Continuous microwave-assisted biodiesel production

NC Nodede
24878502

Dissertation submitted in partial fulfilment of the requirements for the degree Magister Scientiae in Chemical Engineering at the Potchefstroom Campus of the North-West University

Supervisor: Prof S Marx
Co-supervisor: Dr RJ Venter

May 2016
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 m$^2$) 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 m$^2$). 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

November 2015
ACKNOWLEDGEMENTS

“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

I would like to express my sincere gratitude to

❖ Almighty God for the strength and mercies.
❖ Prof S. Marx for giving me the opportunity to this research, and also for her support, and guidance.
❖ Dr R. Venter and Dr I. Chiyanzu with their assistance and advices during course of study
❖ Mr. Adrian for his technical support and my experimental set-up
❖ Gideon and Phindile for their assistance in laboratory work
❖ Eleanor for her help with admin work
❖ My friends and colleagues (Biofuels group) for their help and support (special thanks to Themba, Busi and Banele).
❖ Coega development cooperation, National Research Foundation, and North West University for their financial support.
❖ Last but no list, I would like to thank my family for their prayers and support throughout the study, my parents Mr M. (R.I.P) and Mrs N.C Nodede. My Husband M. Jubhele, my children (Yonelani and Olithemba), and my siblings (Fikile, Vusi, Nontlantla, Neliswa, Zodwa, and Vuyelwa), I have unconditional love for you.
# TABLE OF CONTENTS

ABSTRACT .................................................................................................................. i
DECLARATION ........................................................................................................... ii
ACKNOWLEDGEMENTS ............................................................................................. iii
TABLE OF CONTENTS ............................................................................................... iv
LIST OF ABBREVATIONS ........................................................................................... viii
LIST OF FIGURES ..................................................................................................... x
LIST OF TABLES ....................................................................................................... xii

CHAPTER 1 ................................................................................................................ 1

1. INTRODUCTION .................................................................................................. 1

1.1 Background and motivation .............................................................................. 1
1.2 Problem statement ............................................................................................ 3
1.3 Aim and objectives ........................................................................................... 3

1.3.1 Research aim .................................................................................................. 3
1.3.2 Specific objectives ........................................................................................ 3
1.4 Project scope ...................................................................................................... 3
1.5 References ......................................................................................................... 5

CHAPTER 2 ................................................................................................................ 7

2. LITERATURE REVIEW ......................................................................................... 7

2.1 Global energy ..................................................................................................... 7
2.2 Renewable energy fuels .................................................................................... 7
2.3 Biofuels .............................................................................................................. 8

2.3.1 Types of biofuels .......................................................................................... 8
2.4 Biodiesel as a fuel ............................................................................................ 9

2.4.1 Advantages of biodiesel production ............................................................ 9
2.4.2 Disadvantages of biodiesel production ......................................................... 10
2.4.3 Properties of biodiesel according to South African standards (SANS 1935) .... 10
2.5 Methods for biodiesel production .................................................................... 11

2.5.1 Pyrolysis ...................................................................................................... 11
2.5.2 Dilution......................................................................................................... 11
2.5.3 Micro-emulsion ........................................................................................... 11
2.5.4 Transesterification ....................................................................................... 12

2.5.4.1 Alkali-catalysed transesterification ......................................................... 13
### Results and Discussion

#### 3. EXPERIMENTAL

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Materials</td>
<td>28</td>
</tr>
<tr>
<td>3.1.1 Feedstock</td>
<td>28</td>
</tr>
<tr>
<td>3.1.2 Chemicals</td>
<td>29</td>
</tr>
<tr>
<td>3.2 Experimental reactor</td>
<td>30</td>
</tr>
<tr>
<td>3.3 Experimental procedure</td>
<td>30</td>
</tr>
<tr>
<td>3.4 Separation, purification, and drying</td>
<td>32</td>
</tr>
<tr>
<td>3.5 Biodiesel analyses</td>
<td>32</td>
</tr>
<tr>
<td>3.5.1 Gas chromatography analyses</td>
<td>32</td>
</tr>
<tr>
<td>3.5.1.1 Oil sample preparation</td>
<td>34</td>
</tr>
<tr>
<td>3.5.1.2 Biodiesel sample preparation</td>
<td>34</td>
</tr>
<tr>
<td>3.5.2 FTIR eraspec</td>
<td>34</td>
</tr>
<tr>
<td>3.5.3 Viscometer analysis</td>
<td>35</td>
</tr>
<tr>
<td>3.5.4 Eralystics ERAFLASH</td>
<td>35</td>
</tr>
<tr>
<td>3.5.5 Titrino plus</td>
<td>36</td>
</tr>
<tr>
<td>3.5.6 FTIR IRAffinity-1</td>
<td>37</td>
</tr>
<tr>
<td>3.6 References</td>
<td>38</td>
</tr>
</tbody>
</table>

#### 3.6 References

Refer to page 38 for a list of references.

---

#### 4. RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Effect of energy input on FAME yield</td>
<td>39</td>
</tr>
</tbody>
</table>

Refer to page 39 for a detailed discussion on the effect of energy input on FAME yield.
4.2 Effect of surface area on FAME yield ................................................................. 40
4.3 Physico-chemical properties of biodiesel ......................................................... 41
  4.3.1 Density ........................................................................................................... 42
  4.3.2 Cetane number ............................................................................................ 42
  4.3.3 Flash point .................................................................................................... 43
  4.3.4 Viscosity ....................................................................................................... 43
  4.3.5 Acid value ..................................................................................................... 43
  4.3.6 Water content ............................................................................................... 44
  4.3.7 Oxidation stability ......................................................................................... 44
  4.3.8 Free and total glycerol .................................................................................. 45
4.4 FTIR spectroscopy results for sunflower oil biodiesel ....................................... 45
4.5 References .......................................................................................................... 48

CHAPTER 5 ................................................................................................................. 50
  5.1 Conclusion and recommendations ................................................................... 50
    5.1.1 Conclusion .................................................................................................. 50
    5.1.2 Recommendations ..................................................................................... 50

APPENDIX .................................................................................................................... 52
  A. CALIBRATIONS ..................................................................................................... 52
    A.1 Pump calibrations ......................................................................................... 52
    A.2 Gas chromatograph calibration curves ........................................................ 53
  B. CALCULATIONS ................................................................................................... 57
    B.1 Calculations of sunflower oil molecular weight (MW) ................................... 57
    B.2 Calculations of oil to methanol molar ratio and catalyst loading .................. 58
    B.3 FAME yield calculations .............................................................................. 58
  C. EXPERIMENTAL ERROR .................................................................................... 59
    C.1 FAME yield experimental error calculations ................................................. 59
    C.2 Experimental error data ................................................................................ 59
  D. EXPERIMENTAL DATA ....................................................................................... 61
    D.1 Energy input ................................................................................................... 61
    D.2 Surface area .................................................................................................... 62
    D.3 FAME yield .................................................................................................... 63
  E. BIODIESEL PROPERTIES .................................................................................... 66
    E.1 Free and total glycerol ................................................................................... 66
    E.2 Biodiesel properties ....................................................................................... 66
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>CH$_3$ONa</td>
<td>Sodium methoxide</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>SANS</td>
<td>South African National Standards</td>
</tr>
<tr>
<td>%</td>
<td>Percent</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>ºC</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>Kg</td>
<td>Kilogram</td>
</tr>
<tr>
<td>Cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>mm$^2$/s</td>
<td>Millimetre squared per second</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
</tr>
<tr>
<td>h</td>
<td>Hours</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>cSt</td>
<td>Centistokes</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty acid methyl ester</td>
</tr>
<tr>
<td>FFA</td>
<td>Free fatty acid</td>
</tr>
<tr>
<td>GHz</td>
<td>Gigahertz</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>&lt;</td>
<td>Greater than sign</td>
</tr>
<tr>
<td>&gt;</td>
<td>Less than sign</td>
</tr>
<tr>
<td>ml/min</td>
<td>Millilitre per minute</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transformer Infrared spectrometer</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>ACE</td>
<td>Associated Chemical Enterprise</td>
</tr>
<tr>
<td>TMSH</td>
<td>Trimethylsulphonium hydroxide</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>IS</td>
<td>Internal standard</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen gas</td>
</tr>
<tr>
<td>He</td>
<td>Helium</td>
</tr>
<tr>
<td>m</td>
<td>Metre</td>
</tr>
<tr>
<td>cm/s</td>
<td>Centimetre per second</td>
</tr>
<tr>
<td>µl</td>
<td>Microliter</td>
</tr>
<tr>
<td>kpa</td>
<td>Kilopascal</td>
</tr>
<tr>
<td>s</td>
<td>Seconds</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>RPM</td>
<td>Rounds per minute</td>
</tr>
<tr>
<td>kJ/g</td>
<td>Kilo Joule per gram</td>
</tr>
<tr>
<td>g/g</td>
<td>Grams per gram</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>IP</td>
<td>Induction period</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1-1: South Africa's production of fuel needs .................................................... 2
Figure 2-1: Types of biofuels ....................................................................................... 9
Figure 2-2: Transesterification of triglycerides with alcohol ....................................... 12
Figure 2-3: Proposed mechanism of an alkali catalysed transesterification ............ 13
Figure 2-4: Proposed mechanism of an acid catalysed transesterification .............. 14
Figure 3-1: Domestic microwave setup for continuous biodiesel production ......... 30
Figure 3-2: Continuous biodiesel production processes ............................................ 31
Figure 3-3: Biodiesel separation process ..................................................................... 32
Figure 3-4: GC used to determine fatty acid composition .......................................... 33
Figure 3-5: FTIR eraspec used to determine cetane number and density ............... 34
Figure 3-6: A thermo-scientific viscometer used to determine the viscosity of biodiesel 35
Figure 3-7: Eralystics ERAFLASH used to measure FAME flash point ............... 36
Figure 3-8: Metrohm 848 titrino plus for acid number free fatty acid content determination ................................................................................................................................. 36
Figure 3-9: FTIR IRRAfinity-1 used to determine biodiesel functional groups ......... 37
Figure 4-1: Influence of energy input on FAME yield for a surface area 0.082 m$^2$ (--- lower error limit and --- upper error limit) ................................................................. 39
Figure 4-2: Influence of surface area on FAME yield at different energy inputs (■ 90.55, ■ 104.71 and ■ 120.72 J/g) ............................................................................................................. 41
Figure 4-3: Effect of energy input on cetane number (▲ 0.045, ■ 0.057, ♦ 0.082 m$^2$ and -- SANS 1935) .................................................................................................................. 42
Figure 4-4: The viscosity of various energy inputs (♦ 0.045, ■ 0.057 and ▲ 0.082 m$^2$) 43
Figure 4-5: The oxidation stability of various energy inputs (♦ 0.045, ■ 0.057 and ▲ 0.082 m$^2$) ......................................................................................................................... 44
Figure 4-6: Infrared spectra of A-sunflower oil compared to B-biodiesel produced using reactor coil with surface area 0.045 m$^2$, at 600 W microwave power and 40 s residence time ......................................................................................................................... 46
Figure A-1: 0.082 m$^2$ pump settings ............................................................................ 52
Figure A-2: 0.057 m$^2$ pump settings ............................................................................ 52
Figure A-3: 0.045 m$^2$ pump setting ............................................................................. 53
Figure A-4: C16:0 calibration curve ............................................................................. 53
Figure A-5 C18:0 calibration curve ............................................................................. 54
LIST OF TABLES

Table 2-1: Biodiesel properties according to South African standards .......................... 10
Table 2-2: Summary of optimum conditions in microwave-assisted transesterification 18
Table 3-1: Fatty acid composition of sunflower oil ................................................. 28
Table 3-2: Sunflower oil properties ......................................................................... 28
Table 3-3: Chemicals used for biodiesel production and analyses .............................. 29
Table 3-4: GC operating conditions ........................................................................ 33
Table 4-1: FTIR functional groups of FAME for reactor coil with surface area 0.045 m$^2$, at 600 W microwave power, and 40s residence time ........................................... 46
Table B-1: Calibration curves k-values .................................................................... 57
Table C-1: Experimental error for FAME yield ....................................................... 60
Table D-1: Energy input calculations ...................................................................... 61
Table D-2: Surface area calculation ........................................................................ 62
Table D-3: Effect of energy input on surface area (0.082 m$^2$) ................................. 64
Table D-4: Effect of microwave power on surface area (0.057 m$^2$) ....................... 65
Table D-5: Effect of microwave power on surface area (0.045 m$^2$) ....................... 65
Table E-1: Biodiesel properties for reactor coil 0.082 m$^2$ ....................................... 70
Table E-2: Biodiesel properties at surface area 0.057 m$^2$ ....................................... 71
Table C-6: Biodiesel properties at surface area 0.045 m$^2$ ....................................... 72
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.
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, karanji 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


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).
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)

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirements</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl ester content, % mass fraction</td>
<td>&gt;96,5</td>
<td>EN14103</td>
</tr>
<tr>
<td>Density at 15°C, kg/cm</td>
<td>860-900</td>
<td>ISO 3675</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C, mm²/s</td>
<td>3.5 – 5.0</td>
<td>ISO 3104</td>
</tr>
<tr>
<td>Flash point °C</td>
<td>&gt;120</td>
<td>ISO 3679</td>
</tr>
<tr>
<td>Sulphur content, mg/kg</td>
<td>&lt;10</td>
<td>ISO 20846</td>
</tr>
<tr>
<td>Cetane number</td>
<td>&gt;51</td>
<td>ISO 5165</td>
</tr>
<tr>
<td>Water content, % mass fraction</td>
<td>&lt;0,05</td>
<td>ISO 12937</td>
</tr>
<tr>
<td>Oxidation stability at 110 °C, h</td>
<td>&gt;6</td>
<td>EN 14112</td>
</tr>
<tr>
<td>Acid value, mg KOH/g</td>
<td>&lt;0,5</td>
<td>EN 14104</td>
</tr>
<tr>
<td>Free glycerol, % mass fraction</td>
<td>&lt;0,02</td>
<td>EN 14105</td>
</tr>
<tr>
<td>Total glycerol, % mass fraction</td>
<td>&lt;0.25</td>
<td>EN 14105</td>
</tr>
</tbody>
</table>

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 monohydric aliphatic alcohols having 1-8 carbon atoms are usually used for this reaction (Singh & Singh, 2010).

\[
\begin{align*}
\text{CH}_2\text{-OCOR}^1 & \quad \text{ROCOR}^1 \quad \text{H}_2\text{C-OH} \\
\text{CH-OCOR}^2 + 3\text{ROH} \quad \text{Catalyst} \quad \text{ROCOR}^2 + \text{H}_2\text{C-OH} \\
\text{CH}_2\text{-OCOR}^3 & \quad \text{ROCOR}^3 \quad \text{H}_2\text{C-OH}
\end{align*}
\]

Triglycerides    Alcohol    Esters    Glycerol

**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-Ilic 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).

![Proposed mechanism of an alkali catalysed transesterification](image)

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.

![Proposed mechanism of an acid catalysed transesterification](image)

\[
\begin{align*}
R' & = \text{carbon chain of fatty acid} \\
R & = \text{alkyl group of the alcohol}
\end{align*}
\]

**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-Ilic 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

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

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 increased 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 ≥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 ≥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


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>
<thead>
<tr>
<th>Table 3-1: Fatty acid composition of sunflower oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acid</td>
</tr>
<tr>
<td>Palmatic acid (C16:0)</td>
</tr>
<tr>
<td>Stearic acid (C18:0)</td>
</tr>
<tr>
<td>Oleic acid (C18:1)</td>
</tr>
<tr>
<td>Linoleic acid (C18:2)</td>
</tr>
<tr>
<td>Linolenic acid (C18:3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3-2: Sunflower oil properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>Free fatty acid content</td>
</tr>
<tr>
<td>Water content</td>
</tr>
<tr>
<td>Viscosity @ 40°C</td>
</tr>
<tr>
<td>Density</td>
</tr>
</tbody>
</table>
### 3.1.2 Chemicals

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

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

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.

![Diagram of continuous biodiesel production process](image)

**Figure 3-2: Continuous biodiesel production processes**

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](image)

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

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. 250 µl 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.

\[
M_{is} = M(bd + is) - Mbd
\]

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](image)

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 spindlier 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](image)

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.
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-propanal, 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.
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


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)](image)

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.
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)](image)

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.

![Viscosity graph](image)

**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 m$^2$, 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-CH$_2$-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 CH$_2$ group and asymmetric stretching of the CH$_3$ 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 m$^2$, at 600 W microwave power, and 40 s residence time

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500</td>
<td>O-H hydroxyl stretching vibration associated with water</td>
</tr>
<tr>
<td>3007</td>
<td>=C-H stretching vibration associated with alkenes</td>
</tr>
<tr>
<td>2924</td>
<td>CH$_2$ asymmetric stretching vibrations of C-H associated with alkanes</td>
</tr>
<tr>
<td>2854</td>
<td>CH$_3$ symmetric stretching vibrations of C-H alkane group (methyl)</td>
</tr>
<tr>
<td>1740</td>
<td>C=O ester carbonyl stretching group associated with FAME degradation products (aldehydes, ketones and acids)</td>
</tr>
<tr>
<td>1562</td>
<td>C=O ester carbonyl stretching group</td>
</tr>
<tr>
<td>1458-1435</td>
<td>-CH$_3$ bending associated with methyl</td>
</tr>
<tr>
<td>1363</td>
<td>C-H methyl bending attributed to glycerol</td>
</tr>
<tr>
<td>1195-1168</td>
<td>O-CH$_3$ stretching functional associated with methyl esters</td>
</tr>
<tr>
<td>844</td>
<td>=C-H bending vibrations associated with alkenes</td>
</tr>
<tr>
<td>721</td>
<td>=C-H methylene bending functional group</td>
</tr>
</tbody>
</table>
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 -CH\(_3\) bending methyl ester group, and 1195 cm\(^{-1}\) associated with the stretching methyl group O-CH\(_3\) (Oyerinde & Bello, 2016). The FTIR spectra showed the carbonyl group C=O stretching peak at 1741 cm\(^{-1}\), assigned to the formation of oxidation products, aldehydes, ketones and acids (Furlan \textit{et al.}, 2010). The spectra for biodiesel produced at other two reactor coils are presented in Appendix F.
4.5 References


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 calibrations curve are presented in Figures A-1 – A-3.

![Figure A-1: 0.082 m² pump settings](image1)

![Figure A-2: 0.057 m² pump settings](image2)
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-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

<table>
<thead>
<tr>
<th>FAME</th>
<th>K values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Palmitate (C16:0)</td>
<td>54892</td>
</tr>
<tr>
<td>Methyl Stearate (C18:0)</td>
<td>57966</td>
</tr>
<tr>
<td>Methyl Oleate (C18:1)</td>
<td>54338</td>
</tr>
<tr>
<td>Methyl Linoleate (C18:2)</td>
<td>53461</td>
</tr>
<tr>
<td>Methyl Linolenate (C18:3)</td>
<td>68279</td>
</tr>
</tbody>
</table>

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.

\[ MWoil = (MF * MW16:0) + (MF * MW18:0) + (MF * MW18:1) + (MF * MW18:2) + (MF * MW18:3) \]

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

\[ MWsunflower oil = 3MWFFA + MWglycerol - 3MWwater \]
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.

\[ \text{noil} = \frac{\text{massoil}}{\text{MWoil}} = \frac{450}{875.9} = 0.513 \text{mol} \]

Number of moles for methanol was calculated by dividing noil with 6, as molar ratio is 1:6

\[ n\text{MeOH} = 0.513 \times 6 = 3.078 \text{mol} \]

\[ \text{Mass MeOH} = 3.078 \text{mol} \times \frac{34.02 \text{g}}{\text{mol}} = 98.6 \text{g} \]

\[ \text{Mass KOH} = \frac{1}{100} \times 450 = 4.5 \text{g} \]

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.

\[ \text{Area (FAME)} = K\text{value} \times \text{mass fraction} \]

Then FAME layer was calculated using the following equation

\[ \text{FAME layer (g)} = \text{mass fraction} \times \text{dry biodiesel} \]

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

\[ \text{FAME yield (g/g)} = \frac{\text{FAME produced (g)}}{\text{oil pumped in (g)}} \]
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.

\[
\text{Average}(\bar{x}) = \frac{1}{N} \sum_{i=1}^{N} x_i
\]

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

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

Confidence interval is calculated using the following equation

\[
\text{confidence limit} = \bar{x} \pm \frac{\delta}{\sqrt{n}}
\]

Then the experimental error is calculated using the equation

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

C.2 Experimental error data

The experimental error is presented in Table C-1.
<table>
<thead>
<tr>
<th>Surface Area (m²)</th>
<th>Time (s)</th>
<th>Power (W)</th>
<th>Repeat 1</th>
<th>Repeat 2</th>
<th>Repeat 3</th>
<th>Average</th>
<th>Standard deviation</th>
<th>Confidence limit</th>
<th>Experimental error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.045</td>
<td>40</td>
<td>500</td>
<td>0.51</td>
<td>0.45</td>
<td>0.43</td>
<td>0.46</td>
<td>0.042</td>
<td>0.047</td>
<td>10.17</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>500</td>
<td>0.47</td>
<td>0.44</td>
<td>0.45</td>
<td>0.45</td>
<td>0.015</td>
<td>0.017</td>
<td>3.81</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>500</td>
<td>0.53</td>
<td>0.46</td>
<td>0.44</td>
<td>0.48</td>
<td>0.047</td>
<td>0.053</td>
<td>11.22</td>
</tr>
<tr>
<td>0.057</td>
<td>40</td>
<td>500</td>
<td>0.57</td>
<td>0.64</td>
<td>0.54</td>
<td>0.58</td>
<td>0.051</td>
<td>0.058</td>
<td>9.95</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>500</td>
<td>0.61</td>
<td>0.56</td>
<td>0.58</td>
<td>0.58</td>
<td>0.025</td>
<td>0.028</td>
<td>4.88</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>500</td>
<td>0.60</td>
<td>0.56</td>
<td>0.57</td>
<td>0.58</td>
<td>0.021</td>
<td>0.024</td>
<td>4.08</td>
</tr>
<tr>
<td>0.082</td>
<td>40</td>
<td>500</td>
<td>0.22</td>
<td>0.20</td>
<td>0.20</td>
<td>0.21</td>
<td>0.012</td>
<td>0.013</td>
<td>6.32</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>500</td>
<td>0.22</td>
<td>0.20</td>
<td>0.19</td>
<td>0.20</td>
<td>0.015</td>
<td>0.017</td>
<td>8.50</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>500</td>
<td>0.24</td>
<td>0.21</td>
<td>0.21</td>
<td>0.22</td>
<td>0.017</td>
<td>0.020</td>
<td>8.91</td>
</tr>
</tbody>
</table>
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.

\[
\text{Energy (J)} = \text{Power} \left(\frac{\text{J}}{\text{s}}\right) \times \text{Time (s)}
\]

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

\[
\text{Energy input (J/g)} = \left(\frac{1}{\text{FAME produced (g)}}\right) \times \text{Energy (J)}
\]

Table D-1: Energy input calculations

<table>
<thead>
<tr>
<th>Power (J/s)</th>
<th>Time (s)</th>
<th>Energy (J)</th>
<th>Energy input (J/g)</th>
<th>FAME produced (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>40</td>
<td>16000</td>
<td>53.53</td>
<td>151.06</td>
</tr>
<tr>
<td>400</td>
<td>50</td>
<td>20000</td>
<td>60.26</td>
<td>195.27</td>
</tr>
<tr>
<td>400</td>
<td>60</td>
<td>24000</td>
<td>69.38</td>
<td>171.08</td>
</tr>
</tbody>
</table>
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

\[
Length = Vol \times \frac{22}{7} / \frac{4}{ID^2}
\]

Where vol. is the volume of reactor coil

Table D-2: Surface area calculation

<table>
<thead>
<tr>
<th>Volume (m(^3))</th>
<th>Diameter (m)</th>
<th>Length (m)</th>
<th>Radius (m)</th>
<th>Area (m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0001</td>
<td>0.0088</td>
<td>1.64</td>
<td>0.0044</td>
</tr>
<tr>
<td>2</td>
<td>0.0001</td>
<td>0.007</td>
<td>2.6</td>
<td>0.0035</td>
</tr>
<tr>
<td>3</td>
<td>0.0001</td>
<td>0.0049</td>
<td>5.3</td>
<td>0.00245</td>
</tr>
</tbody>
</table>
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)

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Power (W)</th>
<th>Energy input (J/g)</th>
<th>FAME yields (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>400</td>
<td>69.4</td>
<td>0.65</td>
</tr>
<tr>
<td>40</td>
<td>500</td>
<td>67.9</td>
<td>0.80</td>
</tr>
<tr>
<td>40</td>
<td>600</td>
<td>85.5</td>
<td>0.78</td>
</tr>
<tr>
<td>50</td>
<td>400</td>
<td>113.9</td>
<td>0.49</td>
</tr>
<tr>
<td>50</td>
<td>500</td>
<td>127.0</td>
<td>0.54</td>
</tr>
<tr>
<td>50</td>
<td>600</td>
<td>131.0</td>
<td>0.64</td>
</tr>
<tr>
<td>60</td>
<td>400</td>
<td>140.9</td>
<td>0.48</td>
</tr>
<tr>
<td>60</td>
<td>500</td>
<td>173.7</td>
<td>0.47</td>
</tr>
<tr>
<td>60</td>
<td>600</td>
<td>230.4</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Table D-4: Effect of microwave power on surface area (0.057 m$^2$)

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

Table D-5: Effect of microwave power on surface area (0.045 m$^2$)

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

\[ W = \frac{\text{mass of test portion} \times \text{volume of test portion}}{900} \]

Then the glycerol content was determined using the equation above

\[ \text{Free & total glycerol} = \frac{(B - S) \times N \times 2.302}{W} \]

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 m³)

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 m$^2$

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>400-40</th>
<th>500-40</th>
<th>600-40</th>
<th>400-50</th>
<th>500-50</th>
<th>600-50</th>
<th>400-60</th>
<th>500-60</th>
<th>600-60</th>
<th>SANS 1935</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/ml</td>
<td>0.880</td>
<td>0.878</td>
<td>0.879</td>
<td>0.88</td>
<td>0.877</td>
<td>0.879</td>
<td>0.880</td>
<td>0.880</td>
<td>0.880</td>
<td>0.860 - 0.900</td>
</tr>
<tr>
<td>Cetane No</td>
<td></td>
<td>55.8</td>
<td>57.8</td>
<td>59.2</td>
<td>58.4</td>
<td>58.2</td>
<td>56.2</td>
<td>59.1</td>
<td>56</td>
<td>56.2</td>
<td>51 min</td>
</tr>
<tr>
<td>Acid No</td>
<td>mg KOH/g</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.5 max</td>
</tr>
<tr>
<td>Water content</td>
<td>%</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.05 max</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>h</td>
<td>0.20</td>
<td>0.29</td>
<td>0.27</td>
<td>0.30</td>
<td>0.42</td>
<td>0.31</td>
<td>0.35</td>
<td>0.33</td>
<td>0.34</td>
<td>6 min</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>163.7</td>
<td>163.8</td>
<td>168.8</td>
<td>168.6</td>
<td>168.6</td>
<td>78.7</td>
<td>163.7</td>
<td>163.6</td>
<td>120 min</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>mm$^2$/s</td>
<td>3.2</td>
<td>3.1</td>
<td>3.1</td>
<td>3.0</td>
<td>3.0</td>
<td>3.1</td>
<td>3.2</td>
<td>3.1</td>
<td>3.1</td>
<td>3.5 – 5.0</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>%</td>
<td>0.014</td>
<td>0.02</td>
<td>0.018</td>
<td>0.02</td>
<td>0.019</td>
<td>0.019</td>
<td>0.03</td>
<td>0.021</td>
<td>0.07</td>
<td>0.025 max</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>%</td>
<td>0.18</td>
<td>0.21</td>
<td>0.25</td>
<td>0.23</td>
<td>0.26</td>
<td>0.22</td>
<td>0.26</td>
<td>0.3</td>
<td>0.26</td>
<td>0.25 max</td>
</tr>
</tbody>
</table>
Table E-2: Biodiesel properties at surface area 0.057 m²

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>400-40</th>
<th>500-40</th>
<th>600-40</th>
<th>400-50</th>
<th>500-50</th>
<th>600-50</th>
<th>400-60</th>
<th>500-60</th>
<th>600-60</th>
<th>SANS 1935</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/ml</td>
<td>0.880</td>
<td>0.881</td>
<td>0.881</td>
<td>0.879</td>
<td>0.880</td>
<td>0.880</td>
<td>0.880</td>
<td>0.880</td>
<td>0.880</td>
<td>0.860 – 0.900</td>
</tr>
<tr>
<td>Cetane No</td>
<td></td>
<td>58</td>
<td>62.8</td>
<td>63.9</td>
<td>58</td>
<td>57.5</td>
<td>56.9</td>
<td>63.5</td>
<td>59.8</td>
<td>57.4</td>
<td>51 min</td>
</tr>
<tr>
<td>Acid No</td>
<td>mg KOH/g</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.5 max</td>
</tr>
<tr>
<td>Water content</td>
<td>%</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.05 max</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>h</td>
<td>0.41</td>
<td>0.88</td>
<td>0.76</td>
<td>0.63</td>
<td>0.90</td>
<td>0.51</td>
<td>0.45</td>
<td>0.80</td>
<td>0.54</td>
<td>6 min</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>168.6</td>
<td>168.6</td>
<td>153.6</td>
<td>163.6</td>
<td>163.6</td>
<td>168.6</td>
<td>168.6</td>
<td>168.6</td>
<td>123.7</td>
<td>120 min</td>
</tr>
<tr>
<td>Viscosity</td>
<td>mm²/s</td>
<td>3.2</td>
<td>3.1</td>
<td>3.2</td>
<td>3.3</td>
<td>3.1</td>
<td>3.2</td>
<td>3.1</td>
<td>3.1</td>
<td>3.3</td>
<td>3.5 – 5.0</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>%</td>
<td>0.04</td>
<td>0.021</td>
<td>0.027</td>
<td>0.023</td>
<td>0.027</td>
<td>0.03</td>
<td>0.022</td>
<td>0.019</td>
<td>0.027</td>
<td>0.025 max</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>%</td>
<td>0.24</td>
<td>0.22</td>
<td>0.27</td>
<td>0.3</td>
<td>0.27</td>
<td>0.24</td>
<td>0.21</td>
<td>0.25</td>
<td>0.26</td>
<td>0.25 max</td>
</tr>
</tbody>
</table>
Table C-6: Biodiesel properties at surface area 0.045 m$^2$

<table>
<thead>
<tr>
<th>Properties</th>
<th>Unit</th>
<th>400-40</th>
<th>500-40</th>
<th>600-40</th>
<th>400-50</th>
<th>500-50</th>
<th>600-50</th>
<th>400-60</th>
<th>500-60</th>
<th>600-60</th>
<th>SANS 1935</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/ml</td>
<td>0.886</td>
<td>0.880</td>
<td>0.880</td>
<td>0.880</td>
<td>0.879</td>
<td>0.880</td>
<td>0.880</td>
<td>0.880</td>
<td>0.880</td>
<td>0.860-0.900</td>
</tr>
<tr>
<td>Cetane No</td>
<td></td>
<td>60.4</td>
<td>59.5</td>
<td>56.6</td>
<td>65.2</td>
<td>61.2</td>
<td>58.4</td>
<td>58.5</td>
<td>58.9</td>
<td>57.4</td>
<td>51.0 min</td>
</tr>
<tr>
<td>Acid No</td>
<td>mg</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.5 max</td>
</tr>
<tr>
<td>Water content</td>
<td>%</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.05 max</td>
</tr>
<tr>
<td>Oxidation stability</td>
<td>h</td>
<td>0.20</td>
<td>0.22</td>
<td>0.23</td>
<td>0.17</td>
<td>0.17</td>
<td>0.11</td>
<td>0.17</td>
<td>0.15</td>
<td>0.16</td>
<td>6 min</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>168.6</td>
<td>163.6</td>
<td>168.6</td>
<td>163.7</td>
<td>168.7</td>
<td>168.6</td>
<td>158.7</td>
<td>168.7</td>
<td>168.7</td>
<td>120 min</td>
</tr>
<tr>
<td>Viscosity</td>
<td>mm$^2$/s</td>
<td>3.5</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.2</td>
<td>3.4</td>
<td>3.3</td>
<td>3.4</td>
<td>3.4</td>
<td>3.5 – 5.0</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>%</td>
<td>0.013</td>
<td>0.024</td>
<td>0.024</td>
<td>0.03</td>
<td>0.027</td>
<td>0.04</td>
<td>0.027</td>
<td>0.029</td>
<td>0.021</td>
<td>0.025 max</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>%</td>
<td>0.21</td>
<td>0.20</td>
<td>0.20</td>
<td>0.27</td>
<td>0.28</td>
<td>0.23</td>
<td>0.27</td>
<td>0.24</td>
<td>0.20</td>
<td>0.25 max</td>
</tr>
</tbody>
</table>
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
