (CH₃ONa), and potassium hydroxide (KOH) are the most commonly used alkali catalysts, because they are inexpensive and readily available (Helwani *et al.*, 2009; Juan *et al.*, 2011). Alkali catalysts are inexpensive, have high catalytic activity, and produce high quality biodiesel in a short period of time. However, alkali catalysts are sensitive to water and free fatty acids found in feedstock, which leads to the formation of soap, and difficulties during the separation of glycerol from FAME (Talebian-Kiakalaieh *et al.*, 2013). The mechanism of alkali-catalysed transesterification reaction is shown in Figure 2-3 (Vyas *et al.*, 2010; Koh & Ghazi, 2011).

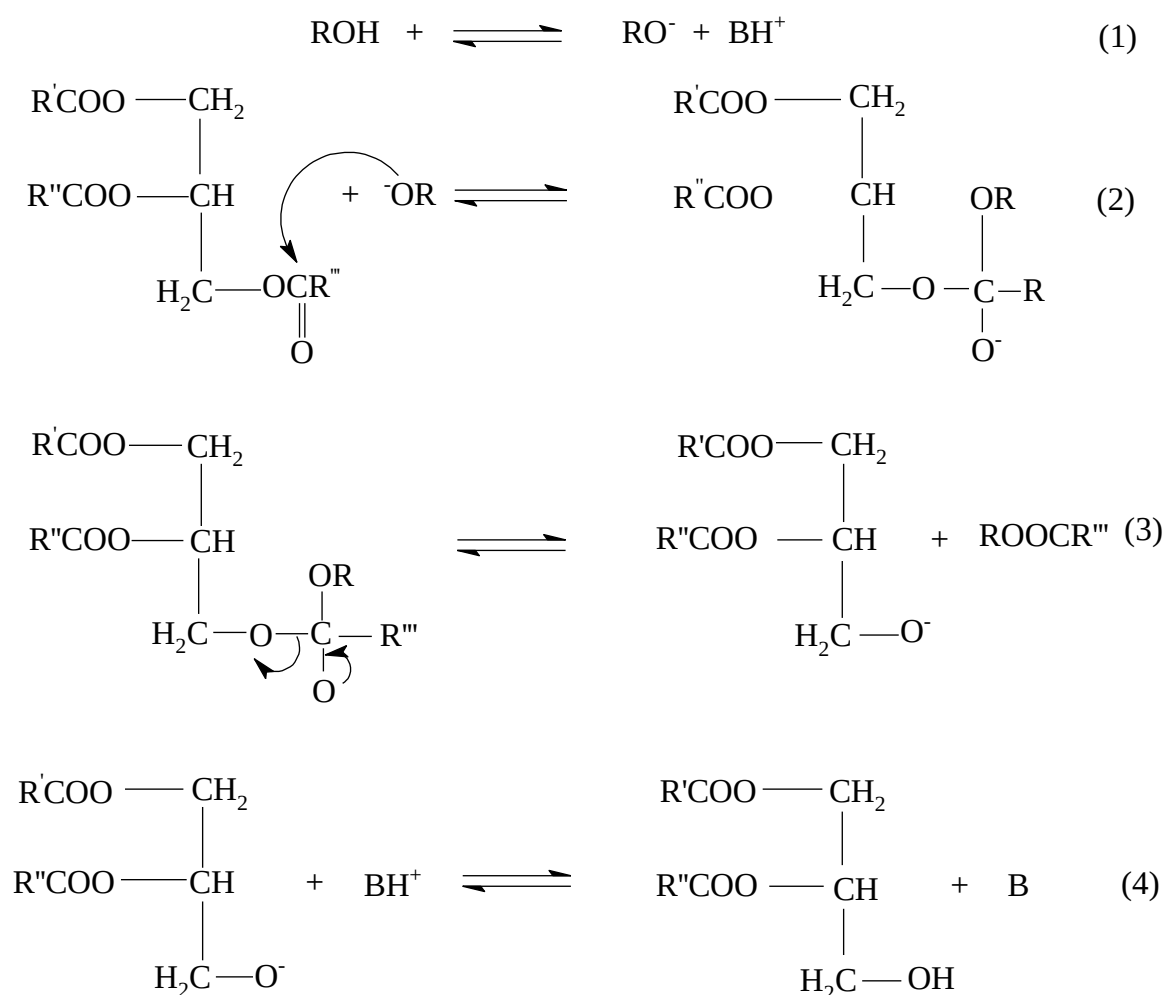


Figure 2-3: Proposed mechanism of an alkali catalysed transesterification (Koh & Ghazi, 2011)

2.5.4.2 Acid-catalysed transesterification

Acid-catalysed transesterification is more suitable for feedstock with high FFAs, which may be of low grade and less expensive. Acid-catalysed transesterification reactions are slower than alkali-catalysed reactions (Helwani *et al.*, 2009). The main advantage of an acid-catalysed reaction is that it can act as catalyst in both esterification and transesterification processes, and can produce biodiesel directly from used cooking oils with high free fatty acid content (Vyas *et al.*, 2010). The only limitation when using acid-catalysed reactions is that high methanol-to-oil molar ratios are required (Bynes *et al.*, 2014). The mechanism for acid-catalysed transesterification is shown in Figure 2-4.

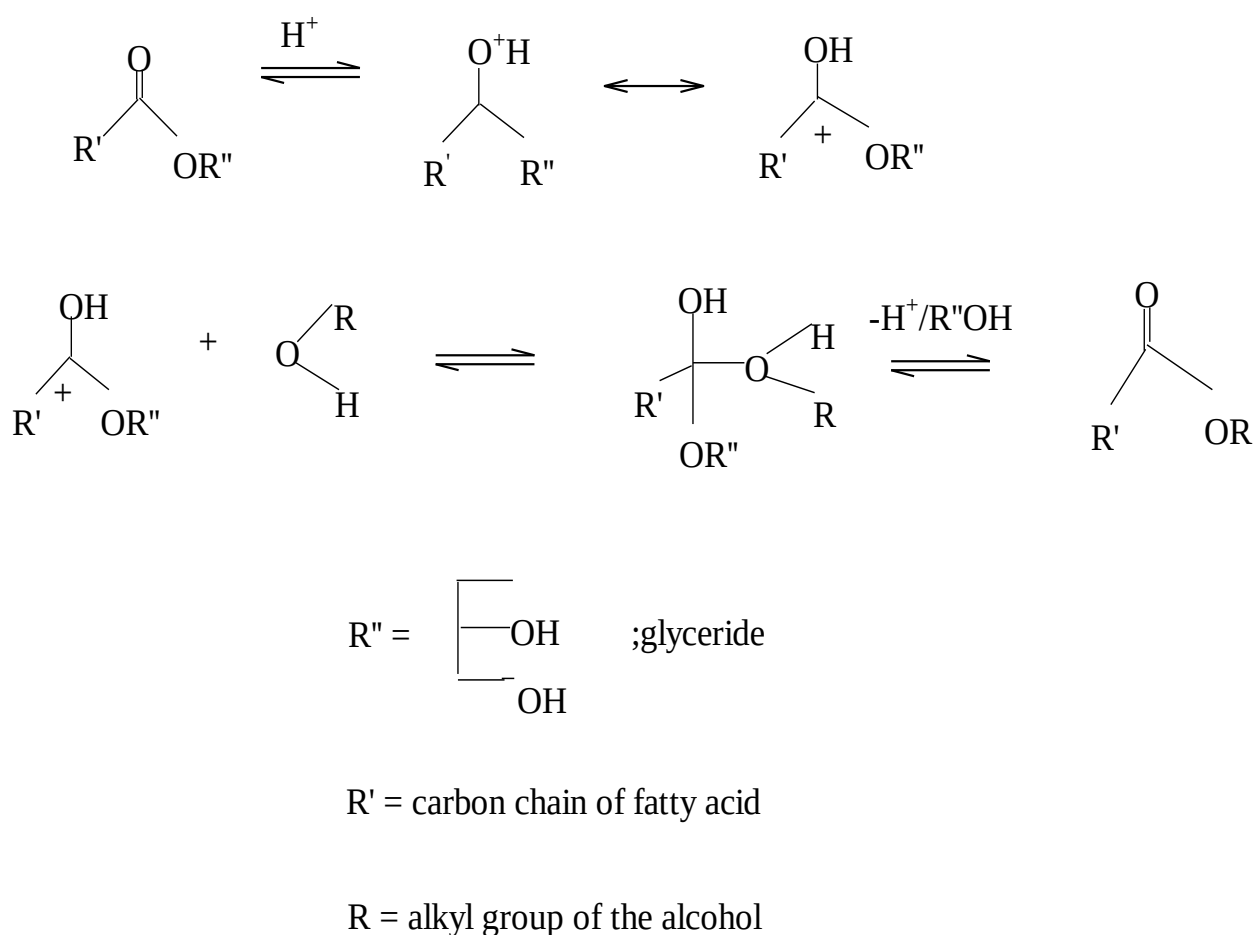


Figure 2-4: Proposed mechanism of an acid catalysed transesterification (Ejikeme et al., 2010; Koh & Ghazi, 2011)

2.5.4.3 Enzyme-catalysed transesterification

Enzyme-catalysed transesterification reactions have been carried out using lipase, and are attractive because of easy product separation, minimal wastewater generated, and the absence of side reactions. Lipase has been seen to favour long-chain fatty alcohols. The reaction yields from enzyme-catalysed transesterification are still unfavourable compared to base-catalysed reactions and therefore render the process impractical and uneconomical (Koh & Ghazi, 2011).

2.5.4.4 Non-catalytic transesterification

Transesterification reactions can also be carried out without any catalyst, using supercritical methanol. However, high temperatures and pressures are required to achieve the supercritical state of the alcohol. In non-catalytic processes, the reaction can be completed within minutes with relatively high yields, while the conventional catalytic transesterification takes several hours (Talebian-Kiakalaieh *et al.*, 2013). No soap formed during supercritical transesterification, and therefore biodiesel purification is much easier. However, high pressure and high temperature conditions imply a high initial capital input for this process (Bankovil-llic *et al.*, 2012).

2.5.5 Microwave-assisted transesterification

Microwave heating is a process that is used as a substitute for conventional heating (Muley & Boldor, 2012). Domestic microwave instruments have wavelengths ranging from 0.01 to 1m and frequency ranging from 0.3 to 300 GHz. Microwave reactors usually operate at a frequency of 2.45 GHz and wavelength of 12.25 cm (Gude *et al.*, 2013).

Microwave irradiation is used in chemical reactions to enhance reaction rates by transferring the energy directly to the reactants, making this form of energy transfer more effective than conventional heating, which allows for the completion of the reaction in a shorter time (Bankovil-llic *et al.*, 2012; Motasemi & Ani, 2012). Advantages of microwave-assisted processes are

- ❖ Higher quality and yield product
- ❖ Lower energy consumption
- ❖ Shorter reaction and separation time
- ❖ Environmental friendly
- ❖ Low methanol-to-oil ratio
- ❖ Less by-products produced

Microwaves are electromagnetic energy that can be directly transferred to the reactants, which negates the necessity of preheating of the reactants (Talebian-Kiakalaieh *et al.*, 2013; Vyas *et al.*, 2010). Biodiesel production using microwave assisted technology (Mittelbach & Remschmidt, 2010), can either be conducted in batch or continuous processes.

2.5.6.1 Batch microwave-assisted transesterification

Bankovil-llic *et al.* (2012) have proved that the reaction time for transesterification could be reduced significantly to minutes compared to conventional transesterification. According to the work done by Refaat *et al.* (2008); Liao & Chung, (2011) biodiesel yields of 100 % were obtained in two minutes using microwave reactors compared to one hour for conventional heating and the separation time was reduced to 30 minutes as compared to eight hours of conventional heating.

Yaakob *et al.* (2009) used jatropha oil and waste frying palm oil for microwave-assisted transesterification and obtained biodiesel yields of 95.3% and 97.89% respectively with a reaction time, temperature and catalyst concentration of seven minutes, 65°C and 1 wt%, respectively. Magida, (2013) conducted experiments on batch microwave-assisted transesterification using sunflower oil and obtained biodiesel yields as high as 98% at a methanol-to-oil molar ratio of 6:1, 1 wt% KOH catalyst loading and 40 s reaction time.

Lin and co-workers (2014) used 0.75 wt% CH₃ONa as catalyst, with 6:1 methanol-to-oil molar ratio, and 750 W microwave power and obtained a 99.7% biodiesel yield. Azcan and Danisman (2008) worked on microwave-assisted transesterification of rapeseed oil. A 93.7% FAME yield was obtained at a temperature of 323K, a reaction time of five minutes, a catalyst loading of 1 wt% KOH and 6:1 methanol-to-oil molar ratio. Using the same conditions with 1 wt% NaOH as catalyst resulted in a 92.2% FAME yield.

2.5.6.2 Continuous microwave-assisted transesterification

The continuous-flow preparation for biodiesel production using a microwave-assisted technique offers a fast, easy route to FAME. Continuous biodiesel production using microwave-assisted methods has been reported by Lertsathapornsuk *et al.* (2008). Transesterification was done at atmospheric conditions and at flow rates of up to 7.2 L/min using a 4 L reaction vessel by Mazo and co-workers (2011).

Barnard *et al.* (2007) studied the continuous microwave-assisted transesterification reaction with either virgin or used vegetable oils at a methanol-to-oil ratio of 6:1, 1 wt% catalyst

loading and microwave power of 600 W. Optimal FAME yields of 97.9% at a flow rate of 2 L/min and 98.9% at a flow rate of 7.2 L/min were obtained. Lertsathapornsuk *et al.* (2008) also reported a biodiesel production yield of 97% when using 3% sodium hydroxide (NaOH) as catalyst with a methanol-to-oil ratio of 12:1 and 30s reaction time.

Tippayawong and Sittisun (2012) produced biodiesel from jatropha oil using a microwave oven. They concluded that their optimal conditions were found to be 30 s residence time, 6:1 methanol-to-oil molar ratio and 1 wt% NaOCH₃ catalyst for a conversion of 96.5%.

It was concluded that a continuous microwave-assisted method is more energy efficient than conventional methods, since such yields are difficult to achieve with the latter method. Summarised optimum conditions of both batch and continuous microwave assisted transesterification are presented in Table 2-2.

Table 2-2: Summary of optimum conditions in microwave-assisted transesterification

Feedstock	Reaction time	Catalyst concentration	Molar ratio	FAME yield	Mode	References
Jatropha oil	7 min	1 wt%	12:1	95.28%	Batch	Yaakob <i>et al.</i> 2009
Waste frying palm oil	7 min	1 wt%	12:1	97.89%	Batch	Yaakob <i>et al.</i> 2009
Sunflower oil	40 sec	1 wt%	6:1	98%	Batch	Magida, 2013
Coconut oil	21.04 min	1 wt%	7:1	99%	Continuous	Kumar <i>et al.</i> 2010
Crude jatropha oil	30 sec	1 wt%	6:1	96.5%	Continuous	Tippayawong & Sittisun, 2012
Waste vegetable oil	2 min	1 wt%	6:1	100%	Batch	Refaat <i>et al.</i> 2008
Karanja oil	8 min	1.2 wt%	11:1	91.2%	Continuous	Iyyaswami <i>et al.</i> 2013
Waste frying palm oil	30 sec	3.0 wt%	12:1	97%	Continuous	Lertsathapornsuk <i>et al.</i> 2008

2.6 Operating parameters affecting biodiesel yield

There are number of variables that influence the FAME yield and quality, such as catalyst concentration, reaction time, flow rate, oil-to-alcohol molar ratio and temperature (Mathiyazhagan & Ganapathi, 2011).

2.6.1 Effect of catalyst concentration

Transesterification reactions can be carried out using alkali, acid or enzyme catalysts. Alkali-catalysed transesterification is much faster than acid-catalysed transesterification, and is most often used commercially (Balat & Balat, 2010). Methoxide and water are produced when an alkali catalyst and methanol are mixed. The presence of water is not desirable in the reaction mixture, because it promotes the formation of soap through hydrolysis, causing a shortage of catalyst to drive the transesterification reaction (Mathiyazhagan & Ganapathi, 2011).

Tippayawong and Sittisun (2012) studied the effect of NaOCH_3 catalyst concentration between 0.25 and 1.5% with 1:6 oil-to-methanol molar ratio, 30s reaction time and 800 W microwave power on a continuous microwave reactor. The highest yield of 96.5% was obtained at a catalyst loading of 1%, and there was no difference observed on FAME yield when the catalyst concentration was increased further. Biodiesel yields of 89% were obtained by Rahimi *et al.* (2014) using 1.2 wt% catalyst loading with 26s residence time. A slight decrease in FAME yield (84%) was observed when the catalyst concentration was increase to 1.8 wt%.

2.6.2 Effect of methanol-to-oil ratio

Methanol-to-oil ratio is another important parameter that influences biodiesel yield from transesterification. The stoichiometry of this reaction is 3 moles of alcohol to 1 mole of oil to produce 3 moles FAME and 1 mole of glycerol (Hossain & Mekhled, 2010). Transesterification is a set of reversible reactions, and therefore excess alcohol is required to shift the reaction to the product side, and increase oil conversion and FAME yield. The molar ratio of 6:1 or higher leads to a higher FAME yield. Lower molar ratios require a longer time for the reaction to be completed. An optimum molar ratio, depending on the type and quality of vegetable oil, produces higher yields and easier separation of glycerol (Balat & Balat, 2010).

Choedkiatsakul *et al.* (2015) reported that a biodiesel yield higher than 96.50% was obtained with four minutes residence time, 1:12 oil-to-methanol molar ratio, 1 wt% catalyst loading and 400 W microwave heating power. The same yields were obtained under the same conditions using 9:1 methanol-to-oil molar ratio and 10 min residence time.

2.6.3 Effect of reaction time

Reaction or residence time plays a crucial role in the production of biodiesel by transesterification. The conversion of oils or fats into biodiesel increases when the reaction time increases (Ferrari *et al.*, 2011). Jagadale and Jugulkar (2012) reported that when transesterification reactions were performed from peanut, cottonseed, sunflower and soybean oil with a molar ratio of 6:1, and catalyst loading of 0.5 wt%, the yield increased with the increasing reaction time, until the equilibrium is reached. An increase in reaction time beyond equilibrium does not increase the yield (Mathiyazhagan & Ganapathi, 2011).

Experiments were carried out at different reaction times (10, 20, 30 and 40s) with 1 wt% NaOCH₃ catalyst concentration, microwave power of 800 W and 1:6 oil-to-methanol molar ratio. It was concluded that the biodiesel yields increased slightly after 30s residence reaching a yield of 96%, with no more conversion when residence increased further (Tippayawong & Sittisun, 2012).

The flow rate is a parameter that affects the biodiesel production, which is related to the residence time. When flow rate increases, the residence time decreases and the biodiesel yield also decreases (Shinde *et al.*, 2011). Flow rates ranging from 70 ml/min to 180 ml/min were tested in a continuous transesterification. A molar ratio of 1:7, 1 wt% catalyst and 65°C were used. It was concluded that the optimum flow rate was 142 ml/min, which gave a yield of $\geq 99\%$ (Kumar *et al.*, 2010).

2.6.4 Effect of temperature

Temperature is one of the vital factors that affects the transesterification reaction. When reaction temperature is high, this leads to shorter reaction times, because of an increase in reaction rate at higher temperatures. However, the reaction temperature should not exceed the boiling point of the alcohol to prevent evaporation of the alcohol (Mathiyazhagan & Ganapathi, 2011). According to Kumar *et al.* (2010), 60°C is the optimum temperature for the production of biodiesel when the methanol-to-oil ratio is 7:1 and a catalyst loading of 1 wt% is used. The maximum biodiesel obtained in these conditions was reported to be $\geq 99\%$.

2.7 Concluding remarks

Biodiesel has developed an attraction in research nowadays in both developed and developing countries. Biodiesel is a mixture of mono-alkyl esters of long-chain fatty acids, derived from vegetable oils and animal fats. Biodiesel can be used as a substitute to transport diesel, because it has similar properties as petroleum diesel and is environmentally friendly. Biodiesel can be produced through four methods, namely pyrolysis, micro-emulsion, dilution and transesterification.

Transesterification reactions carried out using conventional heating takes approximately 90 minutes for the reaction to be completed. Microwave heating is used as an alternative to conventional heating. The use of microwave heating increases biodiesel yields, and shortens reaction times as the heat is transfer directly to the reactants. A use of continuous microwave flow for biodiesel production is energy efficient and it produces high quantities of biodiesel in a short residence time.

2.8 References

- Ahmad, A.L., Yasin, N.H.M., Derek, C.J.C. & Lim, J.K. 2011. Microalgae as a sustainable energy source for biodiesel production: A review. *Renewable and Sustainable Energy Reviews*, 15(1):584-593.
- Arun, N., Sharma, R.V. & Dalai, A.K. 2015. Green diesel synthesis by hydrodeoxygenation of bio-based feedstocks: Strategies for catalyst design and development. *Renewable and Sustainable Energy Reviews*, 48:240-255.
- Atabani, A.E., Silitonga, A.S., Badruddin, I., Anjum, M., Mahlia, T.M.I., Masjuki, H.H. & Mekhilef, S. 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, 16:2070-2093.
- Azcan, N.A. & Danisman, A. 2008. Microwave-assisted transesterification of rapeseed oil. *Fuel*, 87(10-11):1781-1788.
- Bajpai, D. & Tyagi, V.K. 2006. Biodiesel: Source, production, composition, properties and its benefits. *Journal of Oleo Science*, 55(10):487-502.
- Balat, M. & Balat, H. 2010. Progress in biodiesel processing. *Applied Energy*, 87(6):1815-1835.
- Bankovic-llic, I.B., Stamenkovic, O.S. & Veljokovic, V.B. 2012. Biodiesel production from non-edible plant oils. *Renewable and Sustainable Energy Reviews*, 16(6):3621-3647.
- Barnard, T.M., Leadbeater, N.E., Boucher, M.B., Stencel, L.M. & Wilhite, B.A. 2007. Continuous-flow preparation of biodiesel using microwave heating. *Energy and Fuels*, 21:1777-1781.
- Bilgen, S., Keles, S., Sarikaya, I. & Kaygusuz, K. 2015. A perspective for potential and technology of bioenergy in Turkey: Present case and future view. *Renewable and Sustainable Energy Reviews*, 48:228-239.
- Bynes, A.N., Eide, I. & Jorgensen, K.B. 2014. Optimization of acid catalyzed transesterification of jatropha and rapeseed oil with 1-butanol. *Fuel*, 137:94-99.
- Choedkiatsakul, I., Ngaosuwan, K., Assabumrungrat, S., Mantegna, S. & Cravato, G. 2015. Biodiesel production in a novel continuous flow microwave reactor. *Renewable Energy*, 83:25-29.

- Deenanath, E.D., Iyuke, S. & Rumbold, K. 2012. The bioethanol industry in Sub-Saharan Africa: History, Challenges, and Prospects. *Journal of Biomedicine and Biotechnology*:1-11.
- Demirbas, A. 2007. Importance of biodiesel as transportation fuel. *Energy Policy*, 35:4661-4670.
- Demirbas, A. 2009. Progress and trends in biodiesel fuels. *Energy Conversion and Management*, 50(1):14-34.
- Dragone, G., Fernandes, B., Vicente, A.A. & Teixeira, J.A. 2010. Third generation biofuels from microalgae. *Current Research, Technology and Education Topics in Applied Microbiology and Microbial Biotechnology*:1355-1366.
- Ejikeme, P.M., Anyaogu, I.D., Ejikeme, C.L., Nwafor, N.P., Egbuonu, C.A.C., Ukogu, K. & Ibemesi, J.A. 2010. Catalysis in biodiesel production by transesterification process an insight. *E-Journal of Chemistry*, 7(4):1120-1132.
- Elnugoumi, M.G., Ahmed, Z.A.B. & Almsafir, M.K.M. 2012. Current status and challenges of solar energy in Malaysia: A review. *Journal of Advanced Science and Engineering Research*, 2(4):330-337.
- Fattah, I.M.R., Masjuki, H.H., Liaquat, A.M., Ramli, R., Kalam, M.A. & Riazuddin, V.N. 2013. Impact of various biodiesel fuels obtained from edible and non-edible oils on engine exhaust gas and noise emissions. *Renewable and Sustainable Energy Reviews*, 18:552-567.
- Fazal, M.A., Haseeb, A.S.M.A. & Masjuki, H.H. 2011. Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. *Renewable and Sustainable Energy Reviews*, 15:1314-1324.
- Ferrari, R.A., Pighinelli, A.L.M.T. & Park, K.J. 2011. Biodiesel production and quality. (In: (Ed.), Dr. Marco Aurelio Dos Santos Bernardes ed. Biofuel's engineering process technology. InTech. p. 742).
- Gerpen, J.V. 2009. Biodiesel production and fuel quality. *Fuel Processing Technology*, 5(2):153-161.

- Gude, V.G., Patil, P., Martinez-Guerra, E., Deng, S. & Nirmalakhandan, N. 2013. Microwave energy potential for biodiesel production. *Sustainable Chemical Processes*, 1(5):1-31.
- Helwani, Z., Othman, M.R., Aziz, N., Fernando, W.J.N. & Kim, J. 2009. Technologies for production of biodiesel focusing on green catalytic techniques: A review. *Fuel Processing Technology*, 90(12):1502-1514.
- Hossain, A. B.M.S. & Mekhled, M.A. 2010. Biodiesel fuel production from waste canola cooking oil as sustainable energy and environmental recycling process. *Australian Journal of Crop Science*, 4(7):543-549.
- Iyyaswami, R., Halladi, V.K., Yarramreddy, S.R. & Bharathaiyengar, S.M. 2013. Microwave-assisted batch and continuous transesterification of karanja oil: Process variables optimization and effectiveness of irradiation. *Biomass Conversion and Biorefinery*, 3(4):305-317.
- Jagdale, S.S. & Jugulkar, L.M. 2012. Review on various parameters and other factors affecting on production of chicken fat based biodiesel. *International Journal of Modern Engineering Research*, 2(2):407-411.
- Juan, J.C., Kartika, D.A., Wu, T.Y. & Hin, T.Y. 2011. Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: An overview. *Bioresource Technology*, 102:452-460.
- Kajikawa, Y. & Takeda, Y. 2008. Structure of research on biomass and bio-fuels: A citation-based approach. *Technological Forecasting and Social Change*, 75:1349-1359.
- Kapilan, N. & Baykov, B.D. 2014. A review on new methods used for the production of biodiesel. *Petroleum and Coal*, 56(1):62-73.
- Koh, M.Y. & Ghazi, T.I.M. 2011. A review of biodiesel production from jatropha curcas L. oil. *Renewable and Sustainable Energy Reviews*, 15:2240-2251.
- Kumar, G., Kumar, D., Singh, S., Kothari, S., Bhatt, S. & Singh, C. P. 2010. Continuous low cost transesterification process for the production of coconut biodiesel. *Energies*, 3:43-56.

- Lee, R.A. & Lavole, J. 2013. From first to third generation biofuels: Challenges of producing a commodity from a biomass of increasing complexity. *Animal Frontiers*, 3(2):6-11.
- Lertsathapornasuk, V., Pairintra, R., Aryusuk, K. & Krisnangkura, K. 2008. Microwave assisted in continuous biodiesel production from waste frying palm oil and its performance in a 100 kW diesel generator. *Fuel Processing Technology*, 89:1330-1336.
- Leung, D.Y.C., Wu, X. & Leung, M.K.H. 2010. A review on biodiesel production using catalysed transesterification. *Applied Energy*, 87(4):1083-1095.
- Liao, C. & Chung, T. 2011. Analysis of parameters and interaction between parameters of the microwave-assisted continuous transesterification process of jatropha oil using response surface methodology. *Chemical Engineering Research Design*, 89(12):2575-2581.
- Lin, Y.C., Hsu, K.H. & Lin, J.F. 2014. Rapid palm-biodiesel production assisted by a microwave system and sodium methoxide catalyst. *Fuel*, 115:306-311.
- Lokman, I.M., Rashid, U., Zainal, Z., Yunus, R. & Taufiq-Yap, Y.H. 2014. Microwave-assisted biodiesel production by esterification of palm fatty acid distillate. *Journal of Oleo Science*, 63(9):849-855.
- Magida, N.E. 2013. Biodiesel production from sunflower oil using microwave assisted transesterification. Potchefstroom: North-West University. (Dissertation-MSc).
- Mathiyazhagan, M. & Ganapathi, A. 2011. Factors affecting biodiesel production. *Research in Plant Biology*, 1(2):1-5.
- Mazo, P., Restrepo, G. & Rios, L. 2011. Alternative methods for fatty acid alkyl esters production: Microwave, radio-frequency and ultrasound. (In: Stoytcheva, Margarita. ed. Biodiesel-feedstocks and processing technologies. Europe: InTech. p. 458).
- Mazur, A. 2011. Does increasing energy or electricity consumption improve quality of life in industrial nations? *Energy Policy*, 39:2568-2572.
- Mittelbach, M. & Remschmidt, C. 2010. Biodiesel: The comprehensive handbook. 4th ed. Graz: Nora Mittelbach.

Motasemi, F. & Ani, F.N. 2012. A review on microwave-assisted production of biodiesel. *Renewable and Sustainable Energy Reviews*, 16(7):4719-4733.

Muley, P.D. & Boldor, D. 2012. Multiphysics numerical modelling of the continuous flow microwave-assisted transesterification process. *Journal of Microwave Power and Electromagnetic Energy*, 46(3):139-162.

Nolte, M. 2007. Commercial biodiesel production in South Africa: A preliminary economic feasibility study. Stellenbosch: University of Stellenbosch. (Dissertation-MSc).

Ozbugday, F.C. & Erbas, B.C. 2015. How effective are energy efficiency and renewable energy in curbing CO₂ emissions in the long run? A heterogeneous panel data analysis. *Energy*, 82:734-745.

Pragya, N., Pandey, K.K. & Sahoo, P.K. 2013. A review on harvesting, oil extraction and biofuels production technologies from microalgae. *Renewable and Sustainable Energy Reviews*, 24:159-171.

Rahimi, M., Aghel, B., Alitabar, M., Sepahvand, A. & Ghasempour, H.R. 2014. Optimization of biodiesel production from soybean oil in a microreactor. *Energy Conversion and Management*, 79:599-605.

Refaat, A.A., El Sheltaway, S.T. & Sadek, K.U. 2008. Optimum reaction time, performance and exhaust emissions of biodiesel produced by microwave irradiation. *International Journal of Environmental Science and Technology*, 5(3):315-322.

Sarin, A. 2012. Biodiesel: Production and properties. Cambridge: The Royal Society of Chemistry.

Shinde, G.B., Sapkal, V.S., Sapkal, R.S. & Raut, N.B. 2011. Transesterification by reactive distillation for synthesis and characterization of biodiesel. (In: Stoytcheva, Dr. Margarita ed. Biodiesel- feedstocks and processing technologies. InTech. p. 458).

Singh, S.P. & Singh, D. 2010. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews*, 14(1):200-216.

South African National Standard (SANS): 1935. 2004. Automotive biodiesel fuel. 1-14

Talebian-Kiakalaieh, A., Amin, S.A.N. & Mazaheri, H. 2013. A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, 104:683-710.

Tippayawong, N. & Sittisun, P. 2012. Continuous-flow transesterification of crude jatropha oil with microwave irradiation. *Scientia Iranica*, 19(5):1324-1328.

Uriarte, F.A. 2010. Biofuels from plant oils. Jakarta: ASEAN Foundation.

Vyas, A.P., Verma, J.L. & Subrahmanyam, N. 2010. A review on FAME production processes. *Fuel*, 89:1-9.

World Health Organization. 2006. Fuel for life: House hold energy and health. Geneva

Yaakob, Z., Ong, B.H., Kumar, M.N.S. & Kamarudin, S.K. 2009. Microwave-assisted transesterification of jatropha and waste frying palm oil. *International Journal of Sustainable Energy*, 28(4):195-201.

Yusuf, N.N.A.N., Kamarudin, S.K. & Yaakub, Z. 2011. Overview on the current trends in biodiesel production. *Energy Conversion and Management*, 52(7):2741-2751.

CHAPTER 3

3. EXPERIMENTAL

In this chapter, the procedure followed for biodiesel production is described. Materials and chemicals used in the study are presented in section 3.1. Experimental conditions for the transesterification reaction are provided in section 3.2 and the experimental procedure followed is described in section 3.3. Analytical procedures used in the study are described in section 3.4.

3.1 Materials

3.1.1 Feedstock

Sunflower oil used as a biodiesel feedstock in the study, was purchased at a local supermarket. Sunflower oil was analysed using gas chromatograph (GC) Agilent 7820A, to determine its fatty acid composition as shown in Table 3-1. Sunflower oil was characterised, and results are shown in Table 3-2. The calculations of sunflower oil molecular weight and determination of weight percentage (wt %) are shown in Appendix B.1.

Table 3-1: Fatty acid composition of sunflower oil

Fatty acid	Weight %
Palmitic acid (C16:0)	6.2
Stearic acid (C18:0)	3.1
Oleic acid (C18:1)	25
Linoleic acid (C18:2)	65.6
Linolenic acid (C18:3)	1.5

Table 3-2: Sunflower oil properties

Properties	Value
Free fatty acid content	0.08 wt%
Water content	0.02 wt%
Viscosity @ 40°C	7.1 mPas
Density	0.910 g/ml

3.1.2 Chemicals

Chemicals and reagents used in this study are shown in Table 3-3.

Table 3-3: Chemicals used for biodiesel production and analyses

Component	Supplier	Purity	Purpose
KOH	Associated chemical enterprise (ACE)	85 %	Catalyst
MeOH	Rochelle chemicals	99.5 %	Alcohol
Hydrochloric acid (HCL)	ACE	32 %	Acid used to neutralize catalyst
Methyl nonanoate	Sigma-Aldrich	97 %	Internal standard (IS) solvent used for GC samples
Dichloromethane (DCM)	Merck	99 %	Solvent for GC samples
Trimethylsulphonium hydroxide (TMSH)	Sigma-Aldrich	0.25 M	Sample derivative
Isopropanol	Rochelle chemicals	99.7 %	For instrument cleaning and acid number test
Cyclohexane	ACE	99.5 %	Free and total glycerol test
Sodium thiosulphate	ACE	0.1 M	Free and total glycerol test
Periodic acid	Sigma-Aldrich	99 %	Free and total glycerol test
Ethanol	Rochelle chemicals		Free and total glycerol test
Glacial acetic acid	ACE	99.7 %	Free and total glycerol test
Potassium iodide	ACE	100 g/l	Free and total glycerol test

3.2 Experimental reactor

Experiments were carried out using a modified domestic microwave (DEFY model DMO 353) with a power output of 100 W to 1000 W shown in Figure 3-1. The glass tray was removed and a 100 ml glass reactor coil was inserted. The Teflon tubing was connected to the inlet reservoir pump through a stainless steel Tee connector, and to the outlet reservoir at the back of the microwave oven. The temperature was measured with a thermocouple and the measured temperature was displayed on the screen.



Figure 3-1: Domestic microwave setup for continuous biodiesel production

3.3 Experimental procedure

Experiments were carried out with modifications according to the procedure described by Lertsathapornsuk *et al.* (2008). During the transesterification process, sunflower oil, methanol, and potassium hydroxide (KOH) were used to produce biodiesel. All experiments were carried out using an initial amount of 450 g sunflower oil, 1:6 oil-to-methanol molar ratio based on weight of oil, and 1% KOH (catalyst) based on weight of oil.

Experiments were carried out as shown in Figure 3-2. Biodiesel was produced using three different glass tubular reactor coils with same volume (100 ml) and different surface area (0.082, 0.057, and 0.045 m²). Experiments were carried out using one reactor coil and different experimental variables.

KOH pellets were dissolved in MeOH to form a potassium methoxide. The potassium methoxide was added into a beaker with sunflower oil and stirred. The reactants were fed continuously into the reactor system using a peristaltic pump, while stirring. Product was collected in a beaker placed at the reactor outlet.

Experiments were carried out at different microwave powers ranging from 400 W, 500 W and 600 W. The residence time was set between 40s, 50 s, and 60s and flow rate of 150 ml/min, 120 ml/min, and 100 ml/min, respectively. The same procedure was followed for three different reactor coils. The product was neutralised using hydrochloric acid immediately after collection, to ensure that reaction has completely stopped. All experiments were carried out by changing one variable, and kept other variables constant.

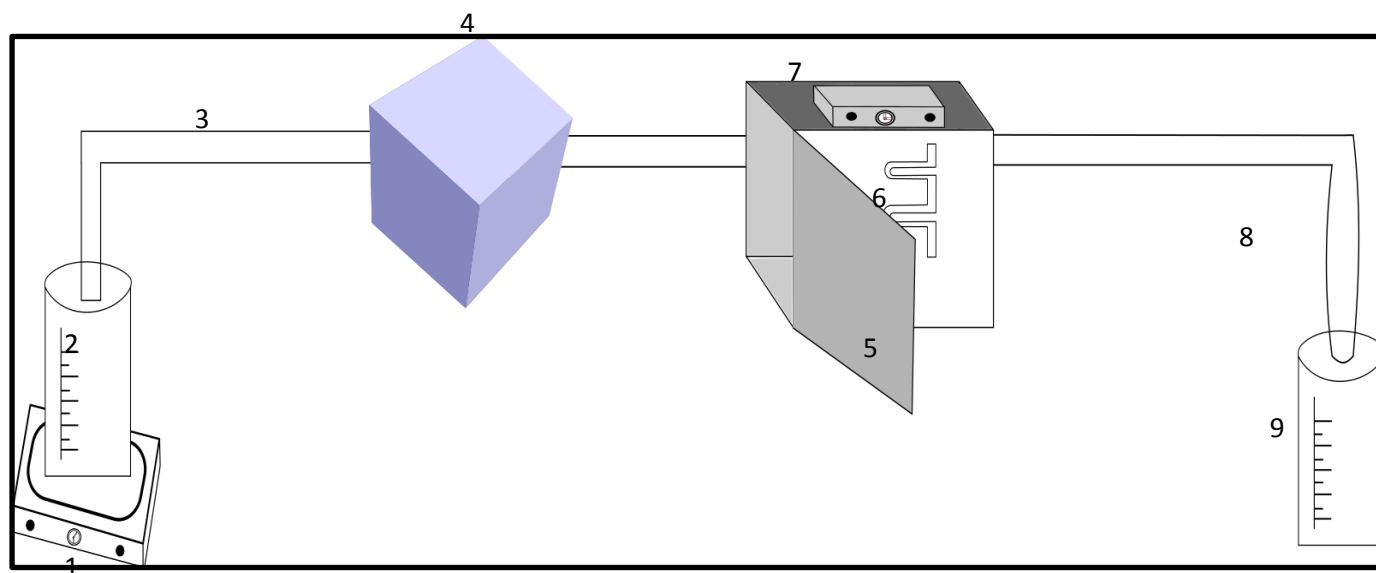


Figure 3-2: Continuous biodiesel production processes

(1. Magnetic stirrer, 2. Beaker with reactants, 3. Inlet reservoir, 4. Peristaltic pump, 5. Domestic microwave oven, 6. Glass reactor coil, 7. Temperature detector, 8. Outlet reservoir, 9. Beaker for sample collection).

3.4 Separation, purification, and drying

After the transesterification process, glycerol has to be removed from the reaction mixture. The reactants were decanted to the separating funnel, where glycerol (which is a by-product) and biodiesel were separated for three hours as shown in Figure 3-3. The bottom layer is glycerol because it is denser than biodiesel, the top layer is crude biodiesel.



Figure 3-3: Biodiesel separation process

When the separation phase has been accomplished, crude biodiesel was purified by washing it with warm deionised water for three to five times, to remove any trace elements. Then, FAME was dried in a conventional oven at 105°C overnight.

3.5 Biodiesel analyses

Produced biodiesel was analysed using gas chromatography (GC), Fourier transformer infrared spectrometer (FTIR) eraspec, Viscometer, Eralytics ERAFLASH, and Metrohm titrino plus.

3.5.1 Gas chromatography analyses

GC Agilent 7890A (Figure 3-4) was used to determine sunflower oil physical characteristics, and biodiesel yields and physical characteristics. Operating conditions of GC are shown in Table 3-4.

Table 3-4: GC operating conditions

Parameter	Value
Column	HP-88 (100m)
Carrier	Helium
Linear velocity	30 cm/s
Inlet	Split/splitless
Split ratio	1/20
Injection	1.0 µl
Inlet temperature	250°C
Inlet pressure	400.0 kpa
Oven temperature	100 °C for 5 min
Detector	FID at 350 °C
Detector gas flows	H2: 40 ml/min Air: 400 ml/min Mode: Constant makeup Makeup (He): 1.0 ml/min
Solvent for needle washes	DCM

**Figure 3-4: GC used to determine fatty acid composition**

3.5.1.1 Oil sample preparation

Oil samples were prepared by filtering the sunflower oil sample, using 0.45 µl and 0.2 µl syringe filters. 250µl filtered oil was then transferred to a clean vial, and 250 µl TMSH. The reaction was vortexed for five minutes, then wait for it to separate. The top layer was removed, and measured 100 µl of the bottom layer. 20 µl of IS was also added to the sample; the sample was diluted with DCM to make 1 ml. The reaction was vortexed to mix it properly, and sent for GC analyses.

3.5.1.2 Biodiesel sample preparation

Biodiesel was filtered using 0.45 µl and 0.2 µl syringe filters. A clean vial was placed in a weighing balance, and tarred the balance. 250 µl filtered biodiesel was added to the vial and recorded a mass. Without tarring the balance, 25 µl IS was added to the vial. The mass of biodiesel and IS was recorded. The equation below was used to calculate the mass of IS.

$$Mis = M(bd + is) - Mbd$$

DCM was added to dilute the sample, without recording its mass. The reaction was vortexed to mix it properly, and injected into a GC.

3.5.2 FTIR eraspec

The FTIR eraspec Figure 3-5 was used to determine biodiesel properties, such as density and cetane number. Propanol was used to clean the FTIR eraspec before and after each sample analysis.

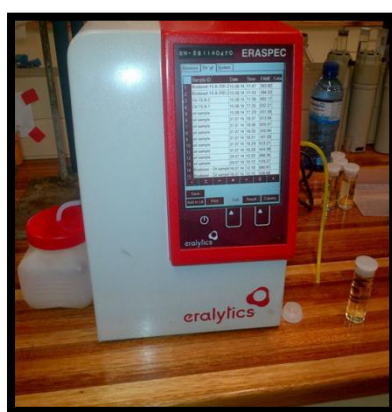


Figure 3-5: FTIR eraspec used to determine cetane number and density

The biodiesel sample was pumped into the FTIR (machine) through a yellow pump. The biodiesel sample was scanned; cetane number and density were displayed on the screen after each scan.

3.5.3 Viscometer analysis

Viscosity is one of the important properties of biodiesel fuel (Esteban *et al.*, 2012). A viscometer thermo scientific Lasec (South Africa) was used to determine the viscosity of biodiesel. Biodiesel samples were heated up to 40°C, then an R2 spindler was used to determine the viscosity of the biodiesel. 200 RPM Spindler's speed was used to measure the biodiesel sample. Results were displayed in the viscometer's screen.



Figure 3-6: A thermo-scientific viscometer used to determine the viscosity of biodiesel

3.5.4 Eralystics ERAFLASH

Eralystics ER 01 ERAFLASH, shown in Figure 3-7, was used to determine biodiesel's flash point. Eralystics ERAFLASH has a temperature range of 25 to 200°C. Using the pipette, the biodiesel sample was filled up into the mark in the cup, with a stirring magnet. The front door of the instrument was opened, and the cup with the biodiesel sample inserted. The sample was labelled on the screen, and the run button was pressed for the sample to be measured. The sample was automatically measured and results were displayed after 15 to 20 minutes. The cup was cleaned after running each sample.

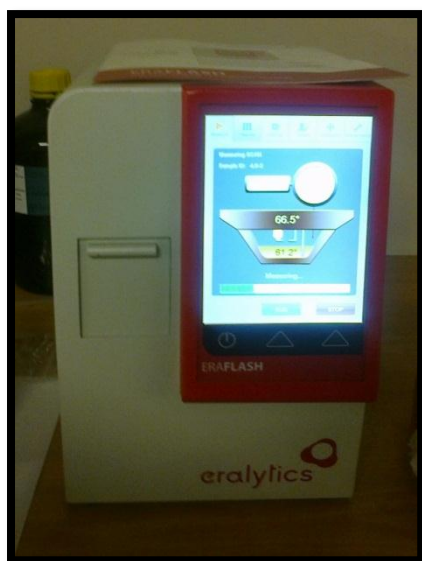


Figure 3-7: Eralytics ERAFLASH used to measure FAME flash point

3.5.5 Titrino plus

Acid number is the measure of the amount of free fatty acids contained in a biodiesel/diesel fuel samples. Acid number is expressed in mg KOH required to neutralise 1 g of FAME (Sarin, 2012). Metrohm 848 titrino plus Figure 3-8 was used to determine the acid number of biodiesel. Approximately 12g of FAME sample was weighed in a clean dry titration glass beaker. The sample was dissolved with 20 ml of 2-propanol, and stirred. It was then titrated with 1M of KOH, and the FAME measured in the titrino plus instrument. Results were shown on the screen, and printed out in an installed small printer.



Figure 3-8: Metrohm 848 titrino plus for acid number free fatty acid content determination

3.5.6 FTIR IRAffinity-1

FTIR IRAffinity-1 (Figure 3-9) with IR resolution software was used to determine the functional groups of biodiesel. The ATR was cleaned with propanol before used, and after each sample. The sample was poured on ATR, no bubbles should be seen in the sample. The ATR was placed carefully on top of a sample holder. The sample was then scanned 45 times, with a wavelength ranging from 400 cm^{-1} to 4000 cm^{-1} .

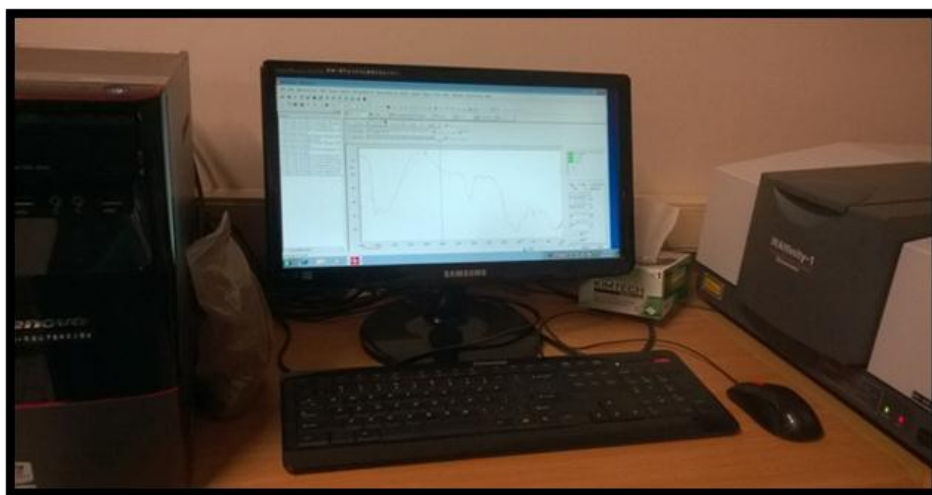


Figure 3-9: FTIR IRAffinity-1 used to determine biodiesel functional groups

3.6 References

Esteban, B., Riba, J., Baquero, G., Rius, A. & Puig, R. 2012. Temperature dependence of density and viscosity of vegetable oils. *Biomass and Bioenergy*, 42:164-171.

Lertsathapornsuk, V., Pairintra, R., Aryusuk, K. & Krisnangkura, K. 2008. Microwave assisted in continuous biodiesel production from waste frying palm oil and its performance in a 100 kW diesel generator. *Fuel Processing Technology*, 89:1330-1336.

Sarin, A. 2012. Biodiesel: Production and properties. Cambridge: The Royal Society of Chemistry.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, all FAME results obtained from continuous microwave-assisted transesterification are discussed. In section 4.1 the influence of energy input on FAME yield is discussed. The effect of reactor surface area on FAME yield is presented in section 4.2. The physico-chemical properties of biodiesel and qualitative analysis are presented in section 4.3 and section 4.4, respectively.

4.1 Effect of energy input on FAME yield

The influence of energy input on FAME yield during continuous microwave-assisted transesterification was investigated using reactors with varying surface areas (0.045, 0.057, and 0.082 m²). The influence of energy input on FAME yield for the reactor with a surface area of 0.082 m² is presented in Figure 4-1. The results for the other two surface areas can be found in Appendix D. The experimental error for the three reactor coils was calculated by repeating experiments three times. Experimental error data and calculations are presented in Appendix C, Table C-1. The experimental error was calculated as 11.22, 9.95, and 8.91% for reactors with surface areas of 0.045, 0.057, and 0.082 m² at a 95% confidence level, and is presented in Figure 4-1 by dotted lines to indicate the average upper and lower limits for the data-set.

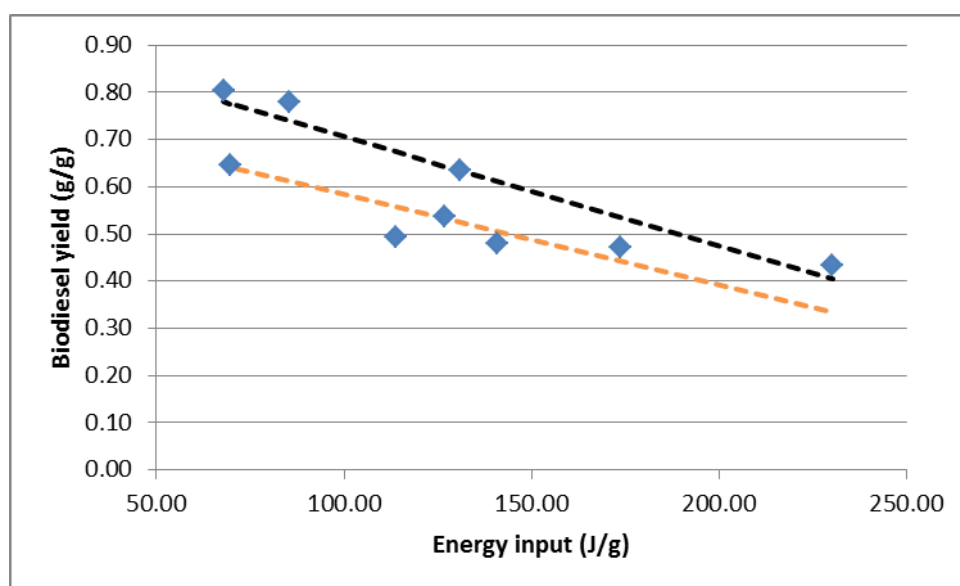


Figure 4-1: Influence of energy input on FAME yield for a surface area 0.082 m² (--- lower error limit and --- upper error limit)

As can be seen in Figure 4-1, a decrease in FAME yield is observed with an increase in energy input. GC-MS analysis of produced diesels showed the presence of 9,17-octadecadienal (a long chain aldehyde) in the diesel. The amount of long-chain aldehyde increased with an increase in energy input, resulting in lower FAME yields observed. The formation of aldehydes during transesterification of oil by an alkaline catalyst has been reported by Zuleta *et al.* (2012) and is the result of degradation of FAME to aldehydes, acids and ketones. Acids, short chain aldehydes and ketones are mostly water-soluble and would have been washed out during the washing of the diesel layer. The boiling point of the aldehyde observed falls within the boiling point range of convention diesel (240-370°C) and therefore the presence of this component does not negatively affects the physico-chemical properties of the diesels negatively. This implies that the fast transfer rate damages the FAME molecules, which causes fast degradation leading to lower oxidation stability (see section 4.3.7).

4.2 Effect of surface area on FAME yield

In microwave reactors, mass and heat transfer increases due to small size and large contact area. Small reactor internal diameters (ID) increase the interaction of the reagents at the molecular level (Da Silva & Oliveira, 2014). As stated in section 3.3, three tubular reactor coils with same volume (100 ml) and different surface area (0.045, 0.057, 0.082 m²) were used. The influence of reactor surface area on FAME yield was investigated and results are presented in Figure 4-2.

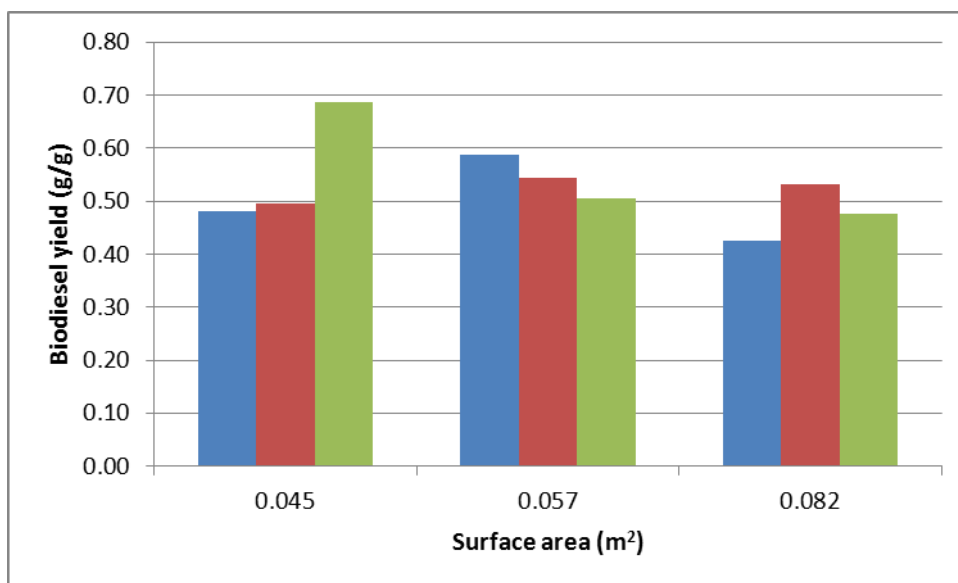


Figure 4-2: Influence of surface area on FAME yield at different energy inputs (■90.55, ■104.71 and ■120.72 J/g)

As seen from Figure 4-2, the effect of reactor surface area did not show any trends on FAME yield. High FAME yields were obtained in the reactor with a surface area of 0.045 m². The larger surface area, corresponding with a smaller internal diameter for the reactor coil, resulted in higher surface transfer area, increasing the heat flux absorbed by the reaction mixture. In addition, this can lead to more degradation products such as long-chain aldehydes being formed, which results in lower FAME yields.

4.3 Physico-chemical properties of biodiesel

The quality of biodiesel is important in order to be used commercially as a fuel. Produced biodiesel was analysed using various analytical instruments, to make sure it meets South African National Standards (SANS). The properties of biodiesel produced, such as density, flash point, cetane number, viscosity, acid value, water content, oxidative stability, as well as free and total glycerol are shown in Figures 4-3 to 4-5. These properties of biodiesel have a great effect on the application of biodiesel (Zhang, 2012). Biodiesel fuel properties are influenced by a number of factors such as feedstock quality, transesterification techniques, and production steps (Guldhe *et al.*, 2016). The properties of biodiesel prepared under different energy inputs and with reactors with different surface areas were determined and compared to the SANS 1935 standard specification.

4.3.1 Density

Density is an important biodiesel parameter that influences the efficiency of atomisation. From Appendix E-2, it can be seen that the measured densities of the diesel produced were all within the SANS 1935 standard specification.

4.3.2 Cetane number

High values of cetane number help to ensure good cold start properties and minimise the formation of white smoke. Biodiesel has a higher cetane number than petroleum diesel. The effect of energy input on cetane number and compared to SANS 1935 standard is shown in Figure 4-3.

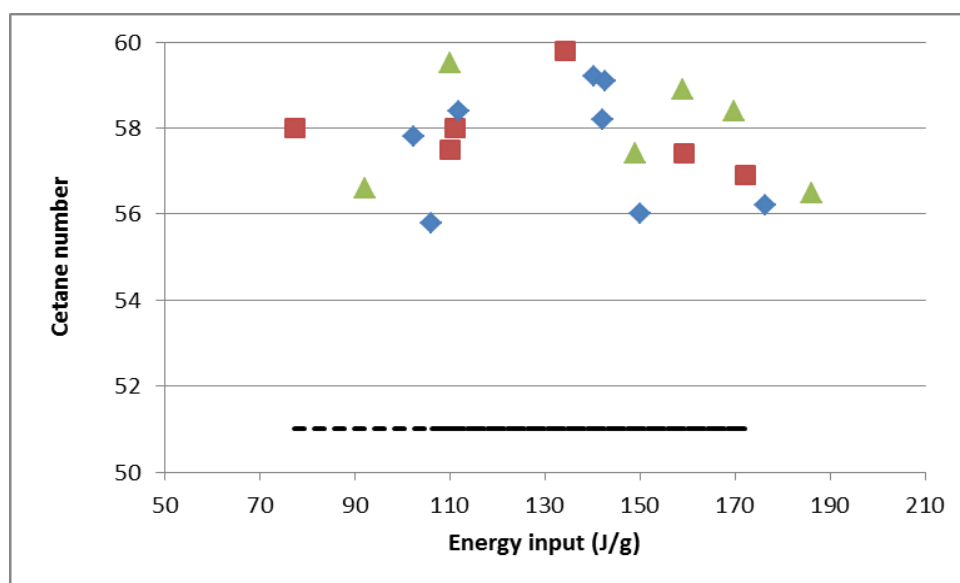


Figure 4-3: Effect of energy input on cetane number (▲ 0.045, ■ 0.057, ◆ 0.082 m² and -- - SANS 1935)

According to ASTM standards the minimum value of cetane number is 51. As observed in Figure 4-3, all values obtained in this study were within the SANS 1935 standard (56.0–65.2). From Figure 4-3, it can be seen that an increase in cetane number is observed initially with increasing energy input up to an energy input of 140 J/g. At higher energy inputs, FAME molecules are degraded to long-chain aldehydes, ketones and acids as can be seen by the decrease in cetane number at energy inputs higher than 140 J/g.

4.3.3 Flash point

Flash point is the minimum temperature at which the fuels will ignite when exposed to flame (Terigar *et al.*, 2010). A high value of FAME flash point shows that there is no unreacted methanol in the sample. The flash point of biodiesel produced ranges between 150 and 170°C (see Appendix E-2), which is above the minimum required by the standard (120°C).

4.3.4 Viscosity

High viscosity can lead to poor atomisation during fuel spraying and can cause engine deposits, and incomplete combustion (Ali *et al.*, 2016; Enweremadu & Mbarawa, 2009). The viscosity of sunflower oil (7.1 mm²/s) used as feedstock was lowered to 3.2 mm²/s for produced biodiesel, and that confirms the transesterification process was effective.

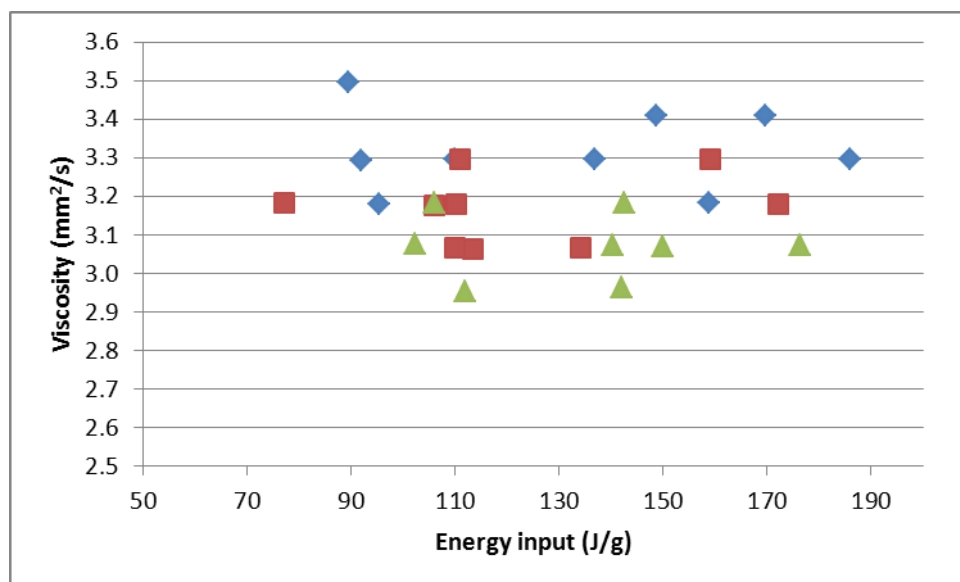


Figure 4-4: The viscosity of various energy inputs (♦ 0.045, ■ 0.057 and ▲ 0.082 m²)

As illustrated in Figure 4-4, the surface area 0.082 m² has lower values of viscosity than the other two reactors. Viscosity values obtained in this study were not within the biodiesel SANS standard specifications. Low values of viscosity could be due to the presence of water-insoluble FAME degradation products.

4.3.5 Acid value

Acid number is the mass of KOH in milligrams that is required to neutralise the acidic constituents in one gram of biodiesel sample (Atabani *et al.*, 2012). Acid value measures the content of free fatty acids contained in biodiesel sample. Acid values ranged between 0.02

and 0.04 mg KOH/g, which is within the minimum requirement of SANS's standard specification (>0.5) (see Appendix E-2).

4.3.6 Water content

Water content of produced biodiesel was determined using Karl Fischer coulometric. According to SANS standards, 0.05% is the maximum water content value for biodiesel. All measured values were below the SANS 1935 standard specification.

4.3.7 Oxidation stability

Biodiesel oxidation stability determines the fuel quality for prolonged storage purposes. The oxidation stability of biodiesel samples were determined by examining the graphs of conductivity versus time. Oxidative stability of biodiesel is affected by fatty acids of FAME, mainly the presence of double bonds, traces of metal and presence of air. A minimum oxidation stability value of 6 h or greater at 110°C is required for SANS standard specification.

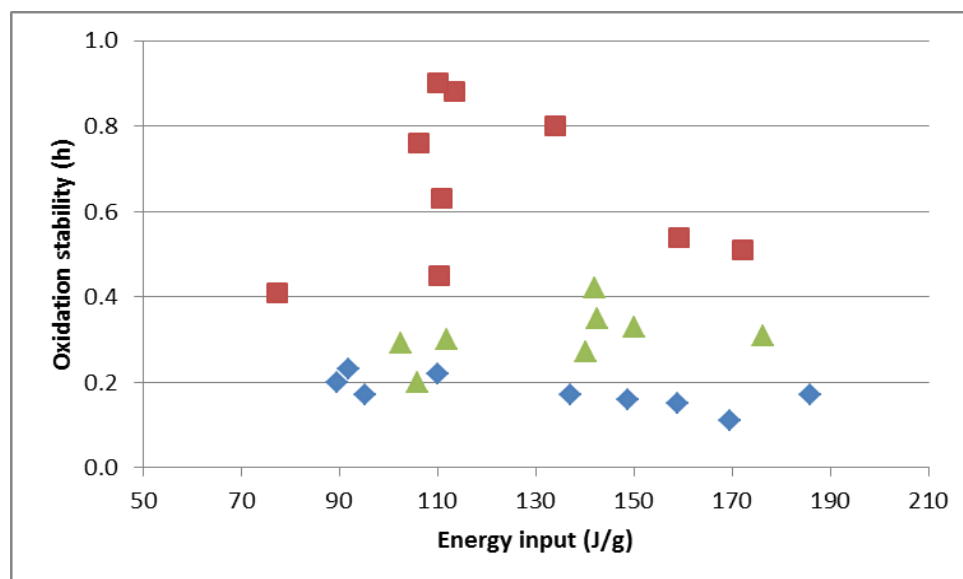


Figure 4-5: The oxidation stability of various energy inputs (♦ 0.045, ■ 0.057 and ▲ 0.082 m²)

As presented in Figure 4-5, oxidation stability values were outside the specified limits of the SANS standard. Low oxidation stability values were observed in all three reactor coils. Low oxidation stability values are observed due to the presence of oxygen groups and the formation of aldehydes in FAME. Oxidation stability increases with increasing energy input

to a certain level, then a further increase in energy input decreases oxidation stability due to the formation of degradation products such as 9,17- octadecadienal.

4.3.8 Free and total glycerol

Glycerol is a by-product of biodiesel production. The incomplete removal of glycerol from biodiesel can lead to fuel separation, engine deposits and material incompatibility (Terigar *et al.*, 2010). Free glycerol represents glycerol molecules and total glycerol represents glycerol molecules and soap molecules. The measured free and total glycerol were within the SANS 1935 standard specification.

4.4 FTIR spectroscopy results for sunflower oil biodiesel

FTIR spectroscopy is a qualitative method employed for the analysis of functional groups of sunflower biodiesel. FTIR spectroscopy is used to determine bands corresponding to bending or stretching vibrations in sunflower oil and biodiesel (Magida, 2013; Ndana *et al.*, 2013). The FTIR spectra of sunflower biodiesel and sunflower oil are shown in Figure 4-6.

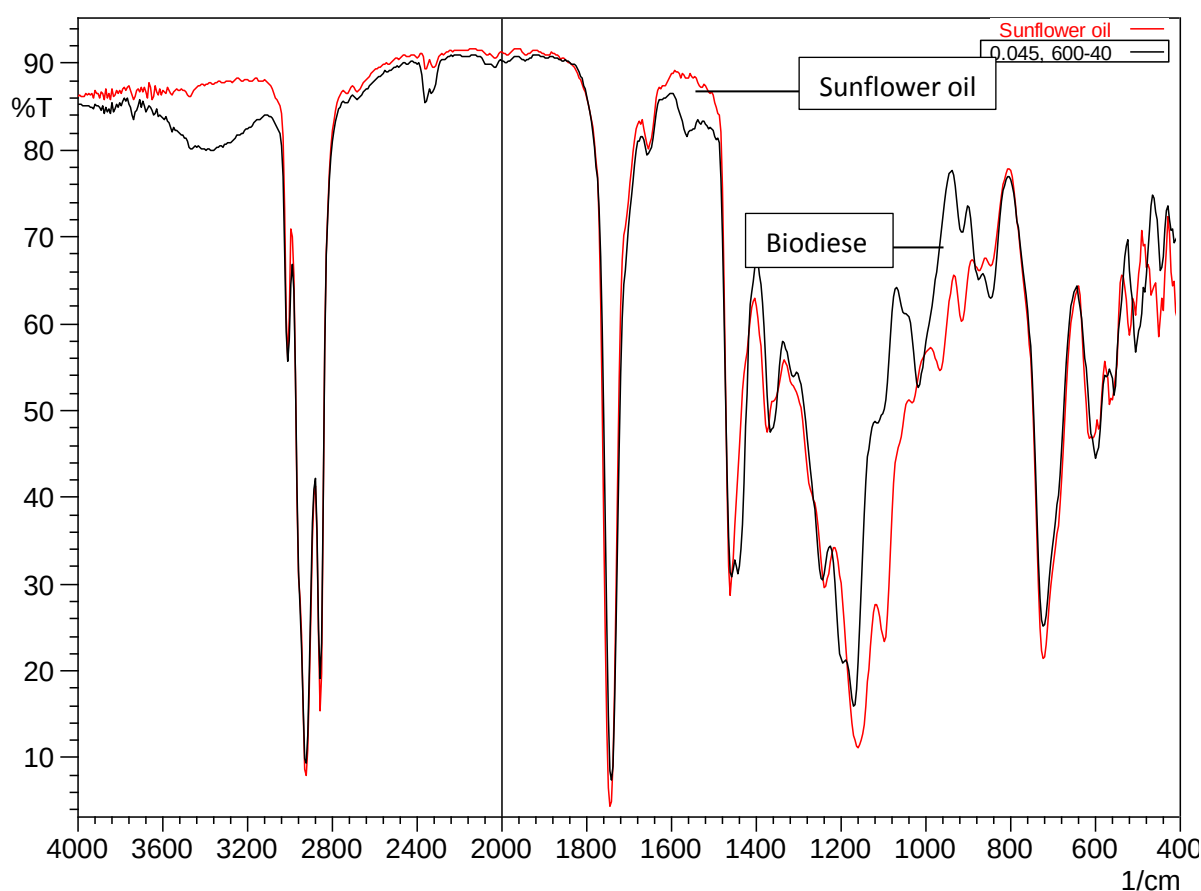


Figure 4-6: Infrared spectra of sunflower oil compared to biodiesel produced using reactor coil with surface area 0.045 m², at 600 W microwave power and 40 s residence time.

For sunflower oil, an absorption peak appeared at 1097 cm⁻¹, which is an indication of C-CH₂-O vibration (Magida, 2013). FAME consists of two strong absorption bands arising from methoxy-carbonyl and CO stretching (Naureen *et al.*, 2015). The FAME spectrum has peaks appeared at 2924 cm⁻¹ and 2854 cm⁻¹ indicating symmetric stretching of the CH₂ group and asymmetric stretching of the CH₃ group, respectively. The summary of sunflower biodiesel functional groups are presented in Table 4-1.

Table 4-1: FTIR functional groups of FAME for reactor coil with surface area 0.045 m², at 600 W microwave power, and 40s residence time

Wave number (cm ⁻¹)	Description
3500	O-H hydroxyl stretching vibration associated with water
3007	=C-H stretching vibration associated with alkenes
2924	CH ₂ asymmetric stretching vibrations of C-H associated with alkanes
2854	CH ₃ symmetric stretching vibrations of C-H alkane group (methyl)
1740	C=O ester carbonyl stretching group associated with FAME degradation products (aldehydes, ketones and acids)
1562	C=O ester carbonyl stretching group
1458-1435	-CH ₃ bending associated with methyl
1363	C-H methyl bending attributed to glycerol
1195-1168	O-CH ₃ stretching functional associated with methyl esters
844	=C-H bending vibrations associated with alkenes
721	=C-H methylene bending functional group

The splitting of the 1161 cm^{-1} absorption peak in the sunflower oil, into the 1168 cm^{-1} and 1195 cm^{-1} absorption peaks in biodiesel, indicates the conversion of sunflower oil to biodiesel. The most important absorption peaks appeared at 1442 cm^{-1} , associated with $-\text{CH}_3$ bending methyl ester group, and 1195 cm^{-1} associated with the stretching methyl group $\text{O}-\text{CH}_3$ (Oyerinde & Bello, 2016). The FTIR spectra showed the carbonyl group $\text{C}=\text{O}$ stretching peak at 1741 cm^{-1} , assigned to the formation of oxidation products, aldehydes, ketones and acids (Furlan *et al.*, 2010). The spectra for biodiesel produced at other two reactor coils are presented in Appendix F.

4.5 References

- Ali, O.M., Mamat, R., Abdullah, N.R. & Abdullah, A.A. 2016. Analysis of blended fuel properties and engine performance with palm biodiesel-diesel blended fuel. *Renewable Energy*, 86:59-67.
- Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T.M.I., Masjuki, H.H. & Mekhilef, S. 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, 16:2070-2093.
- Da Silva, C. & Oliveira, J.V. 2014. Biodiesel production through non-catalytic supercritical transesterification: Current state and perspectives. *Brazilian Journal of Chemical Engineering*, 31(02):271-285.
- Enweremadu, C.C. & Mbarawa, M.M. 2009. Technical aspects of production and analysis of biodiesel from used cooking oil-A review. *Renewable and Sustainable Energy Reviews*, 13:2205-2224.
- Furlan, P.Y., Wetzel, P., Johnson, S., Wedin, J. & Och, A. 2010. Investigating the oxidation of biodiesel from used vegetable oil by FTIR spectroscopy: Used vegetable oil biodiesel oxidation study by FTIR. *Spectroscopy letters*, 43(7-8):580-585.
- Guldhe, A., Singh, P., Kumari, S., Rawat, I., Permaul, K. & Bux, F. 2016. Biodiesel synthesis from microalgae using immobilized *Aspergillus niger* whole cell lipase biocatalyst. *Renewable Energy*, 85:1002-1010.
- Magida, N.E. 2013. Biodiesel production from sunflower oil using microwave assisted transesterification. Potchefstroom: North-West University. (Dissertation-MSc).
- Naureen, R., Taria, M., Yusoff, I., Chowdhury, A.J.K. & Ashraf, M.A. 2015. Synthesis, spectroscopic and chromatographic studies of sunflower oil biodiesel using optimized base catalysed methanolysis. *Saudi Journal of Biological Sciences*, 22:332-339.
- Ndana, M., Grace, J.J., Baba, F.H. & Mohammed, U.M. 2013. Fourier transform infrared spectrophotometric analysis of functional groups in biodiesel produced from oils or *Ricinus Communis*, *Hevea Brasiliensis* and *Jatropha curcas* seeds. *International Journal of Science, Environment and Technology*, 2(6):1116-1121.

Oyerinde, A.Y. & Bello, E.I. 2016. Use of Fourier Transformation Infrared (FTIR) spectroscopy for analysis of functional groups in peanut oil biodiesel and its blends. *British Journal of Applied Science and Technology*, 13(3):1-14.

Terigar, B.G., Balasubramanian, S., Lima, M. & Boldor, D. 2010. Transesterification of soybean and rice bran oil with ethanol in a continuous-flow microwave-assisted system: Yields, quality, and reaction kinetics. *Energy Fuels*, 24:6609-6615.

Zhang, W-B. 2012. Review on analysis of biodiesel with infrared spectroscopy. *Renewable and Sustainable Energy Reviews*, 16(8):6048-6058.

Zuleta, E.C., Baena, L., Rios, L.A. & Calderon, J.A. 2012. The oxidative stability of biodiesel and its impact on the deterioration of metallic and polymeric materials: A review. *Journal of Brazilian Chemical Society*, 23(12): 2159-2175

CHAPTER 5

5.1 Conclusion and recommendations

In this chapter the results obtained in the current study are summarised, and recommendations and challenges experienced during this study are discussed. The main aim of the study was to investigate the effect of surface area of the reactor vessel when producing biodiesel using continuous microwave-assisted transesterification.

5.1.1 Conclusion

The present study successfully produced biodiesel using a continuous microwave-assisted technique on three different reactor coils.

- The effect of surface area on FAME yield was investigated by using various microwave powers and residence time. A high FAME yield was obtained using a reactor with a surface area 0.082 m^2 , with 50s residence time, 400 W microwave power and 67.96 J/g energy input. FAME yield decreased with further increase in energy input. The produced FAME showed degradation with an increase in energy inputs, and also oxidation stability values decreased, due to the presence of aldehydes in FAME.
- The produced FAME was analysed for physico-chemical properties. The results obtained were compared to SANS 1935 standard specifications. All properties measured met the standard requirements, with the exception of viscosity and oxidation stability. The FT-IR results showed presents of ethers, alkanes, ketones and aldehydes in the FAME sample.
- The results obtained from this suggest that different surface area reactor coils can be used in a pilot scale to produce biodiesel using low energy inputs.

5.1.2 Recommendations

As the influence of energy input and surface area on biodiesel yields and properties were investigated in this study, more research still needs to be done, namely:

- The evaluation of different microwave powers and residence time for all different reactor coils. Low FAME yield was obtained on a reactor with a larger surface area, due to residence time reactants being exposed to microwave irradiation.

- A need for further study to evaluate the maximum diesel yield by employing lower power such as 100, 200 and 300 W.
- Low energy inputs should be evaluated for different reactor coils.
- An analysis of FAME content should be determined using both GC and GC-MS for more accurate results.

APPENDIX

A. CALIBRATIONS

A.1 Pump calibrations

Peristaltic pump was used to pump reactants into microwave reactor. The pump was calibrated in order to know the speed corresponding to the flow rate and residence time used. Pump calibration curves are presented in Figures A-1 – A-3.

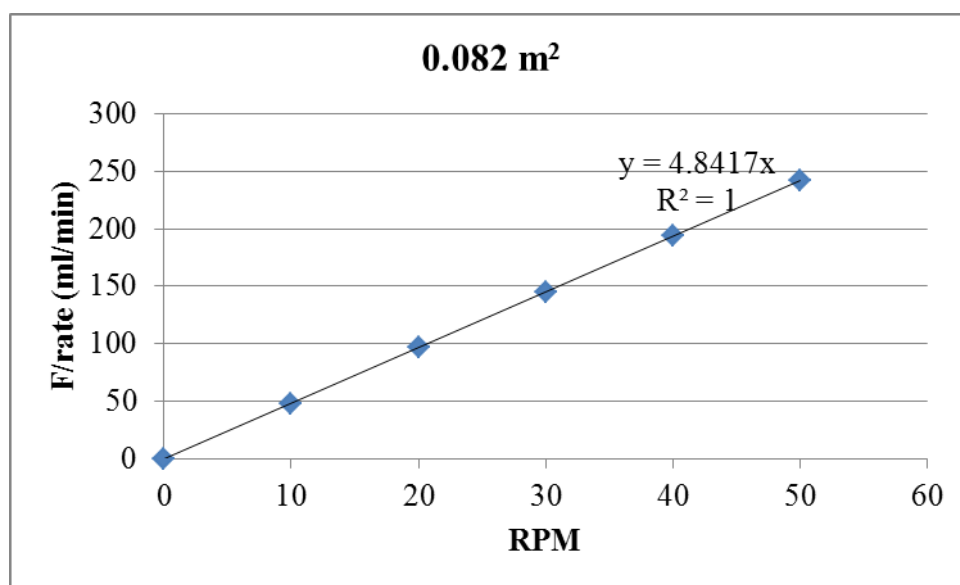


Figure A-1: 0.082 m² pump settings

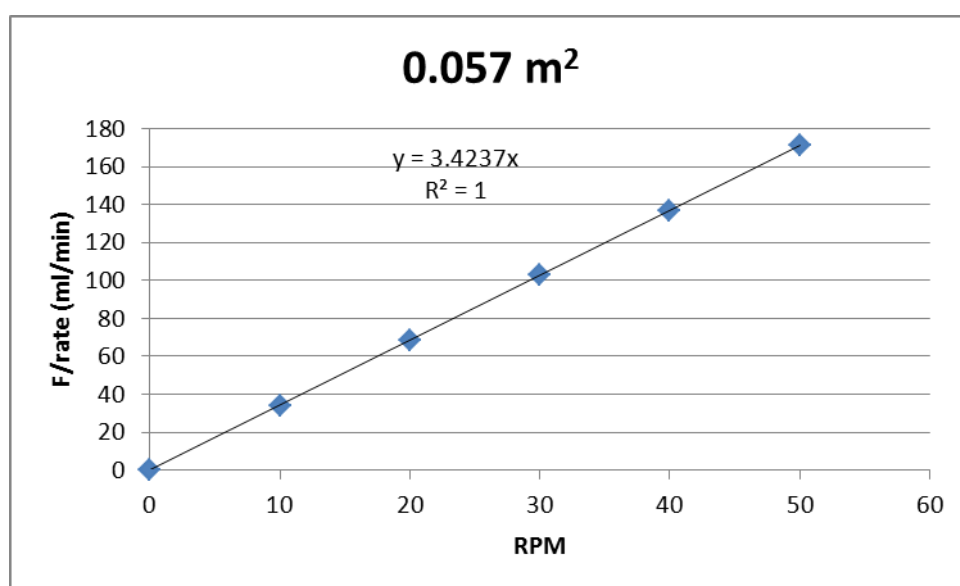


Figure A-2: 0.057 m² pump settings

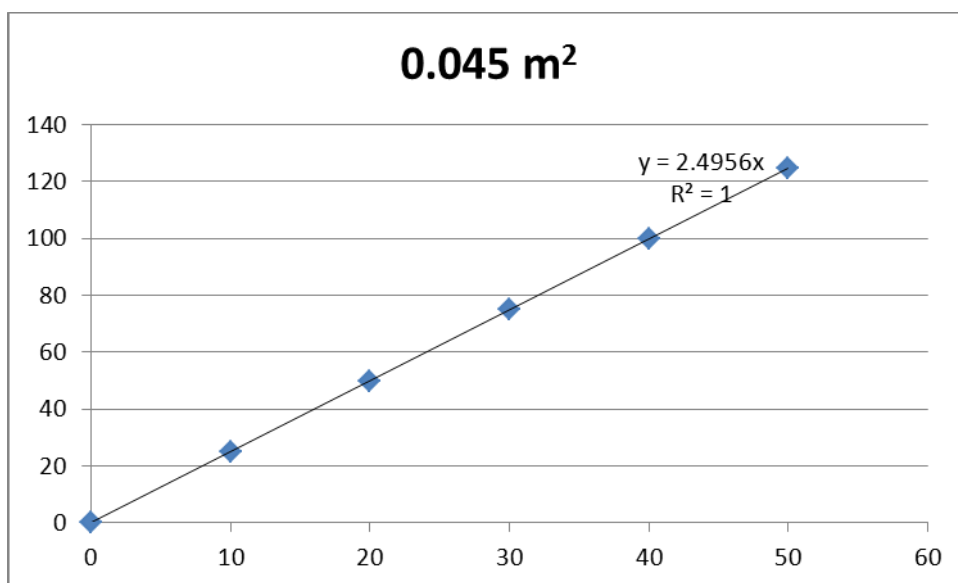


Figure A-3: 0.045 m² pump setting

A.2 Gas chromatograph calibration curves

In order to analyze sunflower oil used in the study, and FAME produced GC was calibrated. The GC calibrations used for calculating the sunflower oil molecular weight and FAME yield are shown in Figure A-4 – A-8, k-values are presented in Table B-1.

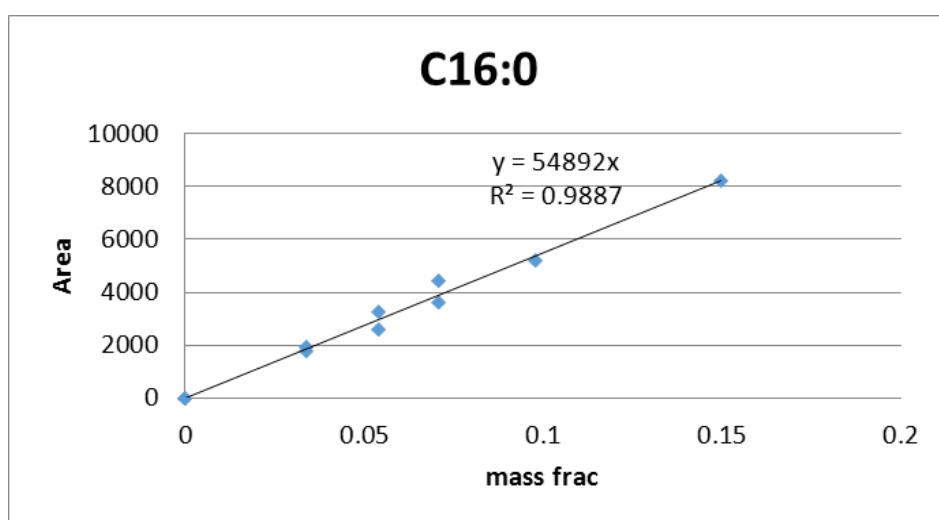


Figure A-4: C16:0 calibration curve

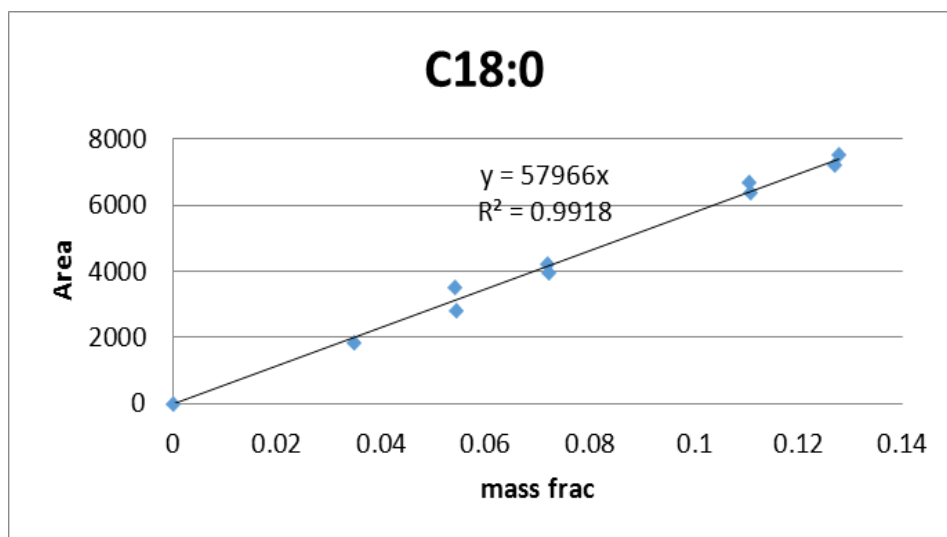


Figure A-5 C18:0 calibration curve

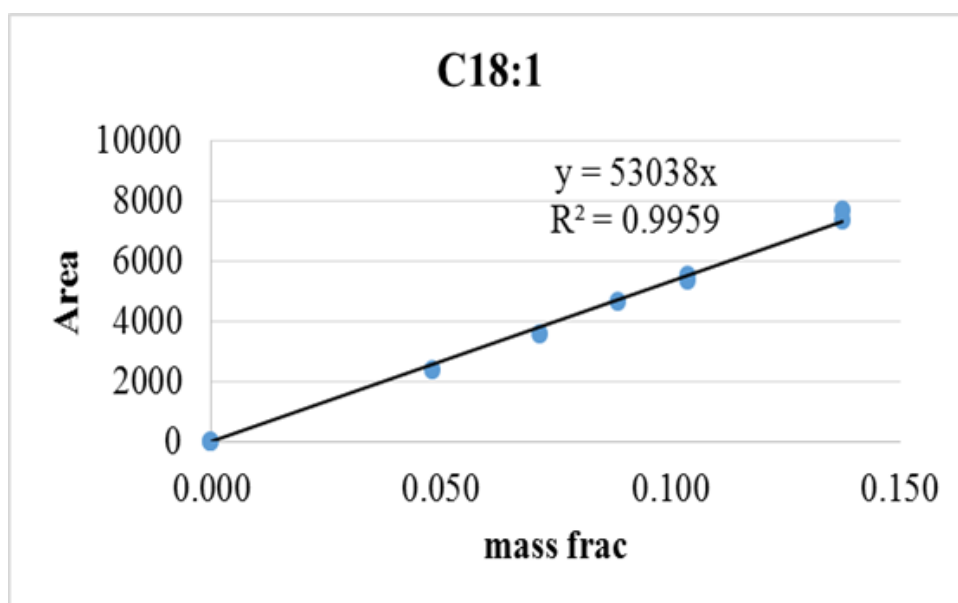


Figure A-6: C18:1(2) calibration curve

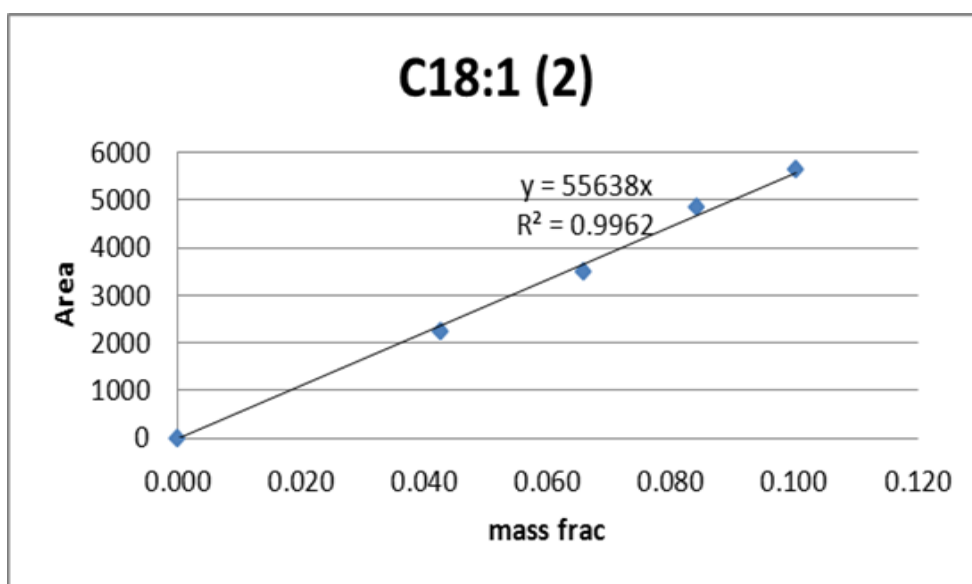


Figure A-7: C18:1 calibration curve

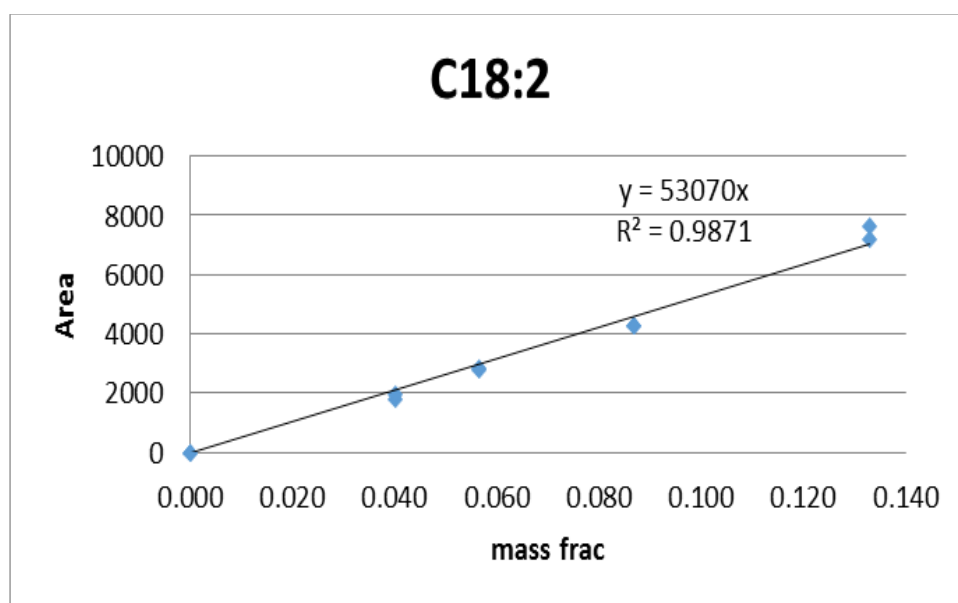


Figure A-8: C18:2 calibration curve

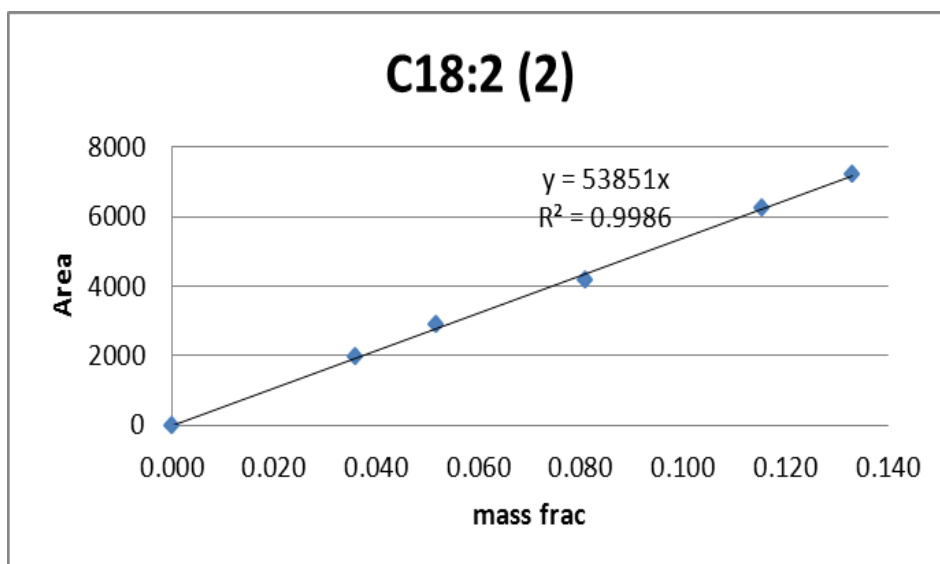


Figure A-9: C18:2(2) calibration curve

B. CALCULATIONS

B.1 Calculations of sunflower oil molecular weight (MW)

Molecular weight of sunflower was calculated in the following manner.

The calibration curve constants (K values) of esters are presented in Table B-1

Table B-1: Calibration curves k-values

FAME	K values
Methyl Palmitate (C16:0)	54892
Methyl Stearate (C18:0)	57966
Methyl Oleate (C18:1)	54338
Methyl Linoleate (C18:2)	53461
Methyl Linolenate (C18:3)	68279

Therefore mass fraction (g) of each component was calculated using the k values and areas of FAME contents. The following equation was used to calculate mass fraction.

$$MF = \frac{Ame}{Kvalue}$$

Where MF is the mass fraction of methyl esters, K value is the slope obtained in calibration curves, Ame is area of free fatty acid.

The average molecular weight of fatty acids triglyceride was calculated by multiplying each component molecular weight by mass fraction obtained above.

$$MW_{oil} = (MF * MW_{16:0}) + (MF * MW_{18:0}) + (MF * MW_{18:1}) + (MF * MW_{18:2}) + (MF * MW_{18:3})$$

Then molecular weight of sunflower oil was calculated by adding average molecular weight of oil with the molecular weight of glycerol and water.

$$MW_{sunflower\ oil} = 3MW_{FFA} + MW_{glycerol} - 3MW_{water}$$

B.2 Calculations of oil to methanol molar ratio and catalyst loading

Mass of methanol and potassium hydroxide were calculated according to the mass of oil added.

For 450 g of oil, then methanol mass was calculated using the following manner.

$$n_{oil} = \frac{mass_{oil}}{MW_{oil}} = \frac{450}{875.9} = 0.513 mol$$

Number of moles for methanol was calculated by dividing n_{oil} with 6, as molar ratio is 1:6

$$n_{MeOH} = 0.513 * 6 = 3.078 mol$$

$$Mass_{MeOH} = 3.078 mol * \frac{34.02 g}{mol} = 98.6 g$$

$$Mass_{KOH} = \frac{1}{100} * 450 = 4.5 g$$

B.3 FAME yield calculations

FAME yield were calculated using K values in Table B-1

The mass fraction of FAME using the following equation is used for calculation.

$$Area(FAME) = Kvalue * mass\ fraction$$

Then FAME layer was calculated using the following equation

$$FAME\ layer\ (g) = mass\ fraction * dry\ biodiesel$$

Finally, FAME yield were calculated by dividing FAME layer/produced with mass oil pumped in to the reactor

$$FAME\ yield\ \left(\frac{g}{g}\right) = \frac{FAME\ produced(g)}{oil\ pumped\ in\ (g)}$$

C. EXPERIMENTAL ERROR

C.1 FAME yield experimental error calculations

The experimental error for the three reactor coils was calculated by repeating experiments three times. The experimental error was calculated for reactions at 500 W microwave power, 50s residence time, and different reactor coils. Experimental error was calculated by firstly calculating the average of experiments conducted.

$$Average(\bar{x}) = \frac{1}{N} \sum_i^N x_i$$

Where N is the number of experimental runs conducted, x_i is the individual data points.

The standard deviation was then calculated using the equation above, in order to calculate 95% confidence limit

$$Standard\ deviation\ (\delta) = \sqrt{\frac{\sum(\bar{x} - x)^2}{N - 1}}$$

Confidence interval is calculated using the following equation

$$confidence\ limit = \bar{x} \pm \frac{\delta}{\sqrt{n}}$$

Then the experimental error is calculated using the equation

$$Experimental\ error\ (\%) = 2 \times \frac{confidence\ limit}{\bar{x}} \times 100$$

C.2 Experimental error data

The experimental error is presented in Table C-1.

Table C-1: Experimental error for FAME yield

Surface									
Area (m²)	Time (s)	Power (W)	Repeat 1	Repeat 2	Repeat 3	Average	Standard deviation	Confidence limit	Experimental error %
0.045	40	500	0.51	0.45	0.43	0.46	0.042	0.047	10.17
	50	500	0.47	0.44	0.45	0.45	0.015	0.017	3.81
	60	500	0.53	0.46	0.44	0.48	0.047	0.053	11.22
0.057	40	500	0.57	0.64	0.54	0.58	0.051	0.058	9.95
	50	500	0.61	0.56	0.58	0.58	0.025	0.028	4.88
	60	500	0.60	0.56	0.57	0.58	0.021	0.024	4.08
0.082	40	500	0.22	0.20	0.20	0.21	0.012	0.013	6.32
	50	500	0.22	0.20	0.19	0.20	0.015	0.017	8.50
	60	500	0.24	0.21	0.21	0.22	0.017	0.020	8.91

D. EXPERIMENTAL DATA

The experimental data of the present study is shown in this section.

D.1 Energy input

Energy input for FAME produced was calculated using the equation below, results are presented in Table D-1.

$$Energy (J) = Power \left(\frac{J}{s} \right) * Time(s)$$

Energy input was calculated by using energy obtained (J) with mass of diesel produced (g)

$$Energy\ input\ (J/g) = \left(\frac{1}{FAME\ produced(g)} \right) * Energy\ (J)$$

Table D-1: Energy input calculations

Power (J/s)	Time (s)	Energy (J)	Energy input (J/g)	FAME produced (g)
400	40	16000	53.53	151.06
400	50	20000	60.26	195.27
400	60	24000	69.38	171.08

D.2 Surface area

The surface area of reactor coils was calculated using the following equation.

$$Surface\ area = 2\pi rl$$

Where $\pi=3.14$, r is the radius and l is the length of reactor.

The radius was calculated using the following equation

$$Radius = \frac{ID}{2}$$

Where ID is the internal diameter of a reactor coil

Length was calculated by

$$Length = Vol * 4 / \left(\frac{22}{7}\right) / ID^2$$

Where vol. is the volume of reactor coil

Table D-2: Surface area calculation

	Volume (m ³)	Diameter (m)	Length (m)	Radius (m)	Area (m ²)
1	0.0001	0.0088	1.64	0.0044	0.045
2	0.0001	0.007	2.6	0.0035	0.057
3	0.0001	0.0049	5.3	0.00245	0.082

D.3 FAME yield

In this section the experimental data and FAME yield calculated according to calibrations curves shown in Appendix A.2. FAME yield for different energy inputs and different surface areas are presented in Figures D-1 – D-3, and Table D-3 – D-5.

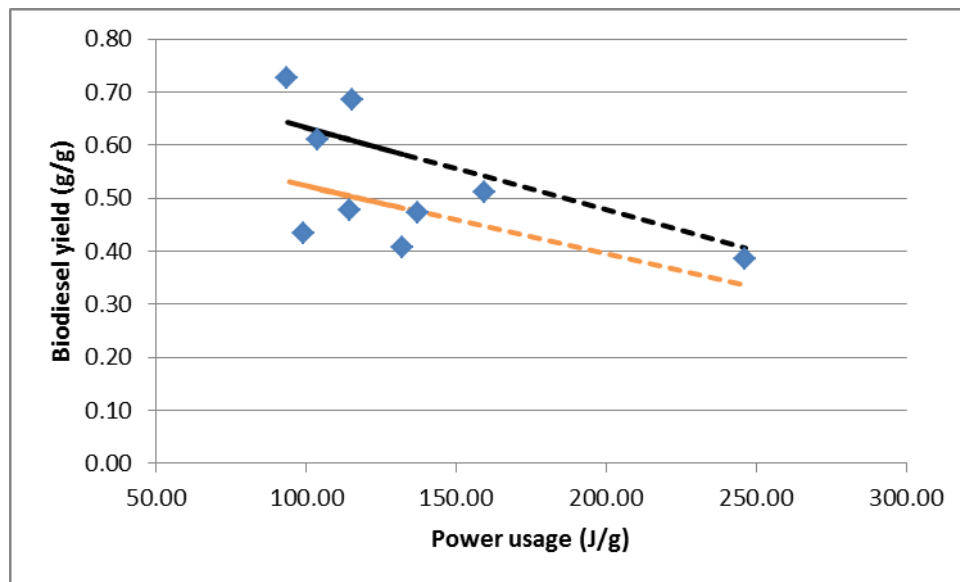


Figure D-1: Influence of various power usages input on FAME yield at for a surface area 0.045 m² (---lower error limit and ---upper limit)

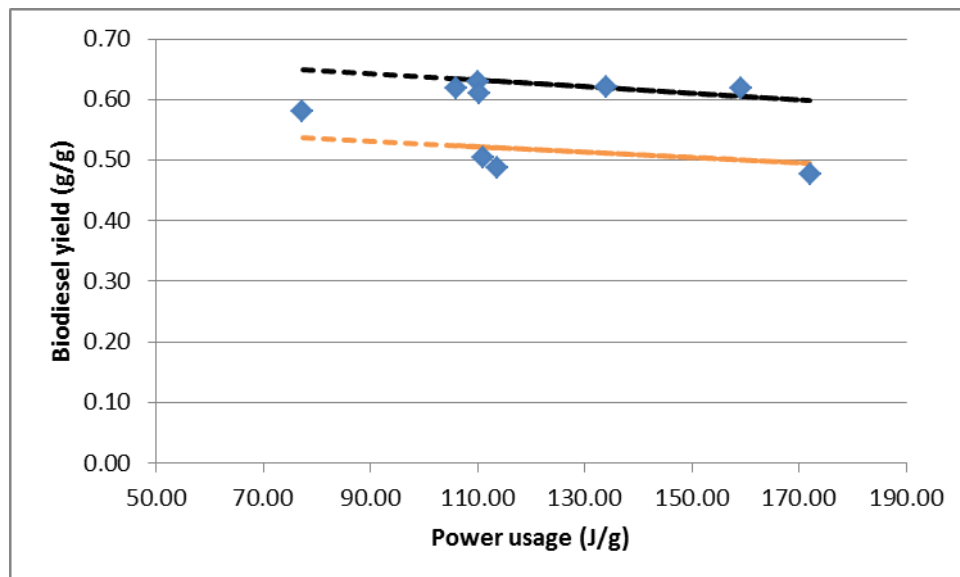


Figure D-2: Influence of various power usages input on FAME yield at for a surface area 0.057 m² (---lower error limit and ---upper limit)

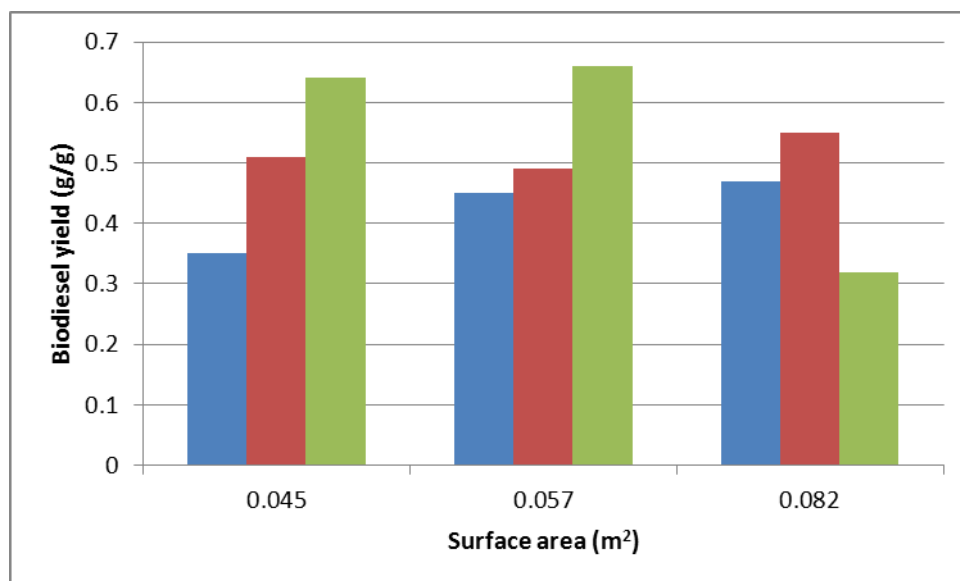


Figure D-3: Influence of surface area on FAME yield at different energy inputs
 (■ 158.95, ■ 159.14 and ■ 204.45 J/g)

Table D-3: Effect of energy input on surface area (0.082 m²)

Time (s)	Power (W)	Energy input (J/g)	FAME yields (g/g)
40	400	69.4	0.65
40	500	67.9	0.80
40	600	85.5	0.78
50	400	113.9	0.49
50	500	127.0	0.54
50	600	131.0	0.64
60	400	140.9	0.48
60	500	173.7	0.47
60	600	230.4	0.43

Table D-4: Effect of microwave power on surface area (0.057 m²)

Time (s)	Power (W)	Energy input (J/g)	FAME yields (g/g)
40	400	69.4	0.65
40	500	67.9	0.80
40	600	85.5	0.78
50	400	113.9	0.49
50	500	127.0	0.54
50	600	131.0	0.64
60	400	140.9	0.48
60	500	173.7	0.47
60	600	230.4	0.43

Table D-5: Effect of microwave power on surface area (0.045 m²)

Time (s)	Power (W)	Energy input (J/g)	FAME yields (g/g)
40	400	99.1	0.43
40	500	114.3	0.48
40	600	103.7	0.61
50	400	131.9	0.41
50	500	93.6	0.73
50	600	115.2	0.69
60	400	136.9	0.47
60	500	159.4	0.51
60	600	246.5	0.38

E. BIODIESEL PROPERTIES

In this section, the physico-chemical properties of produced biodiesel are shown. Calculations for free and total glycerol content are presented in section E-1. Properties of biodiesel produced in different conditions are presented in Tables (E-1- E-3).

E.1 Free an total glycerol

Free and total glycerol were calculated using the same equation. Firstly, the weight of test portion was calculated.

$$W = \frac{\text{mass of test portion} * \text{volume of test portion}}{900}$$

Then the glycerol content was determined using the equation above

$$\text{Free \& total glycerol} = \frac{(B - S) * N * 2.302}{W}$$

Where S is the volume of sample titrant, B is the volume of blank titrant, and N is the normality of sodium thiosulfate solution.

E.2 Biodiesel properties

Properties of biodiesel that did not show any significant differences for different energy inputs and surface areas are presented in Figure E-1 – E-6

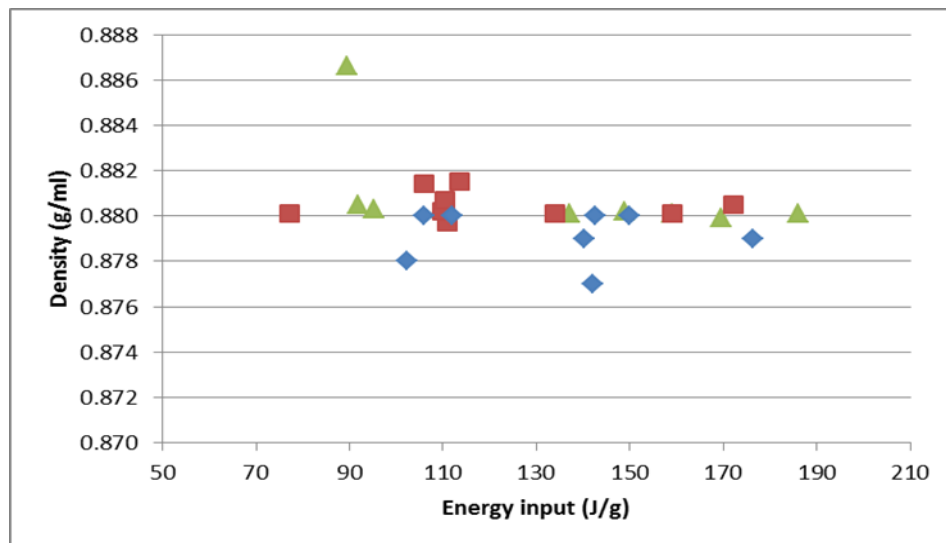


Figure E-1: Effect of energy input on density (▲ 0.045, ■ 0.057 and ◆ 0.082 m²)

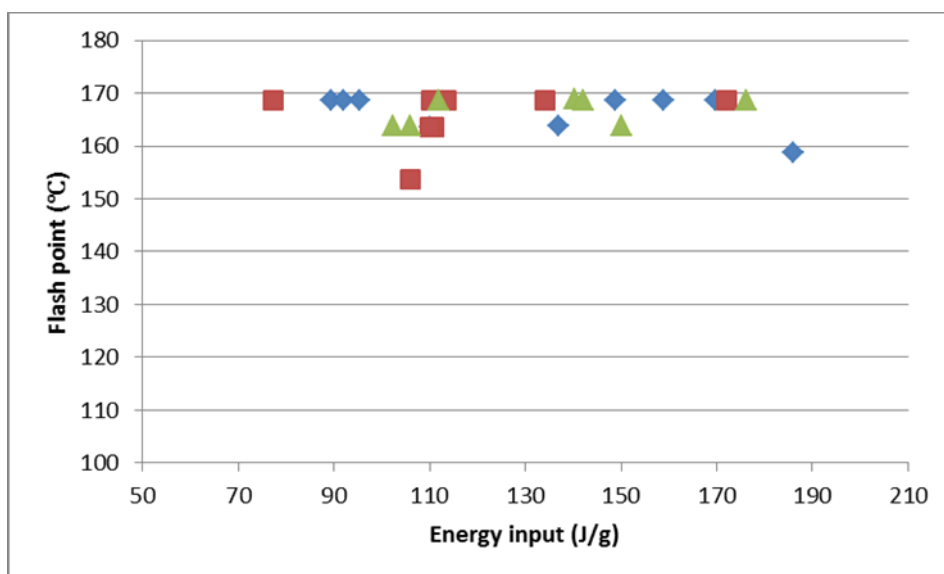


Figure E-2: Effect of energy input on biodiesel flash point (♦ 0.045, ■ 0.057 and ▲ 0.082 m²)

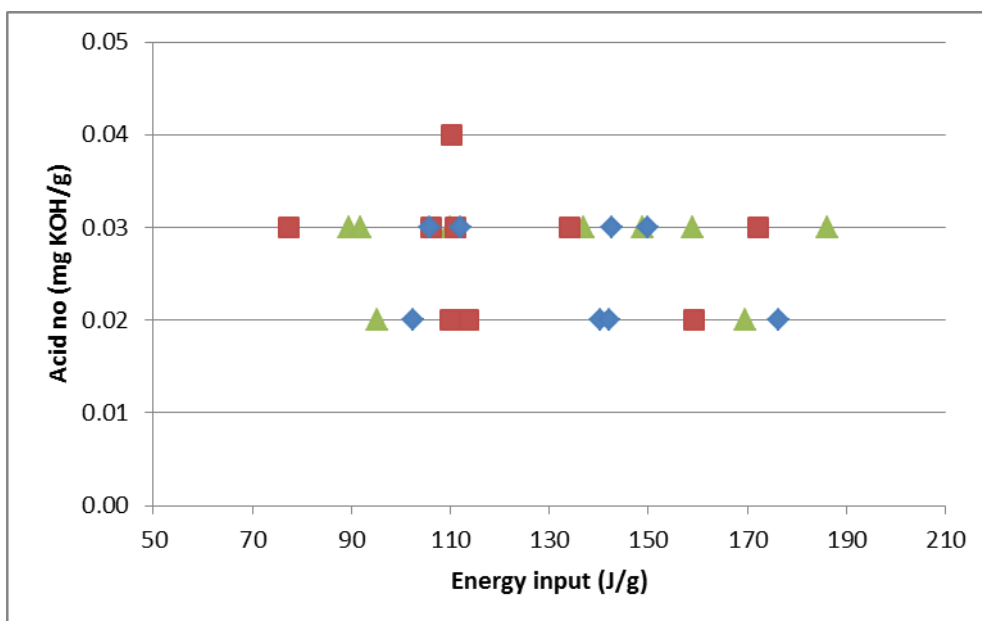


Figure E-3: Effect of energy input on acid value (▲ 0.045, ■ 0.057, ♦ 0.082 m²)

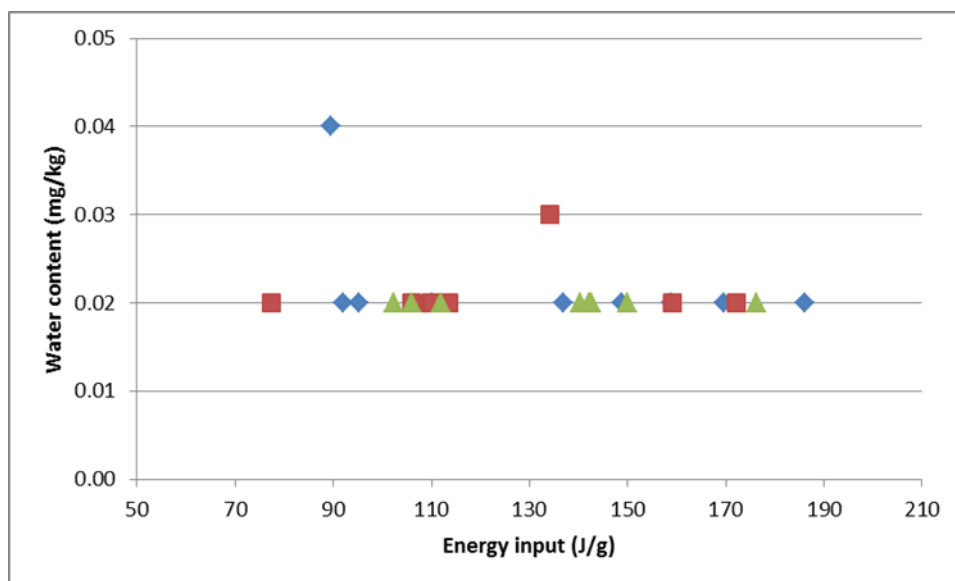


Figure E-4: Effect of energy input on water content (♦ 0.045, ■ 0.057 and ▲ 0.082 m²)

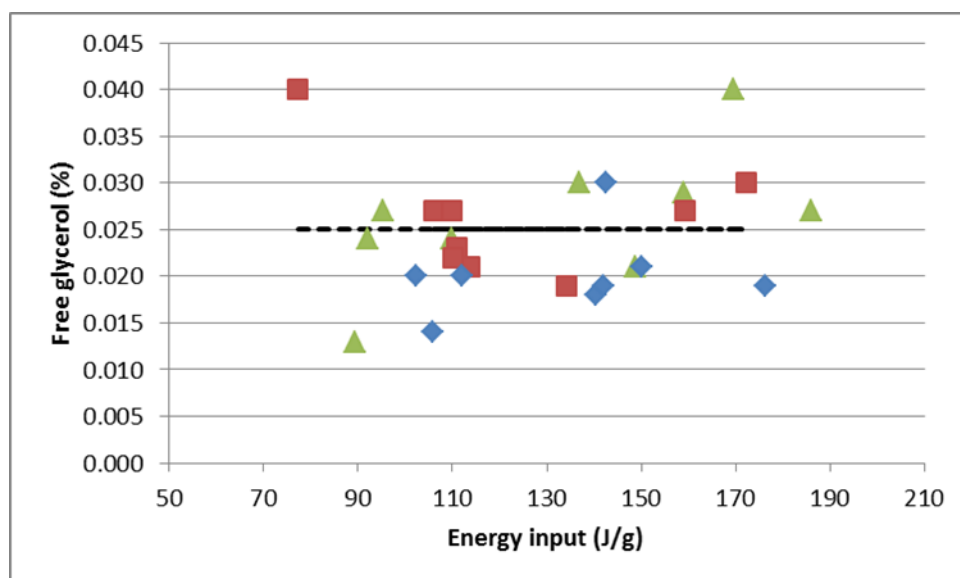


Figure E-5: Effect of energy input on free glycerol (▲ 0.045, ■ 0.057, ♦ 0.082 m² and --- SANS 1935)

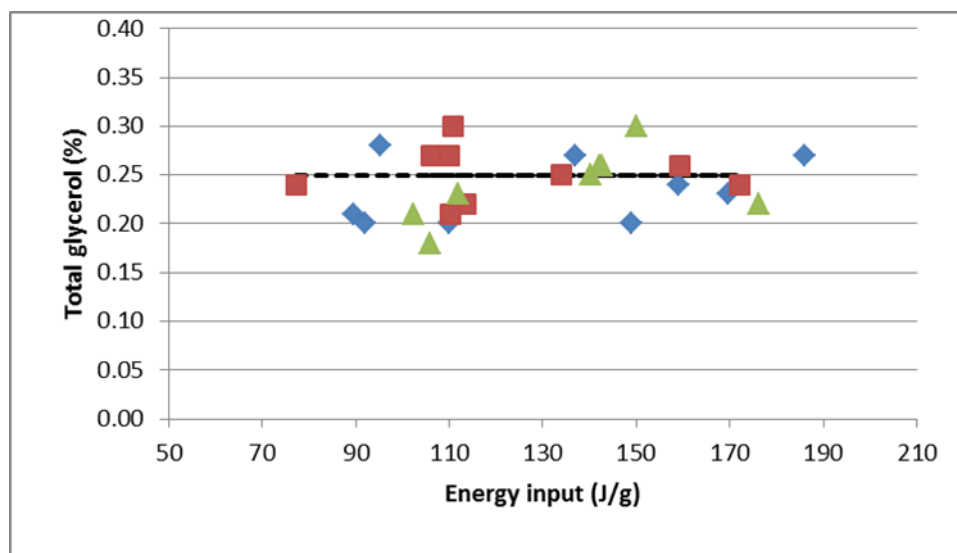


Figure E-6: Effect of energy input on total glycerol (♦ 0.045, ■ 0.057, ▲ 0.082 m² and --- SANS 1935)

Biodiesel physico-chemical properties data is presented in Table E-1 – E-3

Table E-1: Biodiesel properties for reactor coil 0.082 m²

Properties	Unit	400-40	500-40	600-40	400-50	500-50	600-50	400-60	500-60	600-60	SANS 1935
Density	g/ml	0.880	0.878	0.879	0.88	0.877	0.879	0.880	0.880	0.880	0.860 - 0.900
Cetane No		55.8	57.8	59.2	58.4	58.2	56.2	59.1	56	56.2	51 min
Acid No	mg KOH/g	0.03	0.02	0.02	0.03	0.02	0.02	0.03	0.03	0.03	0.5 max
Water content	%	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.05 max
Oxidation stability	h	0.20	0.29	0.27	0.30	0.42	0.31	0.35	0.33	0.34	6 min
Flash point	°C	163.7	163.8	168.8	168.6	168.6	168.6	78.7	163.7	163.6	120 min
Viscosity	mm ² /s	3.2	3.1	3.1	3.0	3.0	3.1	3.2	3.1	3.1	3.5 – 5.0
Free glycerol	%	0.014	0.02	0.018	0.02	0.019	0.019	0.03	0.021	0.07	0.025 max
Total glycerol	%	0.18	0.21	0.25	0.23	0.26	0.22	0.26	0.3	0.26	0.25 max

Table E-2: Biodiesel properties at surface area 0.057 m²

Properties	Unit	400-40	500-40	600-40	400-50	500-50	600-50	400-60	500-60	600-60	SANS 1935
Density	g/ml	0.880	0.881	0.881	0.879	0.880	0.880	0.880	0.880	0.880	0.860 – 0.900
Cetane No		58	62.8	63.9	58	57.5	56.9	63.5	59.8	57.4	51 min
Acid No	mg KOH/g	0.03	0.02	0.03	0.03	0.02	0.03	0.04	0.03	0.02	0.5 max
Water content	%	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.05 max
Oxidation stability	h	0.41	0.88	0.76	0.63	0.90	0.51	0.45	0.80	0.54	6 min
Flash point	°C	168.6	168.6	153.6	163.6	163.6	168.6	168.6	168.6	123.7	120 min
Viscosity	mm ² /s	3.2	3.1	3.2	3.3	3.1	3.2	3.2	3.1	3.3	3.5 – 5.0
Free glycerol	%	0.04	0.021	0.027	0.023	0.027	0.03	0.022	0.019	0.027	0.025 max
Total glycerol	%	0.24	0.22	0.27	0.3	0.27	0.24	0.21	0.25	0.26	0.25 max

Table C-6: Biodiesel properties at surface area 0.045 m²

Properties	Unit	400-40	500-40	600-40	400-50	500-50	600-50	400-60	500-60	600-60	SANS 1935
Density	g/ml	0.886	0.880	0.880	0.880	0.880	0.879	0.880	0.880	0.880	0.860-0.900
Cetane No		60.4	59.5	56.6	65.2	61.2	58.4	56.5	58.9	57.4	51.0 min
Acid No	mg KOH/g	0.03	0.03	0.03	0.03	0.02	0.02	0.03	0.03	0.03	0.5 max
Water content	%	0.04	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.05 max
Oxidation stability	h	0.20	0.22	0.23	0.17	0.17	0.11	0.17	0.15	0.16	6 min
Flash point	°C	168.6	163.6	168.6	163.7	168.7	168.6	158.7	168.7	168.7	120 min
Viscosity	mm ² /s	3.5	3.3	3.3	3.3	3.2	3.4	3.3	3.2	3.4	3.5 – 5.0
Free glycerol	%	0.013	0.024	0.024	0.03	0.027	0.04	0.027	0.029	0.021	0.025 max
Total glycerol	%	0.21	0.20	0.20	0.27	0.28	0.23	0.27	0.24	0.20	0.25 max

F. FTIR spectroscopy analysis

In this section, FTIR analysis is presented for two different reactor coils. The spectrum shows comparison between sunflower oil and produced biodiesel.

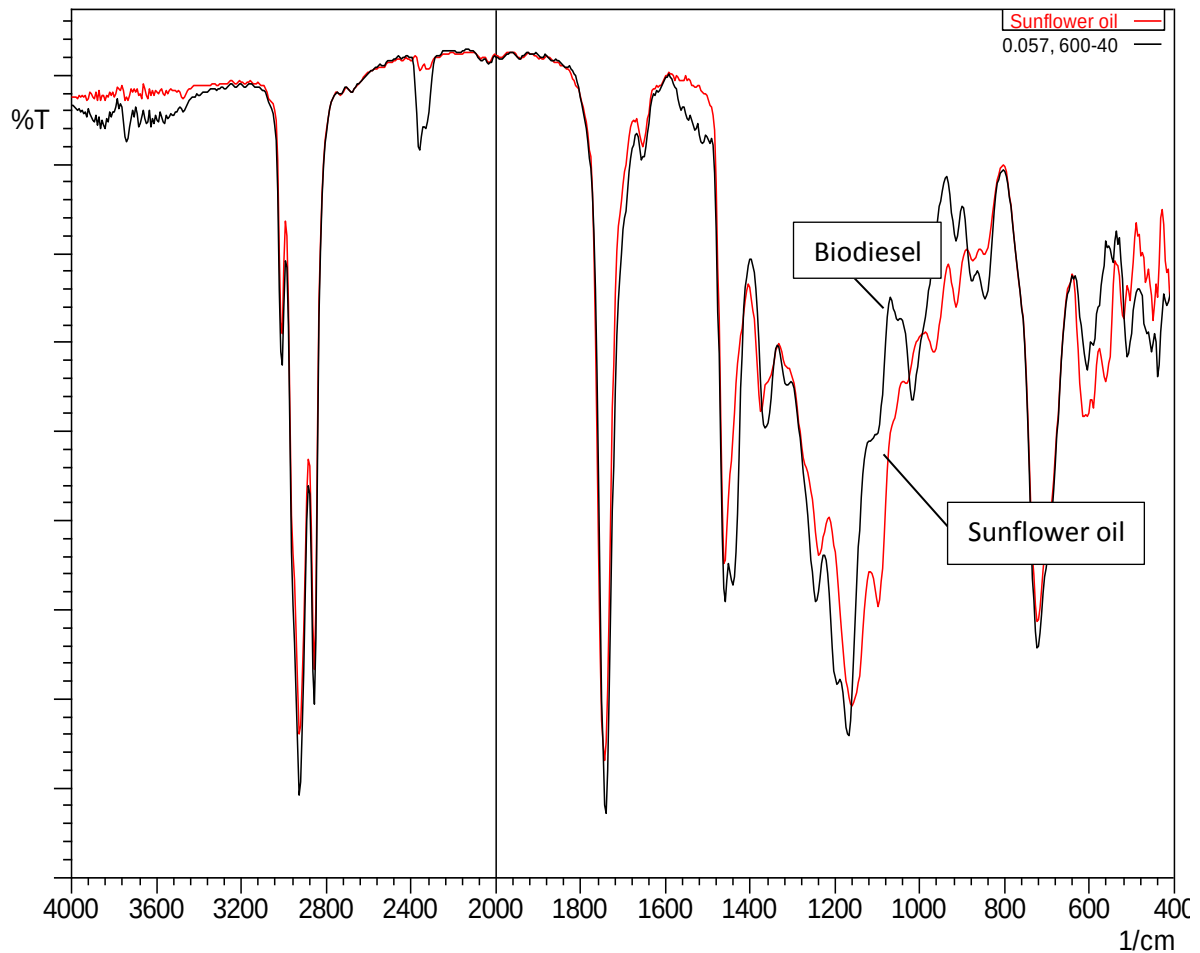


Figure F-1: Infrared spectra of sunflower oil compared to biodiesel produced using reactor coil with surface area 0.057 m^2 , at 600 W microwave power and 40 s residence time.

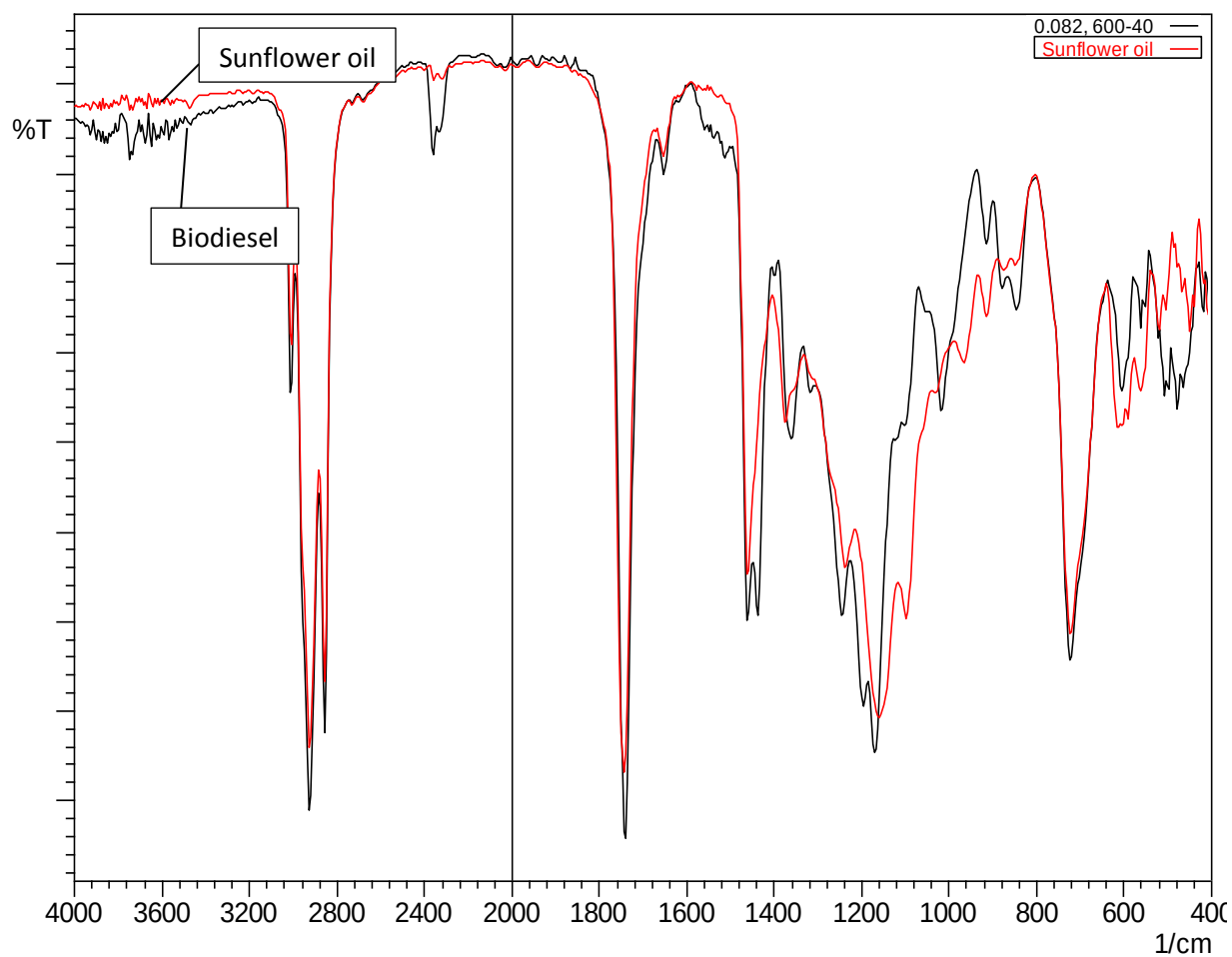


Figure F-2: Infrared spectra of sunflower oil compared to biodiesel produced using reactor coil with surface area 0.082 m^2 , at 600 W microwave power and 40 s residence time.

G. References

AOCS Official Method Ca 14-56. 2011. Total, Free and combined glycerol iodometric-periodic acid method: American Oil Chemists Society.

Oyerinde, A.Y. & Bello, E.I. 2016. Use of Fourier Transformation Infrared (FTIR) spectroscopy for analysis of functional groups in peanut oil biodiesel and its blends. *British Journal of Applied Science and Technology*, 13(3):1-14.