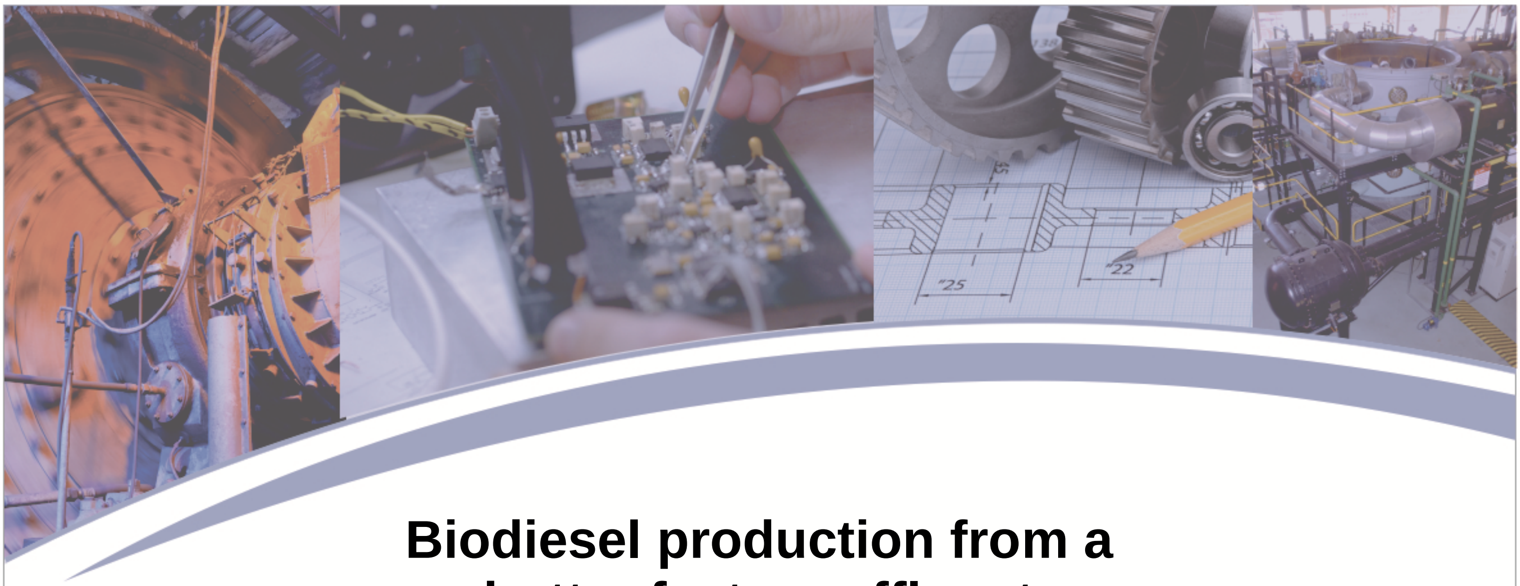

Biodiesel production from a butter factory effluent

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B.Eng. Chemical

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in

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Potchefstroom
2012

It all starts here

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Abstract

The production of biodiesel from a butter factory effluent was the main focus of the study. The alkali transesterification reaction was used to produce the biodiesel.

The effect of the temperature, alcohol to oil molar ratio, catalyst concentration and the reaction time was investigated to determine the optimal reaction conditions. The reaction temperature varied from 45 °C to 65 °C with a 5 °C increment. The alcohol to oil molar ratio varied from 3:1 to 8:1 with an increment of 1:1. The experiments with varying catalyst load were carried out at 0.8 wt%, 1.0 wt% and 1.2wt%. The reaction time was kept constant at 120 minutes, but samples of the reaction mixture were taken at 10 minute intervals.

The optimal reaction conditions according to the results were 50 °C, 6:1 alcohol to oil molar ratio, 1.0 to 1.2 wt% catalyst loads and a reaction time of 60 to 90 minutes. The optimal temperature was also the maximum temperature since a further increase in temperature lowered the ester content. Increasing the alcohol to oil molar ratio above 6:1 had no effect on the ester content. The increase in catalyst load decreased the time needed for the reaction to reach equilibrium.

The purification process was also investigated. The biodiesel was washed with water, Magnesol® D-SOL™ and Purolite® PD-206. The Magnesol® D-SOL™ was the best method for lowering the water content and the acid value of the fuel. A Magnesol® D-SOL™ content of 1.0 wt% was mixed with the biodiesel for 30 minutes in order to lower the water content and the acid value to below the maximum limit.

A kinetic model for the biodiesel reaction was developed. The model was based on the second order reversible reaction. The temperature range for the model is from 45 °C to 55 °C. The forward reaction was found to be exothermic with an endothermic reverse reaction. The activation energy for the exothermic forward reaction varied between 9.478 and 26.937 kJ/mol while the activation energy for the endothermic reverse reaction varied between 74.161 and 136.433 kJ/mol for the reactions with a catalyst load of 1.2 wt%.

The biodiesel was tested according to the SANS 1935:2011 standard. The biodiesel did not meet all the requirements of the standard. The flash point, sulphur content, carbon residue, oxidation stability, free glycerol, total glycerol and cold filter plugging point did not meet the specification of SANS 1935:2011. The biodiesel should be blended with mineral diesel if it is to be used commercially.

The butter factory effluent can be used as a feedstock for the production of biodiesel.

Keywords: Transesterification, butter waste, methanolysis, biodiesel purification, reaction kinetics.

Declaration

I, Hendrik Petrus Visser, hereby declare that I am the sole author of the dissertation entitled:

Biodiesel production from a butter factory effluent

Hendrik Petrus Visser

Potchefstroom

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Nomenclature

Symbol	Description
a	Specific interfacial area
φ	Hold-up of the dispersed phase
d_{32}	Sauter mean drop diameter
d_p	Drop size
H	Height
D	Diameter
σ	Surface tension
n	Agitation speed
d	Diameter of agitator
ρ	Density
C_i	Concentration of component i
C_{i_0}	Initial concentration of component i
r_i	Rate of reaction of component i
t	Time
k_i	Reaction rate constant
X_i	Conversion of component i
m	Mass
A	Peak area
k_c	Calibration constant
$\bar{x}$	Mean
x	Data point
N	Number of data points
δ	Standard deviation
MW_i	Molecular weight of component i

Abbreviation	Description
FAME	Fatty acid methyl ester
FFA	Free fatty acid
GC	Gas chromatograph
FTIR	Fourier transform infrared spectrometer
TG	Triglycerides
G	Glycerol
MeOH	Methanol
HATR	Horizontal attenuated total reflection
CFPP	Cold filter plugging point

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Chapter 1: Introduction

Chapter 1 consists of the background and motivation for the study. The chapter is divided into four sections. The first section is a short background and motivation for the research. Section two contains the problem statement, while section three explains the main objectives of the study. Section four covers the scope of the work that was done.

1.1 Background and motivation

The energy demand of the world is increasing daily with an ever-increasing population, as seen in Figures 1.1 and 1.2. The supply for this increasing demand is limited to the natural resources we have and these resources cannot sustain our thirst for energy, as is clearly seen in Figure 1.2. Fossil fuels are the main components of our energy supply and are very limited, and confined to certain countries.

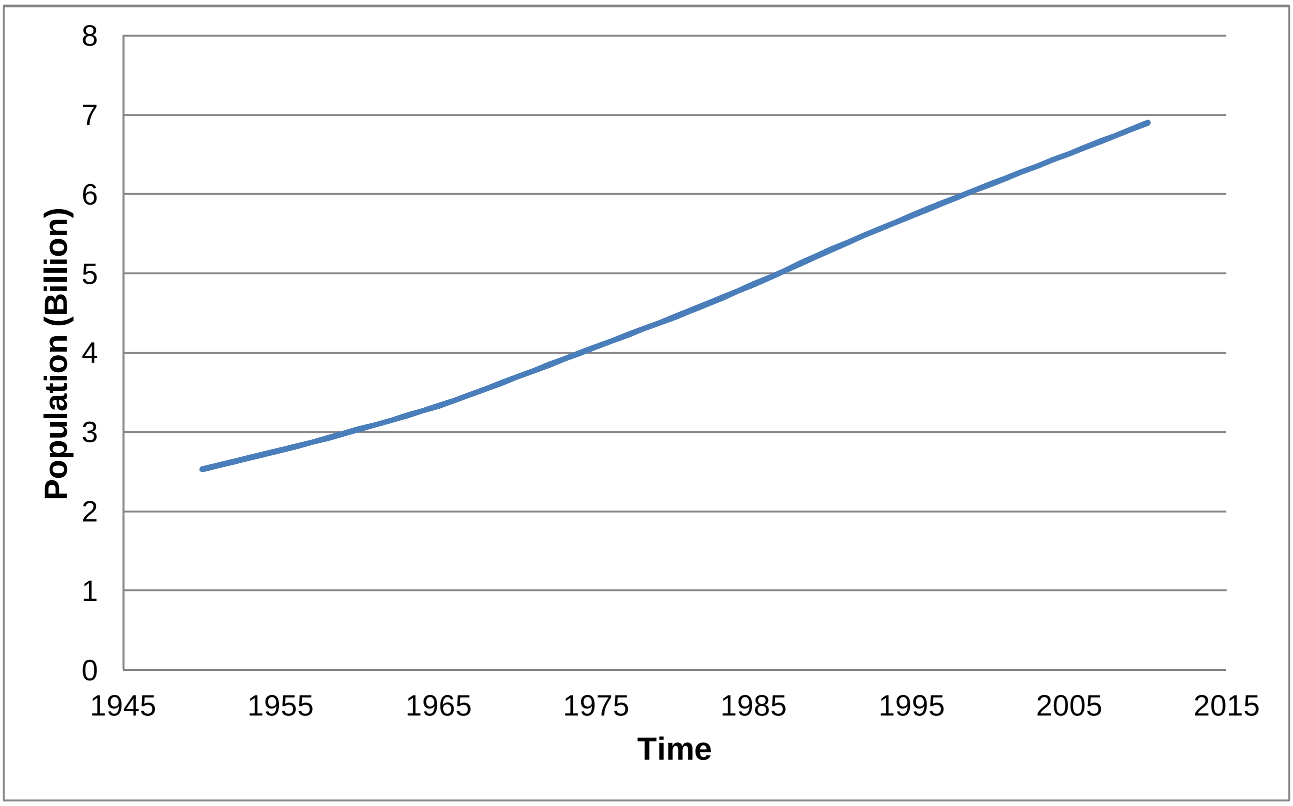


Figure 1.1: World population (— United Nations, 2011).

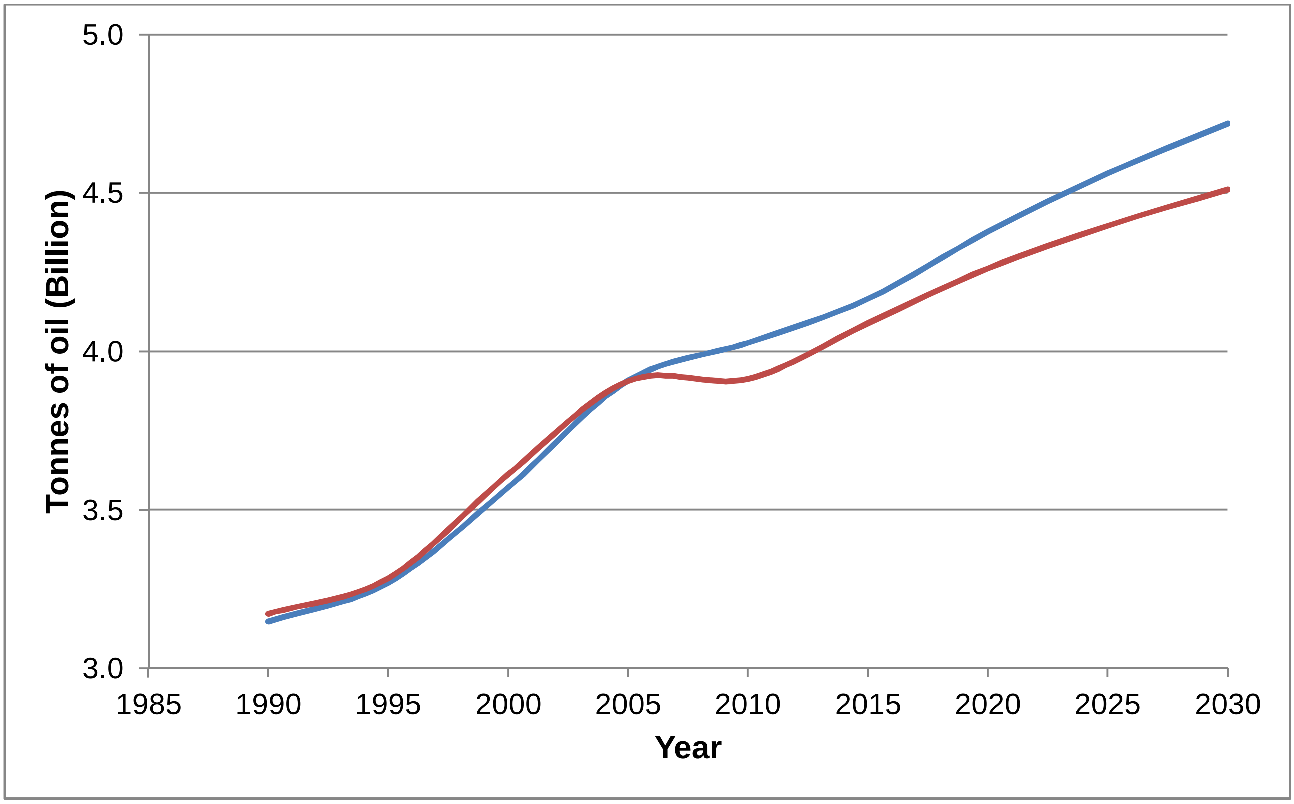


Figure 1.2: Oil demand (—) and consumption (—) (BP, 2012a)

The extreme pressure on the fossil fuel reserves is not the only current problem. The burning of these fuels releases carbon dioxide and nitrogen oxides (Jayed *et al.*, 2009:2453). These gases are said to increase the atmospheric temperature and is contributing to a global warming effect (Alexiadis, 2007:254).

The production of fossil fuels is also limited to certain countries. This is clearly seen in Figure 1.3, in which Asia and Africa are shown to have the lowest oil production, while the Middle East has the highest oil production. The uneven distribution of fossil fuels creates a monopoly and contributes to increasing fuel prices.

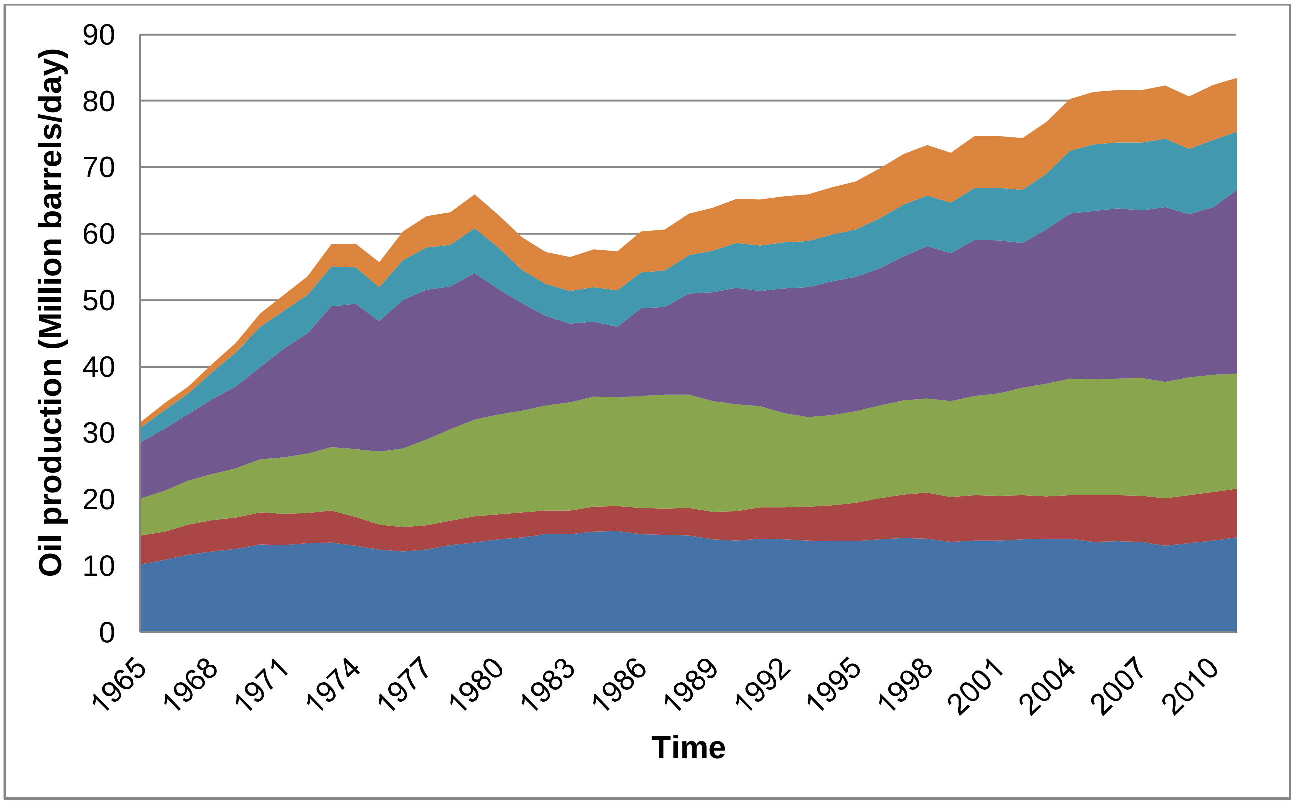


Figure 1.3: Oil production per continent (BP, 2012b).
(🟧 Asia, 🟦 Africa, 🟪 Middle East, 🟩 Europe and Eurasia, 🟥 South and Central America, 🟦 North America)

In order to decrease our dependence on fossil fuels and their harmful emissions, a new renewable and reliable energy source is needed. Biofuels, in the form of bioethanol and biodiesel, have been identified as renewable energy sources for the transport sector (Balat, 2011:88).

Bioethanol is produced by fermenting sugars from biomass (Balat, 2011:88) and biodiesel is derived from oils and fats by the formation or transformation of esters (Meher *et al*., 2006:251).

The use of oils and fats to power normal diesel engines, instead of diesel derived from fossil fuels, will decrease our dependence on fossil fuels and at the same time decrease the amount of carbon dioxide released into the atmosphere (Beer *et al*., 2002:762).

The oils and fats used for biodiesel production range from sunflower oil to animal fat. These oils and fats are also used in the food industry. This is a hurdle for the biodiesel industry to overcome. The use of edible oil for fuel is not a solution to the energy crisis. Using food to fuel motor vehicles is not ethical, since many people around the world are starving (Ewing & Msangi, 2009:522). An alternative feedstock for biodiesel is needed. The use of non-edible oils is a solution to the food versus fuel dilemma but the cultivation of these oils may also lead to food shortages. The use of land for non-edible oil cultivation will decrease arable land, which should be used to plant edible crops.

The only remaining option is to make use of discarded oils and fats. The waste from food industries and other manufacturing plants can be used as alternatives. These waste oils are non-edible and non-competitive to edible oils.

A butter factory (Clover) near Frankfort, South Africa has been identified as a source of waste oil for biodiesel production. According to FAOSTAT (2013), the butter production in South Africa has slightly been increasing from 2005 to 2011. The total butter and ghee production for South Africa in 2011 was 12 400 ton.

There are some losses during the production of butter and margarine. There is an average of five tons of waste oil being produced at the factory every month. These wastes are flushed from the factories and disposed of by municipal utilities, such as sewerage systems and landfill. The disposal of this fatty waste increases production costs, since fines are issued by the municipalities for excessive dumping. The fines are to compensate for the environmental implications of the oil in the wastewater. The wastewater from olive oil mills have been reported as highly toxic to microorganisms, invertebrates, plants and algae (Justino *et al.*, 2012:626). Bucas & Saliot (2002:1391) have found that there are similarities in the environmental impacts of edible oil spills and crude oil spills. The processes to increase the shelve-life of products have decreased their biodegradability (Rajkumar *et al.*, 2010:752). Thus the removal of the oil is essential.

The oil can be used to produce biodiesel, which the factory can use to run machinery or it can even be sold as fuel. Thus the disposal of the waste is done in such a manner that the company can decrease its production costs.

1.2 Problem statement

Butter waste is produced at the Clover factory in Frankfurt, which has been identified as a possible feedstock for biodiesel. The waste can be used at no extra cost to the company which can lower the operating costs and it can even become an additional source of income. Butter waste cannot be used as a biodiesel feedstock due to the lack of a complete production process. The use of butter as feedstock has not been determined in terms of reaction kinetics and no process has been researched to get a final product that meets the standard.

1.3 Aim and objectives

The aim of the study is to determine the optimal reaction conditions of the biodiesel production process and to evaluate the viability of the butter waste as an alternative feedstock.
The individual objectives are listed below:

- Determine the effect of reaction conditions (temperature, alcohol to oil molar ratio, catalyst load and time) on the ester yield.
- Develop reaction kinetics for the production process.
- Develop a process which will ensure that all the standards for biodiesel are met.

1.4 Project scope

To reach the aims and objectives stated in the previous two sections, the project scope should consist of the following:

- Chapter 2: Literature study
  - Feedstock varieties for biodiesel production
  - Background on biodiesel production methods
  - Parameters that affect biodiesel production processes
  - Kinetic parameters developed in previous work
- Chapter 3: Experimental design
  - A brief description of the materials used for the experiments, including the characterisation of the feedstock
  - The experimental set-up for the transesterification reaction
  - The procedure for treatment of samples
  - The analytical methods used
- Chapter 4: Results and Discussion
  - The influence of the variable parameters on the conversion
  - The influence of the variable parameters on other parameters
  - Develop reaction kinetics
  - Compare the biodiesel to the standards
- Chapter 5: Conclusion and Recommendations

Chapter 2: Literature review

An introduction to biodiesel is given in this chapter. The first section is an introduction to different feedstocks for biodiesel production. Biodiesel production processes are discussed in the second and third sections. The reactions involved in the production processes are discussed in Section 2.2. Section 2.3 is a discussion on the various methods to produce biodiesel from the different feedstocks mentioned in Section 2.1. The focus of Section 2.4 is on the transesterification of waste oils and Section 2.5 is a review on reaction kinetics.

2.1 Biodiesel Feedstock

The various feedstocks for biodiesel production are evaluated in this section to understand better the choice for this study. Section 2.1.1 discusses the main edible oils used in biodiesel reactions including their positive and negative attributes. In section 2.1.2 the use of non-edible oils are discussed. Section 2.1.3 reviews the different waste oils used in biodiesel reactions.

2.1.1 Introduction to fats and oils

Fats and oil consist mainly of triglycerides and free fatty acids (O'Brien, 2009:7). The triglycerides contain a glycerine molecule with three fatty acids to form a triacylglycerol molecule (O'Brien, 2009:7). The triacylglycerol is an ester containing three O-C=O bonds. Free fatty acids have not been esterified to form a tri-, di- or monoglyceride molecule (Gunstone, 1967:12). There are other substances like phospholipids, sterols, proteins and carbohydrates in the fats and oils, but these are less than 2% combined (O'Brien, 2009:8, Gunstone, 1967:4-11).

2.1.2 Edible oil

Edible oil can be defined as vegetable oil and animal fat used for flavouring as well as providing heat during the preparation of food. The oil mostly used in the food industry is palm kernel oil (Lam *et al.*, 2009:1457). The properties of the biodiesel produced from palm oil, soybean oil, linseed oil, sunflower oil and rapeseed oil are compared in Table 2.1.

Table 2.1: Properties of biodiesel derived from edible oils.

Property	**Kinematic viscosity (mm^2/s)**	**Density (kg/m^3)**	**Flash point (°C)**	**Cloud point (°C)**	**Cetane number**	**Acid value (mg KOH/g)**	**References**
SANS 1935:2011	3.5 – 5.0	860 – 900	> 101	-	> 51.0	< 0.5	SABS, 2011:6.
Palm	5	878.5	182.7	15.65	79	0.153	Hayyan *et al.*, 2011:924.
Palm	**5.6**	877.9	183.6	15.5	79	0.065	Hayyan *et al.*, 2010:7810.
Soybean	4.3	880	169	-2	-	-	Guzatto *et al.*, 2011:2087.
Soybean	**5.2**	870	166	-1	**47**	**1.8**	Qi *et al.*, 2009:2707.
Linseed	4.2	887	163	-1	-	-	Guzatto *et al.*, 2011:2087.
Sunflower	4.3	886	>110	-2	**46.9**	0.3	Antolin *et al.*, 2002:113.
Rapeseed	**6.35**	888.3	-	-9	**45**	0.31	Yuan *et al.*, 2008:1683.
Butter	**3.097**	-	**91**	5	61.8	0.22	Haas et al., 2010:7682.

As seen in Table 2.1, there are a few oils that do not meet the requirements of SANS 1935:2011 for biodiesel fuel. Biodiesel from the same feedstock may differ due to different processes and because no two feedstocks are the same. According to O'Brien (2009:8) the fatty acid composition of oils and fats can change due to external factors that the plant/organism is exposed to during growth.

The use of edible oils for the production of biodiesel has sparked the food versus fuel debate. The oil can be converted easily to biodiesel without much pre-treatment, but it is also a source of food. There are some countries that cannot support their population due to a lack of nutritional resources (Lam *et al.*, 2009:1461). This creates an ethical dilemma. How can some countries use edible oil for fuel while others are starving? A global increase in food prices of 45% was reported for 2007 to 2008 (Mueller *et al.*, 2011:1630). Thus the use of edible oil for biodiesel production is not in the best interest of everyone.

2.1.3 Non-edible oil

The obvious second choice for a feedstock will be non-edible oils. These oils are also derived from plants but are not suitable for human consumption. The properties of the biodiesel derived from non-edible oils can be seen in Table 2.2.

Using non-edible oils seems to be the solution to the food versus fuel debate since these oils do not compete with edible oils. This is not entirely true. The non-edible oil is still derived from plants which need fertile land. The use of fertile land for non-edible oil production versus edible oil production does not solve the food versus fuel problem.

Table 2.2: Properties of biodiesel derived from non-edible oils.

Property	Kinematic viscosity (mm^2/s)	Density (kg/m^3)	Flash point (°C)	Cloud point (°C)	Cetane number	Acid value (mg KOH/g)	References
SANS 1935:2011	3.5 – 5.0	860 - 900	> 101	-	> 51.0	< 0.5	SABS, 2011:6.
Jatropha	4.016	882	117	-5	-	**6.64**	De Oliveira *et al.*, 2009:452.
Jatropha	3.89	886	459	-	58	0.154	Deng *et al.*, 2011:782.
Castor	**15.17**	-	-	-14	**48.9**	-	Berman *et al.*, 2011:2864.
Castor	**13.75**	**924**	120	-	-	-	Conceicao *et al.*, 2007:968.
Rubber seed	**5.81**	874	130	4	-	0.118	Ramadhas *et al.*, 2005:339.
Rubber seed	4.5	**850**	120	3	-	0.12	Morshed *et al.*, 2011:2986.
Rubber seed	**6.29**	885	235	0.4	**44.81**	**0.9**	Ikwuagwu *et al.*, 2000:58.
Pongamia	**5.34**	900	150	6	-	0.136	Kumar *et al.*, 2011:6619.
Pongamia	4.33	-	174	-	57.6	0.23	Naik *et al.*, 2008:356.

2.1.4 Waste oil

Waste oil consists of both edible and non-edible oil that has expired or is a waste product. An example of waste oil is edible oil that has been used as frying grease in the food industry. The frequent heating and cooling promotes degradation of the oil. After some use, the oil becomes unsuitable for consumption due to accumulation of impurities. The waste frying oil is then disposed of.

Waste oil is not the first choice for biodiesel production when economic feasibility is a determining factor. The waste oil normally contains impurities and free fatty acids. These impurities need to be removed, which adds to the production cost of the biodiesel. Waste oils with free fatty acid contents of 5% or more need more than one process to convert the oil to biodiesel (Zhang & Jiang, 2008:8997). Water is another impurity which should be removed before the feedstock can be used to produce biodiesel (Cvengros & Cvengrosova, 2004:180).

Making use of waste oil instead of edible and non-edible oil is the best option when considering the food versus fuel debate. It is not suitable as a means of producing food and it is also not in competition with edible oil.

Another requirement for a good feedstock is that there should be an assured supply. The definition of a good feedstock for biodiesel production is

- it should be a non-edible oil, preferably a waste oil,
- which is not in competition with edible oils; and
- is continuously available in large quantities.

Table 2.3: Properties of biodiesel derived from waste oils.

Property	Kinematic viscosity (mm^2/s)	Density (kg/m^3)	Flash point (°C)	Cloud point (°C)	Cetane number	Acid value (mg KOH/g)	References
SANS 1935:2011	3.5 – 5.0	860 - 900	> 101	-	> 51.0	< 0.5	SABS, 2011:6.
Waste Palm oil	4.1	-	138	16	-	-	Tan *et al.*, 2011:2087.
Waste cooking oil	4.9	883	175.5	3	-	-	Guzatto *et al.*, 2011:2087.
Waste cooking oil	4.61	885.4	160	11	-	0.41	Charoenchaitrakool & Thienmethangkoon, 2010:117.
Waste cooking oil	**5.23**	877.5	157	12	**48**	0.21	Kumaran *et al.*, 2011:1391-1392
Waste cooking oil	**5.3**	897	120	-	54	0.1	Demirbas *et al.*, 2009:925.
Waste cooking oil	4.89	880	120	3		0.43	Phan & Phan, 2008,3495.
Waste cooking oil	4.36	890	175.4	-	53.4	0.271	Uzun *et al.*, 2012:350.

The Clover butter factory in Frankfort, South Africa, produces butter and ghee. The main ingredient of butter is fat derived from cow's milk. Since it is a part of the food industry, hygiene is of utmost importance. The waste of the plant (spillage, cleaning of equipment etc.) is continuously washed away to ensure safe and pure products. This waste contains large amounts of oil and is separated from the effluent before disposal.

The waste oil from the butter factory is an excellent feedstock for biodiesel production. It complies with the definition of a good feedstock, as previously mentioned and it also contains few impurities. For this reason, the waste oil will be the main focus of this study.

2.2 Biodiesel production reactions

There are two main reactions in biodiesel synthesis. These two reactions are transesterification and esterification. The main product of the two reactions is fatty acid methyl esters, but the main reactant differs. The reactant for the transesterification reaction is a triglyceride while the reactant for the esterification reaction is a free fatty acid.

2.2.1 Transesterification

Transesterification is a reaction where an ester is transformed from one form to another (Santori *et al.*, 2012:115). In the production of biodiesel a triglyceride molecule reacts with three alcohol molecules to form three fatty acid ester molecules and a glycerol molecule (Ma & Hanna, 1999:7). The reaction is illustrated in Figure 2.1.

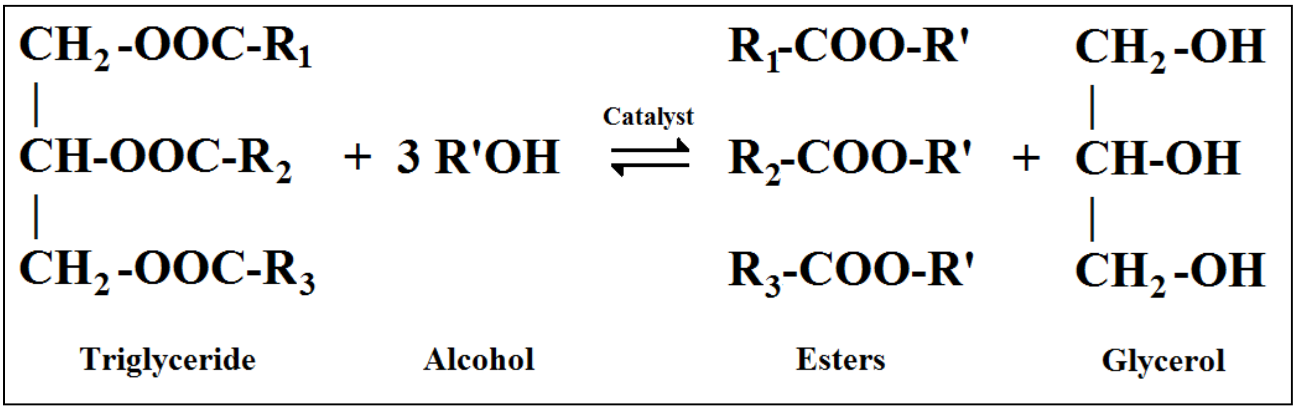


Figure 2.1: Transesterification reaction (Banerjee & Chakraborty, 2009:491).

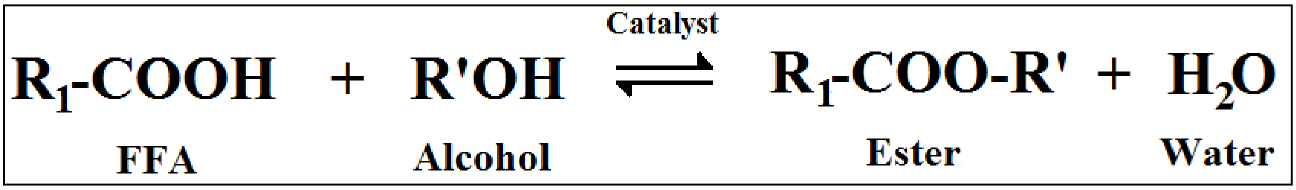
The transesterification reaction is reversible and to ensure that the reaction takes place in the desired direction, an excess of alcohol is usually used (Ma & Hanna, 1999:7). Since the reaction requires at least 3 moles of alcohol for every mole of triglycerides, the molar ratio of alcohol to oil usually exceeds 3:1 (Demirbas, 2008:128).

The reaction in Figure 2.1 is the overall reaction. The transesterification of a triglyceride happens in three steps. In the first step, the triglyceride reacts with alcohol to produce a fatty acid ester and diglyceride. In the second step the diglyceride reacts with alcohol to produce another fatty acid ester and monoglyceride. The third step is the reaction between alcohol and monoglyceride to form the third fatty acid ester and glycerol (Abdullah *et al.*, 2007:2). The transesterification reaction is a series reaction which forms three fatty acid esters and glycerol.

The transesterification reaction can be catalysed by alkalis, acids and enzymes (Balat & Balat, 2010:1823). These catalysts can be homogeneous or heterogeneous. The heterogeneous form eliminates the separation and recovery of the catalyst after the reaction has been completed, but also increases the diffusion resistance (Levenspiel, 1999:378).

2.2.2 Esterification

Esterification is a reaction in which an organic compound is transformed into an ester (McMurry, 2004:781). In the production of biodiesel via esterification, a free fatty acid molecule is transformed into a fatty acid ester and water in the presence of alcohol. The reaction is illustrated in Figure 2.2.



$$\underset{\text{FFA}}{R_1\text{-COOH}} + \underset{\text{Alcohol}}{R'OH} \xrightleftharpoons{\text{Catalyst}} \underset{\text{Ester}}{R_1\text{-COO-}R'} + \underset{\text{Water}}{H_2O}$$

Figure 2.2: Esterification reaction with an acid catalyst (CORRO *et al.*, 2011:117).

The esterification reaction is a reversible reaction and for this reason an excess of alcohol is needed to shift the reaction equilibrium. According to the stoichiometry of the reaction a molar ratio of alcohol to oil of 1:1 is needed for the esterification reaction but, as mentioned above, an excess is needed. The esterification reaction can be catalysed by acid catalysts (Zhang & Jiang, 2008:8996) and enzymes (Jiang *et al.*, 2009:104).

2.3 Biodiesel production processes

There has been an exponential increase in research regarding biodiesel production processes in recent years. The main areas of research according to Mittelbach (2012:134-135), are listed below:

- Feedstock
- Catalyst
- Catalyst free
- Purification methods
- Reaction models

Some of these areas will be discussed in this chapter. The chapter will start with catalyst free processes and move into catalysed reactions.

2.3.1 Supercritical biodiesel production

Biodiesel can be produced under supercritical conditions without the use of a catalyst (Wen *et al.*, 2009:275). A supercritical reaction process is run at high temperatures and pressures. The reactants in a supercritical reaction are exposed to conditions above their critical temperatures and pressures. Under these conditions, a supercritical phase is formed that reduces the diffusion resistance between the alcohol and the oil and makes interaction between the molecules easier (Sharma *et al.*, 2011:1321). There is no need for a catalyst with these reaction parameters since the decrease in diffusion resistance will increase the reaction rate. The separation process that follows the production step is also simplified since no catalyst is used. (Balat & Balat, 2010:1828)

Supercritical transesterification is not influenced by the water and free fatty acid content of the feedstock, which enables the process to make use of a wide range of feedstocks (Balat & Balat, 2010:1828). The free fatty acid content of the feedstock is converted into FAME by the esterifcation reaction. The supercritical method can be used for feedstock that have water contents above 10 wt% and free fatty acid contents of 20% and higher (Tan *et al*., 2010:90).

The supercritical transesterification reaction is not economically viable due to its energy intensive production cost (high temperature and pressure) and the high alcohol to oil molar ratios (30:1 to 60:1) needed (Helwani *et al.*, 2009:1509; Tan *et al.*, 2010:89; Shin *et al.*, 2012:136; Velez *et al.*, 2012:704).

2.3.2 Enzyme-catalysed biodiesel production

An enzyme like lipase can be used during the production of biodiesel. The mechanism of transesterification with an enzyme is a two-step reaction, starting with a hydrolysis reaction followed by an esterification reaction. The triglyceride is hydrolysed by removing the alcohol and using water to produce a free fatty acid. The free fatty acid undergoes esterification to produce an alkyl ester (Miller *et al.*, 1988:927).

Lipase can catalyse the esterification reaction, as well as the transesterification reaction (Véras *et al.*, 2011:9654). This is done by using genetically engineered lipase which can catalyse both reactions (Yan *et al.*, 2012:333).

The use of free enzymes (suspended in the reaction mixture) can increase the production cost since the enzymes are unrecoverable. Thus an immobilised enzyme should be used. The efficiency of the enzymes is also increased by immobilisation (Yan *et al.*, 2012:333).

Enzyme-catalysed biodiesel production has not been used in the industry due to the long reaction times and the high cost of the enzymes (Wu *et al.*, 1999:517, Yan *et al.*, 2012:333). Table 2.4 illustrates the reaction times and alcohol usage for enzyme-catalysed reactions.

Table 2.4: Reaction conditions for enzyme catalysed biodiesel production

Enzyme from	Time	Maximum Yield	Alcohol	Alcohol to oil ratio	Reference
C. cylindracea	12 hours	99%	Methanol	3.5:1	Park *et al.*, 2008:3131-3132.
P. cepacia	12 hours	96.22%	Methanol	4:1	Li & Yan, 2010:3149-3150.
Candida antarctica	2 hours	>90%	Ethanol	5:1	Véras *et al.*, 2011:9654-9655.
Burkholderia	48 hours	97.25%	Methanol	67.93:1	Tran *et al.*, 2012:120-126.
C. Antarctica and *T. lanuginosus*	48 hours	95%	Methanol	1:1 + 2:1 (Additionally added)	Yan *et al.*, 2012:333-336.
Aspergillus niger	16 hours	>90%	Ethanol	5:1 (With additional adding)	Ren *et al.*, 2011:1552-1554.
Thermomyces lanuginosus	6 hours	>80%	Methanol	3.7:1	Sim *et al.*, 2010:1028-1031.

2.3.3 Acid-catalysed biodiesel production

The acid catalysts that are mostly used in esterification reactions are hydrochloric acid and sulphuric acid. The catalyst increases the reaction rate by donating a proton to the alcohol, which increases the reactivity of the alcohol molecule (Demirbas, 2008:128).

Acid catalysts are used to reduce the free fatty acid content. This is done due the fact that acid catalysts are able to catalyse two reactions, the transesterification reaction, as well as the esterification reaction. As previously mentioned the free fatty acids are reduced by reacting with alcohol in the presence of an acid to form a fatty acid ester and water.

The rate of reaction of the acid-catalysed transesterification is relatively slower than the alkali-catalysed rate of reaction (Zhang *et al.*, 2003:3).

A two-step reaction is used due to the slower rate of reaction of acid-catalysed transesterification. The two-step reaction consists of a pre-treatment in which the free fatty acid content is reduced by acid-catalysed esterification and then followed by alkali-catalysed transesterification. The combination of the two reactions gives the highest ester yield that can be achieved with a high free fatty acid content feedstock (Zhang & Jiang, 2008:8997).

The acid-catalysed reaction needs higher alcohol to oil molar ratios than the alkali-catalysed reaction (3:1 to 25: 1) (Thiruvengadaravi *et al.*, 2012:2; Rattanaphra *et al.*, 2012:469; Srilatha *et al.*, 2012:55). This is due to the fact that for every free fatty acid molecule that reacts, one ester and one water molecule are formed, and during the transesterification reaction three ester molecules are formed for every glycerol molecule formed. This indicates a higher concentration of by-products during the esterification reaction; thus a higher alcohol to oil ratio is needed for esterification than for transesterification.

2.3.4 Alkali-catalysed biodiesel production

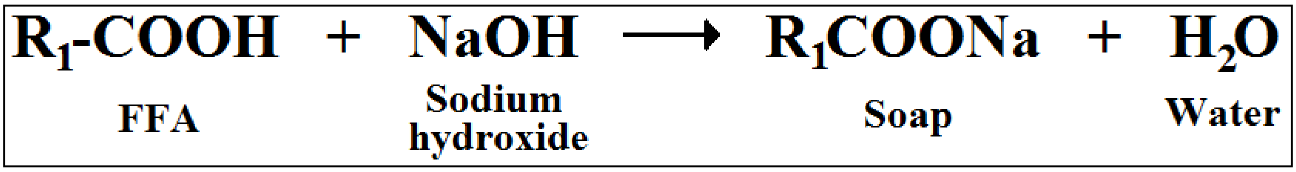
The alkali catalysts mostly used are sodium hydroxide and potassium hydroxide. The catalyst increases the rate of reaction by removing a proton from the alcohol, making it more reactive (Demirbas, 2008:128).

The alkali-catalysed transesterification reaction is the most widely used method of producing biodiesel. This is due to the simplicity of the reaction. The reaction conditions can easily be set up in a laboratory.

The alkali-catalysed reaction is very sensitive to the free fatty acid and water content of the feedstock.

According to Hayyan *et al.* (2011:922), a free fatty acid content of less than 2% is needed before the alkali-catalysed transesterification reaction can be used. According to Meher *et al.* (2006:252), a free fatty acid content of less than 3% is needed and a content of up to 5% can be used according to Van Gerpen, (2005:1104). Thus a free fatty acid content of less than 2% is best for alkali-catalysed transesterification.

The free fatty acids react with the alkali catalyst to form soap and water (Leung *et al.*, 2010:1085). This is a very undesirable side reaction, since it decreases the catalyst and produces more water. This saponification reaction is illustrated in Figure 2.3.



$$R_1\text{-}COOH + NaOH \longrightarrow R_1COONa + H_2O$$

Figure 2.3: Soap formation of sodium hydroxide. (Saponification) (Leung *et al.*, 2010:1085)

The soap formed during the saponification reaction also complicates the separation process when the transesterification reaction is complete (Van Gerpen, 2005:1104). This is due to the polar and non-polar characteristic of soap. There is a biodiesel rich layer and a glycerol rich layer after the transesterification reaction has taken place. The layers separate from each other due to their polar and non-polar characteristics, which will not take place in the presence of soap.

The water content of the feedstock also creates a problem for the transesterification reaction. The water causes a hydrolysis reaction which decreases the triglycerides to form free fatty acids and di- and monoglycerides. The reaction can be seen in Figure 2.4.

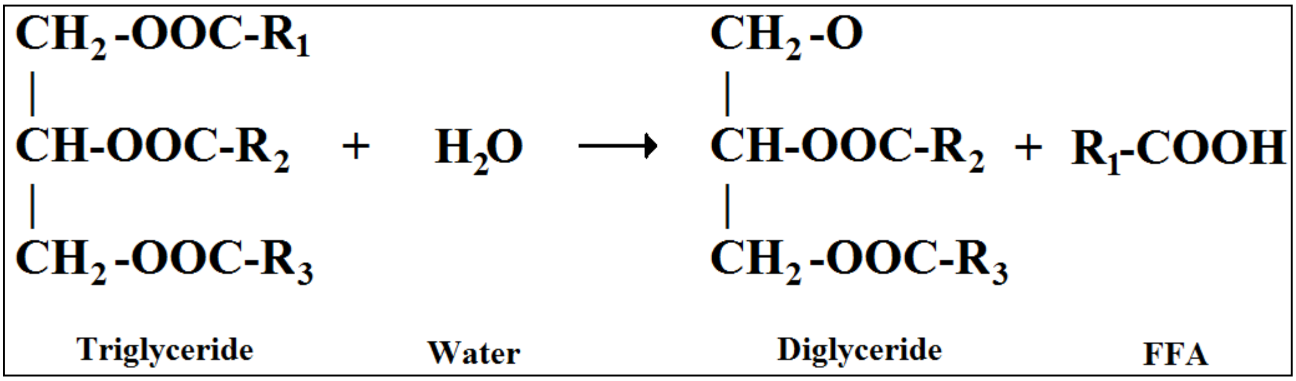


Figure 2.4: Hydrolysis of triglycerides (Leung *et al.*, 2010:1086)

The water content of the feedstock should be kept below 0.1 wt% when using the alkali-catalysed transesterification reaction (Cvengros & Cvengrosova, 2004:180).

These two side reactions can become very problematic since they reduce the yield and recovery of biodiesel. They are also series reactions, so an increase in the rate of one reaction will increase the rate of the other reaction (Leung *et al.*, 2010:1086).

A feedstock with a high free fatty acid and/or high water content can be treated to adhere to the limitations mentioned above. The feedstock can be heated to evaporate the water, but this can also increase the free fatty acid content due to the decomposition of the glycerides. The free fatty acid content can be decreased by adding more alkali catalyst to neutralise the acids or an esterification reaction can be used as a pre-treatment (Leung *et al.*, 2010:1086).

Thus a feedstock with a high free fatty acid content and high water content can be used to produce biodiesel, but with pre-treatment processes. A feedstock with low free fatty acid and water content is ideal.

2.4 Alkali-catalysed transesterification of waste oils

The most suitable feedstocks for biodiesel synthesis are waste oils as determined in Section 2.1.4 and the best production process is alkali transesterification as mentioned in Section 2.3.4. This section will discuss the use of waste oils with the alkali transesterification for biodiesel production.

2.4.1 Effect of catalyst type and load on biodiesel production

A catalyst is a substance that changes the rate of a reaction without being part of the reaction itself. Catalysts are mostly used to increase the reaction rate. The catalyst changes the mechanism of the reaction. The new mechanism has a lower activation energy and thus increases the rate. A catalyst does not affect the equilibrium of a reaction (Arnaut *et al.*, 2007).

Homogeneous and heterogeneous catalysts can be used to produce biodiesel. During the last few years more research has been done on heterogeneous catalysts, with the hope of decreasing the production cost by reusing the catalyst. This has not been the case according to Mittelbach (2012:136-137), since the temperature and pressure needed for the heterogeneous catalysts to work efficiently are much higher than with homogeneous catalysts. The reuse of the heterogeneous catalyst is not promising, according to Agarwal *et al.* (2012:92), who reported a drop in the yield from 96.8% to 83.1% after just 3 cycles. Table 2.5 shows the results of studies on heterogeneous and homogeneous catalysts.

A catalyst load of 1 wt% for homogeneous catalysts has been the norm for optimal biodiesel production, with slight variations as seen in Table 2.5. Homogeneous catalysts are also more effective in terms of alcohol usage and temperature.

An optimal yield is obtained at 1.0 wt% for both sodium and potassium hydroxides. The maximum yield will be obtained with a reaction time of one hour.

Table 2.5: Influence of catalyst on reaction

Catalyst type	Catalyst and load	Time for max yield	Reuse (Yield)	Comment	Reference
Homogeneous	Potassium hydroxide 1wt%	15 min	-	70 °C 6:1 methanol ratio	Agarwal *et al.*, 2012:90-91
Heterogeneous	Potassium hydroxide 5wt%	120 min	96.8% - 83.1% in 3 cycles	70 °C 9:1 methanol ratio	Agarwal *et al.*, 2012:90-92
Homogeneous	Potassium hydroxide 1.2wt%	30 min	-	75 °C 6:1 methanol ratio	Sivakumar *et al.*, 2011:149-150
Homogeneous	Sodium hydroxide 1wt%	60 min	-	60 °C 6:1 methanol ratio	Dias *et al.*, 2008:3573-3575
Heterogeneous	Tri-potassium phosphate 4wt%	120 min	94.4% - 49.1% after 1 cycle with no treatment	30 °C 6:1 methanol ratio	Guan *et al.*, 2009:520-522
Homogeneous	Sodium hydroxide 0.5wt%	30 min	-	70 °C 6:1 methanol ratio	Uzun *et al.*, 2012:348-349.
Heterogeneous	Zinc aluminate 10wt%	120 min	98% - 75% after 2 cycles	>100 °C 40:1 methanol and ethanol ratio	Alves *et al.*, 2012:in press

2.4.2 Effect of alcohol type and load on biodiesel production

Methanol has been used in biodiesel production, mainly due to the size of the molecule and the lower cost (Saravanan *et al.*, 2010:1000; Sanli & Canakci, 2008:2714). The use of ethanol has been investigated by Lam & Lee (2011:1641) and the results have shown that ethanol has better solubility in oil than methanol. The viscosity of biodiesel increases with the increase of alcohol molecular size and the decrease in viscosity is the main objective of transesterification (Al-Widyan *et al.*, 2002:92; Issariyakul *et al.*, 2007:434). The use of bioethanol for biodiesel production is more environmentally friendly, but it is also more expensive, and according to Sanli & Canakci (2008:2715) the ethanol should be very pure – nothing less than a purity of 96%.

The alcohol to oil ratio has another big impact on the ester yield of the biodiesel, as mentioned in Section 2.2.1. Table 2.6 illustrates the effect of alcohol to oil ratio. An increase in alcohol to oil molar ratio, increases the yield. A minimum of 6:1 alcohol to oil molar ratio is needed for a maximum yield.

Table 2.6: Influence of alcohol on reaction

Alcohol	Observation	Reaction parameters	References
Methanol/ Ethanol	Increase in yield with an increase of methanol:ethanol ratio. Higher yield with ethanol than methanol	Two-step reaction Esterification: 5 hours Sulphuric acid 2 wt% Alcohol ratio 3:1 Transesterification: 1 hour Potassium hydroxide 1 wt% 50 °C for methanol and 60 °C for ethanol	Issariyakul *et al.*, 2007:430-432.
Methanol	Increase in alcohol to oil ratio has an increase in yield	1 hour Potassium hydroxide 1 wt% 60 °C	Sanli & Canakci, 2008:2714-2716.
Methanol	Increase in yield to an optimal ratio of 6:1 and a decrease in yield with further increase of alcohol	2 hours Potassium hydroxide 1 wt% 65 °C	Rashid & Anwar, 2008:269.

2.4.3 Effect of temperature on biodiesel production

The yield of the transesterification reaction is dependent on the reaction temperature. The optimal temperature of the reaction is dependent on the alcohol used, since the boiling point of alcohol increases with the increase in alcohol size. A reaction temperature higher than the boiling point of the alcohol will result in more alcohol in the vapour phase than in the reaction mixture. This also increases the energy needed to condense the vapour. The effect of temperature is visible in Table 2.7.

A reaction temperature of at least 50 °C is needed for a maximum yield. An increase in temperature above 75 °C lowers the yield.

Table 2.7: Influence of temperature on reaction

Alcohol	Observation	Reaction parameters	References
Methanol	Increase in yield to optimal temperature of 50 °C	1 hour; Potassium hydroxide 1 wt%; Methanol 30 wt%	Kafuku & Mbarawa, 2010:2563.
Methanol	Increase in yield to optimal temperature of 50 °C	1 hour; Sodium hydroxide 0.5 wt% Methanol 6:1	Sinha *et al.*, 2008:1254.
Methanol	Increase in yield to optimal temperature of 65 °C	2 hours; Potassium hydroxide 1.25 wt% Methanol 6:1	Hoque *et al.*, 2011:1586.
Methanol	Increase in yield to optimal temperature of 75 °C	30 min; Potassium hydroxide 1.2 wt% Methanol 6:1	Sivakumar *et al.*, 2011:149-150.

2.4.4 Effect of mixing on biodiesel production

As mentioned in Section 2.4.2, methanol has is less soluble in oil than ethanol. But methanol is still the mostly used alcohol in biodiesel production due to its molecular size and cost. The solubility issue is addressed by mixing. According to Sivakumar *et al*. (2011:150) there is no change in ester yield when the stirring speed is increased above 350 rpm. And according to Ma *et al*. (1999:291) there is no difference in stirring speed, since the mixture should only be agitated at the beginning of the reaction and then stirring becomes redundant. Ultrasonic assisted biodiesel production has been shown to increase yields with lower alcohol to oil molar ratios, lower catalyst loads and shorter reaction times (Teixeira *et al*., 2009:1166; Yin *et al*., 2012:325).

2.5 Purification

There are two main purification methods in biodiesel production, i.e. wet and dry washing. Wet washing consists of water being added to the reacted biodiesel mixture. The glycerol and catalyst will then dissolve in the water and the entire mixture will separate into two phases. The top layer is the biodiesel rich layer and the bottom (denser) layer is the glycerol rich layer. Wet washing can be done with distilled water or acid water (Faccini *et al*., 2011:560; Manique *et al*., 2012:57; Predojevic, 2008:3523). The acid water is used to neutralise the alkali catalyst. The water used for the purification step is one fifth of the volume of the non-purified biodiesel. According to Faccini *et al*. (2011:560) the washing step is repeated four times while Manique *et al*. (2012:57) reported washing the biodiesel three times. Predojevic (2008:3523) reported repeating the washing process until the wash water had a neutral pH. A neutral pH would indicate neutralisation of the catalyst and removal of the alcohol. Thus repetition of the washing steps until a neutral pH is achieved is the most scientifically correct method in wet washing. The remaining water could then be removed by the addition of sodium sulphate or heating the biodiesel (Predojevic, 2008:3523; Manique *et al*., 2012:57). The increase in temperature can affect the biodiesel quality and is very energy intensive.

Dry washing utilises adsorbents or resins to remove the glycerol, alcohol and catalyst. The most common adsorbents and resins for biodiesel purification are Amberlite BD10 DRY®, Magnesol® D-SOL™ and Purolite® PD-206. The adsorbents and resins work on the principle of active sites that adhere to specified molecules. Magnesol works in a similar way to sodium sulphate. Accoring to Faccini *et al*. (2011:562), Amberlite has the ability to lower the acdi number, soap content, water content, potassium content and methanol content. Magnesol has been reported to lower the acid number, water content, soap content, methanol content, glycerol content and potassium content (Manique *et al*., 2012:60; Faccini *et al*., 2011:562). Purolite has been reported to lower the water content, acid number, soap content, potasium content and methanol content (Faccini *et al*. 2011:562). The effect of these dry washing materials have not been determined in a very wide range (1 and 2 wt%). The resins have a limited re-usability and will need to be regenerated or discarded.

2.6 Reaction kinetics

There has been an increase in the amount of research in biodiesel reaction kinetics during the last few years. This is due to the lack of knowledge about the kinetics for different feedstocks. The variation of reaction kinetics will be discussed in this section.

The kinetic parameters have been studied for a wide range of feedstocks. The kinetics differs for every feedstock and therefore the parameters have to be determined for every individual feedstock. Table 2.8 shows the different feedstocks and parameters.

The overall reaction of transesterification as seen in Figure 2.1 in Section 2.2.1 can be separated into 3 consecutive reversible reactions with the side reactions as stated in Section 2.3.4.

The insolubility of methanol in the oil as mentioned in Section 2.4.2, creates a separation of phases and increases the diffusion resistance of the reaction. The reaction is therefore seen as heterogeneous (Komers *et al.*, 2002:728). Mittelbach & Trathnigg (1990:146) observed a two phase system for the first two minutes of the reaction. The mixture then became homogeneous from five to ten minutes and returned to two phases after that, due to the increase of glycerol. The changes in mass transfer properties for these regimes have a direct effect on the kinetic parameters. Stamenkovic *et al.* (2008:1134-1135) and Avramovic *et al.* (2012:118) have quantified the mass transfer limitations of the reaction. They have included the specific interfacial area in the reaction rate to compensate for the mass transfer limitation. This specific interfacial area is a parameter that can be calculated with equation 2.1.

$$\boldsymbol{a = \frac{6\varphi}{d_{32}}}$$ **Equation 2.1**

Where a is the specific interfacial area, φ is the hold-up of the dispersed phase (alcohol) and d_{32} is the Sauter mean drop diameter.

Slinn & Kendall (2009:2325-2326) and Farajzadeh Bibalan & Sadrameli (2012:51-52) also used the specific interfacial area in their reaction rate equations but calculated the drop size by means of Misek's equation (Equation 2.2).

$$\boldsymbol{d_p = \frac{16.3\left(\frac{H}{D}\right)^{0.46}\sigma e^{(0.087D)}}{n^2 d^2 \rho_c}}$$ **Equation 2.2**

Where H and D are the reactor height and diameter, respectively, σ is the surface tension, n is the agitator speed, d is the diameter of the agitator and ρ_c is the phase density.

These two studies also made use of the empirical calculations to determine the surface tension for the specific feedstock.

The regimes have different reaction orders due to the different conditions of the reaction mixture. The different orders are presented in Table 2.8.

Table 2.8: Reaction kinetics for different feedstock and alcohol

Feedstock	Alcohol	Reaction order	Activation energy (kJ/mol)	References
Sunflower oil	Methanol	1st order irreversible for mass transfer control (Specific interfacial area)	-	Stamenkovic *et al.*, 2008:1137-1138.
		2nd order irreversible for chemical reaction control	53.5	
		2nd order reversible for equilibrium	33.2 (Forward) 34.2 (Reverse)	
Palm oil	Ethanol	2nd order reversible	-	Shahla *et al.*, 2012:2-5.
		2nd order irreversible	42.36	
		1st order irreversible	-	
Sunflower	Ethanol	2nd order irreversible for chemical control	8.3 – 35.1	Marjanovic *et al.*, 2010:666-670.
		2nd order reversible for equilibrium	22.3 – 43.9 (Forward) 3.4 – 34.6 (Reverse)	
Sunflower oil	Methanol (Ultrasound)	1st order irreversible for mass transfer control (Specific interfacial area)	-	Avramovic *et al.*, 2012:118-123.
		2nd order irreversible for chemical reaction control	46.2	

Chapter 3: Experimental design

This chapter explains the experimental set-up. Section 3.1 will describe the materials used (reactants, catalysts and feedstock). The experimental set-up will be discussed in Section 3.2. The sampling method and sample preparation will be discussed in Section 3.3 and the methods of analysis will be discussed in Section 3.4.

3.1 Materials

3.1.1 Feedstock

An oil effluent from a butter factory in Frankfort (Free State Province, S.A.) was used as feedstock. The waste effluent feedstock consists mainly of butter and fat that was washed and collected at a separation point. Some characteristics of the feedstock are summarized in Table 3.1.

Table 3.1: Feedstock characteristics

Characteristic	Value
Water content	0.17 wt%
Free fatty acid content	0.2 wt %
Sulphur content	18 ppm
Density	914 kg/m^3
Viscosity @ 40 °C	46.9 cSt
Viscosity @ 100 °C	7.7 cSt

The effluent is collected in a separation pit where the water is separated from the oil. The water flows into the municipal sewerage system and the oil and fat is removed from the tank with an absorbent material attached to a chain. The process is illustrated in Figure 3.1.

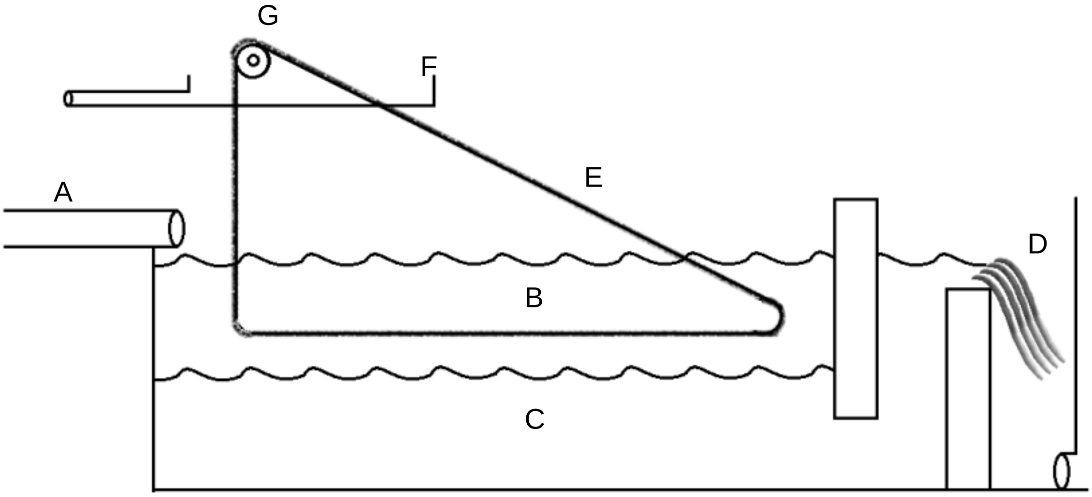


Figure 3.1: Water and fat separation trap.
(A – Effluent from factory; B – Low density fat/oil layer; C – Water layer; D – Water to municipal sewerage; E – Absorbent rope to remove fat/oil; F – Collection tray; G – Motor for rope)

The oil removed from the tank is heated with a steam coil (Steam from the factory is used) to reduce the water content of the oil. The feedstock was used as supplied, without any purification.

3.1.2 Chemicals used

The chemicals used in this study are tabulated in Table 3.2. The reactants, catalyst and analysis chemicals are shown in the table.

Table 3.2: Chemicals used in the biodiesel reaction and analysis

Component	Purity	Supplier	Purpose
Methanol	99.5%	Rochelle Chemicals	Reagent
Potassium hydroxide	85%	Associated Chemical Enterprises	Catalyst
Hydrochloric acid	32% aq	Associated Chemical Enterprises	Catalyst neutraliser
Magnesol® D-SOLTM D-SOL	-	Don't waste another drop (PTY) Ltd	Dry washing agent
Purolite® PD-206 PD206	-	Purolite® PD-206 International South Africa Pty Ltd	Dry washing agent
Dichloromethane	99 %	Merck Chemicals	Solvent – GC
Methyl nonanoate	97 %	Sigma Aldrich	Internal standard - GC
Hydranal	-	Sigma Aldrich	Water analysis (KFC)
Potassium hydroxide	1 M	Sigma Aldrich	Acid value analysis
Potassium iodide	100 g/ℓ aq	Sigma Aldrich	Iodine value analysis
Sodium thiosulphate	0.1 M	Sigma Aldrich	Iodine value analysis
Cyclohexane	99.5 %	Associated Chemical Enterprises	Iodine value analysis
Glacial acetic acid	99.7 %	Associated Chemical Enterprises	Iodine value analysis
Wijs reagent	0.1 M	Sigma Aldrich	Iodine value analysis

3.2 Alkali transesterification

3.2.1 Apparatus

The reaction vessel consists of a three-neck round-bottom flask that was fitted with a condenser, a thermometer and a rubber seal. The condenser ensured that the evaporated alcohol does not leave the system when the reaction is taking place at temperatures near or higher than the boiling point of methanol. Samples were taken during the experiment to determine the progress of the reaction. The rubber stopper was used to keep the vessel closed while samples were taken with a syringe. The syringe creates a vacuum in order to remove the sample from the flask and injecting it directly into the centrifuge tube. The thermometer was used to control the reaction temperature. The reaction vessel was placed in a heating mantle to maintain the temperature of the reaction. The temperature of the heating mantle was controlled by an automatic temperature controller which controlled the heaters power supply. The heater was also equipped with a magnetic stirrer to agitate the reaction mixture. Figure 3.2 illustrates the experimental set up.

3.3.2 Method

The oil and alcohol mixture was heated in the reaction vessel to the desired temperature. The temperature of the heating mantle was controlled at 2 °C higher than the desired reaction temperature. This was to compensate for slow heat transfer through the reaction vessel. The boiling point of methanol had an effect on the temperature control of the reaction. The temperature of the heating mantle may be above the boiling point of methanol but the reaction temperature would not exceed this value until all the methanol was in the vapour phase. This made the control of both temperatures crucial. The potassium hydroxide was dissolved in 20 mℓ of methanol. The reaction of the methanol with the potassium hydroxide is exothermic, so further heating of the catalyst mixture was not needed. The condenser was cooled with tap water. The flow of water through the condenser was not measured but kept constant throughout all of the experiments. The reaction time was started when the catalyst mixture was added to the reaction vessel.

The reaction temperature, alcohol to oil molar ratio and catalyst load were varied, while the reaction time was kept constant. The temperature was set between 45 °C and 65 °C with an interval of 5°C. The alcohol to oil molar ratio was varied between the stoichiometric value of 3:1 with an interval of 1:1 up to a ratio of 8:1. The catalyst load was set at 0.8 wt%, 1.0 wt% and 1.2 wt% and the reaction time was kept constant at 120 minutes. The variable parameters can be seen in Table3.3. A sample of the mixture was taken every ten minutes to track the extent of the reaction. The sample size was kept constant at 30 mℓ.

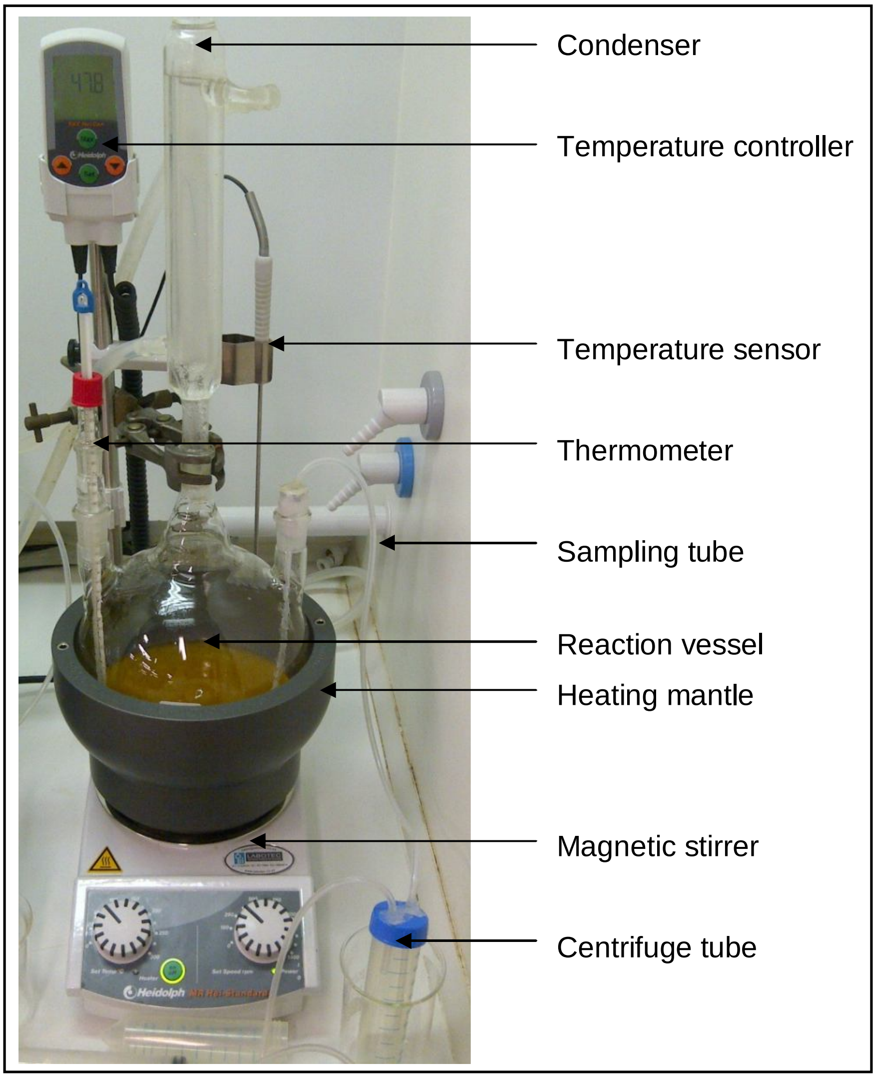


Figure 3.2: Experimental set-up

A hydrochloric acid solution was added to the sample to ensure that the catalyst was neutralised and the reaction had stopped. The sample was then centrifuged for five minutes at 1 200 revolutions per minute to separate the glycerol-rich layer from the biodiesel-rich layer. The glycerol-rich layer was then removed and the sample washed with distilled water at 60 °C. The sample was then centrifuged again and the washing process was repeated five (or more) times. The number of repetitions was determined by the requirement that, finally, the sample had to have a pH of 7 and that the wash water had to be clear.

Table 3.3: Experimental conditions for transesterification reaction.

Parameter	Range	Interval
Temperature	45 °C to 65 °C	5 °C
Alcohol to oil molar ratio	3:1 to 8:1	1:1
Catalyst load	0.8 wt% to 1.2 wt%	0.2 wt%
Time	0 minutes to 120 minutes	10 minutes

3.3 Purification

3.3.1 Apparatus

The samples were taken directly into centrifuge tubes. The centrifuge used was a Rotafix 32 from Hettich Zentrifuger. The remaining reaction mixture was transferred to a separation funnel in order to separate the biodiesel and glycerol layers.

3.3.2 Method

The sample was taken by means of a syringe. The sample size was kept constant at 30 mℓ. The purification took place after neutralising the catalyst. The biodiesel layer was purified by washing with warm (60 °C) water. The use of the warm water increased the solubility of the methanol, glycerol and remaining catalyst in the water layer and also decreased the waiting time for the separation of the two phases. The water layer was then removed and the process repeated five times to ensure that the methanol, glycerol and remaining catalyst were removed. The washing process increases the water content of the biodiesel. The biodiesel was dried in an oven at 105 °C for two hours. The time was increased to five hours for the reaction mixtures that remained at the end of the reaction. The samples were filtered with a PALL Aerodisc Premium 25 mm Syringe filter with GxF/0.2 µm GHP membrane to remove any remaining particles. The biodiesel and glycerol layers are presented in Figure 3.3.

Magnesol® D-SOL^{TM} and Purolite® PD-206 were used as dry washing resins. The biodiesel was heated to 65 °C to remove the remaining methanol and then the resins were added. The resins were added in concentrations of 0.5, 1, 1.5 and 2 weight percentage. The temperature was kept constant at 65 °C and samples were taken at 10, 20 and 30 minutes. The complete work breakdown structure is illustrated in Figure 3.4.

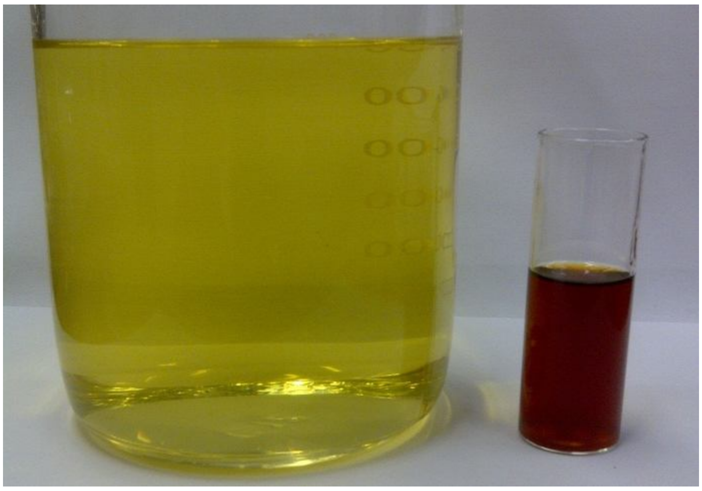


Figure 3.3: Biodiesel (Left) and glycerol (Right) after separtion and filtration.

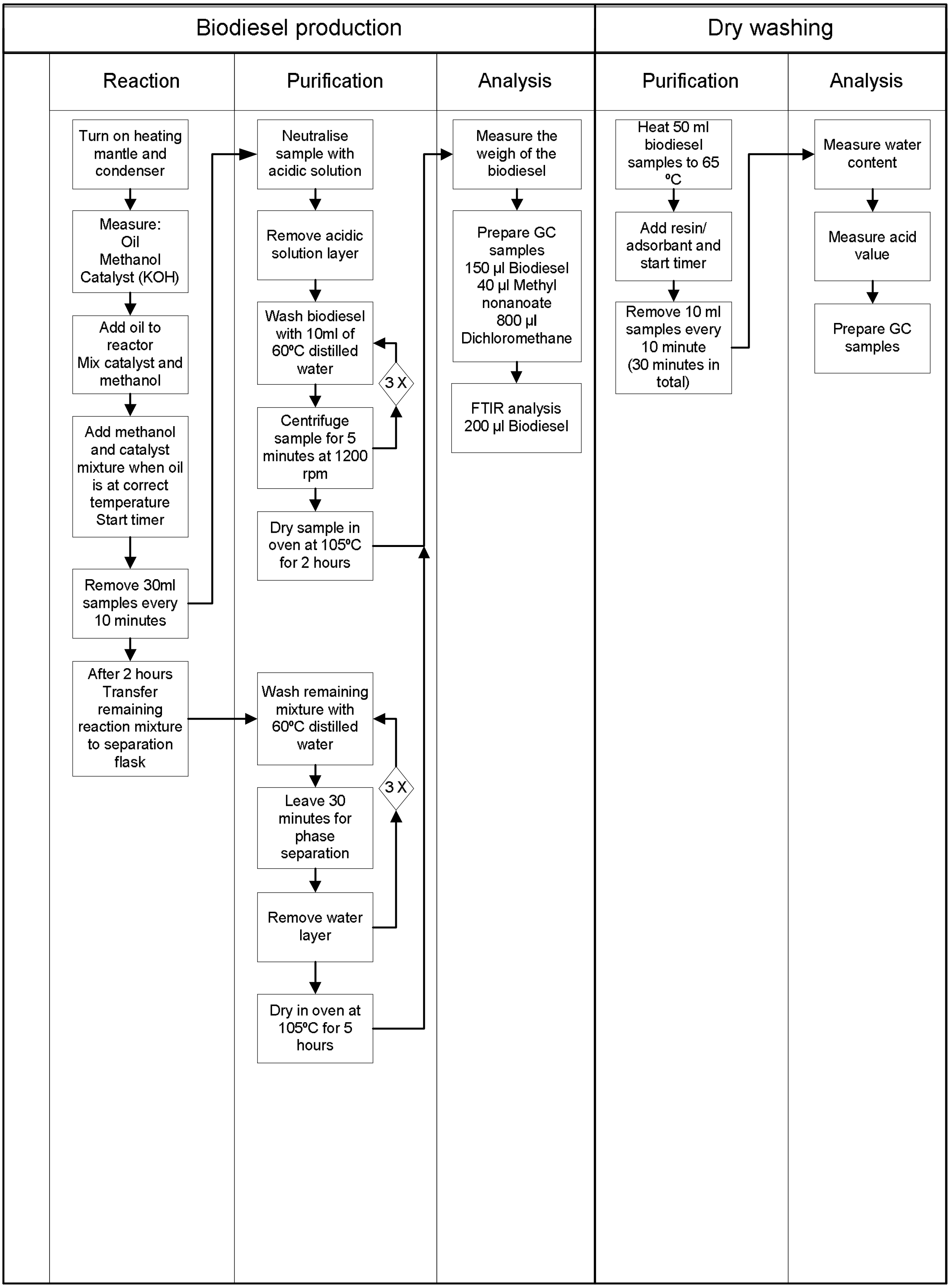


Figure 3.4: Work breakdown structure

3.4 Analytical method

3.4.1 Mass yield

The mass yield of the biodiesel is calculated by measuring the weight of the dried product as seen in Equation 3.1. The mass yield cannot be used to determine the conversion of the reaction, since the biodiesel layer may still contain unreacted feedstock such as di- and monoglycerides. The efficiency of the process can be determined by the mass yield. According to the stoichiometry of the transesterification reaction, the weight of the biodiesel should be more than the weight of the feedstock.

$$\boldsymbol{Mass\ yield} = \frac{\boldsymbol{Mass\ of\ dried\ biodiesel}}{\boldsymbol{Mass\ of\ oil}} \quad \textbf{Equation 3.1}$$

3.4.2 Ester content

The GC (Agilent 7890 A) is set-up to determine the weight percentage of each of the esters (C4 – C18) formed during the reaction. The concentrations of the mono-, di-, triglycerides and esters are needed to determine the reaction kinetics of the three consecutive reactions. The content of the tri-, di- and monoglycerides were not determined and therefore the reaction kinetics of the overall reaction will be examined. Table 3.4 describes the method of the GC analysis and Figure 3.5 shows the GC.

The filtered samples were used for GC analysis. The samples were diluted with dichloromethane and methyl nonanoate (C9 methyl ester) was used as internal standard. The calibration curves and set-up of the sample preparation can be found in Appendix A.1. The GC sample contained 150 µℓ of biodiesel, 40 µℓ methyl nonanoate and 800 µℓ dichloromethane.

Table 3.4: Method for GC analysis.

Parameter	Value
Column	Agilent HP-88 (100m Length, 0.25mm Diameter, 0.2 µm Film)
Carrier gas	Helium
Linear velocity	35 cm/s
Inlet	Split/Splitless
Split ratio	1/50
Injection volume	1 µℓ
Inlet temperature	250 °C
Inlet pressure	381.98 kPa
Oven temperature	100 °C for five minutes; ramp at 10 °C/minute to 120 °C, hold for one minute; ramp at 10 °C/minute to 175 °C, hold for ten minutes; ramp at 5 °C/minute to 210 °C, hold for five minutes; ramp at 5 °C/minute to 230 °C, hold for five minutes.
Detector	Flame Ionisation Detector at 350 °C
Detector gas flows	Hydrogen: 40mℓ/minute; Air: 400mℓ/min
Solvent for needle washes	Dichloromethane

Figure 3.5: Agilent 7890 A Gas Chromatograph

Infrared (IR) spectroscopy is another method to determine the yield of the reaction. With mid-IR spectroscopy the difference in absorption can be seen for FAME and triglycerides (Zhang, 2012:6053). A Fourier transform infrared spectrometer (FTIR) can be used to determine the conversion of the reaction. The individual esters cannot be measured quantitatively as with the GC analysis. FTIR analysis is much faster (one minute) than GC analysis (up to one hour) and if used correctly can decrease the time spent on analysis (Zhang, 2012:6052). A big advantage of FTIR analysis is that it does not need to be recalibrated, as the GC. The GC should be calibrated frequently and every time the column is changed. Sample preparation is also simpler with FTIR analysis. The samples are inserted into the FTIR without any pre-treatment. This makes the FTIR method more cost and time effective.

The sample (200 μℓ biodiesel) was inserted into the Zinc Selenide crystal Horizontal Attenuated Total Reflection (HATR) and analysed by the Shimadzu IRAffinity-1 spectrophotometer. The samples were scanned 25 times with a resolution of 2 cm^{-1} from 400 cm^{-1} to 4000 cm^{-1}. The calibration of the FTIR is explained in Appendix A.2.

The remaining standards were tested according to the specified test methods, unless otherwise stated, and can be seen in Table 3.5.

Table 3.5: Test methods for SANS 1935:2011 standards

Standard	Method	Comments
Density	ISO 12185	Eraspec from Euralytics
Kinematic viscosity	ISO 3104	WearCheck
Flash point	ISO 2719	Bio Services CC
Sulphur content	ASTM D4294	WearCheck (Not ISO as specified)
Carbon residue	ASTM D189	WearCheck (Not ISO as specified)
Cetane number	ISO 5165	Eraspec from Euralytics
Sulphated ash content	ISO 3987	Bio Services CC
Water content	ISO 12937	Auto-titrator
Total contamination	SANS 52662	WearCheck
Copper strip corrosion	ISO 2160	
Oxidation stability	SANS 54112	873 Biodiesel Rancimat from Metrohm
Acid value	SANS 54104	Auto-titrator
Iodine value	SANS 54111	
Linolenic acid methyl ester	Method as described above for ester content (Section 3.4.2)	
Polyunsaturated methyl esters	Method as described above for ester content (Section 3.4.2)	
Methanol content	Method as described above for ester content (Section 3.4.2)	
Monoglyceride content	SANS 54105	N/A
Diglyceride content	SANS 54105	N/A
Triglyceride content	SANS 54105	N/A
Free glycerol	SANS 54105	
Total glycerol	SANS 54105	
Group I metals		WearCheck
Group II metals		WearCheck
Phosphorous content		WearCheck
Cold filter plugging point	SANS 50116	Bio Services CC

Chapter 4: Results and Discussion

The results of the transesterification reaction are discussed in this chapter. The influence of the reaction parameters, as well as the optimal reaction conditions are discussed in Section 4.1. The results of the purification steps are discussed in Section 4.2 and the reaction kinetics are discussed in Section 4.3. The results of the SANS 1935:2011 tests are presented in Section 4.4 and possible solutions for results that do not meet the requirements are also discussed.

4.1 Reaction parameter optimisation

The experimental error for the influence of reaction parameters was determined by repeating an experiment three times and comparing the results. The experimental error of the GC results for the reaction parameters was calculated as 8.069 wt%. A complete discussion on the experimental error calculations can be found in Appendix B.

4.1.1 Influence of reaction temperature

The influence of the reaction temperature on the ester content of the biodiesel was studied at various alcohol to oil molar ratios and catalyst concentrations. The effect of reaction temperature (with an increase in catalyst load) on the ester content is given in Figure 4.1.

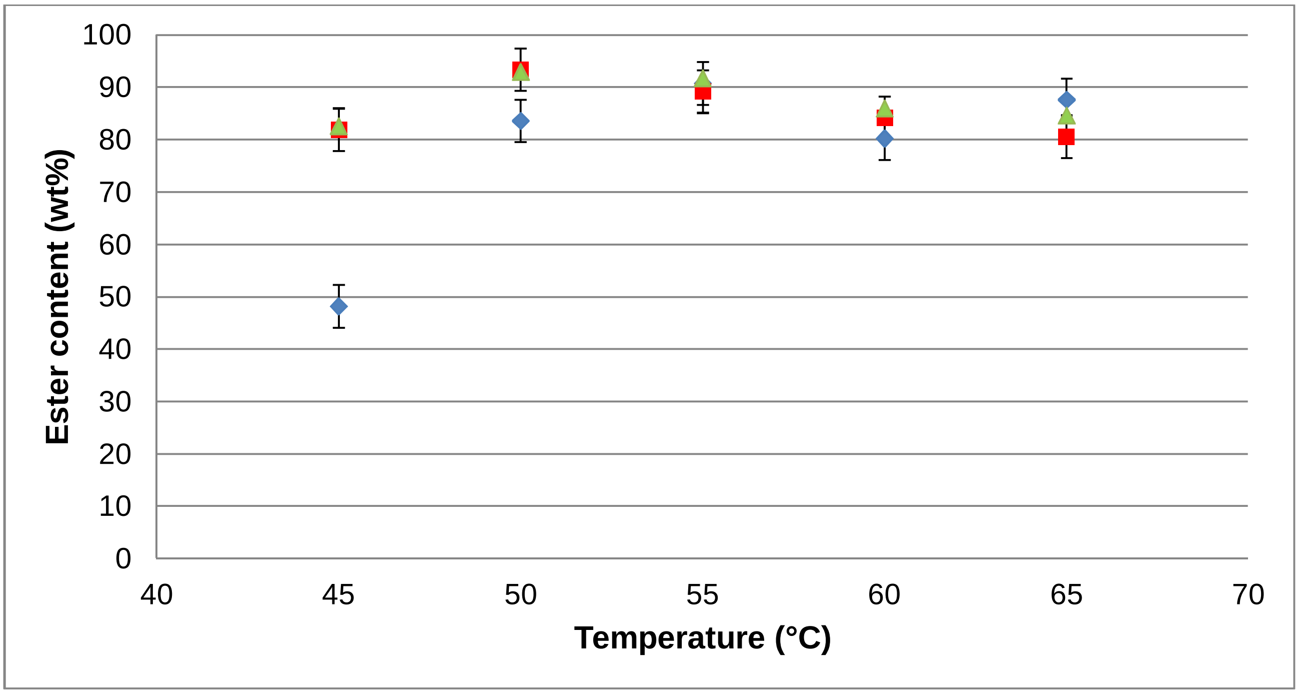


Figure 4.1: Influence of reaction temperature on ester content.
(Alcohol to oil molar ratio of 6:1 and reaction time of 120 minutes with catalyst load of ◆ 0.8 wt%; ■ 1.0 wt%; ▲ 1.2 wt%)

There is a clear increase in ester content with the increase of reaction temperature up to a maximum at 50 °C. The increase in temperature increases the reactivity of the molecules which is explained by the Arrhenius equation (Arnaut *et al.*, 2007:25).

There is no change in ester content with a change in temperature at catalyst loads of 1.0 wt% and 1.2 wt%. The effect of temperature, at different alcohol to oil molar ratios, on the ester content is given in Figure 4.2.

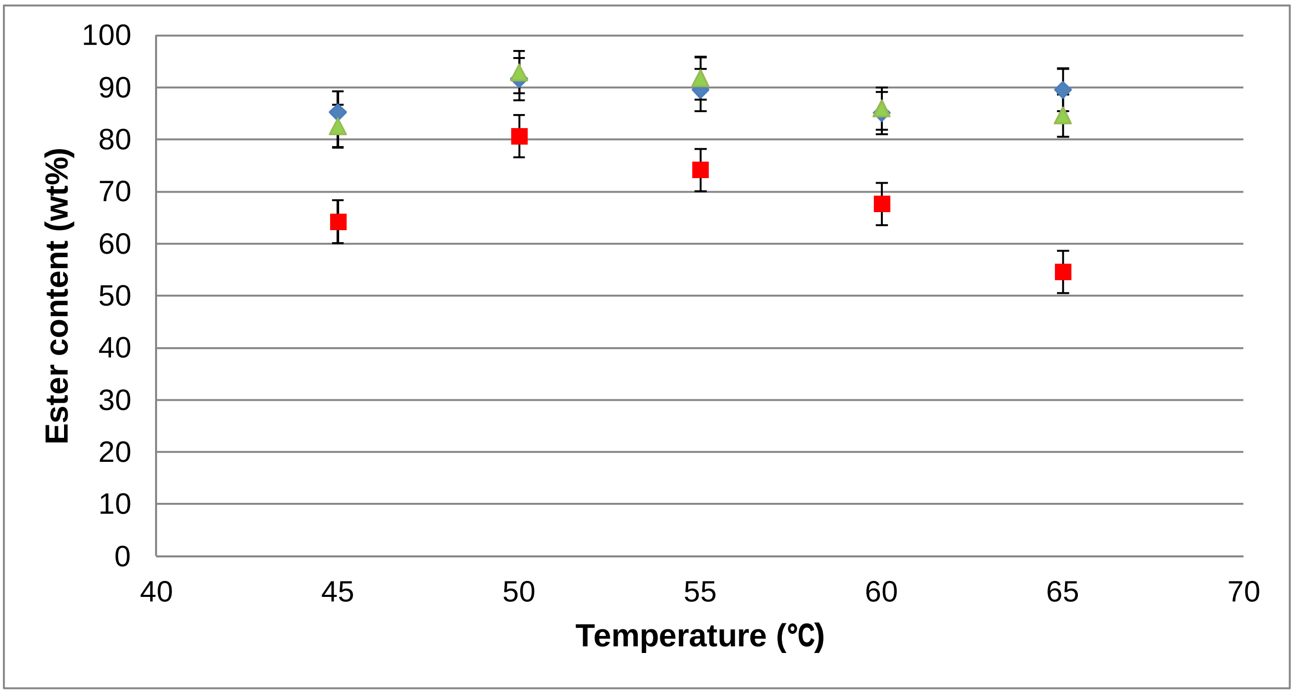


Figure 4.2: Influence of reaction temperature on ester content.
(Catalyst load of 1.2 wt% and reaction time of 120 minutes with alcohol to oil molar ratio of 🟥 3:1; ▲ 6:1; ◆ 8:1)

Increasing the reaction temperature to above 50 °C decreases the ester content. As discussed in Section 2.4.3, the increase in temperature above the boiling point of methanol, decreases the methanol in the liquid phase. The decrease of methanol concentration shifts the reaction equilibrium to the left, which decreases the ester content.

The effect of high temperatures becomes less pronounced with higher alcohol to oil molar ratios. This can be seen in Figure 4.2, where there is little change in ester content with an increase in temperature at alcohol to oil molar ratios of 6:1 and 8:1.

It is clear from both Figures 4.1 and 4.2 that the optimal reaction temperature for catalyst loads of 1.0 wt% and 1.2 wt% is 50 °C. This is coherent with literature as seen in Table 2.7.

4.1.2 Influence of alcohol to oil molar ratio

The influence of alcohol to oil molar ratio was investigated at various temperatures and catalyst loadings. The effect of the molar ratio of alcohol to oil (with a constant temperature and varying catalyst load) can be seen in Figure 4.3.

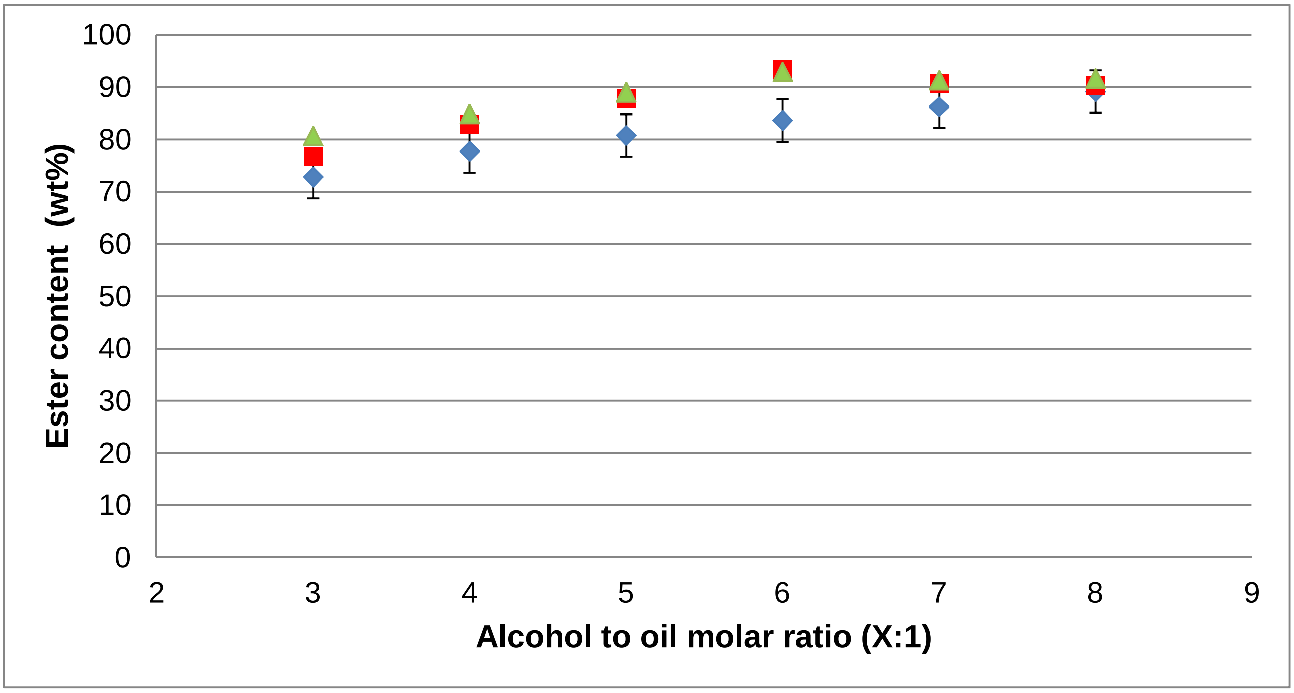


Figure 4.3: Influence of alcohol to oil molar ratio on ester content.
(Reaction temperature of 55 °C and reaction time of 120 minutes with catalyst load of ◆ 0.8 wt%; ■ 1.0 wt%; ▲ 1.2 wt%)

Figure 4.3 shows an increase in ester content with an increase in alcohol to oil molar ratio. The transesterification reaction is reversible, as explained in Section 2.2.1, thus the increase of the ratio shifts the reaction to the right. Higher concentrations are reported with higher catalyst loads, but there are no significant changes in ester content with a change in catalyst load above 1.0 wt%. The effect of the molar ratio of alcohol to oil on the ester content with a change in temperature is displayed in Figure 4.4. The optimal molar ratio is achieved at 6:1. A further increase of alcohol does not increase or decrease the concentration of the esters. The optimal alcohol concentration is chosen from an economic viewpoint i.e. the lowest alcohol concentration with the highest yield is optimal.

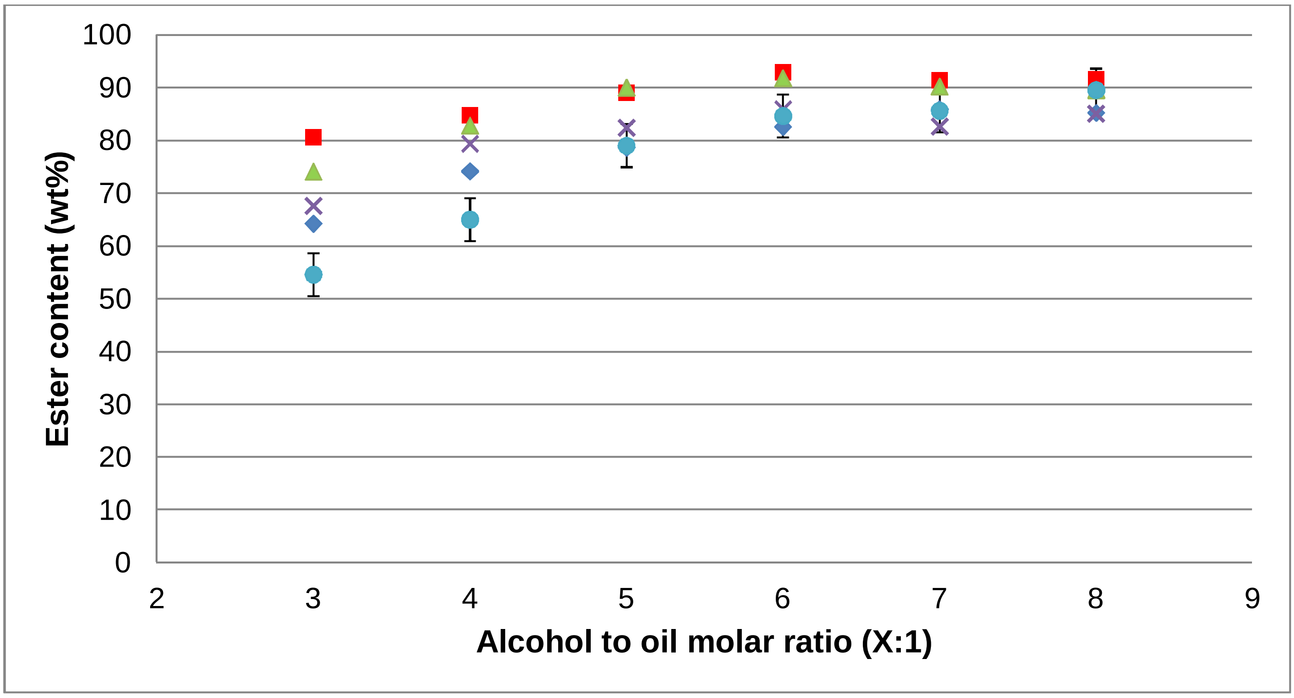


Figure 4.4: Influence of alcohol to oil molar ratio on ester content.
(Catalyst load of 1.2 wt% and reaction time of 120 minutes with reaction temperature of ◆ 45 °C; 🟥 50 °C; ▲ 55 °C; ×60 °C; ● 65 °C)

4.1.3 Influence of catalyst load

The effect of the catalyst concentration on the ester content of the biodiesel is examined in this section. Figures 4.5, 4.6 and 4.7 illustrate the influence of the catalyst load at different temperatures on the ester content.

According to Figure 4.5, there is an increase in ester content with an increase in catalyst concentration at low temperatures (45 °C). The catalyst facilitates the forward reaction to reach equilibrium in a shorter amount of time. The equilibrium of the 0.8 wt% and 1.0 wt% reactions is reached after 40 minutes, but this is lowered to 20 minutes with a catalyst load of 1.2 wt%. The effect of increasing catalyst load is very limited at 55 °C and 65 °C, as seen in Figure 4.6 and Figure 4.7. An increase in temperature increases the reactivity of the molecules. The catalyst is used to lower the activation energy. An increase in catalyst load will not affect the ester content at higher temperatures since the activation energy needed is already supplied by the heat source. This can be seen by comparing Figures 4.6 and 4.7.

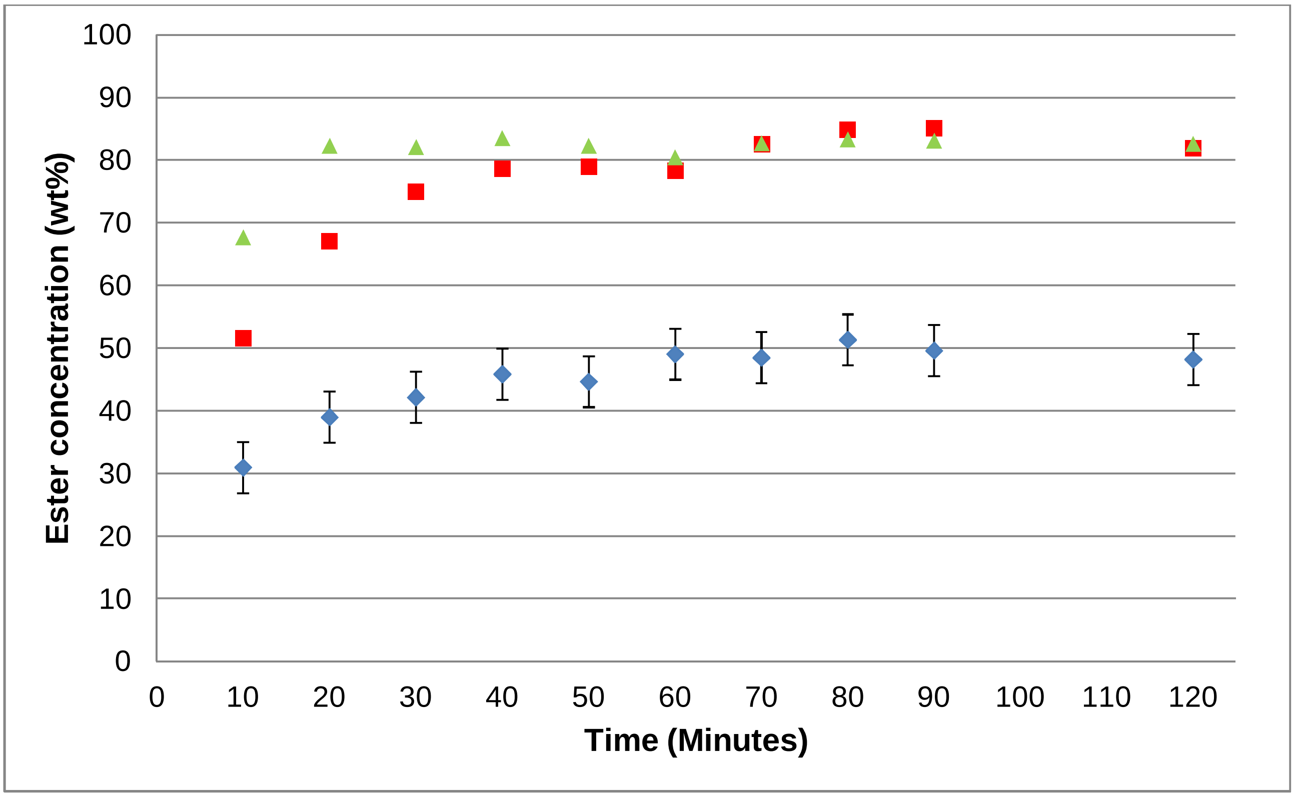


Figure 4.5: Influence of catalyst load on ester content with a reaction temperature of 45°C
(Reaction temperature of 45°C and alcohol to oil molar ratio of 6:1; ◆ 0.8 wt%; ■ 1.0 wt%; and ▲ 1.2 wt%)

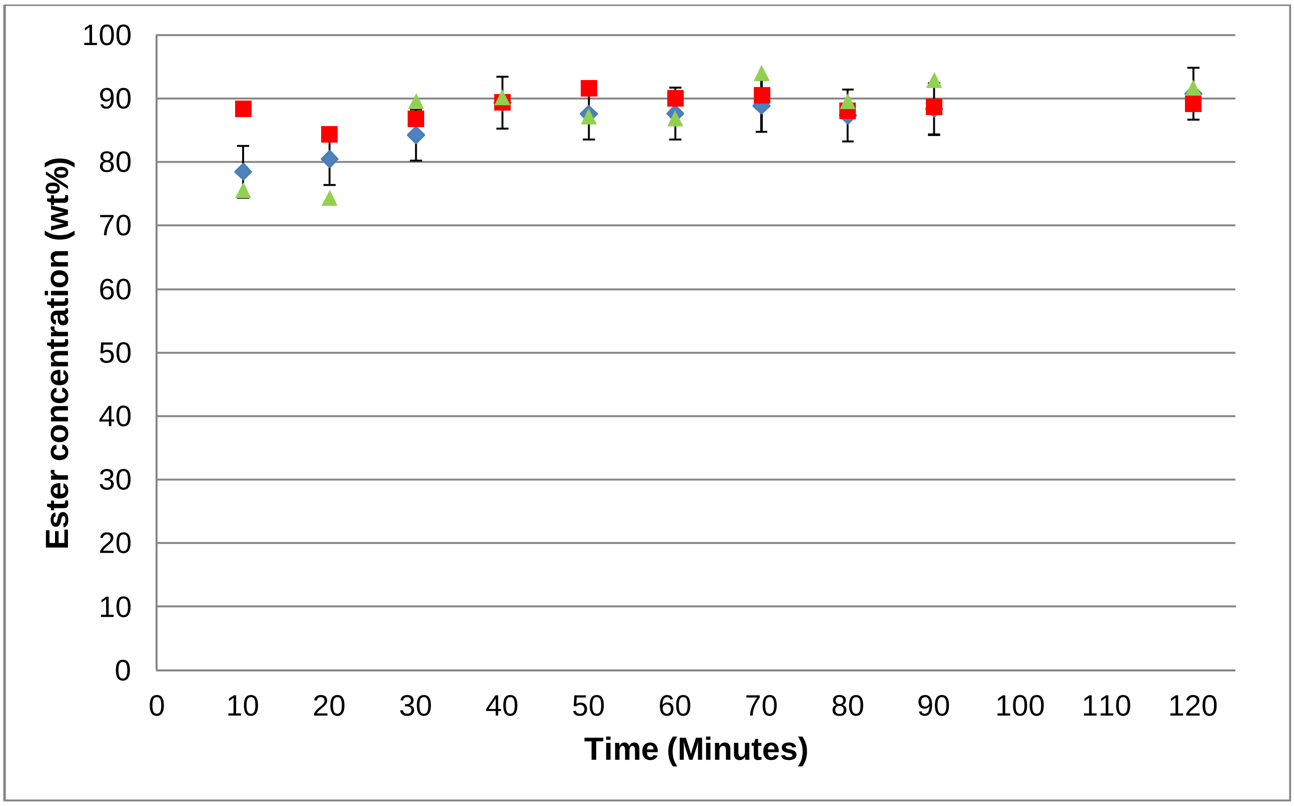


Figure 4.6: Influence of catalyst load on ester content with a reaction temperature of 55°C.
(Reaction temperature of 55°C and alcohol to oil molar ratio of 6:1; ◆ 0.8 wt%; ■ 1.0 wt%; and ▲ 1.2 wt%)

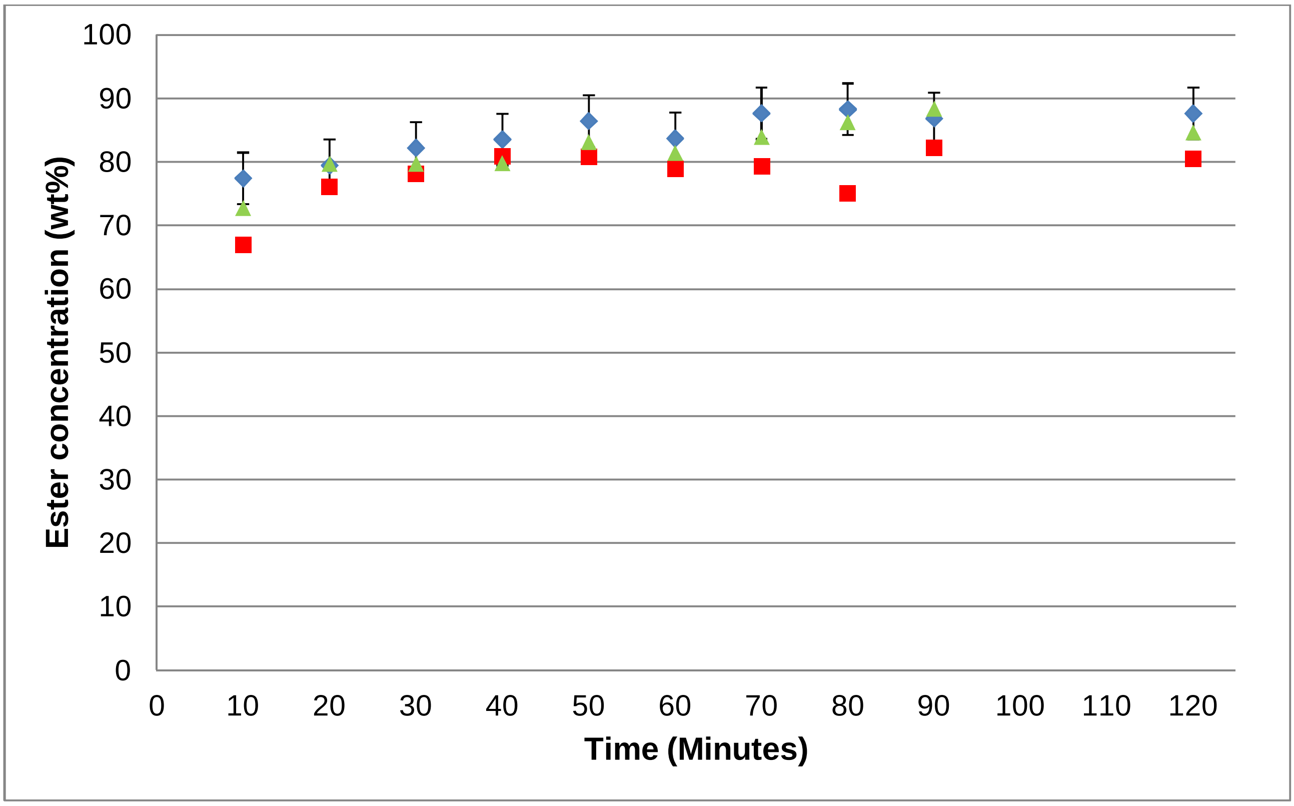


Figure 4.7: Influence of catalyst load on ester content with a reaction temperature of 65°C.
(Reaction temperature of 65°C and alcohol to oil molar ratio of 6:1; ◆ 0.8 wt%; ■ 1.0 wt%; and ▲ 1.2 wt%)

Figures 4.8 and 4.9 show the effect of different alcohol to oil molar ratios on the effectivity of the catalyst loads. There is no significant change in ester content over time with an increase in catalyst load. As explained above, the reaction temperature with the minimum amoutn of catalyst is sufficient to get the reaction over the activation energy threshold. The only noticable difference is the maximum ester content. There is a higher conversion of biodiesel for the 8:1 alcohol to oil molar ratio than the 3:1, which is expected.

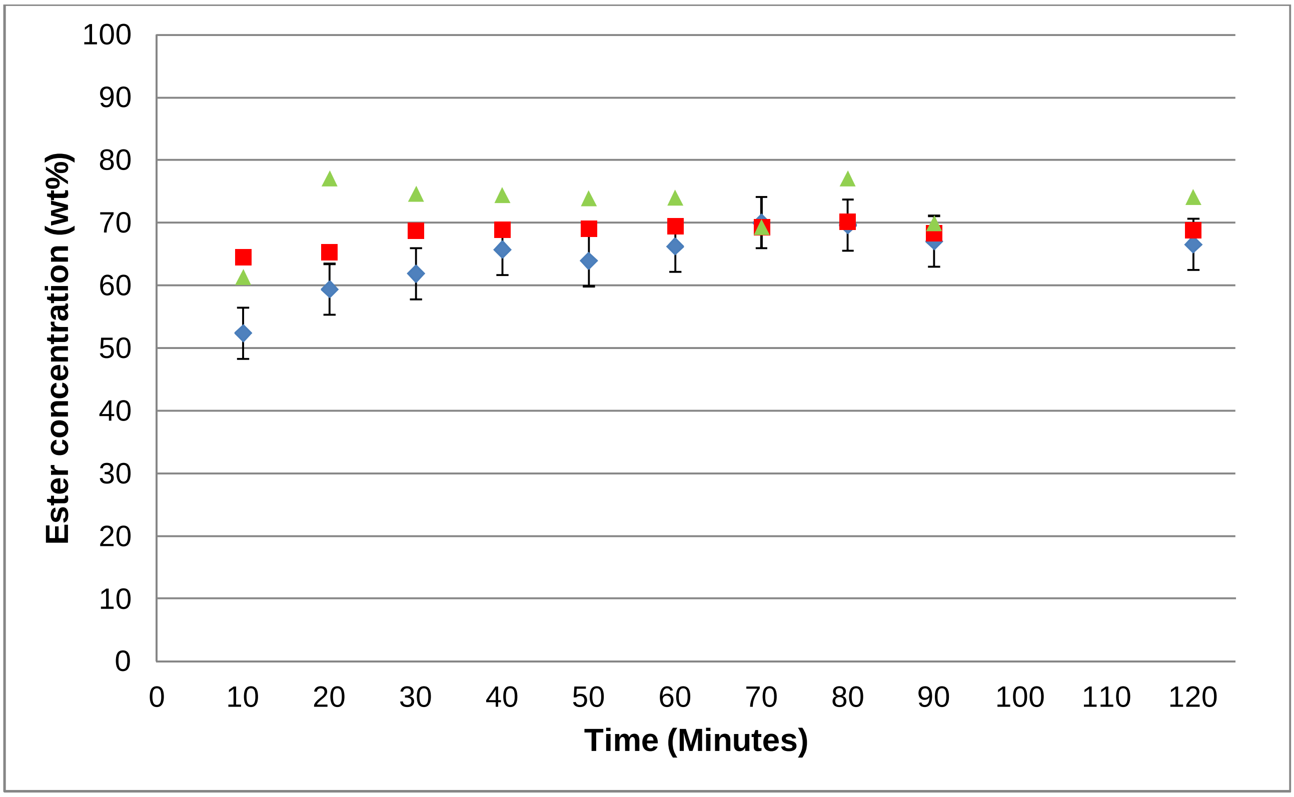


Figure 4.8: Influence of catalyst load on ester content with an alcohol to oil molar ratio of 3:1. (Reaction temperature of 55 °C and alcohol to oil molar ratio of 3:1 with catalyst load of ◆ 0.8 wt%; ■ 1.0 wt%; ▲ 1.2 wt%)

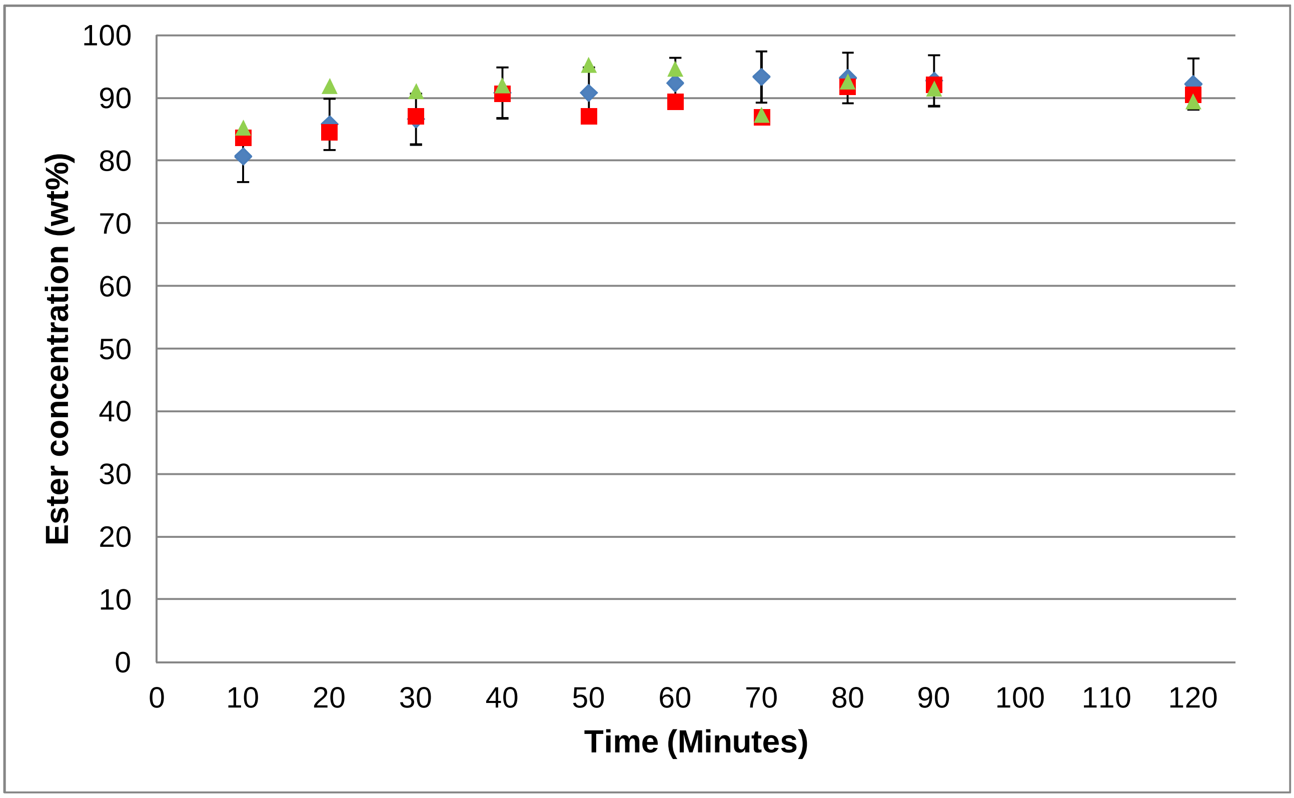


Figure 4.9: Influence of catalyst load on ester content with an alcohol to oil molar ratio of 8:1. (Reaction temperature of 55 °C and alcohol to oil molar ratio of 8:1 with catalyst load of ◆ 0.8 wt%; ■ 1.0 wt%; ▲ 1.2 wt%)

4.1.4. Influence of reaction time

The influence of reaction time on the ester content is discussed in this section. The effect of reaction time on ester concentration with a catalyst load of 0.8 wt% is given in Figures 4.10 and 4.11.

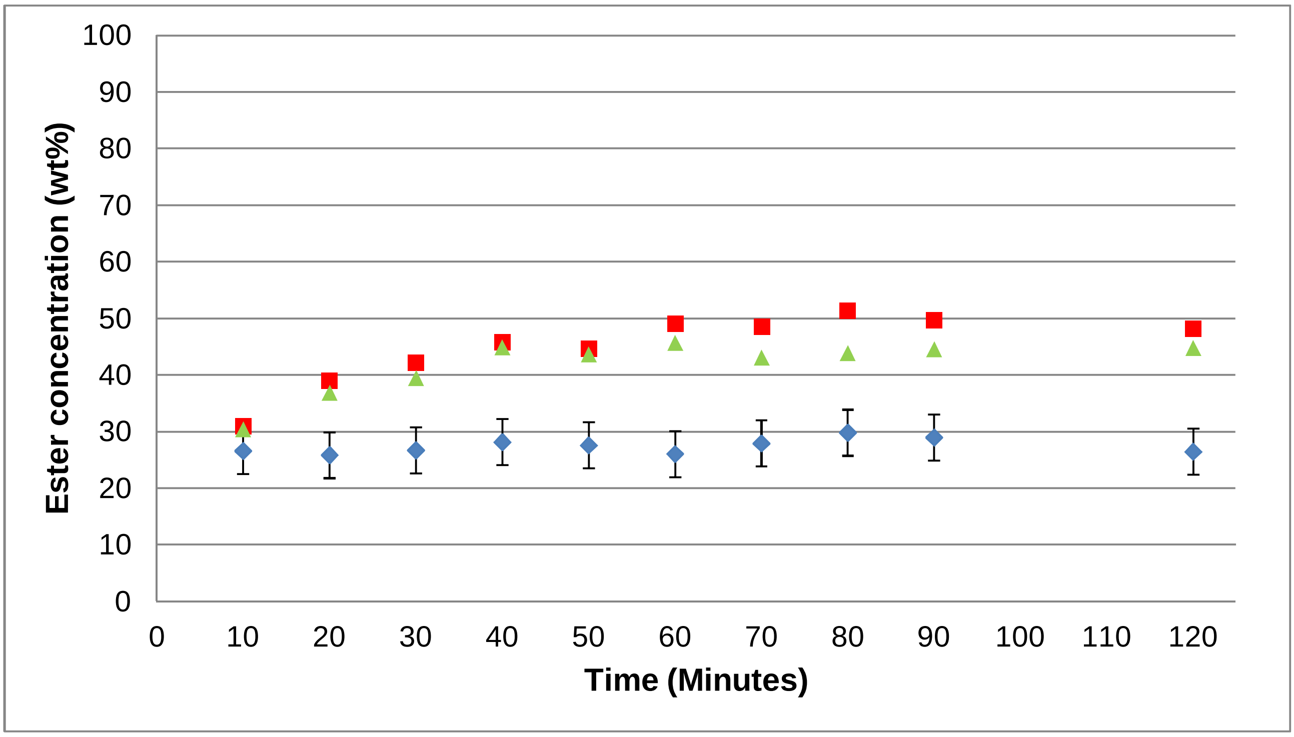


Figure 4.10: Influence of reaction time on ester content with a catalyst load of 0.8 wt%.
(Reaction temperature of 45 °C and a catalyst load of 0.8 wt% with alcohol to oil molar ratios of ◆ 3:1; ■ 6:1; ▲ 8:1)

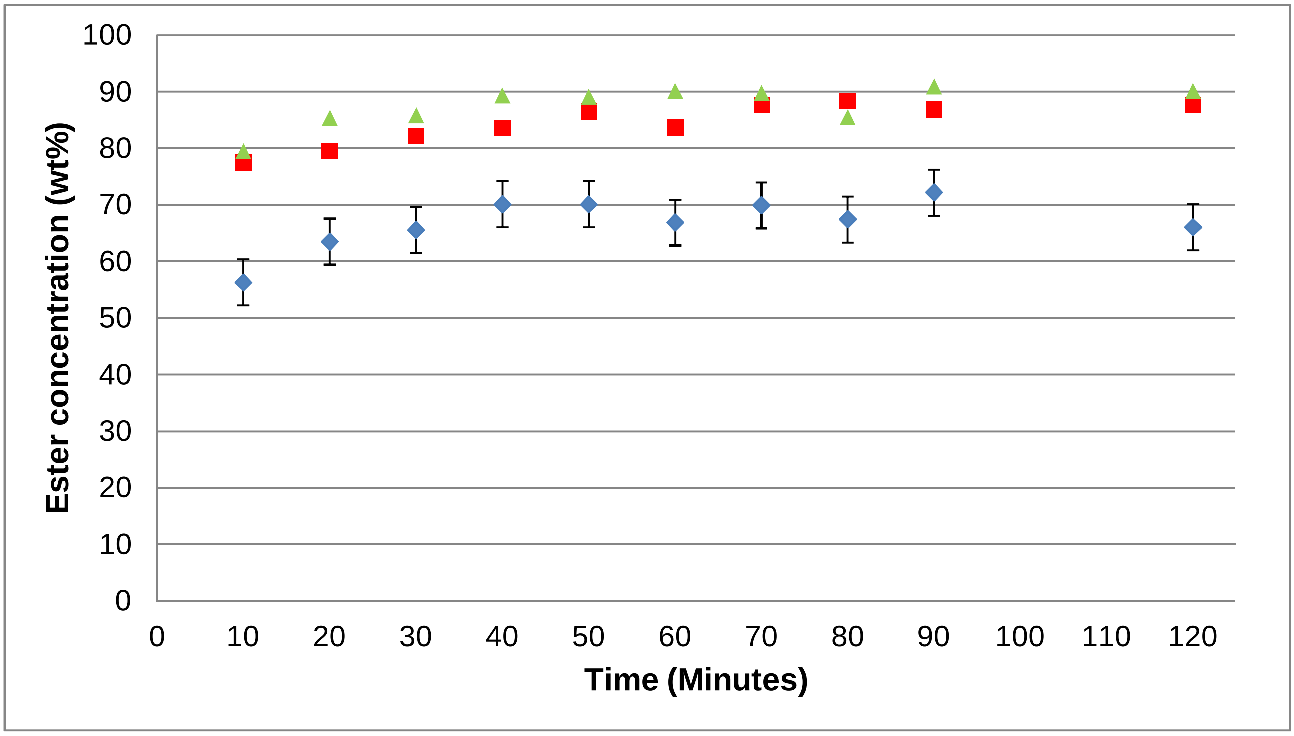


Figure 4.11: Influence of reaction time on ester content with a catalyst load of 0.8 wt%.
(Reaction temperature of 65 °C and a catalyst load of 0.8 wt% with alcohol to oil molar ratios of ◆ 3:1; ■ 6:1; ▲ 8:1)

There are very low yields at low temperatures and low catalyst load as seen in Figure 4.10. The time needed to reach equilibrium is also longer than with higher temperatures. This is expected since an increase in temperature increases the reactivity of the molecules. The reaction time should be in the range of 50 to 70 minutes to reach equilibrium for low catalyst loads and high alcohol to oil molar ratios.

The effect of reaction time on ester content and with a 1.2 wt% catalyst load is shown in Figures 4.12 and 4.13. The time needed for the reaction to reach equilibrium is decreased by the increase in catalyst. This is to be expected since the catalyst lowers the activation energy needed. The reaction time is decreased to less than 30 minutes for higher catalyst loads with higher alcohol to oil molar ratios.

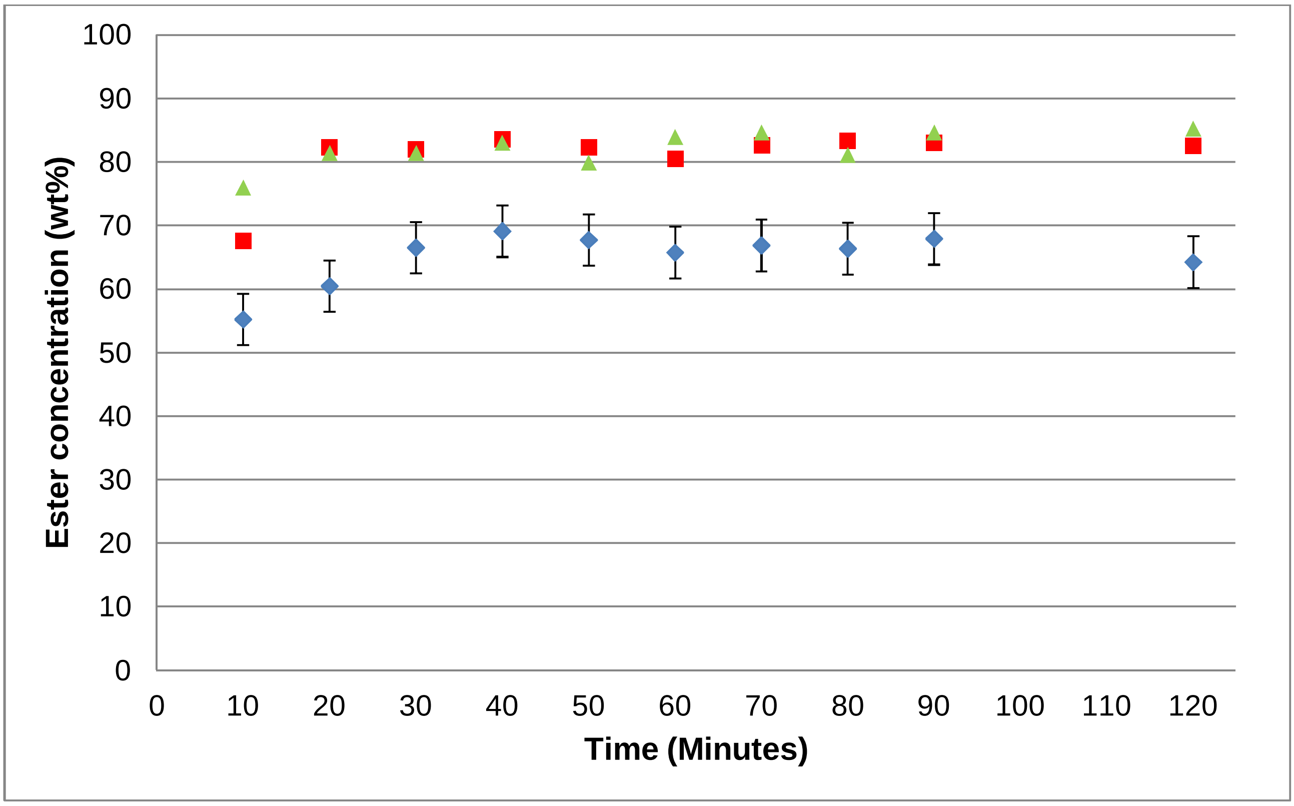


Figure 4.12: Influence of reaction time on ester content with a catalyst load of 1.2 wt%.
(Reaction temperature of 45 °C and a catalyst load of 1.2 wt% with alcohol to oil molar ratios of ◆ 3:1; ■ 6:1; ▲ 8:1)

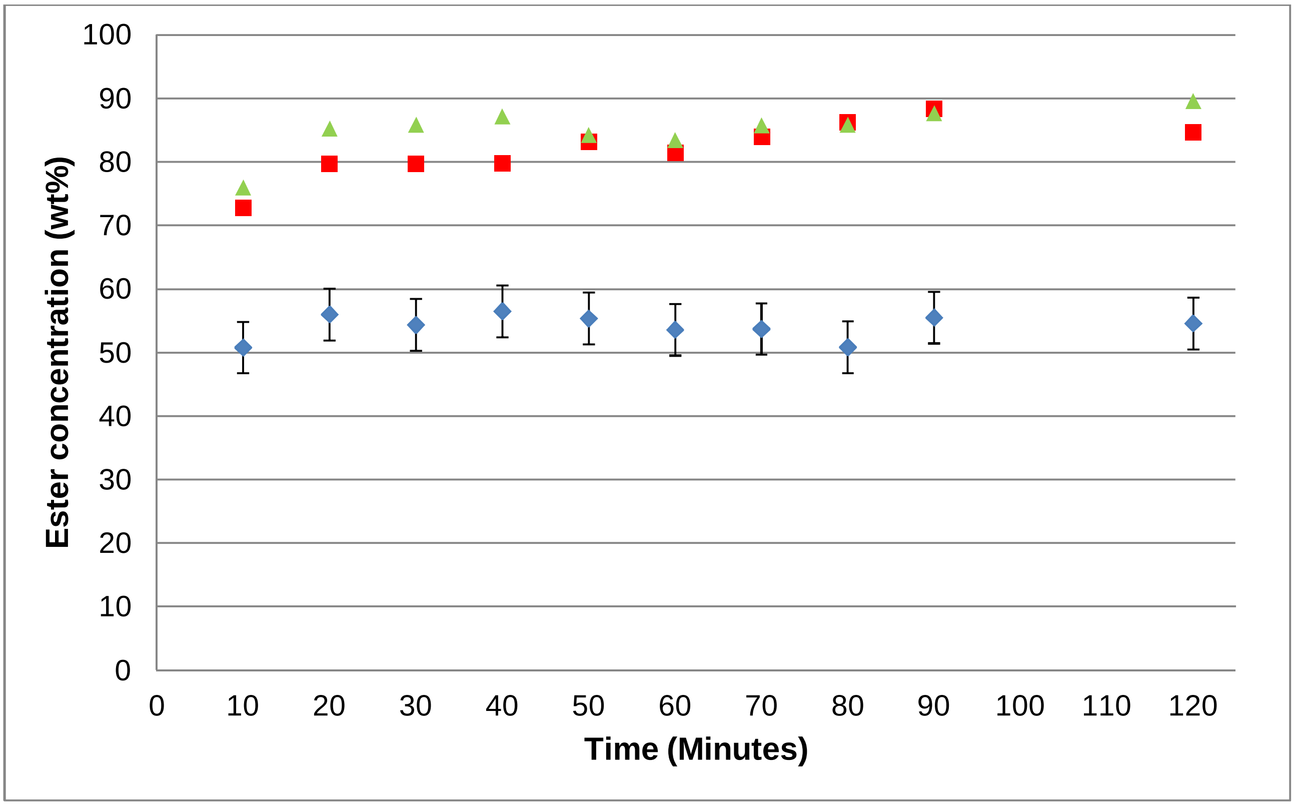


Figure 4.13: Influence of reaction time on ester content with a catalyst load of 1.2 wt%. (Reaction temperature of 65 °C and a catalyst load of 1.2 wt% with alcohol to oil molar ratios of ◆ 3:1; 🟥 6:1; ▲ 8:1)

The optimal reaction conditions for biodiesel production with the alkali-catalysed transesterification reaction are, a reaction temperature of 50 °C, an alcohol to oil molar ratio of 6:1 and a catalyst load of 1.0 wt% to 1.2 wt%. A reaction time of 60 to 90 minutes is needed to reach equilibrium and maximum conversion.

4.2 Purification

The different purification steps are compared in this section. Section 4.2.1 will discuss the effect of washing the biodiesel with water. The effect of dry washing with Magnesol® D-SOL™ will be discussed in Section 4.2.2 and in Section 4.2.3 the effect of dry washing with Purolite® PD-206 will be discussed. The purification processes were carried out on biodiesel produced at the optimal parameters as stated in Section 4.1.

4.2.1 Water washing

The process of water washing, as described in Section 3.3.2, is not the best method to clean biodiesel. The presence of water in the biodiesel layer can produce free fatty acids through the hydrolysis reaction. The drying process after washing is also subjecting the biodiesel to high temperatures for long periods of time (105 °C for 5 hours) in order to lower the water content to less than 500 ppm as specified by SANS 1935:2011. Water washing is also more time consuming because of the repetition needed to remove the methanol and catalyst. The separation is done in a separation funnel or a faster method is by centrifuge.

The acid value of the biodiesel after water washing decreased from 2.77 mg KOH/g to 0.67 mg KOH/g. After the drying process the water content decreased from 917 ppm to 520 ppm. This is not within the range of the SANS 1935:2011 requirements. Thus the drying time should be increased, which will drastically increase the production cost.

The ester content of the biodiesel after water washing was 96.16 ± 4.067 wt%.

The treatment of the waste water after washing is another concern. The waste water will contain unreacted methanol. The methanol should be removed before the water can be discarded. This will increase the production cost even further.

Water washing is not a very efficient process for the purification of biodiesel.

4.2.2 Dry washing with Magnesol® D-SOL™

The effect of dry washing with Magnesol® D-SOL™ on the water content, acid value and ester concentration is discussed in this section. The effect of Magnesol® D-SOL™ on the water content of the biodiesel layer is shown in Figure 4.14. There is a decrease in water content with an increase in time. An increase in the concentration of Magnesol® D-SOL™ results in an increase in water content. This is consistent with the results of Faccini *et al.* (2011:562). There is an experimental error of 2.834% with the water content analysis.

Magnesol® D-SOL™ should be used at a concentration of 0.5 wt% for 20 minutes to reduce the water content of the biodiesel to below the requirement of SANS 1935:2011.

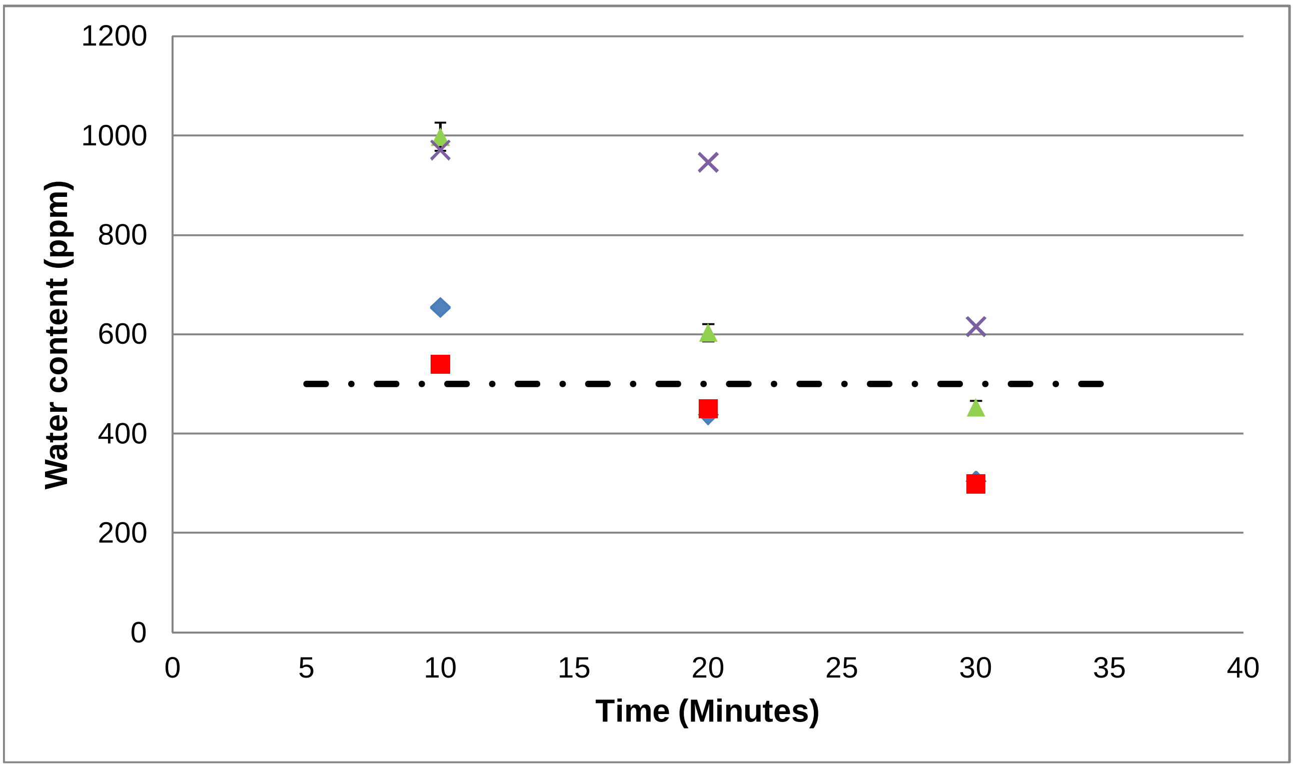


Figure 4.14: The effect of Magnesol® D-SOL™ on the water content of biodiesel.
(◆ 0.5 wt%; 🟥 1.0 wt%; ▲ 1.5 wt%; × 2.0 wt%; — • — SANS 1935:2011 maximum limit)

The effect of the concentration of Magnesol® D-SOL™ on the acid value of the biodiesel is presented in Figure 4.15. The acid value is decreased from 2.78 mg KOH/g to 0.13 mg KOH/g with a concentration of 0.5 wt%. The acid value for every concentration of Magnesol® D-SOL™ is within the requirements of SANS 1935:2011.

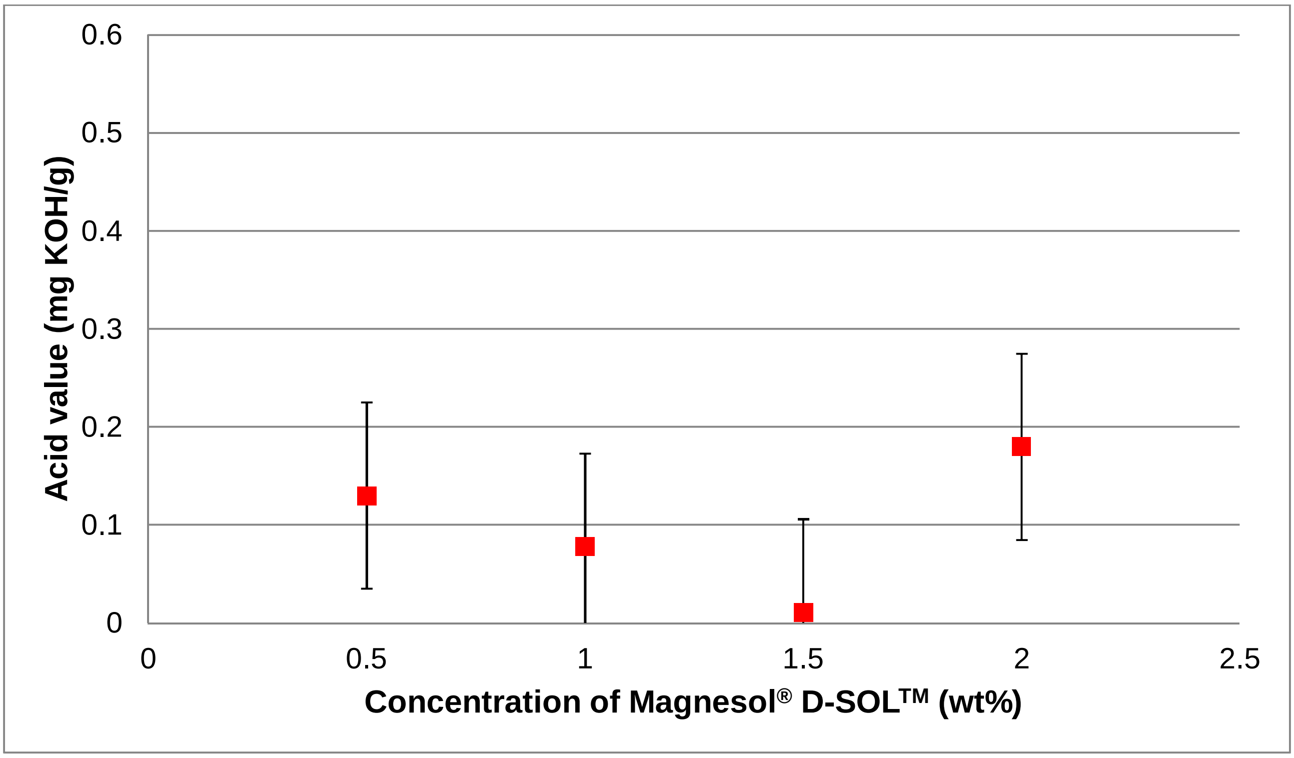


Figure 4.15: The influence of concentration of Magnesol® D-SOL™ on the acid value.
(30 minutes of purification; 🟥 Magnesol® D-SOL™; — • — SANS 1935:2011 maximum limit)

The effect of Magnesol® D-SOL™ concentration on ester content is displayed in Figure 4.16. The ester content before purification was 86.74 ± 4.07 wt%. There is very little change with an increase in time above 10 minutes. The highest ester concentration of 99.94 ± 4.07 wt% is achieved with a Magnesol® D-SOL™ concentration of 2.0 wt% and 30 minute washing time.

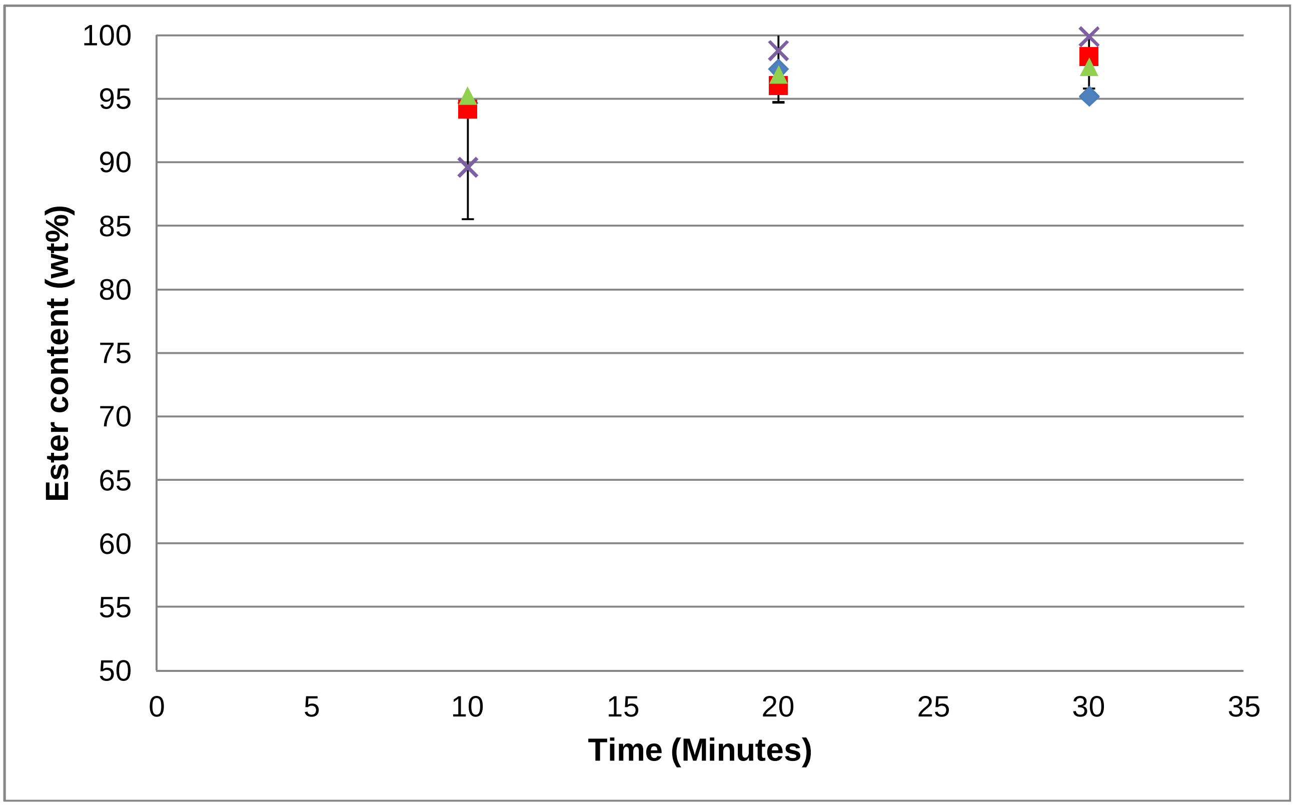


Figure 4.16: The influence of Magnesol® D-SOL™ on the ester content of biodiesel.
(◆ 0.5 wt%; ■ 1.0 wt%; ▲ 1.5 wt%; × 2.0 wt%; ▬ • ▬ SANS 1935:2011 minimum limit)

4.2.3 Dry washing with Purolite® PD-206

The influence of Purolite® PD-206 on the water content, acid value and ester concentration of the biodiesel is discussed in this section. The effect of the concentration of Purolite® PD-206 with a change in time on the water content of the biodiesel is shown in Figure 4.17. There is a decrease in water content with an increase in time for 0.5 wt%, 1.0 wt% and 1.5 wt%. Time has no effect on water content at a concentration of 2.0 wt%. The water content increases with an increase in Purolite® PD-206 concentration. This is not consistent with the results of Faccini *et al.* (2011:562). Purolite® PD-206 reduces the water content to 255 ppm while Magnesol® D-SOL™ only reduces the water content to 300 ppm. Purolite® PD-206 is the best dry washing resin for biodiesel in terms of water content.

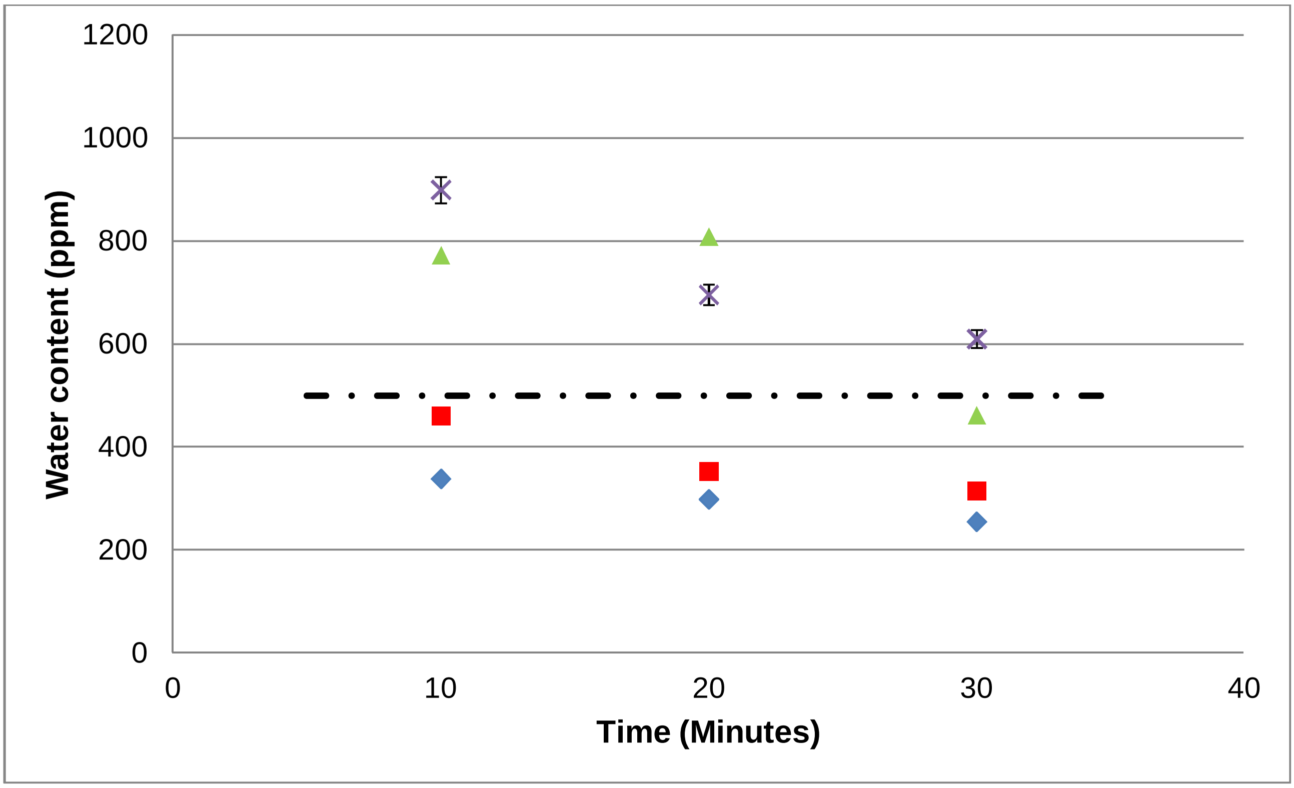


Figure 4.17: Influence of Purolite® PD-206 on the water content of biodiesel.
(◆ 0.5 wt%; ■ 1.0 wt%; ▲ 1.5 wt%; × 2.0 wt%; ▬ • ▬ SANS 1935:2011 maximum limit)

The effect of Purolite® PD-206 concentration on acid value is shown in Figure 4.18. The acid value decreases with an increase in Purolite® PD-206. An acid value of 0.67 mg KOH/g is achieved at a concentration of 2.0 wt%. This is not below the required value of 0.5 mg KOH/g as specified by SANS 1935:2011.

Magnesol® D-SOL™ is the best dry washing resin in terms of acid value of biodiesel.

The effect of Purolite® PD-206 concentration and time on the ester content of biodiesel is shown in Figure 4.19. The ester content before purification was 86.74 ± 4.07 wt%. There is an increase in ester content with an increase in Purolite® PD-206 concentration and time up to 20 minutes. The highest ester content of 99.45 ± 4.07 wt% is achieved at a concentration of 2.0 wt% and 20 minutes washing time.

The mass yield after purification was 87%. The loss of 13% was due to the washing and separation processes. The mass yield could be improved if the purification process is improved.

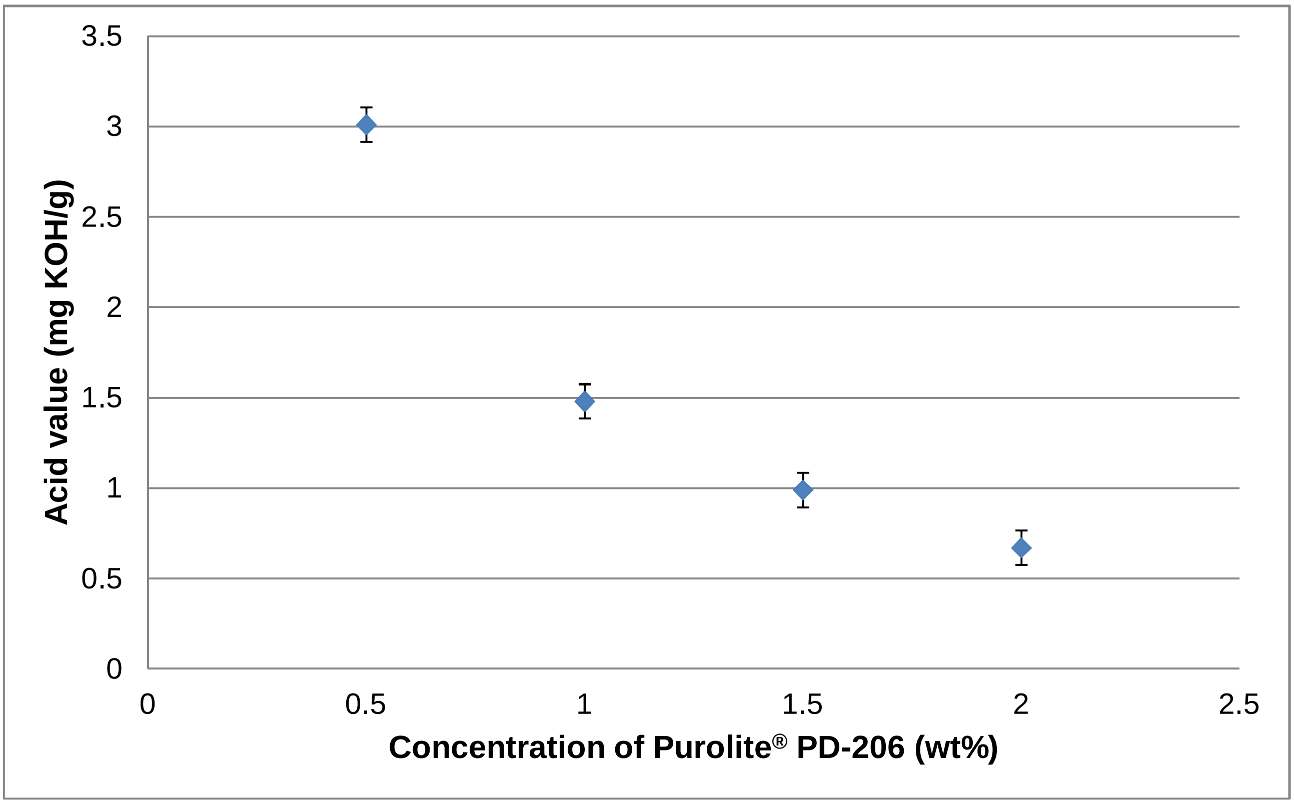


Figure 4.18: The influence of Purolite® PD-206 on the acid value.
(30 minute washing process; ◆ Purolite® PD-206; ▬ • ▬ SANS 1935:2011 maximum limit)

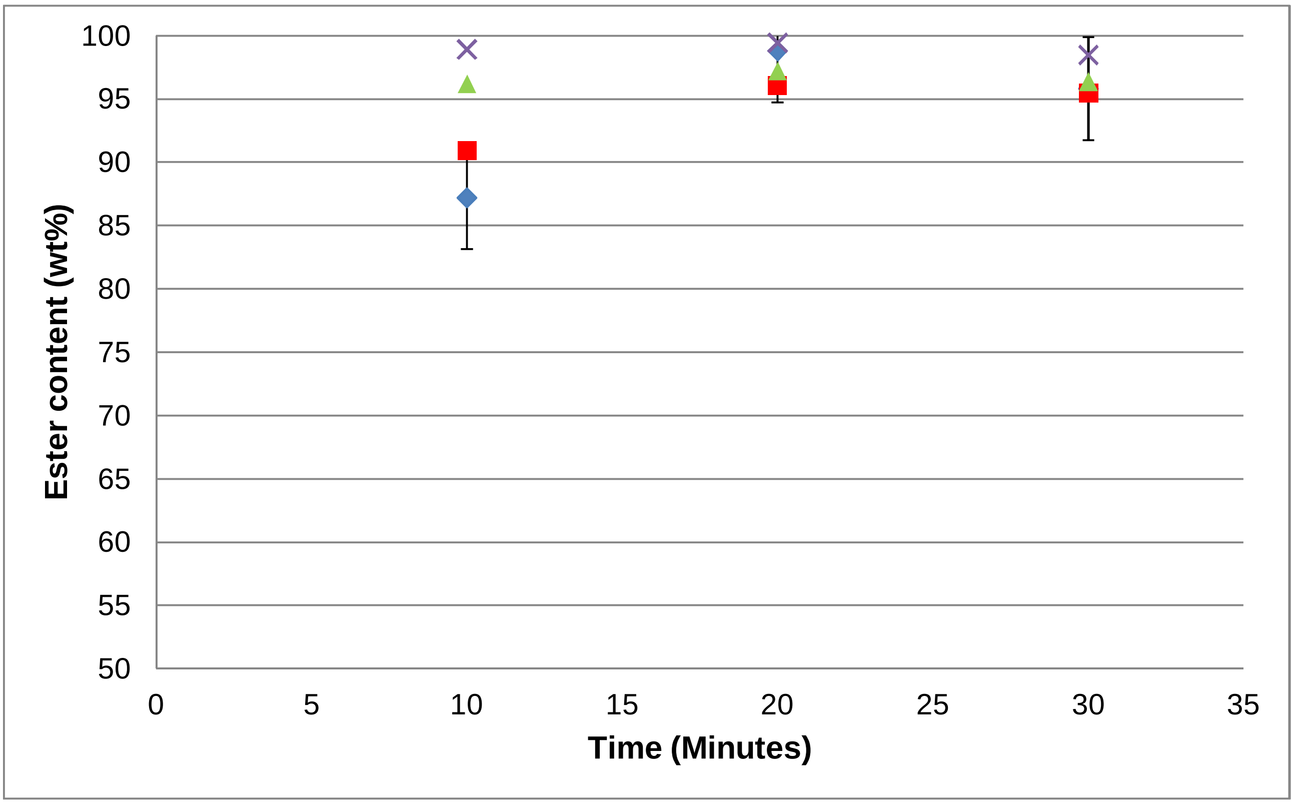


Figure 4.19: The influence of Purolite® PD-206 on the ester content of biodiesel.
(◆ 0.5 wt%; ■ 1.0 wt%; ▲ 1.5 wt%; × 2.0 wt%; ▬ • ▬ SANS 1935:2011 minimum limit)

4.3 Kinetic modelling

The second order reversible reaction (Equation 4.1 and Equation 4.2) was used to describe the reaction. This is a mechanism used by many in literature (Table 2.8). The irreversible first and second order (with respect to triglycerides) reaction was tested to describe the reaction kinetics. The results gave a very poor fit and the use of the irreversible reaction rate was abandoned. The poor fitting was due to the equilibrium phase that could not be taken into account.

$$TG + 3MeOH \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3FAME + G \qquad \textbf{Equation 4.1}$$

$$-r_{TG} = -\frac{dC_{TG}}{dt} = k_1 C_{TG} C_{MeOH} - k_2 C_{FAME} C_G \qquad \textbf{Equation 4.2}$$

Where r_{TG} is the rate of disappearance of triglycerides, k_1 is the reaction rate constant for the forward reaction, C_{TG} is the concentration of triglycerides, C_{MeOH} is the concentration of methanol, k_2 is the reaction rate constant of the reverse reaction, C_{FAME} is the concentration of the fatty acid methyl esters and C_G is the concentration of the glycerol.

The change of concentration over time was determined with the finite difference method (Fogler, 2006:258-259). Equations 4.3 to 4.5 are the equations used in the finite difference method.

$$\left(\frac{dC_A}{dt}\right)_{t_0} = \frac{-3C_{A0} + 4C_{A1} - C_{A2}}{2\Delta t} \qquad \textbf{Equation 4.3}$$

$$\left(\frac{dC_A}{dt}\right)_{t_i} = \frac{C_{A(i+1)} - C_{A(i-1)}}{2\Delta t} \qquad \textbf{Equation 4.4}$$

$$\left(\frac{dC_A}{dt}\right)_{t_f} = \frac{C_{A(f-2)} - 4C_{A(f-1)} + 3C_{Af}}{2\Delta t} \qquad \textbf{Equation 4.5}$$

The concentrations in Equation 4.2 were changed to conversion to give Equation 4.6.

$$-\frac{dX_{TG}}{dt} = k_1\left(C_{TG_0} - C_{TG_0}X_{TG}\right)\left(C_{MeOH_0} - MC_{TG_0}X_{TG}\right) - k_2\left(MC_{TG_0}X_{TG}\right)\left(C_{TG_0}X_{TG}\right) \qquad \textbf{Equation 4.6}$$

Where M is the stoichiometric ratio of methanol/fatty acid methyl esters to triglycerides and C_{A0} are the initial concentrations of the components.

Polymath 5.1 was used to determine the reaction rate constants by non-linear regression. The calculated values from the finite difference method were used with the conversion of triglycerides like in Equation 4.6. The model fitting can be seen in Figure 4.20.

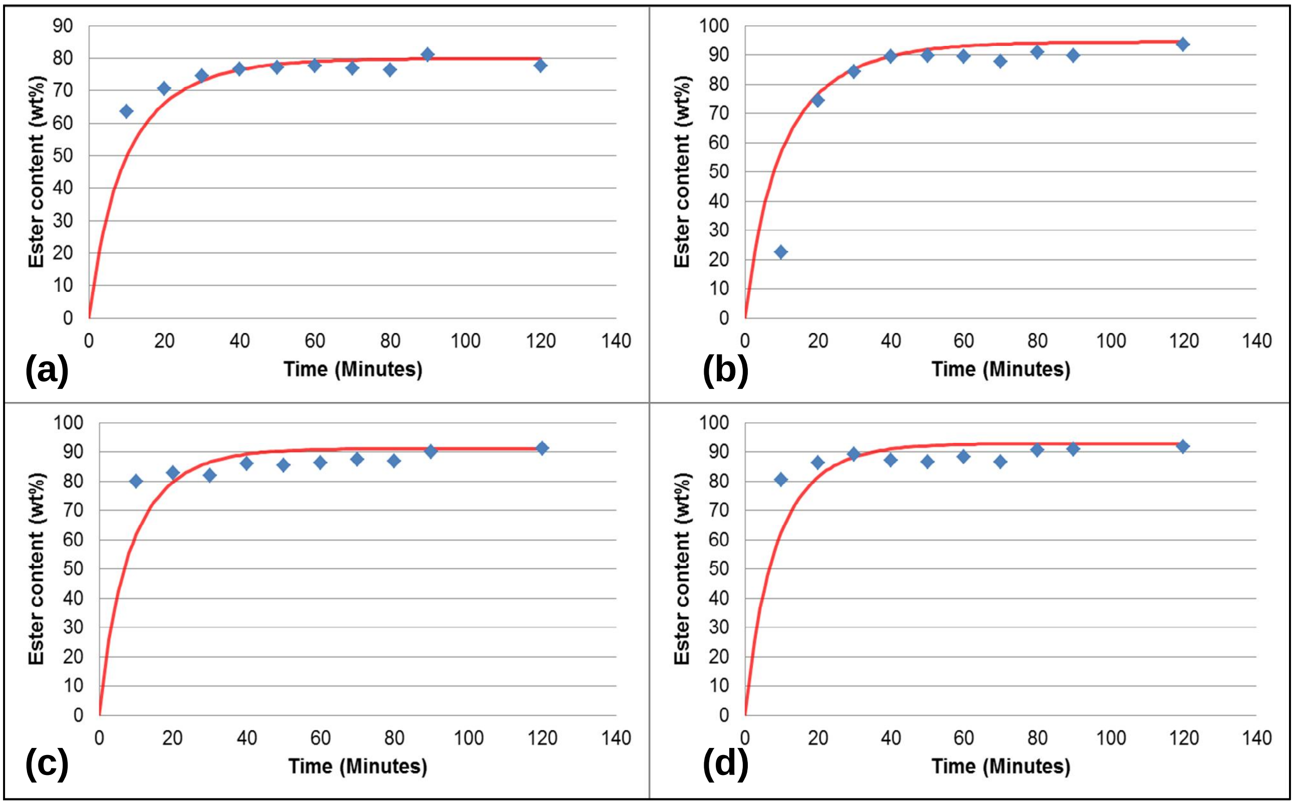


Figure 4.20: The comparison of ester content calculated by model and experimental values at 50°C.
((a) 4:1 alcohol to oil molar ratio and 0.8 wt% catalyst; (b) 6:1 alcohol to oil molar ratio and 1.0 wt%;
(c) 7:1 alcohol to oil molar ratio and 1.2 wt% catalyst; and (d) 8:1 alcohol to oil molar ratio and 1.2 wt% catalyst)

The activation energy for each k value for the forward reaction is illustrated in Figure 4.21. The forward reaction is exothermic as seen from the slope of Figure 4.21 which is consistent with literature (Table 2.8). The activation energy is also lowered by the addition of more catalyst, which is to be expected.

The activation energy from the k values for the reverse reactions is illustrated in Figure 4.22. The reverse reaction is endothermic as seen from the slope of Figure 4.22. This is not consistent with literature (Table 2.8). The endothermic characteristic of the reverse reaction is a good explanation for the decrease in ester content at higher temperatures. Thus the reverse reaction is favoured at higher temperatures. The decrease in methanol due evaporation is only visible above 60 °C and is very low. This is for an atmospheric pressure of 0.87 bar (North-West University, 2012).

The activation energy ranges from 9.478 to 26.937 kJ/mol for the forward reaction with a catalyst load of 1.2 wt% and from 74.161 to 136.433 kJ/mol for the reverse reaction. The activation energy for the forward reaction ranges from 73,080 to 92.867 kJ/mol and 223.729 to 313.438 kJ/mol for the reverse reaction with a catalyst load of 0.8 wt%. There is an increase in activation energy for both the forward and reverse reaction with a decrease in catalyst load. The calculations for the kinetic data can been in Appendix D.

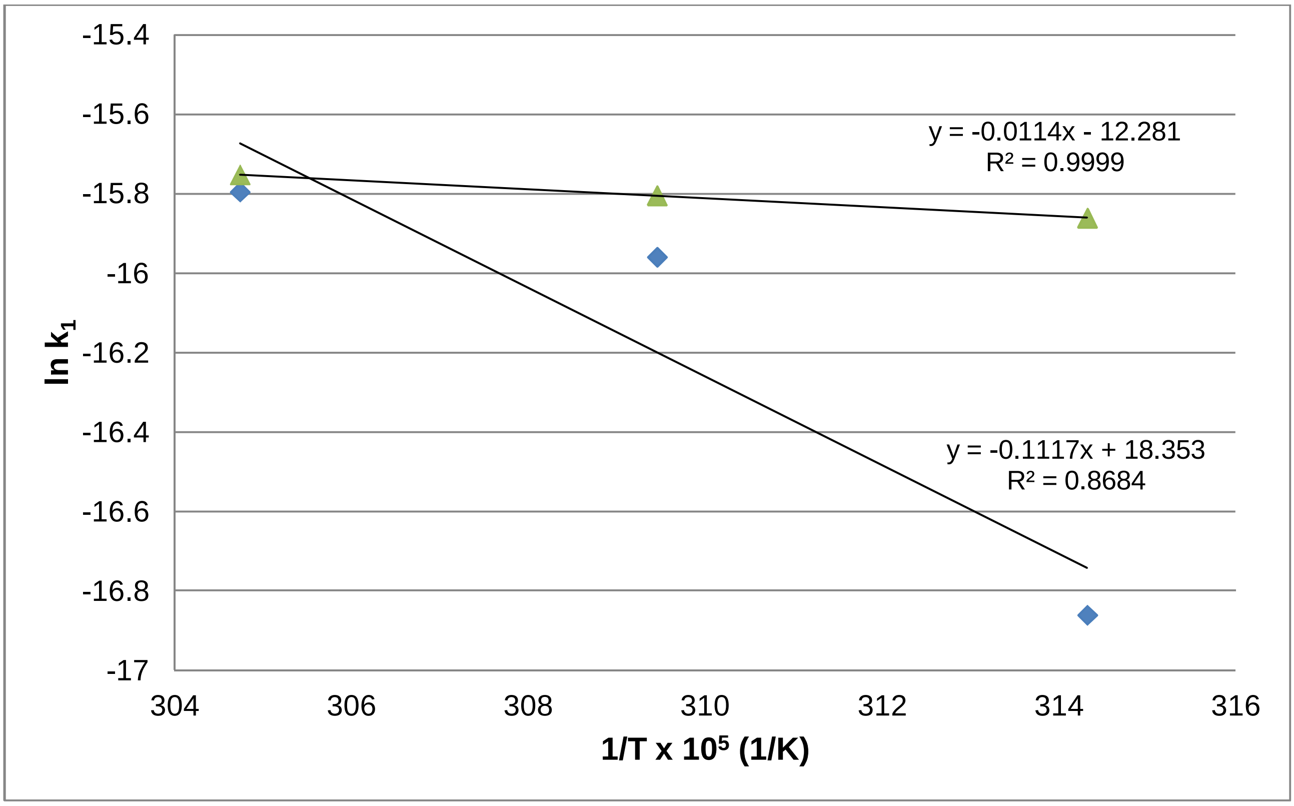


Figure 4.21: The Arrhenius plot for the forward k_1 value of the reversible second order reaction. (8:1 alcohol to oil molar ratio with ◆ 0.8 wt% and ▲ 1.2 wt%)

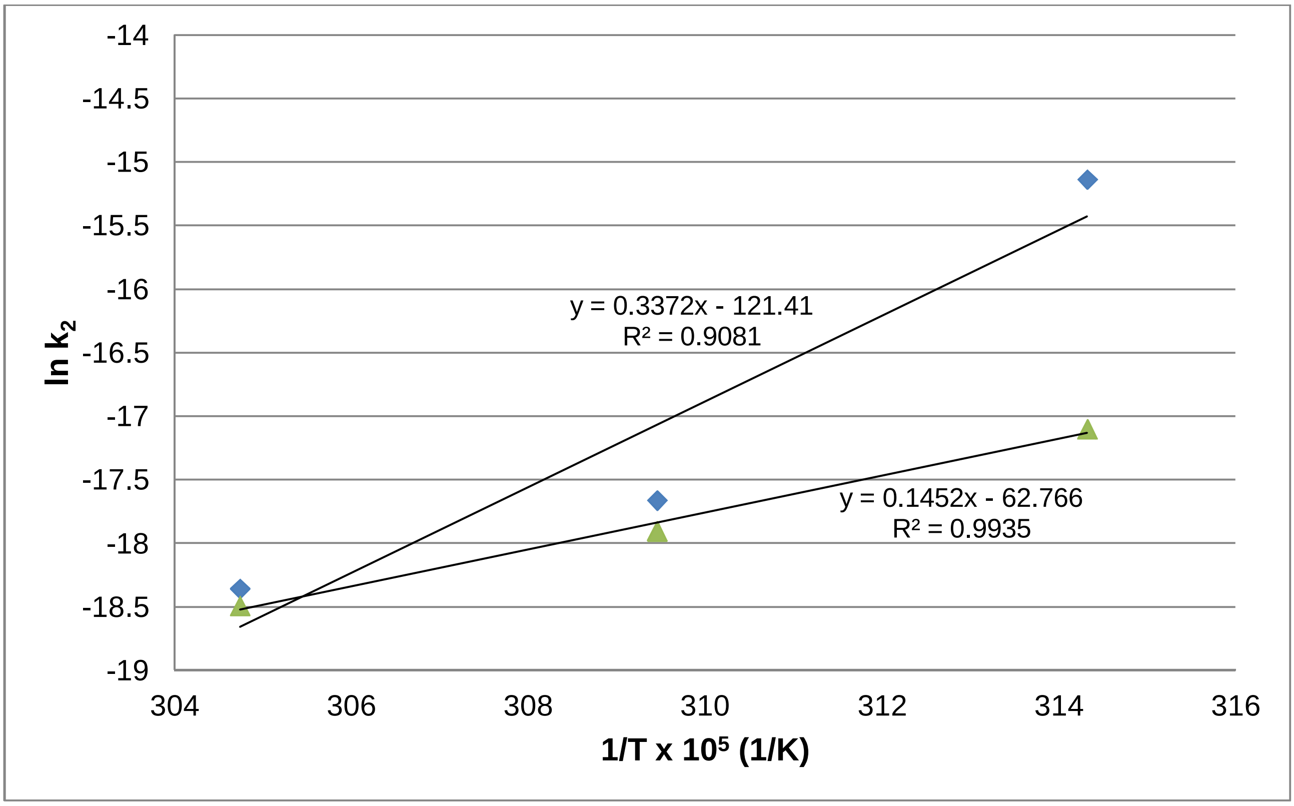


Figure 4.22: The Arrhenius plot for the reverse k_2 value of the reversible second order reaction. (8:1 alcohol to oil molar ratio with ◆ 0.8 wt% and ▲ 1.2 wt%)

Table 4.1: Reaction rate constants for the transesterification of butter waste. (Alcohol to oil molar ratio of 8:1 and catalyst load of 1.2 wt%)

Temperature (°C)	Forward reaction rate constant (dm^3/mol.min)	Reverse reaction rate constant (dm^3/mol.min)
45	1.29	0.374
50	1.37	0.168
55	1.44	0.0932

4.4 SANS 1935:2011 specifications

The SANS specification are discussed in this section. The results of all the specifications are discussed in Section 4.4.1. The results that do not meet the requirements are discussed in Section 4.4.2.

4.4.1 SANS 1935:2011 results

The results for the SANS 1935:2011 specifications are shown in Table 4.1. The results are for biodiesel produced at the optimal conditions as stated in Section 4.1; 50 °C, 6:1 methanol to oil molar ratio and 1.2 wt% catalyst. The purification was done with Magnesol® D-SOL™. The purification was done with 1.0 wt% Magnesol® D-SOL™ for 30 minutes. The results that do not meet the requirements of SANS 1935:2011 are displayed in bold in Table 4.2. These parameters will be discussed in the following section to develop a process to improve each parameter.

Table 4.2: The SANS 1935:2011 parameters of biodiesel produced from butter waste.

Property	**SANS 1935:2011**	**Result**
Ester content, wt%, min	96.5	96.16 ± 4.07
Density at 15 °C, kg/m^3	860 – 900	877.4
Kinematic viscosity at 40 °C, mm^2/s	3.5 – 5.0	4.2
Flash point, °C, min	**101**	**68**
Sulphur content, mg/kg, max	**10.0**	**50**
Carbon residue (on 10% distillation residue), wt%, max	**0.3**	**1.3**
Cetane number, min	51.0	68.8
Sulphated ash content, wt%, max	0.02	0.001
Water content, mg/kg, max	500	315
Total contamination, mg/kg, max	24	5
Copper strip corrosion (3h at 50 °C), rating, min	Class 1	Class 1
Oxidation stability, at 110 °C, h, min	**6**	**0.8**
Acid value, mg KOH/g, max	0.5	0.078
Iodine value, g of iodine/100 g of FAME, max	140	45
Linolenic acid methyl ester, wt%, max	12	1.328
Polyunsaturated (>= 4 double bonds) methyl ester, wt%, max	1	N/D
Methanol content, wt%, max	0.2	N/D
Monoglyceride content, wt%, max	0.8	N/A
Diglyceride content, wt%, max	0.2	N/A
Triglyceride content, wt%, max	0.2	N/A
Free glycerol, wt%, max	**0.02**	**0.04**
Total glycerol, wt%, max	**0.25**	**0.27**
Group I metals (total of Na and K), mg/kg, max	5.0	0
Group II metals (total of Ca and Mg), mg/kg, max	5.0	2
Phosphorous content, mg/kg, max	4	1
Cold filter plugging point		
Winter, °C, min	**-4**	**+8**
Summer, °C, min	**+3**	

4.4.2 SANS 1935:2011 parameter improvement

The parameters that do not conform to the standards of SANS 1935:2011 will be discussed in this section.

The parameters that will be discussed are as follows:

- Flash point
- Sulphur content
- Carbon residue
- Oxidation stability
- Free glycerol
- Total glycerol
- Cold filter plugging point

4.4.2.1 Flash point

The flash point can be described as the lowest temperature where enough combustible vapour is emitted to create a flame (Carrero & Perez, 2012:102-103). The average flash point of biodiesel is above 150 °C (Boog *et al.*, 2011:906; Kumar *et al.*, 2012:5). The flash point is usually lowered by unreacted methanol and can lower the flash point from 178 °C to 105 °C with the addition of 0.123 wt% methanol (Boog *et al.*, 2011:906).

The methanol content of the biodiesel was undetectable with GC analysis. The biodiesel produced from the butter waste has a broad range of esters. The biodiesel contains small amounts of short chain esters. The ester concentration and flash points of these short chain esters are presented in Table 4.3.

Table 4.3: The ester concentration and flash point of short chain esters in biodiesel from butter waste.

	Ester concentration (wt%)	Flash point (°C)	Reference
Methyl butyrate (C4)	1.680	14	Sigma-Aldrich, 2012a:4.
Methyl hexanoate (C6)	1.755	43	Sigma-Aldrich, 2012b:4.
Methyl octanoate (C8)	1.170	69	Sigma-Aldrich, 2012c:4.
Methanol	-	9.7	Sigma-Aldrich, 2012d:4.

The concentrations of these esters are higher than the concentration increase in methanol reported by Boog *et al.* (2011:906), which resulted in a decrease in flash point of 73 °C. Thus the shorter chain esters can be responsible for the low flash point.

A solution to the low flash point is to remove the short chain esters by distillation or to blend with mineral diesel.

A B10 and B20 blend of biodiesel in diesel gave a flash point of 52 °C and 55 °C, respectively. This is lower than specified by SANS 1935:2011 (SABS, 2011:6) but the B20 blend is above the minimum of 55 °C as specified by the SANS 342:2006 standard for diesel (SABS, 2006:7).

4.4.2.2 Sulphur content

The sulphur content of the biodiesel is above the maximum level, but is within the range of SANS 342:2006. Thus a blend of the biodiesel with a low sulphur content (50 ppm) diesel will be within specification. This might be a problem for future specification for biodiesel since the standard for sulphur content is decreasing.

4.4.2.3 Carbon residue

The carbon residue is an indication of the amount of impurities in the biodiesel that will be left behind after combustion of the fuel. The impurities may cause engine failures due to blockage of the fuel injectors (Carrero & Perez, 2012:104). The biodiesel can be filtered or blended with mineral diesel to lower the carbon residue.

4.4.2.4 Oxidation stability

The oxidation stability is an indication of the storage conditions needed for the biodiesel. The oxidation stability is measured by heating the biodiesel to 110 °C and aerating the sample. The air is then dissolved in water and the change in conductivity is measured. The oxidation stability induction period is determined when a sudden increase in conductivity is measured. Low oxidation stability increases the acid value and decreases the kinematic viscosity of the biodiesel (Carrero & Perez, 2012:101). The oxidation stability can be improved by the addition of antioxidants or by blending with mineral diesel, which contains antioxidants. Figure 4.23 illustrates the change in oxidation stability of biodiesel blends.
A biodiesel/diesel blend of up to 40 vol% can be used to improve the oxidation stability.

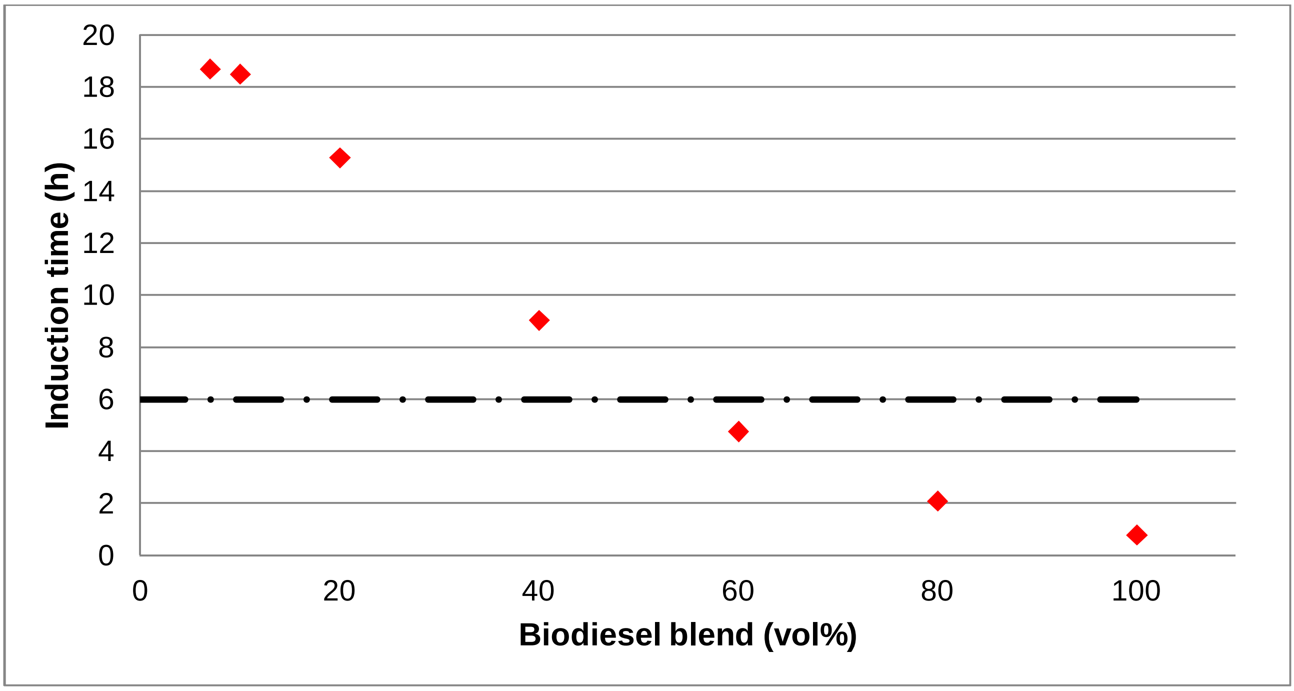


Figure 4.23: Influence of biodiesel/diesel blends on oxidation stability.
(▬ • ▬ SANS 1935:2011 minimum limit)

The use of commercial antioxidants increases the production cost of biodiesel. The essential oil with the highest anti-oxidative properties is clove bud oil (Teixeira *et al.*, 2013:594).

The effect of different clove bud oil concentrations on the oxidative stability is presented in Figure 4.24.

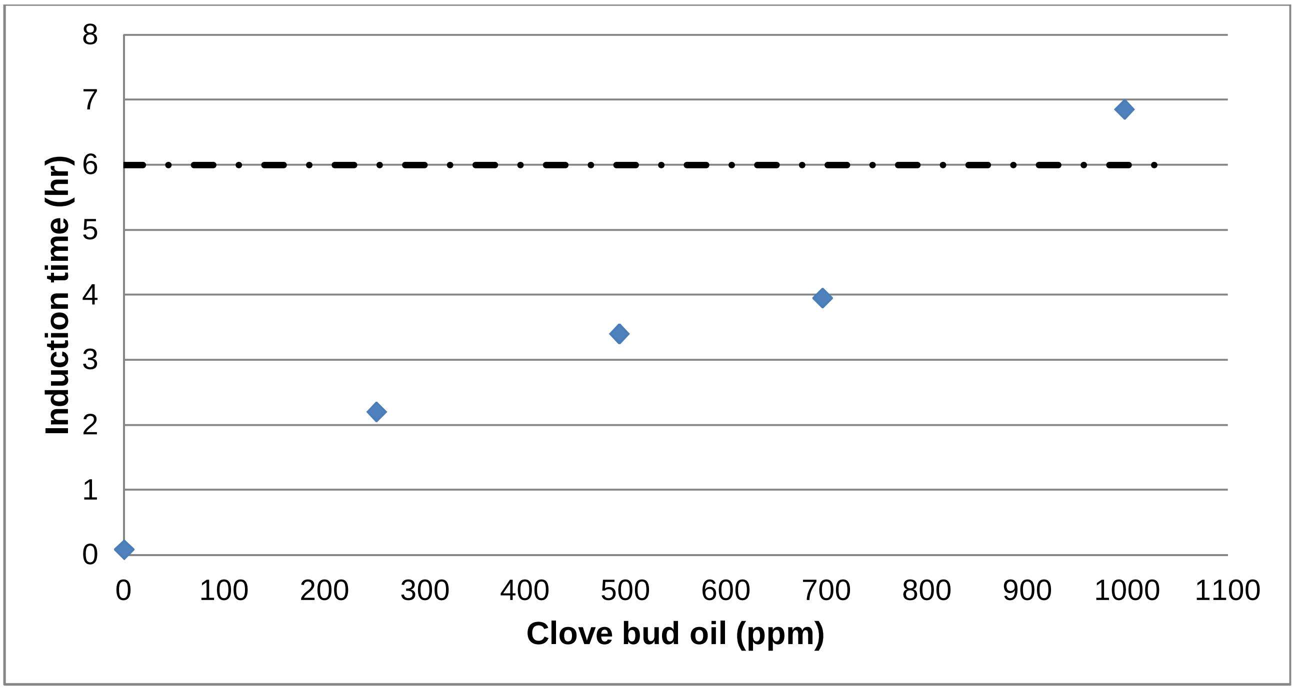


Figure 4.24: The effect of clove bud oil concentration of the oxidation stability.
(▬ • ▬ SANS 1935:2011 minimum limit)

The addition of a 1 000 ppm of clove bud oil improved the oxidative stability to meet the SANS 1935:2011 requirements. A very inexpensive essential oil can be used as an antioxidant.

4.4.2.5 Free and total glycerol

The use of dry washing resins like Magnesol® D-SOL™ and Purolite® PD-206 can decrease the glycerol content of the biodiesel (Berrios & Skelton, 2008:461-463).

This is due to the ability of the resins to remove free glycerol and glycerides. The free glycerol content of the biodiesel was reduced from 0.145 wt% to 0.04 wt% with 1.0 wt% Magnesol® D-SOL™ in 30 minutes and the total glycerol content was reduced from 0.87 wt% to 0.27 wt%. This is still not within the specifications of SANS 1935:2011 but can be reduced with further purification.

4.4.2.6 Cold filter plugging point

The cold filter plugging point is a temperature similar to the melting point of the biodiesel. The CFPP is determined by cooling the biodiesel until it is unable to flow through a filter within a specified time. This parameter determines the environmental conditions that the biodiesel can be used in. A biodiesel that does not meet the CFPP requirements will block fuel filters and pipelines (Carrero & Perez, 2012:104). The specific ester concentration is responsible for this parameter. An increase in unsaturated esters decreases the CFPP, while an increase in chain length of esters increases the CFPP. The ester concentrations and melting points of the long chain saturated and unsaturated esters are displayed in Table 4.4.

Table 4.4: The concentrations and melting points of various long chain esters in biodiesel from waste butter.

	Ester concentration (wt%)	Melting point (°C)	Reference
Methyl decanoate (C10:0)	2.577	-14 to -11	Sigma-Aldrich, 2012e:4.
Methyl laurate (C12:0)	3.157	4 to 5	Sigma-Aldrich, 2012f:4.
Methyl myristate (C14:0)	9.485	18	Sigma-Aldrich, 2012g:4.
Methyl palmitate (C16:0)	28.557	32 to 35	Sigma-Aldrich, 2012h:4.
Methyl palmitoleate (C16:1)	2.832	-0.5 to 0.5	Sigma-Aldrich, 2012i:4.
Methyl stearate (C18:0)	11.021	37 to 41	Sigma-Aldrich, 2012j:4.
Methyl linoleate (C18:2)	6.619	-35	Sigma-Aldrich, 2012k:4.

The ester composition and degree of unsaturation is a major factor in the CFPP. The biodiesel can be blended with mineral diesel in order to reduce the CFPP.

The CFPP was reduced from 8 °C to -5 °C and -9 °C with a biodiesel/diesel blend of B20 and B10, respectively, which is well within the range of SANS 1935:2011 and SANS 342:2006.

Chapter 5: Conclusions and recommendations

The conclusions of the study are discussed in this section. The objectives of the study are discussed in Section 5.1 and recommendations for further research in biodiesel production from waste butter are discussed in Section 5.2.

5.1 Conclusions

5.1.1 Main aim of the study

The main objective of the study was to determine whether the effluent from a butter factory can be used as an alternative feedstock for biodiesel production. This was done by determining the optimal reaction parameters for the alkali transesterification reaction, developing a kinetic model to describe the reaction conversion and analysing and improving the final product to meet the SANS 1935:2011 specifications.

5.1.2 Optimal reaction conditions

The optimal reaction conditions for the alkali transesterification of the butter waste were investigated. The optimal conditions were the point where the best yield at the lowest temperature, alcohol to oil molar ratio and catalyst load with the shortest reaction time was achieved. The optimal reaction conditions were found to be at a temperature of 50 °C, an alcohol to oil molar ratio of 6:1 and a catalyst load of 1.2 wt%. The time needed to reach equilibrium was 60 minutes at these conditions.
An increase in reaction temperature decreased the yield so a maximum point was determined. An increase in alcohol to oil molar ratio had no effect on the yield, therefore, from an economic point of view, the least amount of alcohol needed would be optimal. The shortest reaction time was achieved with a catalyst load of 1.2 wt%.

5.1.3 Reaction kinetics

A model for the prediction of the conversion of triglycerides was developed. The model was based on a second order reversible reaction. The model consisted of a single regime. The mass transfer regime was omitted since no effect of the mass transfer controlled reaction was observed. The activation energy of the forward reaction was consistent with reported values for activation energy. The reverse reaction was found to be endothermic, which has not been reported in the literature. This is an interesting observation, since it explains the effect of increasing reaction temperature on the ester content. The equilibrium shifts to the right with an increase in temperature due to the endothermic characteristic of the reverse reaction. The original explanation of the increasing vapour phase of the methanol is incorrect since the vapour phase of methanol is only detectible above 60 °C at the atmospheric pressure in Potchefstroom (0.87 bar).

5.1.4 SANS 1935:2011 specifications

The biodiesel produced from the effluent did not meet all the specifications of SANS 1935:2011. Possible solutions for the parameters that did not meet the requirements were investigated. The only solution that ensured that all the specifications were met was achieved by blending the biodiesel with mineral diesel.

5.2 Recommendations

The underlying reaction mechanism should be investigated to completely understand the reaction kinetics. The tri-, di- and monoglycerides should be analysed to develop a complete kinetic model. This should shed more light on the working of the exothermic and endothermic reaction characteristics.

The standards for biodiesel should be revised and adapted to incorporate biodiesel/diesel blends. This will ensure a uniform product, since there are no specifications for blends. The high standard for biodiesel is limiting the application thereof. More research is needed to improve the parameters of an ever-growing range of diverse biodiesel feedstocks.

Appendix A: Calibration

A.1 GC calibration

The gas chromatograph was used to determine the ester content of the biodiesel. The calibration of the GC will be discussed in this section. The retention times for all the FAME in Table 3.1 were determined and are presented in Table A.1. The internal standard for the calibration and analysis was chosen, based on the retention times of the esters.

Table A.1: Retention times of HP-88 column.

FAME	Retention time (Minutes)
Dichloromethane (Solvent)	5.553
Methyl butyrate (C4:0)	5.952
Methyl hexanoate (C6:0)	7.217
Methyl octanoate (C8:0)	9.611
Methyl nonanoate (C9:0)	11.127
Methyl decanoate (C10:0)	12.629
Methyl laurate (C12:0)	15.567
Methyl myristate (C14:0)	18.569
Methyl myristoleate (C14:1)	19.708 and 20.265 (cis and trans)
Methyl palmitate (C16:0)	22.390
Methyl palmitoleate (C16:1)	23.599
Methyl stearate (C18:0)	27.134
Methyl oleate (C18:1)	27.922 and 28.205 (cis and trans)
Methyl linoleate (C18:2)	29.813
Methyl linoleneate (C18:3)	32.188

Uneven carbon esters like methyl heptanoate, methyl heptadecanoate and methyl nonadecanoate were used as internal standard in many studies (Darnako & Cheryan, 2000:1264; Rattanaphra *et al.*, 2012:468; Shin *et al.*, 2012:135). The lack of uneven carbon esters in feedstock for biodiesel production is the reason for the choice of internal standard. Methyl nonanoate was chosen as internal standard for this study due to the retention time gap that is available between methyl octanoate and methyl decanoate.

The calibration curve was set up in order to calculate wt% values of esters in the sample. The calibration samples were prepared with a constant mass of internal standard and varying the mass of the esters. A peak is produced at the specific retention time for the various esters, and the GC software determines the peak area. The area is then used to quantify the esters. The samples are analysed three times to reduce the error of the calibration curves.

Tables A.2 to A.14 contain the mass and peak areas of the esters used in this study.

Table A.2: Methyl butyrate calibration curve samples and mass and area ratios.

Mass C4:0 (g)	Mass C9:0 (g)	Mass C4:0 / Mass C9:0	Area C4:0 (pA)	Area C9:0 (pA)	Area C4:0 / Area C9:0
0.009	0.018	1273.33	1257.00	3812.00	0.33
0.026	0.018	4068.67	4061.00	4030.00	1.01
0.045	0.018	6988.33	7022.00	3879.00	1.80
0.058	0.018	9123.33	9066.00	3869.00	2.34
0.072	0.018	10903.33	10870.00	4070.00	2.67

Table A.3: Methyl hexanoate calibration curve samples and mass and area ratios.

Mass C6:0 (g)	Mass C9:0 (g)	Mass C6:0 / Mass C9:0	Area C6:0 (pA)	Area C9:0 (pA)	Area C6:0 / Area C9:0
0.022	0.018	4271.00	4237.00	4282.00	0.99
0.03	0.019	5888.67	5840.00	4178.00	1.40
0.045	0.019	8541.67	8554.00	4316.00	1.98
0.058	0.019	11140.00	11050.00	4109.00	2.69
0.072	0.018	13910.00	13900.00	4197.00	3.32

Table A.4: Methyl octanoate calibration curve samples and mass and area ratios.

Mass C8:0 (g)	Mass C9:0 (g)	Mass C8:0 / Mass C9:0	Area C8:0 (pA)	Area C9:0 (pA)	Area C8:0 / Area C9:0
0.021	0.018	5248.33	5222.00	4347.00	1.20
0.031	0.018	6880.00	6880.00	4383.00	1.57
0.044	0.018	10024.33	10100.00	4268.00	2.36
0.058	0.018	12776.67	12810.00	4120.00	3.11
0.073	0.018	15393.33	15270.00	3947.00	3.87

Table A.5: Methyl decanoate calibration curve samples and mass and area ratios.

Mass C10:0 (g)	Mass C9:0 (g)	$\frac{\text{Mass C10:0}}{\text{Mass C9:0}}$	Area C10:0 (pA)	Area C9:0 (pA)	$\frac{\text{Area C10:0}}{\text{Area C9:0}}$
0.019	0.017	5409.67	5394.00	4485.00	1.20
0.031	0.019	7708.67	7625.00	4366.00	1.75
0.048	0.018	10790.00	10780.00	4322.00	2.49
0.058	0.017	13883.33	13910.00	3843.00	3.62
0.072	0.017	16463.33	16360.00	3748.00	4.36

Table A.6: Methyl laurate calibration curve samples and mass and area ratios.

Mass C12:0 (g)	Mass C9:0 (g)	$\frac{\text{Mass C12:0}}{\text{Mass C9:0}}$	Area C12:0 (pA)	Area C9:0 (pA)	$\frac{\text{Area C12:0}}{\text{Area C9:0}}$
0.023	0.018	5306.33	5253.00	3845.00	1.37
0.032	0.018	6663.67	6630.00	3603.00	1.84
0.044	0.018	9508.33	9458.00	3685.00	2.57
0.058	0.019	13260.00	13180.00	3895.00	3.38
0.072	0.018	16830.00	17110.00	4159.00	4.12

Table A.7: Methyl myristate calibration curve samples and mass and area ratios.

Mass C14:0 (g)	Mass C9:0 (g)	$\frac{\text{Mass C14:0}}{\text{Mass C9:0}}$	Area C14:0 (pA)	Area C9:0 (pA)	$\frac{\text{Area C14:0}}{\text{Area C9:0}}$
0.017	0.019	5997.67	5964.00	4399.00	1.36
0.032	0.019	8137.33	8135.00	4224.00	1.93
0.045	0.018	11556.67	11560.00	4232.00	2.74
0.059	0.019	14993.33	14990.00	4262.00	3.51
0.074	0.019	18576.67	18620.00	4099.00	4.54

Table A.8: Methyl myristoleate calibration curve samples and mass and area ratios

Mass C14:1 (g)	Mass C9:0 (g)	$\frac{\text{Mass C14:1}}{\text{Mass C9:0}}$	Area C14:1 (pA)	Area C9:0 (pA)	$\frac{\text{Area C14:1}}{\text{Area C9:0}}$
0.023	0.019	5514.67	5464.00	4118.00	1.32
0.03	0.019	8109.33	8141.00	4248.00	1.92
0.046	0.019	11680.00	11620.00	4173.00	2.80
0.061	0.019	14990.00	14990.00	4274.00	3.51
0.077	0.018	18310.00	18240.00	4101.00	4.44

Table A.9: Methyl palmitate calibration curve samples and mass and area ratios.

Mass C16:0 (g)	Mass C9:0 (g)	$\frac{\text{Mass C16:0}}{\text{Mass C9:0}}$	Area C16:0 (pA)	Area C9:0 (pA)	$\frac{\text{Area C16:0}}{\text{Area C9:0}}$
0.024	0.018	6661.67	6648.00	4525.00	1.48
0.028	0.018	7789.33	7748.00	4406.00	1.76
0.074	0.017	19753.33	19730.00	4214.00	4.66
0.009	0.017	2279.33	2280.00	4267.00	0.53
0.028	0.017	6748.00	6799.00	3802.00	1.79

Table A.10: Methyl palmitoleate calibration curve samples and mass and area ratios.

Mass C16:1 (g)	Mass C9:0 (g)	$\frac{\text{Mass C16:1}}{\text{Mass C9:0}}$	Area C16:1 (pA)	Area C9:0 (pA)	$\frac{\text{Area C16:1}}{\text{Area C9:0}}$
0.023	0.018	5608.00	5552.00	3834.00	1.44
0.032	0.019	7843.33	7948.00	4017.00	1.98
0.046	0.018	11333.33	11390.00	3619.00	3.14
0.061	0.019	14893.33	14950.00	3820.00	3.92
0.074	0.018	17716.67	17670.00	3821.00	4.63

Table A.11: Methyl stearate calibration curve samples and mass and area ratios.

Mass C18:0 (g)	Mass C9:0 (g)	$\frac{\text{Mass C18:0}}{\text{Mass C9:0}}$	Area C18:0 (pA)	Area C9:0 (pA)	$\frac{\text{Area C18:0}}{\text{Area C9:0}}$
0.021	0.019	5568.00	5542.00	4349.00	1.27
0.033	0.017	8991.00	8941.00	3940.00	2.28
0.06	0.018	15840.00	15730.00	3651.00	4.30
0.071	0.019	17516.67	17620.00	4023.00	4.38
0.083	0.018	20146.67	20120.00	3846.00	5.27

Table A.12: Methyl oleate calibration curve samples and mass and area ratios.

Mass C18:1 (g)	Mass C9:0 (g)	$\frac{\text{Mass C18:1}}{\text{Mass C9:0}}$	Area C18:1 (pA)	Area C9:0 (pA)	$\frac{\text{Area C18:1}}{\text{Area C9:0}}$
0.024	0.019	6615.33	6575.00	3997.00	1.65
0.033	0.019	8575.67	8561.00	4058.00	2.10
0.047	0.019	12333.33	12310.00	4118.00	2.98
0.061	0.02	15756.67	15760.00	3984.00	3.93
0.077	0.019	19230.00	19090.00	3913.00	4.92

Table A.13: Methyl linoleate calibration curve samples and mass and area ratios

Mass C18:2 (g)	Mass C9:0 (g)	$\frac{\text{Mass C18:2}}{\text{Mass C9:0}}$	Area C18:2 (pA)	Area C9:0 (pA)	$\frac{\text{Area C18:2}}{\text{Area C9:0}}$
0.023	0.019	6225.33	6157.00	4160.00	1.47
0.035	0.018	8999.00	8954.00	4103.00	2.18
0.047	0.018	12080.00	12120.00	4102.00	2.96
0.064	0.019	16460.00	16410.00	4151.00	3.96
0.08	0.018	19970.00	19900.00	4027.00	4.96

Table A.14: Methyl linolenate calibration curve samples and mass and area ratios.

Mass C18:3 (g)	Mass C9:0 (g)	$\frac{\text{Mass C18:3}}{\text{Mass C9:0}}$	Area C18:3 (pA)	Area C9:0 (pA)	$\frac{\text{Area C18:3}}{\text{Area C9:0}}$
0.017	0.018	6024.00	6015.00	4236.00	1.42
0.032	0.018	8896.33	8880.00	4190.00	2.12
0.046	0.019	12270.00	12220.00	4154.00	2.94
0.06	0.019	16026.67	15980.00	4210.00	3.79
0.075	0.019	19300.00	19020.00	4103.00	4.66

The calibration curves were calculated with Equation A.1.

$$\frac{m_i}{m_{C9:0}} = k_{ci}\frac{A_i}{A_{C9:0}}$$ **Equation A.1**

where m_i is the mass of the ester, $m_{C9:0}$ is the mass of the internal standard, k_{ci} is the calibration constant for the ester, A_i is the peak area of the ester and $A_{C9:0}$ is the peak area of the internal standard. The constant can be calculated as the slope of Equation A.1.

Figures A.1 and A.2 show the calibration curves of the esters.

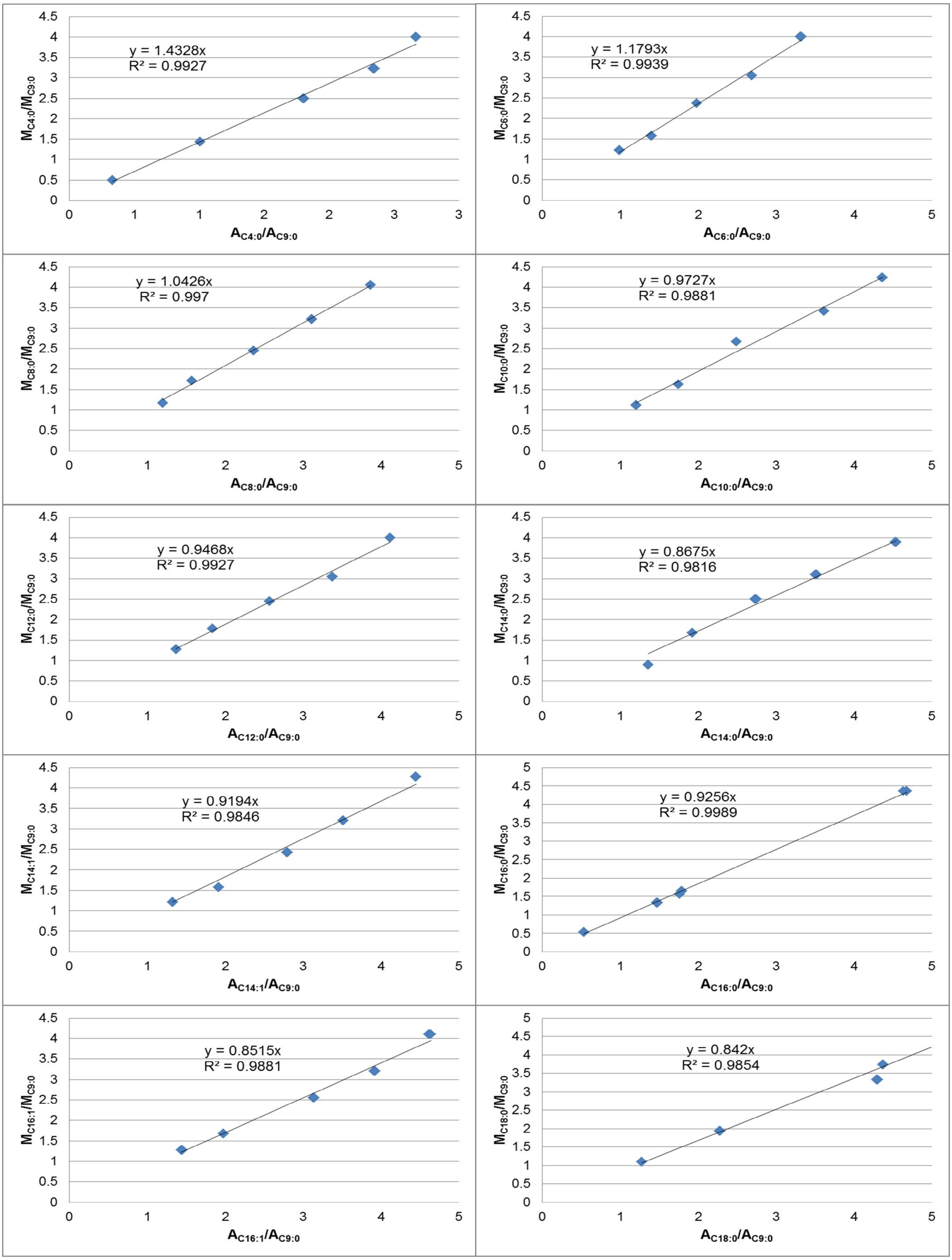


Figure A.1: Calibration curves for C4:0 to C18:0.

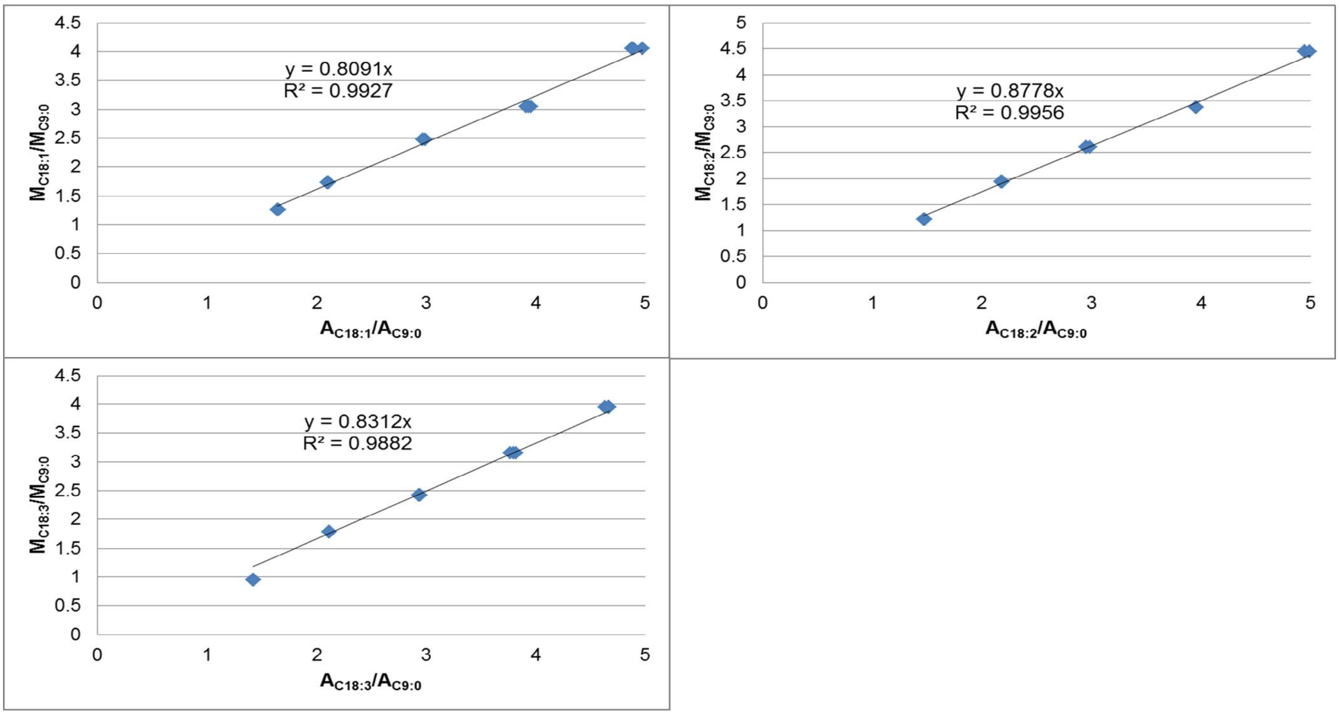


Figure A.2: Calibration curves for C18:1 to C18:3.

The calibration curve constants for the esters are presented in Table A.15.

Table A.15: Calibration constants for esters.

FAME	k_c-values
Methyl butyrate (C4:0)	1.4328
Methyl hexanoate (C6:0)	1.1793
Methyl octanoate (C8:0)	1.0426
Methyl decanoate (C10:0)	0.9727
Methyl laurate (C12:0)	0.9660
Methyl myristate (C14:0)	0.8675
Methyl myristoleate (C14:1)	0.9194
Methyl palmitate (C16:0)	0.9178
Methyl palmitoleate (C16:1)	0.8515
Methyl stearate (C18:0)	0.842
Methyl oleate (C18:1)	0.809
Methyl linoleate (C18:2)	0.8779
Methyl linoleneate (C18:3)	0.8313

A.2 FTIR calibration

The FTIR was calibrated to determine the ester content which will be used to verify the GC results. The calibration of the FTIR was done in a similar way to the GC calibration. The fatty acid concentration of the feedstock has an effect on the calibration of the FTIR. A feedstock that differs in fatty acid concentration will have different values when analysed with a FTIR. Thus a calibration curve is needed for every feedstock used.

The calibration was done with varying concentrations of biodiesel with oil. The biodiesel was prepared by using an excess of methanol to oil molar ratio, 10:1, and a catalyst load of 1.2 wt%. The reaction temperature was kept constant at 50 °C. The reaction was repeated three times in order to ensure that the biodiesel is free of glycerides. The standards were prepared by increasing the biodiesel to oil weight percentage from 50 wt% to 100 wt% with increments of 5 wt%. The increments were lowered to 1 wt% between 90 wt% and 100 wt% to ensure that the values closer to the SANS1935:2011 standard was correct.

The variance and squared correlation for the calibration curve are illustrated in Figures A.3 and A.4. The calibration was done with Shimadzu IRsolution 1.60. The peak height was evaluated to determine the calibration curve. The evaluation of the peak height was done for the wavenumber range of 1000 to 1500 cm^{-1}. This range gave the best linear fit. According to Figure A.3 and A.4 the range selected has a variance and a very good correlation.

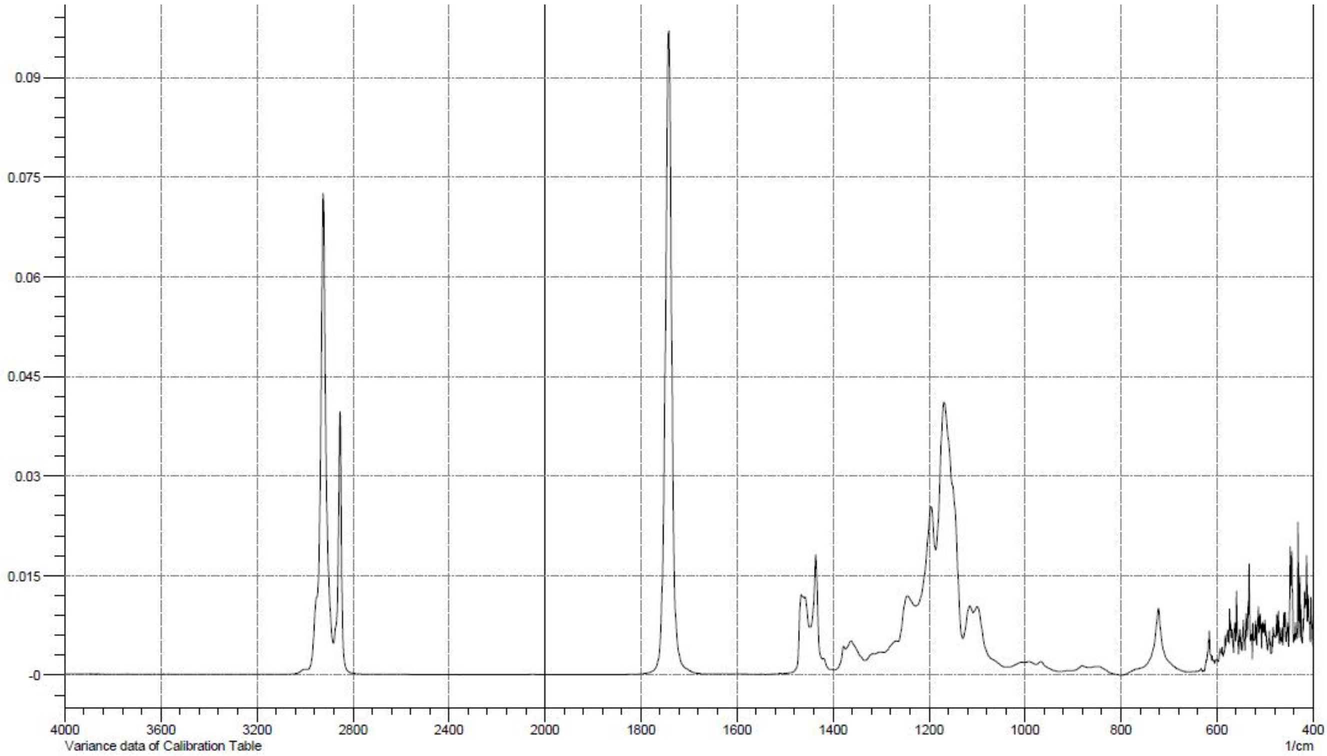


Figure A.3: The variance of the calibration data.
(x-axis: Wavenumber and y-axis: Variance)

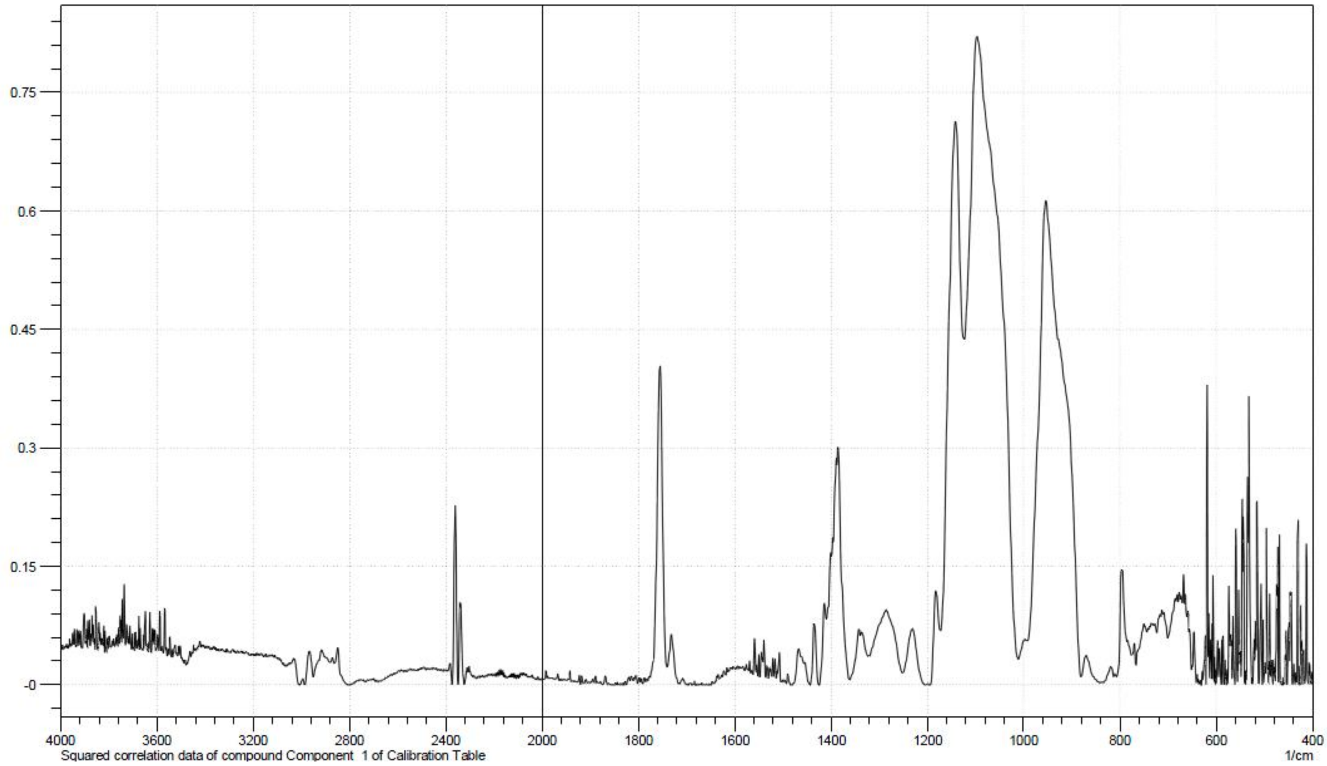


Figure A.4: Squared correlation of calibration data.
(x-axis: Wavenumber and y-axis: Squared correlation)

From Figures A.3 and A.4, it is clear that the region between 1000 and 1500 cm^{-1} should be used. The spectometry of the samples were determined and compared to the peak heights in the specified range of the calibration model. This is done by the software. The model has an R^2 value of 0.99.

Appendix B: Experimental error

B.1 Ester content

The experimental error for the ester content was determined by repeating an experiment three times and calculating the standard deviation. The experimental error was determined at the reaction temperature of 65 °C, an alcohol to oil molar ratio of 3:1 and a catalyst load of 0.8 wt%. Figure B.1 shows the GC data for the three experiments.

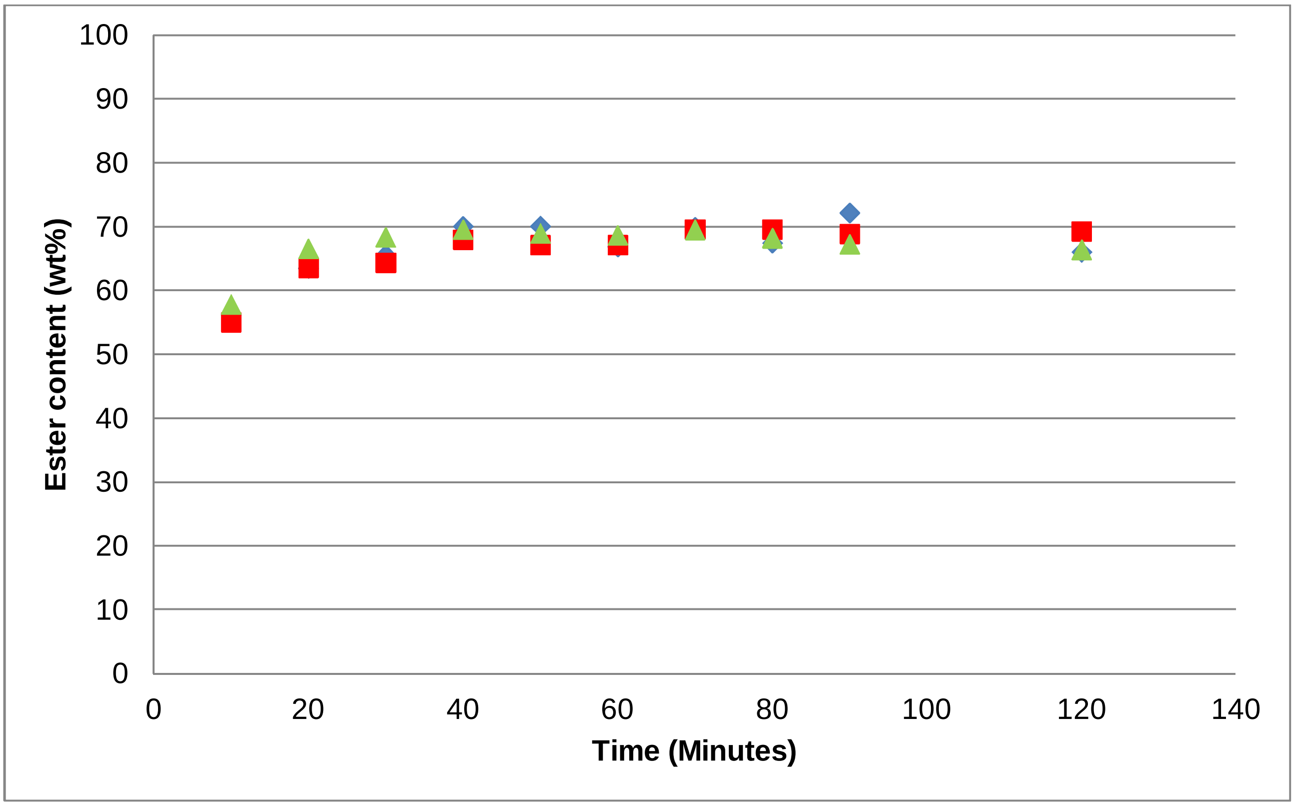


Figure B.1: Experimental error of ester content
(◆ Repeat 1, ■ Repeat 2, ▲ Repeat 3).

The experimental error is calculated by determining the average of the values measured for each of the repeated experiments. The average was calculated with Equation B.1.

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$$ **Equation B.1**

Where $\bar{x}$ is the average, N is the number of data points and x_i is the individual data points.

The standard deviation of the values is then determined. The calculation is done with Equation B.2.

$$\delta = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{(N-1)}}$$ **Equation B.2**

Where the standard deviation is represented by δ.

The experimental error is determined for a 95% conidence interval. The confidence interval has a 95% probability that the data lies within the range of the error. The confidence interval is calculated with the normal confidence interval function (CONFIDENCE.NORM(alpha,standard deviation, size)) in Excel®. Where alpha is 0.05 for a 95% confidence interval, the standard deviation is used as calculated with Equation B.2 and the size is equal to N and metioned above.

The experimental error is then calculated with Equation B.3.

$$Experimental\ error = 2 \times \frac{Confidence\ interval}{\bar{x}} \times 100\% \qquad \text{Equation B.3}$$

The ester content error calculations are presented in Table B.1.

Table B.1: Experimental error of the ester content

Time (Minutes)	Repeat 1	Repeat 2	Repeat 3	Average	Standard deviation	Experimental error (%)
10	56.274	55.053	57.835	56.387	1.394	5.596
20	63.499	63.566	66.530	64.532	1.731	6.070
30	65.549	64.384	68.342	66.092	2.034	6.966
40	70.090	67.993	69.539	69.207	1.087	3.556
50	70.097	67.132	68.944	68.724	1.495	4.923
60	66.880	67.157	68.675	67.571	0.966	3.236
70	69.939	69.579	69.525	69.681	0.225	0.732
80	67.445	69.584	68.216	68.415	1.084	3.584
90	72.195	68.903	67.295	69.464	2.498	**8.138**
120	66.033	69.284	66.396	67.238	1.781	5.995

The maximum error is used as the experimental error. The error for the ester content with GC analysis is 8.138%.

The GC results were also compared to the FTIR results. The comparison is shown in Figure B.2.

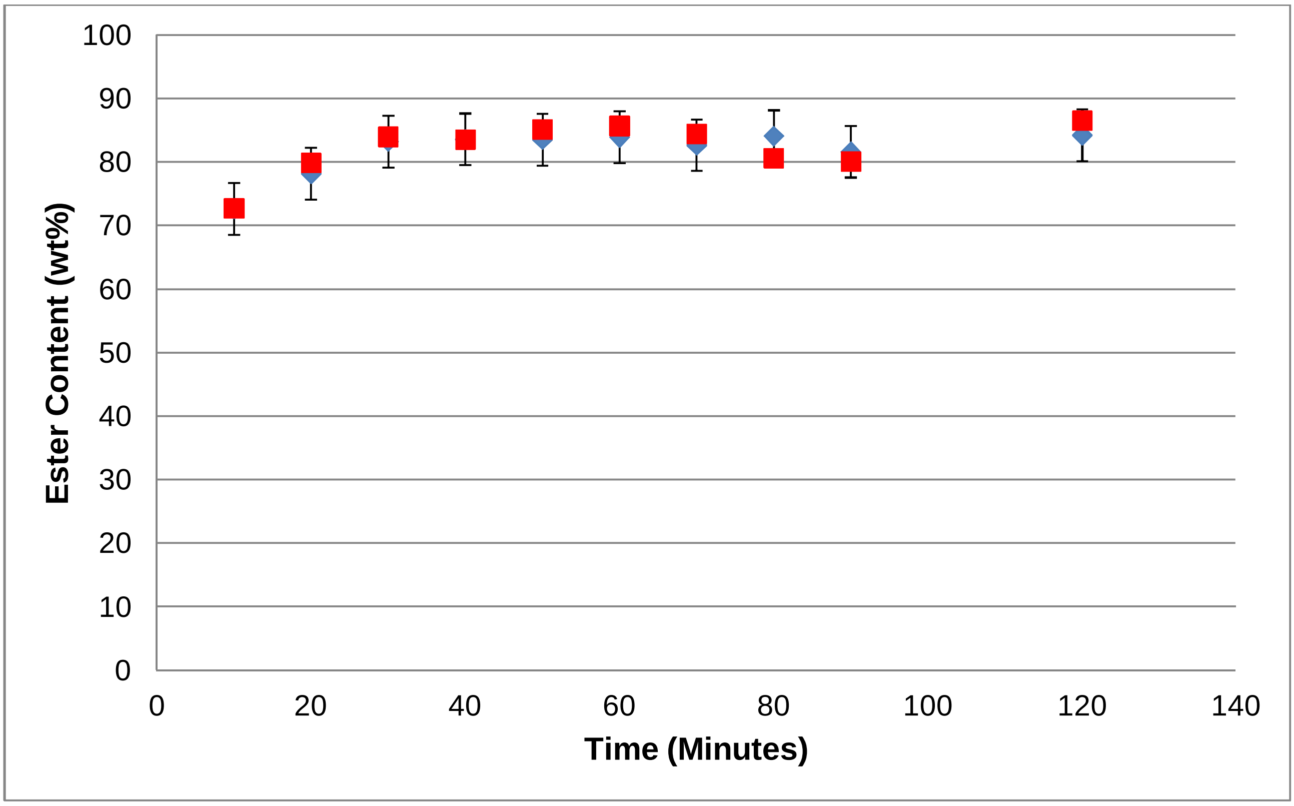


Figure B.2: Comparison of FTIR and GC results.
(◆ GC results; ■ FTIR results)
The values of the FTIR are all within the experimental error range. Thus it is safe to assume that the GC results are correct and that the FTIR can be used to determine the ester content.

B.2 Water content

The water content of the biodiesel was measured with a Karl Fischer coulometric titrator. The error of the titrator was calculated by analysing the same sample three times.
The error of the titrator is summarised in Table B.2.

Table B.2: Experimental error of the KFC titrator

Repeat	Water content (ppm)
1	917.2781
2	937.1598
3	937.7515
Average	930.7298
Standard deviation	11.65325
Experimental error	2.833615

B.3 Acid value

The acid value was determined with an automatic tritator. The experimental of the tritator was detemrined and the results are shown in Table B.3.

Table B.3: Experimental error of the acid value titrator

Repeat	Acid value (mg KOH/g)
1	2.39
2	2.49
3	2.58
Average	2.486667
Standard deviation	0.095044
Experimental error	7.491254

Appendix C: Experimental data

The experimental data for the study is shown in this section. Section C.1 contains the ester content of the experiments done for the optimisation of the reaction conditions as well as the kinetic study. The data from the Magnesol® D-SOL™ experiments are shown in Section C.2. The Purolite® PD-206 data is presented in Section C.3.

C.1 Ester content

The ester content experimental data is presented in this section. The ester content as determined with the calibration curves are shown in the following tables (Table C.1 to Table C.18).

Table C.1: Ester content (wt%) for an alcohol to oil molar ratio of 3:1 and catalyst load of 0.8 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	26.594	25.860	26.712	28.152	27.595	26.080	27.916	29.823	28.976	26.470
50	52.988	58.370	63.233	66.239	67.223	68.301	71.621	71.920	71.608	72.813
55	52.425	59.422	61.918	65.767	63.989	66.267	70.064	69.675	67.084	66.589
60	42.862	44.233	44.132	45.756	47.102	45.995	46.538	46.868	44.701	46.819
65	56.274	63.499	65.549	70.090	70.097	66.880	69.939	67.445	72.195	66.033

Table C.2: Ester content (wt%) for an alcohol to oil molar ratio of 3:1 and catalyst load of 1.0 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	42.491	46.153	49.702	50.599	47.161	49.522	49.935	49.972	49.260	48.065
50	62.403	69.917	75.292	73.992	76.350	72.299	74.992	79.219	75.583	76.878
55	64.525	65.411	68.782	68.942	69.081	69.474	69.400	70.200	68.376	68.853
60	69.501	69.242	72.429	74.928	74.204	71.359	72.918	74.877	72.195	73.608
65	41.371	43.391	47.235	47.320	48.700	47.799	45.617	47.626	49.904	49.889

Table C.3: Ester content (wt%) for an alcohol to oil molar ratio of 3:1 and catalyst load of 1.2 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	55.262	60.496	66.549	69.150	67.756	65.778	66.897	66.401	67.949	64.263
50	69.568	77.214	75.259	77.682	80.384	77.373	77.463	76.593	77.738	80.649
55	61.358	77.091	74.698	74.445	74.000	74.061	69.314	77.159	69.948	74.123
60	60.033	68.317	69.655	68.333	70.017	68.536	64.874	65.671	66.613	67.642
65	50.824	56.034	54.381	56.530	55.380	53.631	53.740	50.869	55.542	54.627

Table C.4: Ester content (wt%) for an alcohol to oil molar ratio of 4:1 and catalyst load of 0.8 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	27.642	31.368	34.945	33.873	33.112	34.786	35.136	35.181	34.453	37.883
50	63.461	70.736	74.490	76.543	77.263	77.718	76.955	76.238	80.994	77.735
55	69.463	77.612	76.918	78.850	78.187	80.413	80.194	80.442	81.103	81.871
60	54.460	56.210	59.660	58.103	58.393	58.053	57.680	60.483	63.210	60.935
65	65.782	73.801	76.386	78.041	78.121	75.635	80.615	82.339	80.731	78.554

Table C.5: Ester content (wt%) for an alcohol to oil molar ratio of 4:1 and catalyst load of 1.0 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	46.699	52.428	56.385	53.316	56.233	56.526	56.793	55.413	55.443	56.362
50	69.918	75.998	79.742	77.628	81.289	81.665	81.193	81.557	84.828	82.916
55	62.109	73.307	76.781	76.828	77.628	78.787	79.282	75.206	78.046	77.498
60	79.411	80.976	84.615	86.769	85.287	84.997	86.777	88.036	85.172	80.002
65	33.893	53.434	61.247	65.267	63.369	64.471	61.808	61.845	63.710	63.310

Table C.6: Ester content (wt%) for an alcohol to oil molar ratio of 4:1 and catalyst load of 1.2 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	65.949	68.858	72.591	73.121	75.189	75.192	73.370	74.928	74.408	74.175
50	70.217	82.457	85.223	83.724	85.098	83.615	84.665	84.949	83.959	84.892
55	78.201	83.253	84.627	84.302	84.986	85.730	80.445	84.594	85.967	82.803
60	67.484	73.197	72.947	77.018	77.247	75.047	74.303	73.379	78.482	79.411
65	59.153	64.910	66.857	65.132	67.479	66.802	66.294	67.644	64.255	65.035

Table C.7: Ester content (wt%) for an alcohol to oil molar ratio of 5:1 and catalyst load of 0.8 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	34.051	38.672	41.549	42.055	45.290	45.582	45.644	42.532	44.184	43.477
50	73.036	80.316	82.880	82.457	80.954	80.968	78.526	81.090	84.147	80.789
55	75.472	76.414	79.418	79.557	83.163	83.544	82.251	81.430	84.329	87.436
60	59.515	64.505	68.383	66.387	71.385	69.242	70.347	72.202	70.948	72.067
65	75.331	79.558	82.448	81.247	81.148	80.481	83.035	85.112	84.752	83.914

Table C.8: Ester content (wt%) for an alcohol to oil molar ratio of 5:1 and catalyst load of 1.0 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	55.984	62.877	64.984	69.621	69.136	71.568	72.440	71.215	69.394	69.643
50	64.869	80.594	85.076	87.021	88.073	87.782	90.011	89.394	85.886	87.806
55	80.421	82.757	86.106	86.286	85.255	87.946	89.439	85.489	86.465	89.247
60	80.468	79.379	79.560	82.429	82.959	81.208	85.762	83.583	83.393	82.426
65	62.388	71.693	71.782	70.995	74.674	69.515	73.776	73.372	78.507	72.659

Table C.9: Ester content (wt%) for an alcohol to oil molar ratio of 5:1 and catalyst load of 1.2 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	58.291	70.170	74.641	81.082	79.002	79.216	76.999	79.955	80.768	78.691
50	71.369	85.617	85.825	86.461	85.273	88.166	86.625	90.517	92.224	89.046
55	77.976	84.714	87.998	89.904	88.680	88.161	89.544	87.442	88.141	90.043
60	77.162	78.662	78.204	79.066	78.483	79.318	81.317	82.185	84.147	82.428
65	65.383	71.577	77.510	79.010	74.930	75.442	76.806	76.572	73.542	79.033

Table C.10: Ester content (wt%) for an alcohol to oil molar ratio of 6:1 and catalyst load of 0.8 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	30.976	39.014	42.178	45.869	44.683	49.076	48.499	51.348	49.630	48.225
50	76.458	82.704	81.133	83.461	85.635	84.892	85.951	83.215	84.369	83.633
55	78.535	80.530	84.309	89.394	87.643	87.678	88.925	87.365	88.433	90.805
60	67.114	72.932	73.492	78.674	80.712	79.627	82.627	81.354	81.349	80.274
65	77.449	79.484	82.257	83.569	86.471	83.728	87.697	88.323	86.886	87.659

Table C.11: Ester content (wt%) for an alcohol to oil molar ratio of 6:1 and catalyst load of 1.0 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	51.560	67.097	74.954	78.632	78.955	78.354	82.520	84.892	85.055	81.949
50	69.433	74.557	84.349	89.559	89.776	89.359	87.756	91.068	89.807	93.415
55	88.414	84.450	86.817	89.441	91.637	90.053	90.513	88.121	88.768	89.228
60	72.653	78.202	83.274	83.606	83.577	83.927	82.691	84.117	81.673	84.241
65	66.934	76.125	78.122	80.976	80.868	78.923	79.339	75.066	82.279	80.604

Table C.12: Ester content (wt%) for an alcohol to oil molar ratio of 6:1 and catalyst load of 1.2 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	67.693	82.330	82.097	83.543	82.344	80.533	82.711	83.405	83.102	82.600
50	81.780	85.746	90.776	93.338	90.132	89.046	91.672	90.831	91.510	92.934
55	75.616	74.443	89.672	90.272	87.199	86.919	94.069	89.633	92.979	91.790
60	85.413	85.784	85.880	86.849	85.366	85.918	87.138	86.984	85.455	85.981
65	72.818	79.777	79.787	79.881	83.205	81.463	83.933	86.310	88.459	84.639

Table C.13: Ester content (wt%) for an alcohol to oil molar ratio of 7:1 and catalyst load of 0.8 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	30.133	34.766	40.443	40.655	41.857	37.663	44.422	44.585	44.487	43.799
50	71.479	79.138	84.672	82.273	82.895	80.238	85.184	83.380	87.473	86.259
55	80.493	90.206	90.888	93.401	90.846	93.836	90.392	91.230	90.504	91.073
60	76.504	83.991	85.428	89.831	86.974	83.894	85.849	80.847	86.094	85.265
65	77.011	82.718	89.520	90.506	90.277	90.263	90.431	89.666	89.948	88.848

Table C.14: Ester content (wt%) for an alcohol to oil molar ratio of 7:1 and catalyst load of 1.0 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	63.710	71.844	75.146	79.438	84.358	87.213	85.541	84.998	83.403	87.110
50	82.265	89.540	86.422	90.466	90.477	87.714	93.512	90.467	93.418	90.726
55	89.864	87.569	91.448	89.473	89.097	88.914	88.936	88.715	90.742	89.691
60	77.094	76.933	81.977	85.808	82.496	83.796	84.206	84.492	86.201	83.672
65	71.000	74.785	80.716	76.614	84.188	80.842	78.531	85.007	87.159	88.454

Table C.15: Ester content (wt%) for an alcohol to oil molar ratio of 7:1 and catalyst load of 1.2 wt%.

Temperature	Time (Minutes)									
(°C)	10	20	30	40	50	60	70	80	90	120
45	71.062	81.714	85.405	84.677	86.243	88.125	86.078	84.052	84.986	85.953
50	79.875	82.948	81.924	85.891	85.458	86.230	87.583	87.002	90.118	91.368
55	88.413	92.700	94.477	90.596	92.190	92.061	91.895	88.927	91.318	90.209
60	80.069	82.417	85.196	81.936	83.576	80.649	82.412	85.315	82.235	82.641
65	71.976	84.714	87.896	88.508	91.379	91.227	90.784	88.483	85.697	85.671

Table C.16: Ester content (wt%) for an alcohol to oil molar ratio of 8:1 and catalyst load of 0.8 wt%.

Temperature (°C)	Time (Minutes)									
	10	20	30	40	50	60	70	80	90	120
45	30.402	36.915	39.458	44.966	43.626	45.670	43.068	43.916	44.592	44.852
50	70.657	84.748	86.100	86.235	85.288	84.943	86.731	85.821	86.822	89.171
55	80.755	85.885	86.712	90.909	90.897	92.446	93.452	93.278	92.846	92.295
60	81.414	87.211	91.275	90.722	90.836	88.256	84.483	87.154	91.309	91.103
65	79.519	85.330	85.805	89.304	89.083	90.147	89.822	85.447	90.926	90.181

Table C.17: Ester content (wt%) for an alcohol to oil molar ratio of 8:1 and catalyst load of 1.0 wt%.

Temperature (°C)	Time (Minutes)									
	10	20	30	40	50	60	70	80	90	120
45	58.085	71.740	79.491	84.081	84.741	85.418	84.385	86.506	85.186	87.536
50	77.751	84.157	87.457	91.668	94.707	90.826	88.525	90.325	92.565	90.289
55	83.693	84.609	87.198	90.764	87.153	89.441	86.953	91.931	92.154	90.562
60	79.060	79.446	80.577	85.740	87.084	82.570	84.696	82.595	85.154	85.506
65	73.819	82.453	79.636	85.149	83.543	83.135	85.167	81.929	83.347	89.428

Table C.18: Ester content (wt%) for an alcohol to oil molar ratio of 8:1 and catalyst load of 1.2 wt%.

Temperature (°C)	Time (Minutes)									
	10	20	30	40	50	60	70	80	90	120
45	76.012	81.486	81.506	83.076	79.929	84.012	84.734	81.203	84.729	85.262
50	80.457	86.345	89.122	87.250	86.455	88.358	86.506	90.612	91.064	91.662
55	85.322	92.036	91.221	92.063	95.413	94.728	87.443	92.733	91.611	89.572
60	78.722	82.739	87.380	86.111	87.704	85.111	87.545	87.721	86.720	85.130
65	75.969	85.250	85.929	87.237	84.299	83.513	85.758	85.857	87.712	89.578

C.2 Magnesol® D-SOL™ experimental data

The water content, acid value and ester content for Magnesol® D-SOL™ is shown in Tables C.19 to C.21.

Table C.19: Water content (ppm) of biodiesel treated with Magnesol® D-SOL™

Time (Minutes)	Magnesol® D-SOL™ load (wt%)			
	0.5	1.0	1.5	2.0
10	654.0252	539.1685	997.7591	971.0027
20	438.1643	451.2019	603.6364	946.3268
30	304.7059	299.6063	452.9412	615.9817

Table C.20: Acid value (mg KOH/g) of biodiesel treated with Magnesol® D-SOL™ (30 minutes)

Magnesol® D-SOL™ load (wt%)			
0.5	1.0	1.5	2.0
0.130	0.078	0.011	0.180

Table C.21: Ester content (wt%) of biodiesel treated with Magnesol® D-SOL™

Time (Minutes)	Magnesol® D-SOL™ load (wt%)			
	0.5	1.0	1.5	2.0
10	94.699	94.218	95.288	89.660
20	97.375	96.108	96.979	98.836
30	95.231	98.350	97.561	99.937

C.3 Purolite® PD-206 experimental data

The water content, acid value and ester content for Purolite® PD-206 are shown in Tables C.22 to C.24.

Table C.22: Water content (ppm) of biodiesel treated with Purolite® PD-206

Time (Minutes)	Purolite® PD-206 load (wt%)			
	0.5	1.0	1.5	2.0
10	338.179	460.714	772.850	899.129
20	298.561	352.620	808.602	695.826
30	255.031	315.365	461.602	609.984

Table C.23: Acid value (mg KOH/g) of biodiesel treated with Purolite® PD-206 (30 minutes)

Purolite® PD-206 load (wt%)			
0.5	1.0	1.5	2.0
3.01	1.48	0.99	0.67

Table C.24: Ester content (wt%) of biodiesel treated with Purolite® PD-206

Time (Minutes)	Purolite® PD-206 load (wt%)			
	0.5	1.0	1.5	2.0
10	87.218	90.972	96.224	98.929
20	98.800	96.065	97.247	99.449
30	95.844	95.501	96.394	98.479

Appendix D: Kinetic data

The kinetic data calculations are explainen in this section.

The conversion of triglycerides to fatty acid methyl esters is needed to determine th kinetic parameters. The experimental data is available in weight percentage of esters, thus Equation D.1 was used to convert the experimental data to conversion.

$$-r_{TG} = -\frac{dC_{TG}}{dt} = k_1 C_{TG} C_{MeOH} - k_2 C_{FAME} C_G \qquad \text{Equation 4.2}$$

$$-\frac{dX_{TG}}{dt} = k_1\left(C_{TG_0} - C_{TG_0}X_{TG}\right)\left(C_{MeOH_0} - MC_{TG_0}X_{TG}\right) - k_2\left(MC_{TG_0}X_{TG}\right)\left(C_{TG_0}X_{TG}\right)$$

Equation 4.6

$$X_{TG} = \frac{C_{TG_0} - C_{TG}}{C_{TG_0}} \qquad \text{Equation D.1}$$

$$C_{TG} = \frac{x_{TG} \times \rho_{TG}}{MW_{TG}} = 3 \times \frac{(100 - x_{FAME})\rho_{TG}}{MW_{TG}} \qquad \text{Equation D.2}$$

Where x_{TG} is the weight percentage of triglycerids, x_{FAME} is the weight percentage of FAME, ρ_{TG} is the density of the triglycerides (914 mol/dm^3) and MW_{TG} is the molecular weight of the triglycerides (790 g/mol). The molecular weight of the oil was determined by using the percentage of the specific triglycerides multiplied with the molecular weight of each triglyceride. The molecular weight calculation is shown in Table D.1.

Table D.1: Molecular weight of oil

Ester	Molecular weight of ester	wt% of ester (GC result)	Mol Ester	Mol TG	Molecular weight of TG	Molecular weight contribution
C4:0	102.132	2.150	0.021	0.007	302.363	6.500
C6:0	130.185	2.099	0.016	0.005	386.523	8.112
C8:0	158.238	1.663	0.011	0.004	470.682	7.825
C10:0	186.291	3.085	0.017	0.006	554.842	17.116
C12:0	214.344	3.117	0.015	0.005	639.001	19.917
C14:0	242.398	9.659	0.040	0.013	723.161	69.849
C14:1	240.382	2.552	0.011	0.004	717.113	18.302
C16:0	270.451	29.023	0.107	0.036	807.320	234.311
C16:1	268.435	3.080	0.011	0.004	801.273	24.680
C18:0	298.504	10.364	0.035	0.012	891.480	92.390
C18:1	296.488	24.015	0.081	0.027	885.432	212.633
C18:2	294.472	7.390	0.025	0.008	879.384	64.987
C18:3	292.456	1.532	0.005	0.002	873.337	13.380
					Total molecular weight	**790.004**

The conversion was calculated with the concentration of the triglycerids. The values of the calculated conversion and the values of the mass fraction of FAME was identical, thus the mass fraction of the esters where used as the conversion of the reaction (Equation D.3).

$$X_{TG} = \frac{C_{TG}}{100} \qquad \text{Equation D.3}$$

The initial concentration of triglycerides was constant for all the reactions since the mass of oil used was constant (300g). The reaction mixture was assumed to be hetergeneous throughout the reaction. The alcohol concentration is presented in Table D.2.

Table D.2: Concentration of methanol in reaction mixture.

Alcohol to oil molar ratio	Mass of methanol (g)	Concentration (mol/dm^3)
3:1	38	939.089
4:1	51	1260.356
5:1	64	1581.623
6:1	77	1902.890
7:1	90	2224.157
8:1	102	2520.712

The left side of Equation 4.6 was calculated by the finite difference method as explained in Section 4.3. The right side of the equation was compared with the left side with variables k_1 and k_2 by means of the non-linear regression function in Polymath 5.1.

The k values are shown in Tables D.3 to D.5.

Table D.3: k values for a reaction temperature of 45 °C.

Alcohol to oil molar ratio	Catalyst load (wt%)	k_1 value (dm^3/mol.min)	k_2 value (dm^3/mol.min)
3:1	0.8	1.20E-07	6.81E-07
	1.0	1.95E-07	1.54E-07
	1.2	2.53E-07	3.58E-08
4:1	0.8	8.92E-08	3.78E-07
	1.0	1.58E-07	1.33E-07
	1.2	2.27E-07	3.74E-08
5:1	0.8	8.96E-08	2.78E-07
	1.0	1.51E-07	6.68E-08
	1.2	1.55E-07	3.13E-08
6:1	0.8	6.26E-08	1.86E-07
	1.0	1.10E-07	2.66E-08
	1.2	1.48E-07	2.70E-08
7:1	0.8	5.30E-08	2.82E-07
	1.0	1.21E-07	2.58E-08
	1.2	1.36E-07	2.38E-08
8:1	0.8	4.76E-08	2.67E-07
	1.0	9.52E-08	2.26E-08
	1.2	1.29E-07	3.74E-08

Table D.4: k values for a reaction temperature of 50 °C.

Alcohol to oil molar ratio	Catalyst load (wt%)	k_1 value (dm^3/mol.min)	k_2 value (dm^3/mol.min)
3:1	0.8	2.41E-07	1.85E-08
	1.0	2.82E-07	2.55E-09
	1.2	3.13E-07	3.34E-09
4:1	0.8	2.15E-07	2.77E-08
	1.0	2.38E-07	1.57E-08
	1.2	2.33E-07	5.87E-09
5:1	0.8	1.97E-07	2.79E-08
	1.0	1.70E-07	6.98E-09
	1.2	1.88E-07	9.07E-09
6:1	0.8	1.72E-07	2.62E-08
	1.0	1.59E-07	8.63E-09
	1.2	1.86E-07	5.85E-09
7:1	0.8	1.37E-07	3.07E-08
	1.0	1.58E-07	1.19E-08
	1.2	1.55E-07	2.02E-08
8:1	0.8	1.17E-07	2.14E-08
	1.0	1.33E-07	1.45E-08
	1.2	1.37E-07	1.68E-08

Table D.5: k values for a reaction temperature of 55 °C.

Alcohol to oil molar ratio	Catalyst load (wt%)	k_1 value (dm^3/mol.min)	k_2 value (dm^3/mol.min)
3:1	0.8	2.37E-07	3.04E-08
	1.0	2.98E-07	2.38E-08
	1.2	2.65E-07	2.23E-09
4:1	0.8	2.34E-07	1.66E-08
	1.0	2.07E-07	2.37E-08
	1.2	2.65E-07	9.65E-09
5:1	0.8	2.07E-07	2.13E-08
	1.0	2.20E-07	1.01E-08
	1.2	2.11E-07	6.52E-09
6:1	0.8	1.79E-07	1.38E-08
	1.0	2.04E-07	1.15E-08
	1.2	1.75E-07	1.16E-08
7:1	0.8	1.54E-07	7.65E-09
	1.0	1.76E-07	1.38E-08
	1.2	1.70E-07	8.05E-09
8:1	0.8	1.38E-07	1.07E-08
	1.0	1.45E-07	1.73E-08
	1.2	1.44E-07	9.32E-09

Appendix E: Article

WASTE BUTTER AND MARGARINE AS FEEDSTOCK FOR BIODIESEL PRODUCTION

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ABSTRACT: The resulting bio-waste from butter and margarine factories should be disposed of in an environmentally friendly manner. Currently the bio-waste is either flushed into the municipal sewerage system or moved to landfill sites. The bio-waste from butter and margarine factories provides a potential alternative feedstock for biodiesel production, being both non-edible and non-competitive with edible oils. A butter factory (Clover) near Frankfort, South Africa, has been identified as a source of bio-waste for biodiesel production. This facility produces 60 tons of fatty bio-waste per annum. In this study fatty acid methyl esters (FAME) were produced using cow's milk butter, margarine, as well as the actual butter factory's bio-waste as feedstock. Even though yields in excess of 90% were obtained, the biodiesel produced from the butter factory's bio-waste failed to meet the specifications for sulphur (18 wt ppm) and oxidation stability. Unless further purification methods are considered, the resulting biodiesel cannot meet the 10 wt ppm specification. The problem with regards to oxidation stability and sulphur content can be addressed by blending with ultra-low sulphur biodiesel. The oxidation stability can also be improved by the addition of a commercial antioxidant formulation.

Keywords: biodiesel, biofuels, transesterification, waste disposal.

1 INTRODUCTION

Due to the depletion of fossil fuels the world is constantly searching for alternative, renewable energy sources. The energy obtainable from biomass is one possibility that shows a lot of promise and has enjoyed an equal amount of interest and research.

The production of biodiesel from vegetable oils and fats is one of the ways in which energy can be obtained from biomass. The biodiesel product formed during transesterification can be used in a diesel engine without any adaptations made to the engine and thus the production of biodiesel is very feasible from a technical point of view [1].

Apart from the fact that biodiesel can be produced from renewable sources, the biodiesel product is a cleaner burning fuel and shows increased engine performance than its petroleum derived counterpart [2].

The best feedstock for biodiesel production, from a production and process point of view, is refined vegetable oils and animal fats. However, these are normally used for human consumption, and competition between these two markets causes increases in feedstock prices which, in turn, cause high production costs [3]. Due to the high production costs, biodiesel cannot economically compete with its petroleum derived counterpart. There is a need for a cheap source of feedstock which can be used for biodiesel production. Using waste feedstock from a butter factory might be viable due to the low costs associated with waste oils and fats as well as the added benefit of consuming waste products which might have a negative effect on the environment [4].

The disadvantage of waste oils and fats is the large amounts of free fatty acids and moisture normally present in these feedstock which might influence the alkali catalyzed transesterification reaction [5]. There are, however, methods to reduce these impurities and make the feedstock suitable for alkali catalyzed transesterification [6].

According to Cheng [1] transesterification is the preferred method for biodiesel production from triglycerides as this method shows the highest yield of biodiesel product that has a low enough viscosity to prevent carbon deposits in engines. There are a few important factors that influence the final yield of biodiesel [1]:

- Moisture and free fatty acid (FFA) content of feedstock
- Type and amount of catalyst
- Type of alcohol and molar ratio of alcohol to oil
- Reaction temperature

It is important to obtain the FFA and moisture contents of the feedstock used during transesterification as these two parameters affect the choice and concentrations of alcohol and catalyst used during the reaction step [6].

1.1 Type and amount of catalyst

Catalysts used during transesterification include alkaline, acidic, enzymatic and heterogeneous catalysts [7]. It is possible to convert triglycerides without catalyst using methanol in its supercritical state [8]. When methanol enters its supercritical state the dielectric constant lowers which makes it soluble in the oil, therefore excluding the necessity of a catalyst to speed up the reaction rate.

The use of chemical catalysts is, however, most often used due to the availability and the high operating costs when using other catalysts/non-catalytic processes [1]. Alkaline catalysts such as KOH and NaOH are normally used. The use of these catalysts result in fast reaction rates, and the optimum concentrations in terms of biodiesel yield is 1 wt% of oil [4]. As mentioned before the quality of the feedstock determines the type of catalyst used during transesterification. According to Yuan *et al.* [4] alkaline catalysts will form soap in the presence of FFA and moisture. FFA and moisture contents should be lower than 1% and 0.5% respectively to permit the use of alkaline catalysts [9].

Acidic catalysts can be used when the FFA and moisture content excludes the use of alkaline catalysts. However, acidic catalysts are not as effective as their alkaline counterparts [6]. Acids normally used during transesterification include sulphuric acid, hydrochloric acid and phosphoric acid [1]. According to Al-Widyan and Al-Shyoukh [10] sulphuric acid is the most effective at concentrations of 2.25 M.

1.2 Alcohol to oil molar ratio

An excess of alcohol is added to the reaction mixture to shift the equilibrium to the right. The amount of excess alcohol used during transesterification depends on the quality of feedstock used. As mentioned before alkaline catalysts are the most effective. During transesterification using alkaline catalysts, the optimum alcohol to oil molar ratio was found to be 6:1 [5,6].

Given a feedstock with a high FFA and moisture content necessitates the use of an acidic catalyst. The disadvantage of using acidic catalysts is the decrease in reaction rate associated with these catalysts and therefore higher alcohol to oil ratios needed to obtain the same conversion when compared to alkaline catalyzed transesterification [6]. According to Cheng [1] the optimum alcohol to oil molar ratio for acidic catalyzed transesterification is 15:1.

1.3 Reaction temperature

Normally transesterification reactions are carried out close to the boiling point of the specific alcohol used during reaction [1]. This might be to increase the reaction rate without boiling of the alcohol. There is however optimum temperatures at which transesterification can be carried out. According to Banerjee and Chakraborty [6] these temperatures depend on the quality of the feedstock used during transesterification.

Although the optimum temperature for transesterification of refined oils and fats is close to 60 °C (the boiling point of methanol), various researchers have found that the optimum temperature for transesterification of waste cooking oils and fats are lower than 60 °C, close to 50 °C [4,5,8].

2 MATERIALS AND METHODS

2.1 Materials

Two butter brands (Kerrygold and Clover butro), two margarine brands (House Brand and Sunshine D), as well as an oil effluent from a butter factory were used as feedstock. The feedstock was boiled under continuous agitation on a hot plate equipped with a magnetic stirrer. When a temperature of 110 ºC was reached the feedstock was removed from the hot plate and placed in an oven at 105 ºC for 1 hour. The dried feedstock was analysed for water and FFA content, as shown in Table I.

Table I: Water and FFA content of the feedstock

Feedstock	Water (ppm)	FFA (wt%)
Kerrygold Butter	464	0.46
Clover Butro Butter	522	0.34
House Brand Margarine	226	0.28
Sunshine D Margarine	240	0.36
Butter factory waste	490	0.20

From Table I it can be seen that all the feedstocks had a low enough water and FFA content to allow alkali catalyzed transesterification.

As this study specifically focuses on the possibility of using bio-waste as feedstock the butter factory waste was further characterised and it was found that the feedstock had a sulphur content of 18 ppm, a density of 914 kg/m^3, and a viscosity of 46.9 cSt at 40 ºC.

2.2 Chemicals

Methanol was used as the alcohol during the alkali transesterification. This is due to the lower cost when compared to other alcohols. Methanol is not as soluble in oil as ethanol but according to Issariyakul *et al.* (2007) and Demirbas (2009) the yield obtained from methanol is higher than that of ethanol [11,12].

The alkali catalyst used was KOH, as potassium hydroxide gives the highest yield for the largest range of feedstock [13,14]. During the treatment of biodiesel samples sulphuric acid was used to remove any unreacted reagents and neutralize the alkali catalyst.

2.3 Experimental procedure

The experimental procedure for all five feedstocks was identical. 300 g of dried feedstock was heated to the reaction temperature in a three neck round bottom flask, fitted with a condenser, a thermometer and a rubber seal using a hot plate with magnetic stirrer. The KOH was dissolved in the methanol (1 wt% KOH/wt% oil) and added to the reaction mixture.

The temperature dependant experiments for the butter and margarine were conducted at four specific temperatures, ranging from 40 ºC to 70 ºC. In the case of the butter factory waste the temperatures were varied from 50 ºC to 65 ºC, in order to determine the optimum temperature.

The molar ratio dependent experiments for the butter and the margarine were conducted at four specific alcohol to oil molar ratios, ranging from 5:1 to 8:1. The molar ratio was varied from 3:1 to 8:1 in the case of the butter factory waste.

The reaction was left at the set conditions for 1 hour, after which the biodiesel was separated from the glycerol. The biodiesel product was washed with distilled water and dried at 100 ºC for 2 hours.

2.4 Analytical method

The individual ester content of the biodiesel was measured by gas chromatography (GC). The GC was set up as follows:

A HP-88 100m column with a split ratio of 1:50 and helium as carrier gas was used. The oven was set at 100 °C for 5 minutes and then ramped at 10 °C/min up to 120 °C, which was then kept constant for 1 minute. The oven was then heated 10 °C/min to 175 °C and held constant for 10 minutes. The next ramp was 5 °C/min up to 210 °C and held for 5 minutes. The final ramp was 5 °C/min to 230 °C and held constant for 5 minutes. The FID was set at 350 °C.

Fourier Transform Infrared spectroscopy (FTIR) was also used to determine the total ester content. The mid-infrared range was used. The Eraspec by Eralytics was used for analysis.

The biodiesel quality was determined according to SANS 1953 standards.

3 RESULTS AND DISCUSSION

3.1 Temperature

The effect of temperature on the FAME yield for the butter and margarine is shown in Figure 1.

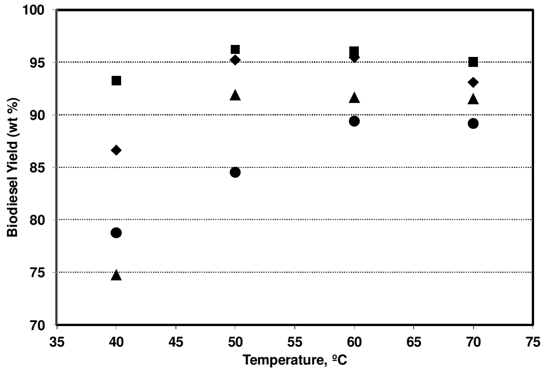

Figure 1: Effect of temperature on biodiesel yield during alkali catalyzed transesterification (■ Sunshine D ◆ Housebrand ● Kerrygold ▲ Clover)

With an increase in temperature, there was an increase in biodiesel yield for both the butter and the margarine. The maximum biodiesel yield obtained at an alcohol to oil molar ratio of 6:1 using Kerrygold was 89.4±0.7 wt% at 60 ºC. There is no significant change in biodiesel yield for the Clover Butro between 50 ºC and 70 ºC, with a maximum yield of 91.9±0.5 wt% at 50 ºC.

The optimum temperature in the case of the margarine was also found to be 60 ºC. The steady decline in yield above 60 ºC can be attributed to the boiling point of methanol, which is 64.7 ºC. A maximum yield of 96.2±0.6 wt% and 95.5±1.4 wt% were reported for the Sunshine D and Housebrand respectively.

The optimum temperature for transesterification found for both the butter and margarine is similar to the optimum temperatures reported by researches using refined vegetable oils with low FFA and water contents as feedstocks [15].

The experiment was repeated with an alcohol to oil ratio of 6:1 using the butter factory waste as feedstock. The effect of temperature on the FAME yield for the butter factory waste is shown in Figure 2.

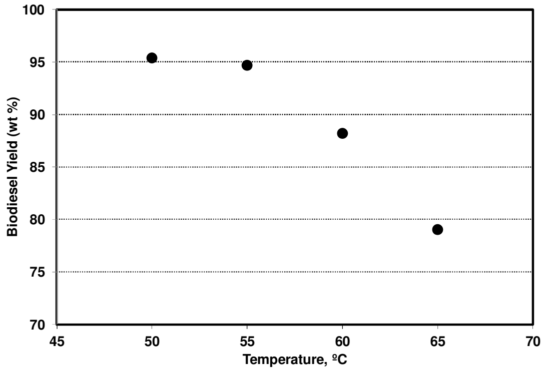

Figure 2: Effect of temperature on biodiesel yield during alkali catalyzed transesterification of butter factory waste

The optimal temperature for the butter factory waste was 50 °C. A further increase in temperature decreases the biodiesel yield. As previously mentioned, the decrease in yield is due to the increase of methanol in the vapour phase. A maximum yield of 95.37±1.67wt% was obtained at 50 °C for a 6:1 alcohol to oil molar ratio and 1.2 wt% (with respect to the oil) catalyst load.

3.2 Alcohol to oil molar ratio

The effect of the alcohol to oil ratio on the biodiesel yield at a reaction temperature of 60 ºC is shown in Figure 3.

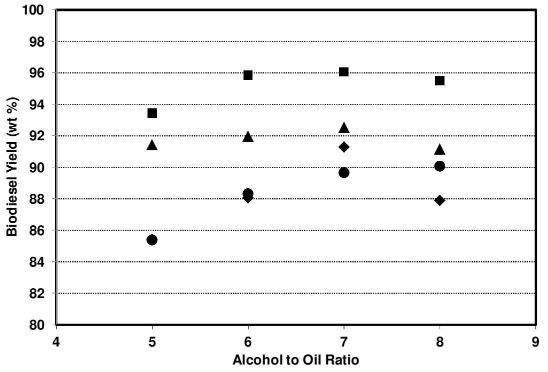

Figure 3: Effect of alcohol to oil ratio on biodiesel yield during alkali catalyzed transesterification (■ Sunshine D ◆ Housebrand ● Kerrygold ▲ Clover)

With an increase in alcohol to oil ratio, there was an increase in biodiesel yield for all of the feedstocks. With the exception of the Kerrygold butter, all the feedstocks showed an optimum alcohol to oil ratio of 7:1. There was a decrease in biodiesel yield at higher alcohol to oil ratios. The optimum biodiesel yields of 96.0±0.5 wt%, 92.5±0.5 wt% and 91.3±0.4 wt% were reported for the Sunshine D, Clover Butro and Housebrand respectively. The optimum biodiesel yield for the Kerrygold was found to be 90.1±0.7 wt% at an alcohol to oil ratio of 8:1.

The experiment was repeated at a temperature of 50 ºC using the butter factory waste as feedstock. The effect of a change in alcohol to oil ratio on the FAME yield for the butter factory waste is shown in Figure 4.

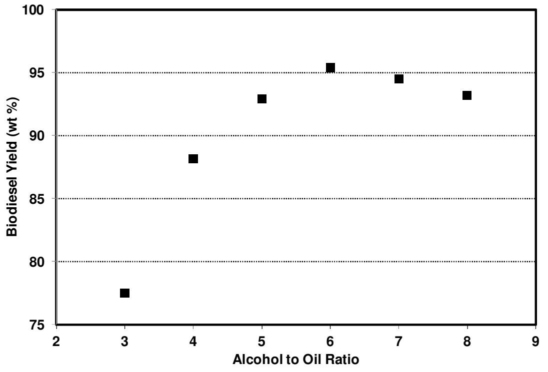

Figure 4: Effect of alcohol to oil ratio on biodiesel yield during alkali catalyzed transesterification of butter factory waste

As with the butter and margarine, an increase in alcohol to oil ratio, led to an increase in yield. The maximum yield of 95.37±1.67 wt% was obtained at an alcohol to oil molar ratio of 6:1.

The increase in yield with an increase in alcohol to oil ratio can be attributed to the fact that the biodiesel transesterification reaction is a reversible reaction. An increase in excess methanol will generally push the reaction to the right. The decrease in yield at a higher ratio of 8:1 can be ascribed to the excess methanol causing an increase in solubility of the glycerol in the biodiesel layer [16].

The 7:1 ratio (margarine and butter) is, however, in line with similar studies done using refined or waste oils and fats, *i.e.* 6.5:1 and 7:1 [4,5,15].

3.3 Catalyst loading

The effect of the catalyst load on the biodiesel yield of the butter factory waste, is represented in Figure 5. The effect of the catalyst was evaluated with a constant reaction temperature of 50 °C and an alcohol to oil ratio of 6:1.

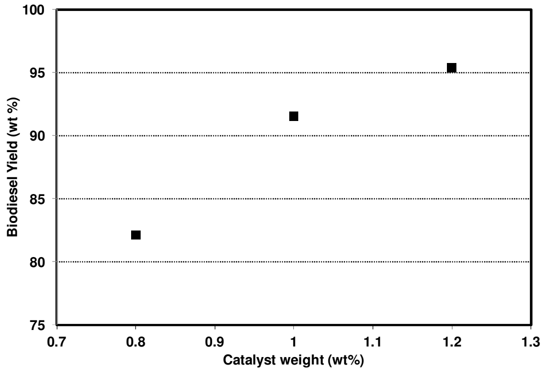

Figure 5: Effect of catalyst loading (wt%) on biodiesel yield during alkali catalyzed transesterification of butter factory waste

An increase of biodiesel yield was observed with an increase of catalyst. The optimal biodiesel yield, 95.37±1.67 wt%, was at a catalyst load of 1.2 wt%. According to Agarwal *et al.* [17], a catalyst load of more than 1 wt% leads to a decrease in yield due to soap formation. The waste oil used by Agarwal *et al.* [17], has an acid value of 1.95 mg KOH/g while the butter factory waste has an acid value of 0.04 mg KOH/g. Thus an increase in catalyst will not lead to an increase of soap formation for this feedstock, but will lead to higher yields. The optimal catalyst load for this study is in line with literature on low acid value feedstock [18].

3.4 Biodiesel quality

A batch of biodiesel was produced from the butter factory waste at the optimum conditions, *i.e.* a temperature of 50 °C, an alcohol to oil ratio of 6:1, and a catalyst loading of 1.2 wt%. This biodiesel batch was analysed to determine whether the biodiesel conforms to the SANS 1935 standard. The results are shown in Table II.

Table II: Results of the analysis of waste butter FAME

Parameter	Waste butter biodiesel	SANS 1935
Ester content	96.5 vol%	95.37±1.67 vol%
Density	803 g/cm^3	860 - 900 g/cm^3
Kinematic viscosity @ 40°C	4.5 cSt	3.5 – 5.0 cSt
Sulphur content (max)	18 ppm	10 ppm
Cetane number (min)	57.95	51.0
Water content (max)	0.03 wt%	0.05 wt%
Copper strip corrosion (max)	Class 1	Class 1
Oxidation stability (min)	0.395 h	6 h
Acid value (max)	0.03 mg KOH/g	0.5 mg KOH/g
Iodine value (max)	26 g/100 g	140 g/100 g
Linolenic acid methyl ester (max)	0.266 wt%	12 wt%
Polyunsaturated methyl ester (max)	N/D	1 wt%
Methanol content (max)	N/D	0.2 wt%
Group I metals (Na and K) (max)	N/D	5.0 ppm
Group II metals (Ca and Mg) (max)	1 ppm	5.0 ppm
Phosphorous content (max)	2 ppm	4 ppm

The parameters that do not meet the standards (density, sulphur content and oxidative stability) can be improved to meet the requirements of both biodiesel and diesel standards. A 40 vol% blend of biodiesel in diesel increases the oxidative stability to over 20 hours.

4 CONCLUSIONS

The optimum temperature and alcohol to oil ratio for biodiesel production from butter and margarine were found to be 60 °C and 7:1 respectively. Biodiesel yields greater than 90 wt% was obtained at these conditions, showing that butter and margarine are suitable feedstocks in the production of biodiesel. These parameters were used as guidelines in the production of biodiesel from butter factory waste.

The highest biodiesel yield of 95.37±1.67 wt% was achieved with the butter factory waste at a temperature of 50 °C, an alcohol to oil ratio of 6:1, as well as a catalyst loading of 1.2 wt%.

Waste butter is a viable option for biodiesel production. The biodiesel should, however, be blended with ultra-low fossil diesel to meet the specifications for density, sulphur content and oxidative stability.

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