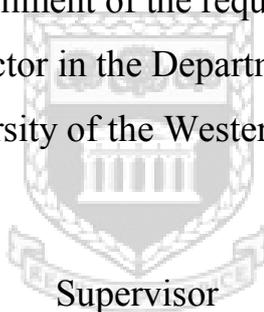


OPTIMISATION OF BIODIESEL PRODUCTION VIA DIFFERENT CATALYTIC AND PROCESS SYSTEMS

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Keywords

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Abstract

Abstract

The production of biodiesel (methyl esters) from vegetable oils represents an alternative means of producing liquid fuels from biomass, and one which is growing rapidly in commercial importance and relevance due to increase in petroleum prices and the environmental advantages the process offers. Commercially, biodiesel is produced from vegetable oils, as well as from waste cooking oils and animal fats. These oils are typically composed of C₁₄-C₂₀ fatty acid triglycerides. In order to produce a fuel that is suitable for use in diesel engines, these triglycerides are usually converted into the respective mono alkyl esters by base-catalyzed transesterification with short chain alcohol, usually methanol.

In the first part of this study, the transesterification reactions of three different vegetable oils; sunflower (SFO), soybean (SBO) and waste cooking oil (WCO) with methanol was studied using potassium hydroxide as catalyst in a conventional batch process. The production of biodiesel from waste cooking oil was also studied via continuous operation systems (employing the use of low frequency ultrasonic technology and the jet loop reactor). The characterisation of the feedstock used and the methyl ester products were determined by different analytical techniques such as gas chromatography (GC), high performance liquid chromatography (HPLC) and thin layer chromatography (TLC). The effects of different reaction parameters (catalyst amount, methanol to oil ratio, reaction temperature, reaction time) on methyl ester/FAME yield were studied and the optimum reaction conditions of the different process systems were determined. The optimum reaction conditions for production of methyl esters via the batch process with the fresh oil samples (SFO and SBO) were established as follows: a reaction time of 60 min at 60 °C with a methanol: oil ratio of 6:1 and 1.0 KOH % wt/wt of oil; while the optimum reaction conditions for the used oil (WCO) was observed at a reaction time of 90 min at 60 °C, methanol: oil ratio of 6:1 and 1.5% KOH wt/wt of oil. The optimum reaction conditions for the transesterification of the WCO via ultrasound technology applied in a continuous system in this study were: a reaction time of 30 min, 30 °C, 6:1 methanol/oil ratio and a 0.75 wt%

Abstract

(KOH) catalyst concentration. The ultrasound assisted transesterification reactions performed at optimum conditions on the different oil samples led to higher yields of methyl esters (96.8, 98.32 and 97.65 % for WCO, SFO and SBO respectively) compared to methyl esters yields (90, 95 and 96 % for WCO, SFO and SBO respectively) obtained when using conventional batch procedures. A considerable increase in yields of the methyl esters in the ultrasound assisted reaction process were obtained at room temperature, in a remarkably short time span (completed in 30 min) and with a lower amount of catalyst (0.75 wt % KOH) while the results from the continuous jet loop process system showed even better results, at an optimum reaction condition of 25 min of reaction, a methanol: oil ratio of 4:1 and a catalyst amount of 0.5 wt%. This new jet loop process allowed an added advantage of intense agitation for an efficient separation and adequate purification of the methyl esters phase at a reduced time of 30 min.

The use of homogeneous catalysts in conventional processes poses many disadvantages; heterogeneous catalysts on the other hand are attractive on the basis that their use could enable the biodiesel production to be more readily performed as a continuous process resulting in low production costs. Consequently, a solid base catalyst (KNO_3/FA) prepared from fly ash (obtained from Arnot coal power station, South Africa) and a new zeolite, FA/Na-X synthesized from the same fly ash were used as solid base catalysts in the transesterification reactions in the conversion of a variety of oil feedstock with methanol to methyl esters. Since fly ash is a waste product generated from the combustion of coal for power generation, its utilization in this manner would allow for its beneficiation (as a catalytic support material and raw material for zeolite synthesis) in an environmentally friendly way aimed at making the transesterification process reasonably viable. Arnot fly ash (AFA) was loaded with potassium (using potassium nitrate as precursor) via a wet impregnation method while the synthesized zeolite FA/Na-X was ion exchanged with potassium (using potassium acetate as precursor) to obtain the KNO_3/FA and FA/K-X catalysts respectively. Several analytical techniques were applied for characterization purposes. The results of the XRD and XRF showed that the AFA predominantly contained some mineral phases such as quartz, mullite, calcite and

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lime. The high concentration of CaO in AFA was apparent to be beneficial for the use of fresh fly ash as a support material in the heterogeneous catalysed transesterification reactions. XRD characterisation of KNO₃/FA results indicated that the structure of KNO₃/FA gradually changed with the increase in KNO₃ loading. The catalyst function was retained until the loading of KNO₃ was over 10 %. IR spectra showed that the KNO₃ was decomposed to K₂O on the fly ash support during preparation at a calcination temperature of 500 °C. The CO₂-TPD of the KNO₃/FA catalysts showed that two basic catalytic sites were generated which were responsible for high catalytic abilities observed in the transesterification reactions of sunflower oil to methyl esters. On the other hand, XRD results for the as-received zeolite synthesized from AFA showed typical diffraction peaks of zeolite NaX. SEM images of the FA /NaX showed nano platelets unique morphology different from well known pyramidal octahedral shaped crystal formation of faujasite zeolites and the morphology of the FA /KX zeolite did not show any significant difference after ion exchange. The fly ash derived zeolite NaX (FA /NaX) exhibited a high surface area of 320 m²/g. The application of the KNO₃/FA catalysts in the conversion reactions to produce methyl esters (biodiesel) via transesterification reactions revealed methyl ester yield of 87.5 % with 10 wt% KNO₃ at optimum reaction conditions of methanol: oil ratio of 15:1, 5 h reaction time, catalyst amount of 15 g and reaction temperature 160 °C, while with the use of the zeolite FA/K-X catalyst, a FAME yield of 83.53 % was obtained for 8 h using the ion exchanged Arnot fly ash zeolite NaX catalyst (FA/KX) at reaction conditions of methanol: oil ratio of 6:1, catalyst amount of 3 % wt/wt of oil and reaction temperature of 65 °C. Several studies have been carried out on the production of biodiesel using different heterogeneous catalysts but this study has been able to uniquely demonstrate the utilization of South African Class F AFA both as a catalyst support and as a raw material for zeolite synthesis; these catalyst materials subsequently applied successfully as solid base catalysts in the production of biodiesel.

November 2011

Declaration

Declaration

I declare that “*Optimisation of biodiesel production via different catalytic and process systems*” is my own work, that it has not been submitted before for any degree or assessment in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references.

Omotola Oluwafunmilayo Babajide



Signature.....

November 2011

Dedication

Dedication

To

God Almighty

My “ALL IN ALL”

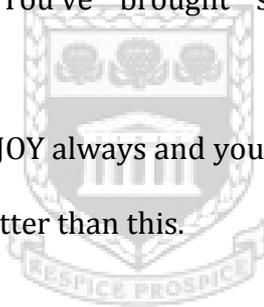
My Husband

Olalekan; for completing me and and bringing out the best in me.

My Kids

Oyinkansola; for making my life so gracefully beautiful and making my dreams worth pursuing. You’ve brought so much SWEETNESS and BRIGHTNESS.

Ayomikun; you fill me with JOY always and you make motherhood worth the trouble. I wouldn’t wish it better than this.



My Mom

Mom; for enduring the pain of yester-years and sacrificing so much, you dared to stay in the face of hardship, proved your love with so much diligence and patience while always holding your head up high with a strong assurance that all will be well. *“All indeed has ended well”*.

My Dad

Dad; for being a survivor; overcoming more than what a man should face and emerging so strong and polished. I am so really proud of you.

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"Eye hath not seen, nor ear heard, neither have entered into the heart of man, the things which God hath prepared for them that love Him. (1 Cor. 2 v 9)

Thank you Lord!

Great Things

Great things must be done greatly

With

A great purpose

A great mind

A great courage

A great energy and most especially

A great persistent patience

Elizabeth B. Browning

Culled from the Merry Mayflower



List of Abbreviations

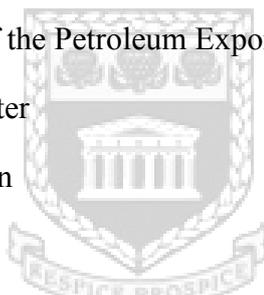
AAS	Atomic absorption spectroscopy
AFA	Arnot fly ash
AV	Acid value
AFR	Stoichiometric air/fuel ratio
AOCS	American Oil Chemists' Society
ASTM D	American Standards and Measurements
ATR	Attenuated Total Reflectance
B5/20/100	Volume % of biodiesel.
BET	Brunauer Emmett Teller
CCR	Conradson carbon residue
CM /NaX,	Commercial Na-X catalyst
CN	Cetane Number
CFPP	Cold-filter plugging point
CO	Carbon monoxide
CO ₂	Carbon dioxide
DG	Di-glyceride
EDS	Energy Dispersive Spectroscopy
EDX	Energy Dispersive X-ray Spectroscopy
EN	European National Standard
ER	Eley-Rideal
EU	European Union
DOE	Department of Energy
ECOD	Economic Co-operation and Development
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid

List of Abbreviations

FA	Fly ash
FA/NaX	Fly ash synthesised zeolite Na- X catalyst
FA/KX	Fly ash synthesised zeolite K-X catalyst
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GDP	Gross Domestic Product
GHG	Green House gases
GL	Glycerol
HC	Hydrocarbons
HCL	Hydrochloric acid
HPLC	High Performance Liquid Chromatography
HRTEM	High resolution transmission electron microscopy
IEA	International Energy Agency
IEE	Institute of Energy and Environment
ICDD	International Centre for Diffraction Data
ICPS	Inductively coupled plasma spectroscopy
IPCC	International Panel on Climate Change
ISO	International Standards Organisation
IV	Iodine value
JIC	Joint Implementation Committee
KNO ₃ /FA	Fly ash loaded with potassium nitrate
K	Potassium
KOH	Potassium Hydroxide
M	Mullite
Mag	Magnetite

List of Abbreviations

MG	Mono-glycerides
Mt/y	Million tonnes per year
MW	Molecular weight
LCA	Life cycle assessment
Na	Sodium
NaOH	Sodium Hydroxide
NA	Not Applicable
ND	Not Detected
NO ₂	Nitrogen dioxide
NO _x	Nitrous oxide
OPEC	Organisation of the Petroleum Exporting Countries
PM	Particulate Matter
ppm	Parts per million
Q	Quartz
RETs	Renewable energy technologies
SANS	South African National Standard
SDC	Sustainable Development Commission
SBO	Soybean oil
SFO	Sunflower oil
SEM	Scanning electron microscopy
SV	Saponification value
TBD	1, 5, 7 Triazabicyclo dec-5-ene
TCD	Temperature Crystalline Desorption
TCG	1, 2, 3 tricyclohexylguanidine
TPD	Temperature Programmed Desorption



List of Abbreviations

TG	Triglycerides
TLC	Thin Layer Chromatography
TR	Transesterification Reaction
UN	United Nations
USEPA	United States Environmental Protection Agency
UNECA	United States Economic Commission for Africa
US	United States
UFOP	Union zur Förderung von Oel- und Proteinpflanzen
WEC	World Economic Council
Wt	Weight
w.r.t	with respect to oil
WCO	Waste cooking oil
XRD	X-ray diffraction
XRF	X-ray fluorescence

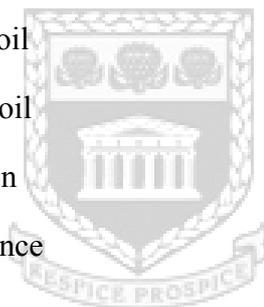


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Academic Output

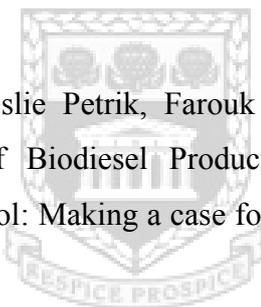
Academic Output

Publications

- Omotola Babajide, Leslie Petrik, Nicholas Musyoka, Bamikole Amigun & Farouk Ameer (2010). Application of Coal Fly Ash as a Solid Basic Catalyst in Producing Biodiesel: Petroleum & Coal 52 (4) 261-272, 2010, ISSN 1337-7027.
- Omotola Babajide, Leslie Petrik, Bamikole Amigun & Farouk Ameer (2010). Low-Cost Feedstock Conversion to Biodiesel via Ultrasound Technology. Energies 3, 1691-1703.

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- Omotola Babajide, Leslie Petrik, Farouk Ameer & Bamikole Amigun (2011). A Review of Biodiesel Production and New Value Added Applications of Glycerol: Making a case for Africa. South African Journal of Science.



Presentations

- The West Africa Biofuel Summit held at the International Conference Centre, Abuja. Nigeria. 22nd – 24th April, 2008. **Paper presented:** Optimization of Biodiesel Production Using Suitable Heterogeneous Solid Acid Catalysts: A Critical Review.
- The 39th Convention of the South African Chemical Institute, Stellenbosch, South Africa, 2nd -5th December, 2008. **Oral presentation:** Optimisation of Biodiesel Production from Low Cost Feedstock using Ultrasonication Technology.

Academic Output

- The 4th African Biofuels Conference, Midrand, Johannesburg, South Africa. 30th March to 2nd April 2009. **Oral presentation:** Biodiesel production using the Jet reactor and the Ultrasound.
- The 42nd IUPAC Congress, Chemistry Solutions, held at the SECC Glasgow, Scotland, UK. 2nd to 7th August, 2009, **Poster presentation:** Catalytic Esterification of Waste vegetable oil in Biodiesel Production Using DOTO & Zeolite Y.
- The 10th Annual AIChE Meeting held at the Salt Palace Convention Center, Salt Lake City, Utah, USA. 7th to 12th November, 2010, **Oral presentation:** Application of Coal Fly Ash as a Solid Basic Catalyst in Producing Biodiesel.



Chapter 1

Introduction

1. Introduction

This chapter deals with the introduction to the study in which the background of the study, the problem statement, aims and objectives, research questions and research approach are presented.

1.1 Background

The major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas with the exception of hydroelectricity and nuclear energy. However these sources are limited, and could be exhausted by the end of the next century (Schuchardta et al., 1998) thus, looking for alternative sources of energy is of vital importance. Securing the supply of fossil fuel has seen wars, human rights abuses and environmental destruction just to control the source of this fuel. Vegetable oils are known to be a renewable source of energy though its energy balance is still disputable (Zhou et al., 2008).

Historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oils as fuel for diesel engines (Lang et al., 2001). In the following decades, the studies became more systematic and, nowadays, much is known about its use as fuel. Despite being energetically favourable, the direct use of vegetable oils in fuel engines is problematic. Due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. In Rudolph Diesel's 1893 paper "The Theory and Construction of a Rational Heat Engine" the German inventor described a revolutionary engine in which air would be compressed by a piston to a very high pressure thereby causing a sufficiently high temperature to ignite non volatile oils. His first working engine could run on various vegetable oils, leading him to envision in 1911 that "the diesel engine can

be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it” (Balat and Balat, 2008). Since then nearly all research has focused on how to improve the performance of the engine when using biologically based diesel fuel.

The term biofuel includes liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. A variety of fuels can be produced from biomass resources including liquid fuels, such as ethanol, methanol, biodiesel, gaseous fuels, such as hydrogen and methane. Liquid bio fuels are primarily used to fuel vehicles, but can also fuel engines or fuel cells for electricity generation. World production of bio fuels rose by some 20 percent to an estimated 54 billion litres in 2007 and these gains meant bio fuels accounted for 1.5 percent of the global supply of liquid fuels, up by just 0.25 percent from the previous year (Worldwatch Institute, 2011; Monfort, 2008). The justification for biodiesel as an alternative fuel is that it is remarkably the only alternative fuel currently available that has an overall positive life cycle energy balance. It yields as much as 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle compared to only 0.83 units for petroleum diesel (Sheehan et al., 2005). However, it is widely accepted that bio fuels are neither a panacea, nor without their disadvantages and risks. Major drawback is that converting edible vegetable oils like sunflower, soybean and canola to fuel will almost certainly compromise food security (especially within the global market context).

The vegetable-oil derivative ‘biodiesel’ offers several advantages as an alternative fuel for diesel engines. These include improved fuel performance and lubricity, a higher cetane rating than petro-diesel, a higher flashpoint that makes it safe to handle, lower toxicity to plants and animals, reduced exhaust emissions, and the fact that it is simple to phase in and out of use (Ma and Hanna, 1999; Zhang et al., 2003; Encinar et al., 2002; Sivaprakasam and Saravanan 2007). It is a local renewable source of energy and highly biodegradable (Meng et al., 2008; Ahn et al 1995).

Economically it reduces imports and affords improved security of energy supply. It also improves the quality of the environment with less and far less pernicious

soot generated from the exhaust of vehicles. Biodiesel can be blended at any level with petroleum diesel to create a biodiesel blend that can be used in compression-ignition (diesel) engines with little or no modification as the superior lubricating properties of biodiesel increases functional engine efficiency. Biodiesel not only has low viscosity, lower carbon monoxide emissions (Ryan et al., 1984) but also is simple to use, non toxic, essentially free of sulphur (Alcantra et al., 2000) and aromatics (Srivastava and Prasad, 2000). Its higher flash point makes it safer to store and the presence of a higher amount of oxygen (up to 10%) ensures more complete combustion of hydrocarbons.

Historically, energy continues to be the pivot of the economic and social development of all countries around the world and Africa is endowed with significant quantities of both fossil and renewable energy (RE) resources. According to Davidson et al., (2007), although energy has brought great economic prosperity, the way it is produced and used is inefficient and has adversely affected local, regional and global environments, hence the ongoing debate about making the energy systems more environmentally friendly. Strategies to develop energy resources must be extremely mindful of both the environmental pollution problems (through carbon monoxide, ozone forming hydrocarbons, hazardous particulates, acid rain-causing sulphur dioxide etc.) and the threat of “climatic change” associated with the use of fossil fuels, the latter as a result of the accumulation of certain greenhouse gases (GHGs) in the atmosphere (mainly carbon dioxide, methane and nitrous oxide that trap heat in the lower atmosphere and leads to global warming).

As adopted by the third conference of parties (COP3) in Kyoto, Japan in 1997, attempts have been made to agree to legally binding obligations on most developed countries to reduce their GHG emissions by an average of 5.2% below 1990 levels by 2012 (Amigun, et al., 2008a). In South Africa, the transport sector contributes some 16% of its greenhouse gas emissions, the greatest in Africa (Nolte, 2007). Of this, diesel fuel contributes about 17 % or 11,705,000 tonnes of CO₂ equivalent. An additional 1,622,000 tonnes is released from diesel fuel used for electricity generation (Wedel, 1999). Therefore South Africa has chosen to set

a limit on its green house emissions and increase its use of renewable energy sources. Reports indicate that greenhouse gas emissions are predicted to quadruple unless the government alters course (Schalkwyk, 2008).

In December 2006, the draft bio fuels strategy was approved by the South African cabinet to be implemented in consultation with industries. The draft strategy proposes a 4.5 % bio fuels industry development in South Africa and will achieve 75 % of the country's renewable energy target of over a billion litres of bio fuels by 2013. It has however not made good progress in developing its bio fuels policy, hampering the potential growth of the sector in Africa's biggest economy. Recent progress in the Brazilian and other developed countries bio fuels programme has highlighted the enormous opportunities that are open to African countries to reduce their dependency on imported oil and make meaningful contributions towards minimizing GHG emissions (Al Zuhair, 2007).

The Stern Review on the economics of climate change has also publicized the economic necessity to limit global warming (Stern, 2006). An accelerated release of fossil entombed CO₂ due to human activity is now generally accepted as a major factor contributing to the green house effect (Houghton et al., 2001). The poor distribution of fossil fuel resources makes over 70 % of countries on the African continent dependent on imported energy resources, which again supports the development of abundant renewable energy resources.

The topic of this dissertation focuses on different catalytic systems applicable in the process of producing biodiesel. A comparative and a process optimisation study of the transesterification catalytic processes which is an important goal in reducing production costs in biodiesel productions investigated and presented.

1.2 Research motivation

There are several reasons why bio fuels production needs to be considered as a relevant technology by both developing and industrialized countries, these include energy security, environmental concerns, foreign exchange savings, and

socioeconomic issues related to the rural sector. The sustainability, environmental and inflationary problems associated with conventional fuels has led to a global search for renewable biofuel (Amigun et al., 2008b).

Government support for bio fuels is gaining momentum and plans are being proposed and developed to promote the planting, harvesting and processing of crops such as maize, sugar cane, soy beans, cassava and oil seeds from trees and sorghum into bio ethanol and biodiesel feedstock for use in the liquid fuels industry (DST 2003). To this end the South African government has established a joint implementation committee (JIC) for the biodiesel industry. The JIC comprises a range of interested parties such as the South African Petroleum Industry Association, farmers, oil companies and unions. A biodiesel standard has been completed with the assistance of the South African Bureau of Standards, and the JIC is currently developing a pricing model for the local biodiesel industry (SADC, 2005).



1.3 Problem statement

Biodiesel presents a suitable renewable substitute for petroleum based diesel. Despite the successes experienced in the biodiesel industry as stated previously there still remain major challenges in the biodiesel industry, as production costs of biodiesel are still rather high compared to petroleum-based diesel fuel; the two main factors affecting the cost of biodiesel include the cost of raw materials and the cost of processing (Demirbas, 2009).

The current and majority of commercial biodiesel production processes are made by transesterification of vegetable oils and animal fats with methanol or ethanol, through a batch reaction (stirred tank reactors) in the presence of base or acid catalysts. There are however some challenges related to this process which include; (i) reaction rate can be limited by mass transfer between the oils and alcohol because they are immiscible, (ii) transesterification itself is a reversible reaction and therefore there is an upper limit to conversion in the absence of

product removal (iii) most commercial processes are run in a batch mode and thus do not gain some of the advantages of continuous operation.

In order to overcome these problems, an obvious method to avoid or minimise these difficulties is to use a continuous production process. In order to achieve this, it is necessary to have a good knowledge of the chemical transformations reactions and underlying this is the requirement to be able to analyse the conversion on a dynamic basis (Qiu et al., 2010). The continuous production process therefore permits the reaction conditions to be monitored and optimised. Hence, the need for the development of a new process intensification technology to improve mixing and mass/heat transfer between the two liquid phases to reduce production costs as current conventional techniques involves long reaction times, high molar ratio of alcohol to oil and catalyst concentration. Long residence times, high operating cost and energy consumption required to purify biodiesel and recover excess amount of alcohol and high catalyst during downstream processing amounts to waste and incur low production efficiency (Bournay et al., 2005).

Due to an increase of population which causes an increase in demand in diesel fuels, the quest for alternative fuels is widely focused. One possible alternative is using feedstocks for biodiesel production which consist of methyl esters from vegetable oil or animal fats that can be produced with the use of acid or base catalysts. Biodiesel production is effected by base catalysts such as NaOH, KOH and CH_3COONa but the separation of homogeneous catalyst from the esters is difficult (Ma and Hanna, 1999). This problem can be solved by the use of heterogeneous catalysts. In addition to these, the benefits of the use of heterogeneous catalysts could also include simplification of the separation and purification of the reaction products, elimination of the water washing procedure currently needed for the neutralisation of the biodiesel during production process, easy reuse of the catalyst in the reactor and reduced corrosion problems.

1.4 Research aims

Literature review has shown that there are a variety of options for the production of biodiesel. These are all disadvantaged in one way or the other to enable biodiesel production to be more readily performed as a continuous process; this work therefore addresses the following specific objectives.

- i. To determine the physical, chemical compositions of some identified fresh and used oil samples.
- ii. To evaluate the effects of the different reaction parameters on the yield and conversion rates of the different feedstock to their corresponding methyl esters
- iii. To maximize process parameters and evaluate the process optimisation of the different reaction systems used in producing the methyl esters.
- iv. To determine the characteristics of the methyl esters produced with each of the oil types investigated under different process conditions to meet industrial specification.
- v. To study biodiesel production under a continuous process via different process intensification technologies such as ultrasound or jet-loop mixing which may enhance physical process such as heat, mass, and momentum transfer compared to the conventional biodiesel process.
- vi. To utilize South African class F Arnot fly ash as catalyst support and the application of Arnot fly ash based zeolite Na-X as heterogeneous catalysts in the production of biodiesel.
- vii. To investigate the influence of various reactions parameters affecting all the tested reactions with respect to FAME yields and conversions.
- viii. To make a comparison of the transesterification catalytic processes involved in the different process intensification technique and biodiesel produced during these processes will be tested to ascertain if some standard parameters are met.

1.5 Research questions

This study aims to address the following questions;

- i. What are the optimum reaction parameters to process the fresh and used oil samples to biodiesel of high quality?
- ii. What are the optimum parameters for biodiesel production using either the homogenous or heterogeneous transesterification catalytic reactions systems?
- iii. Can a continuous scale up process (ultrasound and jet loop reactor) improve FAME yield and fuel quality of used cooking oil when used as feedstock and can the use of this scale up process (ultrasound and jet loop reactor) reduce the cost of production?
- iv. Can South African Class F Arnot fly ash be used as a support and raw material in the preparation of heterogeneous catalysts that could lead to potentially favourable yield of methyl esters from sunflower oil and easier refining of the produced biodiesel?
- v. Will the use of fly ash based materials present a catalytic system that is environmentally benign processes?
- vi. Will the biodiesel produced from these homogenous and heterogeneous transesterification catalytic reactions systems and process intensification meet or compare with standard quality specifications?

1.6 Research approach

The research approaches used in this study in order to achieve the aims and objectives of the study are hereby highlighted.

Homogeneous catalysis of vegetable oils to biodiesel

Characterization of fresh and used oil samples were carried out by analytical methods such as Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC) and Thin Layer Chromatography (TLC) to determine the chemical compositions of the samples to establish baseline data.

Transesterification reactions were conducted on the oil samples (sunflower, soybean and waste cooking oil samples) using homogeneous catalysts (KOH and NaOH) to obtain methyl esters (biodiesel) via the batch and continuous reactors to determine the best process parameters.

Heterogeneous catalysis of vegetable oils to biodiesel

This part of the thesis involves heterogeneous catalysts (KNO_3/FA) prepared from fly ash (obtained from Arnot coal power station, South Africa) and as-received fly ash based zeolite, $\text{FA}/\text{Na-X}$ obtained from the same fly ash. These catalysts were used in the transesterification reactions of a variety of feedstock with methanol to form methyl esters. The Arnot fly ash (AFA) was loaded with potassium (using potassium nitrate as precursor) via a wet impregnation method while the synthesized zeolite $\text{FA}/\text{Na-X}$ was ion exchanged with potassium (using potassium acac as precursor) to obtain the KNO_3/FA and $\text{FA}/\text{K-X}$ catalysts respectively, the use of these materials could improve dispersion of the active species, K_2O and provide available adsorption sites for the reagents (methanol and triglycerides) prior to the conversions to methyl esters.

Characterization of fresh fly ash and prepared fly ash based samples were carried out by XRF, XRD, SEM-EDS, and TPD analyses to determine their chemical and mineralogical compositions.

1.7 Research hypothesis

- i. Continuous processing using the jet loop and ultrasound will enhance process intensification and improve the reaction conditions necessary for the transesterification reaction.
- ii. The use of KNO_3/FA and AFA -zeolite $\text{FA}/\text{K-X}$ heterogeneous catalysts in transesterification reactions would present a process that is environmentally benign and leads to potentially favourable yield of methyl esters and easier refining of the produced biodiesel, and improved recovery of the catalyst.

1.8 Scope and delimitation

Three oil samples; sunflower, soybean and waste cooking oil were used as feedstock in the synthesis of methyl esters via transesterification reactions conducted under homogeneous and heterogeneous catalytic processes.

The homogeneous catalytic process was further enhanced using an ultrasonic homogeniser and a jet-loop reactor. Optimum conditions under the different processes were determined. The product (FAME) characterisations from the different processes were performed and results were compared to the conventional batch reaction process.

To address the limitations of the homogeneous catalytic process, heterogeneous catalysts prepared from fly ash were characterised and used for the transesterification reactions required to produce methyl esters at bench scale in a stirred batch reactor system. This catalytic process was developed and optimised; a product characterisation was also performed and compared to standard specifications.

Finally, a comparison study of the different process systems was conducted.

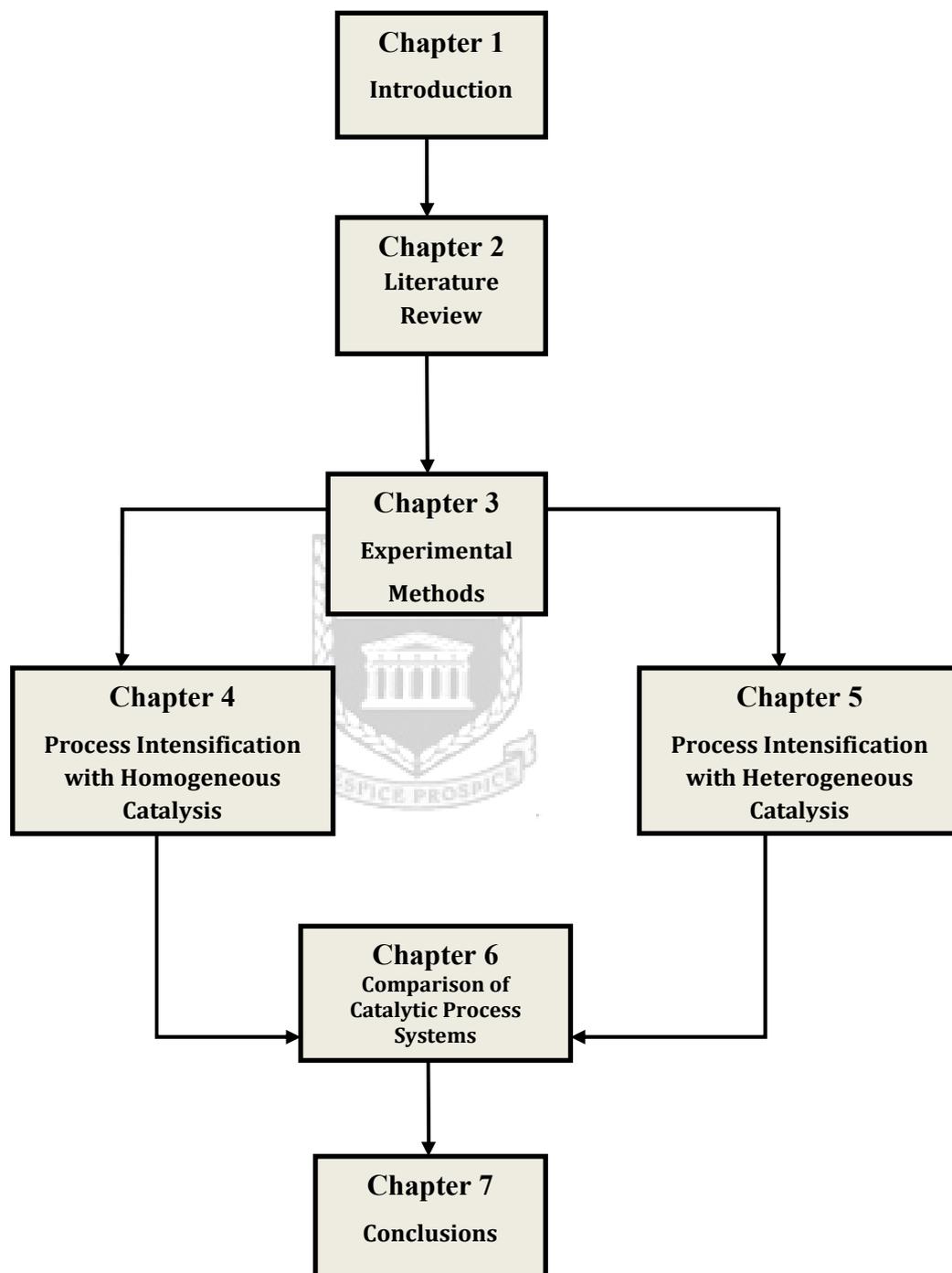
Delimitation

This study did not cover the following;

- i. Esterification reactions using an acidic catalyst (in the case of feedstock with high amounts of free fatty acids (FFA)).
- ii. Determination of the purity and yield of the glycerol (by product) from the transesterification reactions conducted in the course of the study was not investigated.
- iii. A study of the transesterification reactions via the ultrasound and the jet loop reactor with the heterogeneous catalyst were not investigated.

1.9 Thesis structure

This thesis is broken down into seven chapters.



Outline of the subsequent chapters**Chapter Two: Literature review**

The chapter deals with the review of the literature. It reviews the history, use, advantages and disadvantages of bio fuels and biodiesel in particular, world biodiesel production and the chemistry of biodiesel production. Biodiesel feedstock requirements and characteristics are also discussed in this chapter. The chapter also reviews literature on coal fly ash and the application of fly ash as a catalyst in biodiesel production. The properties and quality control of biodiesel and its role in biodiesel production is emphasized in the literature review.

Chapter Three: Experimental and analytical methods

Chapter three sets out the methodology applied in the course of the study. This chapter features the list of materials used, the research design and methods. A theoretical background of the analytical techniques applied in this study is also presented briefly. The experimental consists of a general section that explains the laboratory procedures conducted common to the work in general, and those specific to each milestone covered.

Chapter Four: Biodiesel synthesis via homogeneous catalysis

Chapter four details the optimisation results of the transesterification reactions of the different triglycerides (sunflower, soybean, waste cooking oil) into their respective methyl esters via homogeneous catalysis; in this case the catalysts used was KOH for both the conventional continuous batch process and continuous operation by applying the low frequency ultrasonic homogeniser as well as the larger scale jet reactor (a continuous system developed mainly for the intense agitation necessary to enhance the emulsifying of the liquid reactants into FAME). The influence of relevant process parameters and variables that affects the conversion and yield of FAME from the different feedstock are reported.

Chapter Five: Biodiesel synthesis via heterogeneous catalysis

This chapter presents and discusses the results of the characterisation of the heterogeneous catalysts prepared and used for transesterification reactions. The results of the characterization and the catalytic activity of the heterogeneous catalysts, KNO_3/FA and zeolite $\text{FA}/\text{K-X}$ were studied and discussed in this chapter. The influence of the catalysts on the different reaction parameters with regards to the heterogeneous catalytic transesterification reactions were also investigated and results presented.

Chapter Six: A comparative study of the catalytic processes

A comparative study of the different catalytic and reaction alternatives involved in the overall biodiesel production processes systems conducted in this study is the main focus of this chapter.

Chapter Seven: Conclusions and recommendations

Finally, in this chapter, the overall conclusions and the findings from this study are summarized and recommendations for future studies are made.

This chapter is followed by all the references that have been consolidated into a list.

Chapter 2

Literature Review

2. Introduction

The main focus of this chapter is a review of literature which is also based on the main perspective, rationale and motivation as presented in the previous chapter.

2.1 Renewable energy /Bio-energy

The development level of a country is directly related to its economic and social development. One of the most important factors that play an active role in achieving such development is energy. Energy can only be an impulsive force in industrialization and overall sustainable development of societies if it is supplied on time, in sufficient quantity, under reliable economic conditions with consideration and mitigation of the environmental impacts. The demand for energy increases rapidly in parallel with the population increase, industrialization and technological developments in developing countries (Tunç et al., 2007).

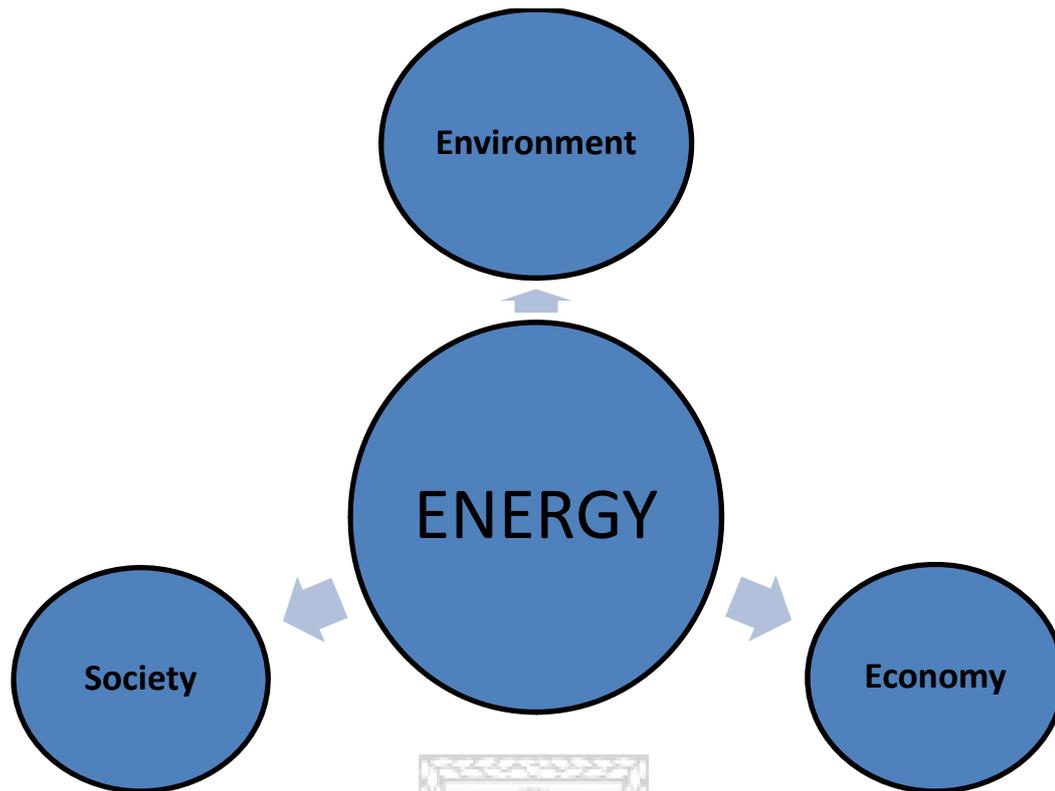


Figure 2.1: Interrelationships between energy and sustainable development (Amigun et al., 2011).

Africa currently constitutes 14 % of the world's population but accounts for only 2 % of its gross domestic product (GDP). Although the continent produces 7% of the world's total energy, it consumes only 3 % of it (Davidson 2007). According to the World Energy Council (2002), the energy intensity in Africa is twice the world average. The use of modern energy services is closely linked to development, poverty reduction and the provision of vital services. However the consumption of modern energy sources in sub Saharan Africa is extremely low owing to the region's reliance on traditional biomass. This access to secure, sustainable and affordable energy is therefore a pre-requisite for sustainable development in this part of the world. This access to affordable energy is an essential component of achieving the millennium development goals with respect to facilitating education and communication, enhancing health care services and responding to climate change.

Renewable energy sources are abundant in Africa, with more than 1.1 million gigawatts of exploitable hydropower capacity, more than 9000 megawatts of geothermal potential, substantial biomass and solar potential. However use of renewable energy sources is rather limited. With a total energy demand of approximately 267 million tons of oil equivalent in Sub-Saharan Africa in 1990, modern renewable energy sources account for less than 2 % of the region's primary energy demand (Elmissiry and Punungwe, 1998). Sub Saharan Africa also has significant amounts of renewable energy yet to be exploited, as renewable energy technologies (RETs) have demonstrated a growing potential to meet energy needs where conventional energy supply options have failed. If Africa were to take its place in the blossoming renewable energy market, the advantages would be plenteous. The potential to develop modern biomass technologies in Africa such as biogas, bio ethanol and biodiesel fuel specifically offers Africa some prospect of self reliant energy supplies at national and local levels with economic, ecological or environmental, social and security benefits (Figure 2.1). Energy consumption in Africa is largely dominated by combustible renewable resources. Energy from biomass accounts for more than 30% of the energy consumed in Africa and more than 80% in some African countries. Biomass constitutes the main energy resource for the large majority of African households for cooking, drying and space heating. From 1994 to 2004, primary energy consumption increased by 24 % in Africa according to reports on Energy for Sustainable Development in AFRICA (Figure 2.2a). Fossil fuels are however expected to continue supplying much of the energy used worldwide. Although liquid fuels remain the largest source of energy, the liquids share of world marketed energy consumption will fall from 35 % in 2007 to 30 % in 2035 (GENI, 2003), as projected high world oil prices lead many energy users to switch away from liquid fuels when feasible, making a way for renewable energy sources.

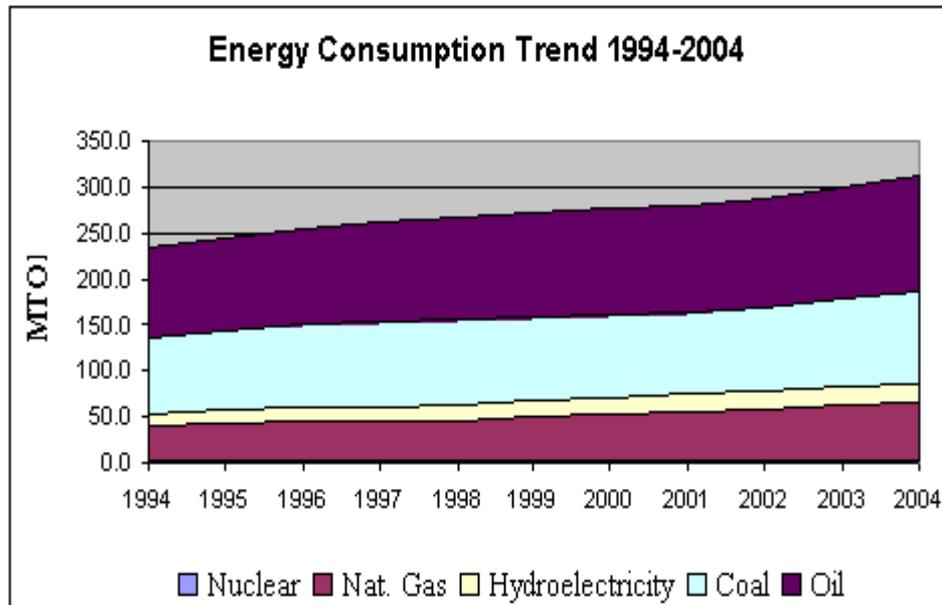


Figure 2.2a: Modern Energy Consumption trend in Africa (UNECA, 2006)

Energy use in the transportation sector includes the energy consumed in moving people and goods by road, rail, air, water. The transportation sector is second only to the industrial sector in terms of total end-use energy consumption. Almost 30 percent of the world's total delivered energy is used for transportation, most of it in the form of liquid fuels. The transportation share of world total liquids consumption increase is projected from 53 % in 2007 to 61 % in 2035 in the *IEO2010* reference case, accounting for 87 % of the total increase in world liquids consumption (IEA 2010). Over 25 % of total U.S. greenhouse gas (GHG) emissions come from the transportation sector (see Figure 2.2b), making transportation the second largest source of GHG emissions in the United States after the electric power sector. Thus, understanding the development of transportation energy use is one of the most important factors in assessing future trends in demand for liquid fuels.

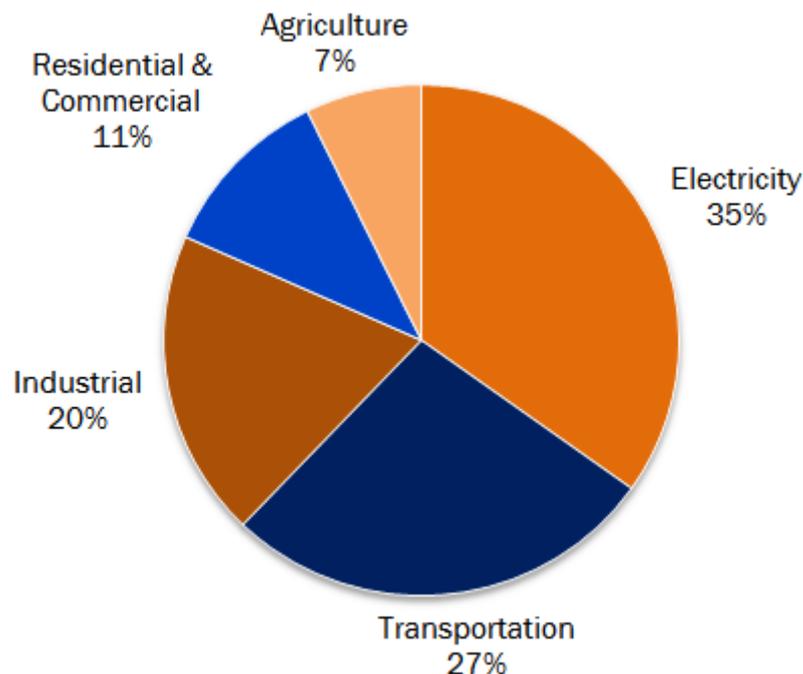


Figure 2.2b: Sectors contributing to GHG (USEPA, 2008)

2.2 Bio-fuels

Biofuels are not a recent discovery. The transesterification of vegetable oils has been widely known and employed since the 19th century. In fact, the process currently in use for making bio fuels from biomass is the same inherited from the past. The feedstocks utilised for their preparation were also very similar. Peanut, hemp and corn oil and animal tallow were conventionally used and have been partially replaced by soybean, rapeseed, recycled oil, forest wastes and trees and sugar cane. But the history of bio fuels is more political and economical than technological.

Biofuels can be broadly defined as any sort of fuel that is made from organic matter (biomass). The most common bio fuels are biodiesel and bio alcohols, including bio ethanol and bio butanol (also called bio gasoline).

Liquid bio fuels for transport have been used since the early days of the automobile industry. Nikolaus August Otto, the German inventor of the internal

combustion engine conceived his invention to run on ethanol. In 1898, Rudolph Diesel used peanut oil (the “original” biodiesel) in the first demonstration of his compression ignition engine at the World’s Exhibition in Paris. Vegetable oils were used in diesel engines until the 1920’s when an alteration was made to the engine, enabling it to use a residue of petroleum (currently known as No. 2 diesel fuel).

Diesel was not the only person to believe that bio fuels could be the way forward for the transportation industry. Henry Ford was also so convinced that renewable resources were the key to the success of his automobiles that he designed them (from the 1908 Model T) to be run with ethanol. He also built an ethanol plant in the Midwest and established a partnership with Standard Oil to sell it in their distributing stations.

At the beginning of World War II, both the Allies and Germany utilized biomass fuels in their machines. Wartime Germany experienced extreme oil shortages. The vehicles were then powered with blends including Reichskraftsprit that was a blend of gasoline with alcohol fermented from potatoes. In Britain, grain alcohol was blended with petrol by the Distillers Company Ltd. Under the name Discol and marketed through Esso’s affiliate Cleveland. Despite their use during World War II, bio fuels have since remained in obscurity to which they had been forced by fossil fuels (petroleum). Until the 70s, the solid petrol-based industry establishment made the world very dependent on foreign oil. However, the supply of crude oil, as are all supplies of fossil fuels, is limited. In 1973, the first of two oil crises was experienced. The second one came five years later in 1978. The Organisation of the Petroleum Exporting Countries (OPEC) that controls the majority of the global oil reduced supplies and increased prices. (Luque et al., 2008).

The potential of bio fuels reappeared in the public consciousness, brought back by various bio-energy programs including the Programa Nacional do Alcool (Proalcool) established in Brazil in 1975 (which was critical in the development of ethanol fuel) and international organisations such as the International Energy Agency (IEA) Bioenergy, established in 1978 by the Organisation for Economic

Co-operation and Development (OECD), that aimed to improve cooperation and information exchange between countries that have national programs in bio energy research, development and implementation.

On a worldwide scale, the United Nations (UN) International Biofuels Forum is formed by Brazil, China, India, South Africa, the United States and the European Commission, the United States, Brazil, France, Sweden and Germany being the world leaders in biofuel development and use.

The global development of the bio fuels industry over the years has been triggered by a global crisis caused by an increased use of fossil fuels, resulting in limitations of supply, high inflationary prices and negative environmental impact. With respect to Africa, energy resources are unevenly distributed and a majority of African countries are net energy importers as they import petroleum products at a cost that places an economic burden and reduces energy security and sovereignty (Amigun et al., 2011). However Africa possesses vast biomass resources which are presently under-utilised or not used at all despite the large resource base, and thus possesses the potential to become an important source of bio-fuels and such use could make a considerable contribution to poverty relief of rural African communities (Amigun et al., 2008).

Southern Africa is believed to have the largest untapped potential of bio fuels in the world (Mwakasonda, 2007). The biodiesel development in the Southern Africa region and the whole of Africa is however, still in its infancy and considerable interest, has recently attracted debates among policy makers, development practitioners, donors and other stakeholders with respect to the development of bio fuels in the African context.

The continuous use of non-renewable fossil fuels causes serious damage to the environment, while oil reserves are rapidly being depleted with increased global consumption resulting in limited supply and increasing fluctuations in the price of crude oil. For the most part, it is the concern about the health and environmental effects of diesel that has spurred this recent upsurge in interest as diesel soot is

known to cause cancer (Zmirou et al., 2000) and it has been reported that burning diesel is a major contributor to global man-made CO₂ production (Peterson and Hustrulid, 1998).

According to Sustainable Development Commission (SDC) the use of bio fuels can lead to a reduction in Green House Gases (GHG). To render this reduction achievable, a series of careful measures are required. The use of bio fuels has to be balanced against any environmental and social detriment amongst other factors (Amigun et al., 2011). There are several reasons for bio-fuels to be considered as relevant technologies by both developing and industrialized countries (Demibras, 2008) which include: source of foreign exchange saving activity especially for oil-deprived countries (development and use of locally-produced renewable fuel, and reduction of demand for imported petroleum), boosting of local agriculture productions and additional markets and revenue to farmers; leading consequently to the increase of rural people's purchasing powers and quality of life, beneficial environmental impact through the use of organic municipal solid waste materials to generate a higher value end-product, reduced level of carbon dioxide emitted by motor engines and thus preservation of the quality of the atmosphere. Ideally, the biofuel alternatives should reduce (or even remove) the dependence on oil as well as contributing as much as possible to meet the GHG emissions target. However, it is also widely accepted that joint efforts from politicians, regulators, scientists and consumers will be needed to support an independent oil/ GHG controlled scenario in the future.

In South Africa, the transport sector contributes about 16% of its greenhouse gas emissions, the greatest in Africa. This sector accounts for 26 % of global CO₂ emissions (Chapman, 2007), of which roughly two thirds originate from the wealthiest 10 % of countries (Lenzen and Hamilton, 2003). Of these, diesel fuel contributes about 17% or 11,705,000 tonnes of CO₂ equivalent. An additional 1,622,000 tonnes is released from diesel fuel used for electricity generation (Nolte, 2007). In order to reduce CO₂ emission from road transport, a significant modal shift onto a more environmentally benign source of energy is required

(Waterson et al., 2003). Oils of vegetable and animal origin, unlike fossil fuels, have the potential to provide energy not only on a sustainable basis but could also be greenhouse gas neutral, or at the very least, emit substantially less greenhouse gases per unit energy. The need for a secure energy supply for transportation makes it essential to explore bio fuels as an alternative to mineral oil based fuels.

The share of bio-fuel in the automotive fuel market has been predicted to grow fast in the next decade according to reports by Thurmond (2010). An exponential increase in the consumption of these bio fuels has taken place in the last few years in the European Union (EU) according to reports by the IEA (2007) (Figure 2.3). In order for bio-fuels to be a viable alternative to conventional fuels, it is recommended to provide net energy gain, be environmentally beneficial, economically competitive and available in large quantities without reducing food supplies.

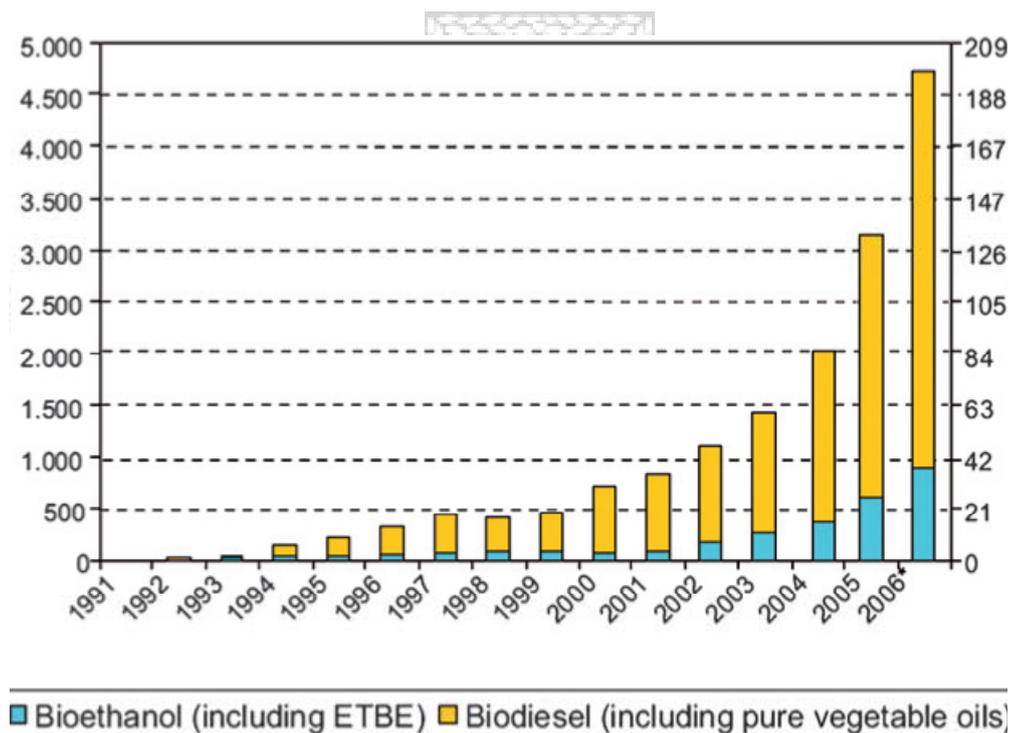


Figure 2.3: Biofuels consumption (1991–2006) in the EU 27 (Luque et al., 2009)

2.3 Biodiesel

In the 1920's, technological changes made it possible to use smaller diesel engines which required lower viscosity fuels. In 1977 a Brazilian scientist, Expedito

Parente created the first true biodiesel fuel, using the process called transesterification, he was the first to receive a patent for biodiesel fuels, and it is following his process that all biodiesel fuels were created. The first compression ignition engine was however patented by Rudolf Diesel where he used large injectors to prevent clogging by using viscous heavy fuels (unrefined vegetable oils and petroleum oil). Engines of large warship and vegetable oil powered heavy duty vehicles used in South Africa before World War II was among the mobile users of Diesel's technology. Then the petroleum industry began producing inexpensive medium weight diesel fuels which essentially shut down the bio-fuel market (Bradely, 2008). The history of biodiesel began at the Paris world exposition in 1900, where one of the five diesel engines exhibited at the exposition ran on peanut oil. The French Government at that time was interested in a local energy source for its African colonies as Rudolf Diesel's research with respect to the use of vegetable oils as fuel for diesel engines. As previously mentioned, this was the first known use of a vegetable oil as a diesel fuel.

According to Friedrich (2003), biodiesel is defined as the fatty acid alkyl derived from the transesterification of vegetable oils or animal fats. Thus it is the product obtained when a vegetable oil or animal fat (triglyceride) reacts with an alcohol in the presence of a catalyst and glycerol is produced as a by-product.

In South Africa, biodiesel is restricted by the SANS 1935 automotive standard to being a fatty acid ester (FAME) derived only from vegetable oils (The South African Bureau of Standards, 2006). This means that either oilseeds or their subsequent crude vegetable oil can be used for the production of biodiesel or FAME (fatty acid methyl ester) in South Africa. Table 2.1 gives a description of the similar properties and performance parameters of biodiesel and fossil diesel.

Table 2.1: Selected properties and performance parameters of fossil and biodiesel diesel (Anton et al., 2008)

Fuel property	Diesel Biodiesel	
Fuel standard	ASTM D 975	ASTM D6751
Fuel composition	C ₁₀ -C ₂₁ HC	C ₁₂ -C ₂₂ FAME
Kinetic viscosity, mm ² /s (at 40 °C)	1.3–4.1	1.9–6.0
Specific gravity, kg/L	0.85	0.88
Boiling point, °C	188–343	182–338
Flash point, °C	60–80	100–170
Pour point, °C	-15 to5	15-10
Cetane number (Ignition quality)	40-45	48-65
Stoichiometric air/fuel ratio (AFR)	15	13.8
Life-cycle energy balance (energy units produced per unit energy consumed)	0.83/L	3.2/L

HC, Hydrocarbons; FAME, Fatty acid methyl esters

An important characteristic of diesel fuels is the ability to auto-ignite which is quantified by the cetane number (cetane index). Biodiesel not only has a higher cetane number than petroleum diesel but also has a higher flash point, meaning better and safer performance. Blends of biodiesel and petroleum diesel are designated by a “B” followed by the volume % of biodiesel. B5 and B20, the most common blends, can be used in unmodified diesel engines. Remarkably, biodiesel is the only alternative fuel currently available with an overall positive life-cycle energy balance (Figure 2.5), producing 3.2 units of fuel product energy per unit of fossil energy consumed, as compared to barely 0.83 units for petroleum diesel. The presence of oxygen in biodiesel (~10%) improves combustion and reduces CO, soot, and hydrocarbon emissions while slightly increasing the NO_x emissions (Anton et al., 2008).

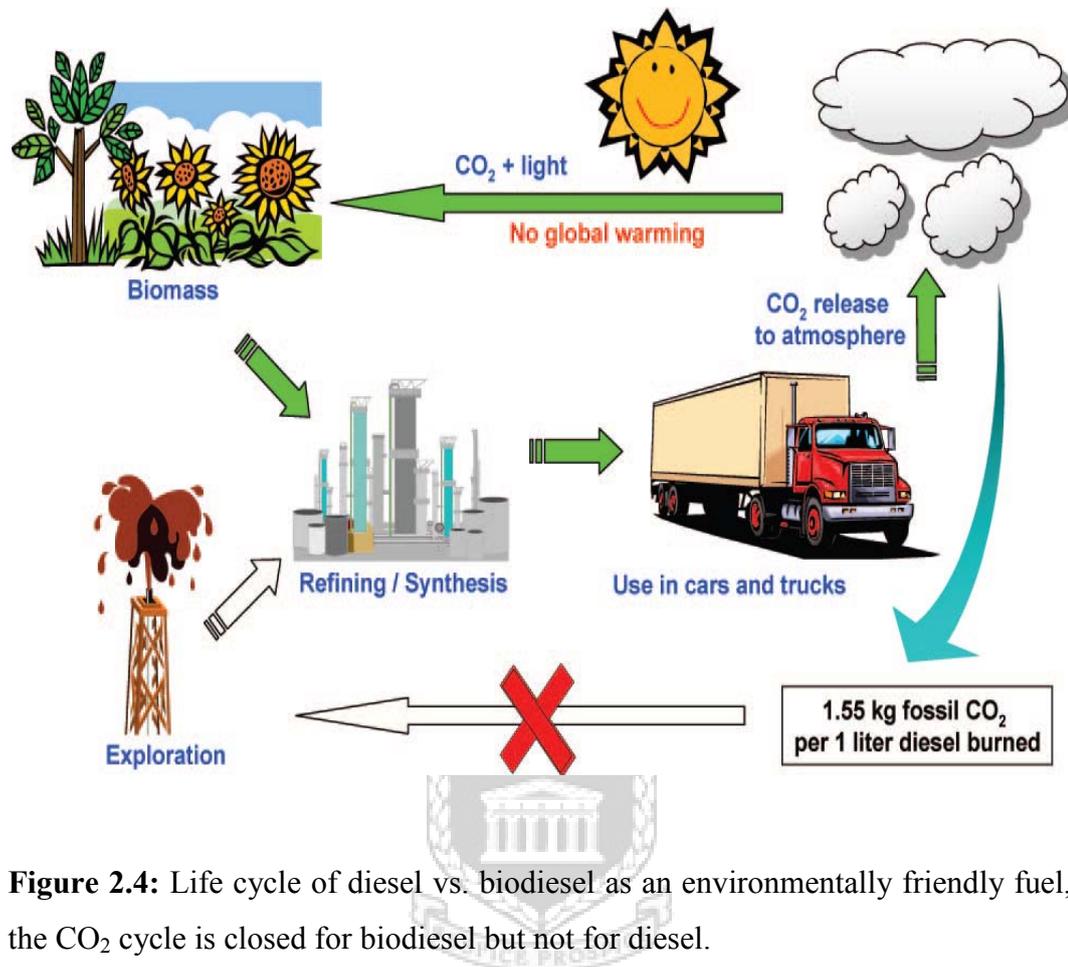


Figure 2.4: Life cycle of diesel vs. biodiesel as an environmentally friendly fuel, the CO₂ cycle is closed for biodiesel but not for diesel.

2.3.1 Advantages of biodiesel use

Biodiesel can lead to 50 % or more reduction in Particulate Matter (PM), Hydrocarbons (HC) and Carbon oxides (CO) following a report summarized by the United States Environmental Protection Agency (see Figure 2.5)

Economically, biodiesel reduces imports and affords improved security of energy supply. It also improves the quality of the environment with less and far less pernicious soot generated in the exhaust of vehicles. Biodiesel can be blended at any level with petroleum diesel to create a biodiesel blend that can be used in compression-ignition (diesel) engines with little or no modification as the superior lubricating properties of biodiesel increases functional engine efficiency.

Biodiesel not only has low viscosity, lower carbon monoxide emissions but also is simple to use, non toxic, essentially free of sulphur and aromatics. Its higher flash point makes it safer to store and the presence of a higher amount of oxygen ensures more complete combustion of hydrocarbons.

It burns up to 75 % cleaner than conventional fossil diesel as it substantially reduces unburned hydrocarbons, carbon monoxide and particulate matter and eliminates sulphur dioxide emissions in exhaust fumes and its ozone-forming potential is nearly 50 % less than fossil diesel fuel. Biodiesel is a renewable energy source as it is plant-based and adds no CO₂ to the atmosphere.

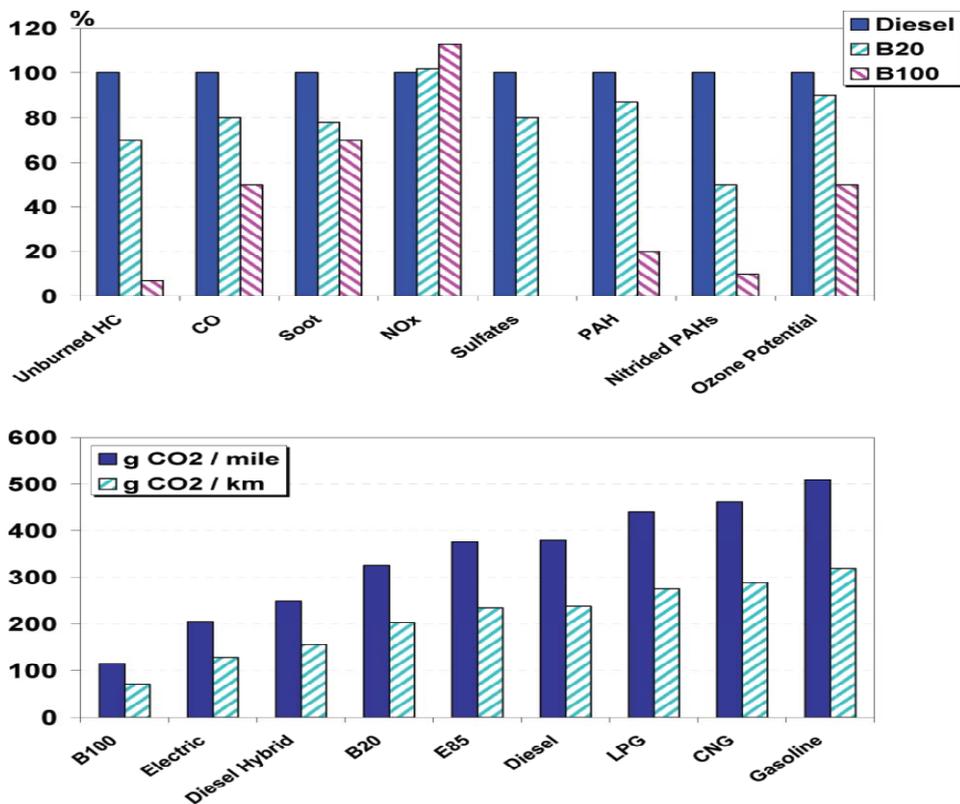


Figure 2.5: Biodiesel vs petroleum diesel emissions (top). Comparison of CO₂ emissions for most common fuels (bottom) (USEPA 2002).

2.3.2 Disadvantage of biodiesel use

Although the advantages make biodiesel seem very appealing, there are also several disadvantages to consider when using biodiesel which include the following; (i) Due to the high oxygen content, it produces relatively high NO₂ levels during combustion but these can be reduced to below fossil diesel fuel levels by adjusting engine timing and using a catalytic converter (ii) storage conditions of biodiesel must be monitored strictly as biodiesel has lower oxidation stability and oxidation products that may be harmful to vehicle components could be produced (iii) contact with humid air must be avoided due to its hygroscopic nature. (iv) it has a higher cold-filter plugging point temperature than fossil diesel meaning it will crystallize into a gel at low temperatures when used in its pure form (v) it can cause dilution of engine lubricant oil, requiring more frequent oil change than in standard diesel-fuelled engines, (vi) it is a strong solvent and scrubs out all the tars, varnishes, and gums left by fossil diesel in the fuel system which means that the fuel filter will have to be replaced a few times during the initial stages of biodiesel use (vii) modified refuelling infrastructure is needed to handle biodiesel which adds to total cost of production (Nolte, 2007).

2.3.3 Biodiesel feedstock requirements

Traditionally, conventional major feedstocks for the “methyl ester process” are cotton seed oil, soybean, sunflower and peanut oil (Weber, 2009). Another suitable feedstock for the “methyl ester process”, which can be used and grown in Southern Africa, is *Jatropha*, attractive in view of the uncertainty of conventional feedstock and also to avoid conflict between energy and food, since it is non-edible oil.

The type and quality (composition and purity) of the feedstock affect the yield of the final products. These are decisive factor on the technical design of a transesterification plant and respectively on the corresponding material and energy flows, which are not only indicators of technical efficiency, but also affect the economic efficiency of biodiesel production. When selecting a feedstock to produce biodiesel it is important to consider the yield per hectare, environmental

and social impacts as well as the quality of the material. The yield per hectare of feedstock determines the economic viability of the biodiesel. The higher the feedstock yield, the lower the production cost. A detailed evaluation of feedstocks on the basis of a specification of the significant characteristics of oils and fats has been identified, analysed and studied (Amigun et al., 2011).

The various potential feedstocks for biodiesel production that are currently available in Southern Africa which can be considered suitable on first sight are presented in Table 5 (see appendix 5). A whole range of oil producing crops that possess potential for use as biodiesel feedstock are also grown globally (see appendix 6). However, only a limited number of these feedstocks are currently grown and/or have the potential to be grown in Southern Africa. Sunflower and soybean are already being widely grown in the region and their production can easily be expanded wherever there is irrigation and water. Their impact on employment is high. They are already widely grown by both large and smallholder farmers as a food crop and an industrial crop. Expanded use for biodiesel can create additional demand and stimulate production, and this can be achieved within one season by increasing the area under production. Although, the yield of sunflower is better than soybean (yield is highly influenced by seed selection, plant density, and pest and weed control), the availability and price of these seed oils are high and low respectively. For these reasons, these seed oils were the choice as feedstock for the transesterification reactions.

The limited availability of recycled oil is a big constraint to large-scale production of biodiesel using this feedstock. This is the primary feedstock used for the production of biodiesel in most small to medium scale biodiesel plants in South Africa. The collecting and recycling of used oils is a highly competitive business. For example, yellow grease is a potential feedstock for the manufacture of soap, textiles, cleansing creams, inks, glues, solvents, clothing, paint thinner, rubber, lubricants and detergents, to list but a few. It is also possible to use it as a livestock feed additive. It makes the feed less dusty and adds lubrication to the feed, reducing wear on milling machinery. It is a dense source of energy, which is important for animals like cattle and horses that have a hard time eating. Apart

from the quantity constraint, the quality of the oil can have a knock on effect on the quality of the biodiesel produced (Nigam and Singh, 2010).

A viable biodiesel industry in Southern Africa cannot survive primarily on recycled oil due to their limited supply and availability. To meet the long-term feedstock need of the industry in the Southern Africa, a dedicated biodiesel oilseed(s) will need to be identified and developed.

The “second generation” biodiesel feedstock which is the use of algae has the potential to dramatically expand the resource base for the production of biodiesel in the future. This approach can contribute to solving two major problems of air pollution from CO₂ and the future crises of food competition with energy production. Algae can be grown using waste materials such as sewage and without displacing land currently used for food production. However, the production of algae to harvest oil for biodiesel has not been conducted on a commercial scale, but the potential is promising. The potential of microalgae as an alternative and sustainable energy source has generated significant research and business interest in the past few years and currently, many companies are pursuing algae bio-reactors for various purposes, including scaling up biodiesel production to commercial levels. Specifically, the Biodiesel 2020 study by Thurmond, (2008) reported that algae may hold the key to meeting large-scale, sustained feedstock shortages in the US, Europe and Asia.

Generally, it is important to note that no single agricultural feedstock or recycled product can supply sufficient feedstock to meet national biofuel (biodiesel) targets. Constraints on land suitable for any single feedstock and competing demands from other markets (e.g., food, feed, wood products) preclude such a research or production focus. A wide array of feedstock will lead to more geographic diversity, less resource pressure on any one location, and greater resilience to drought, pests, and other production shocks. Research on feedstock that increases yield for existing feedstock and reduces pressure on cropland should be carried out for sustainable biodiesel development in the Southern Africa.

2.3.4 Biodiesel feedstock characteristics

The sources of triglycerides are diverse, ranging from single fatty acids to waste oils with edible soybean oil being the oil most frequently used for research (Demibras, 2009). Other vegetable oils such as rapeseed, sunflower, palm kernel and canola oil follow in terms of frequency of application (Ma and Hanna, 1999). Animal fats and used cooking oils have also been studied from the motivation to use cheap oil sources or the desire to meet the regional oil availability but their irregular chemical composition makes application difficult. In chemical terms, each oil source has a specific composition of fatty acids as shown in Figure 2.6.

The fatty acid profile of a particular oil sample is the amount of the different fatty acids present in the sample. The fatty acid profile can be used to predict both physical and performance properties of the biodiesel product. For example, biodiesel produced from tallow, a highly saturated fat, tend to have a higher freezing point that can inhibit cold flow properties. In chemistry, a fatty acid is a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28 (IUPAC, 1997).

Fatty acids are usually derived from triglycerides or phospholipids. When they are not attached to other molecules, they are known as "free" fatty acids (FFAs). These fatty acids are used for the production of soap within the transesterification reaction. The FFA content of an oil sample can also be used as a guide to determine the extent of deterioration of its quality. A triglyceride molecule is made up of three fatty acid units attached to a three-carbon backbone. If all carbon atoms of the free acid are connected in single bonds they are called saturated; a triglyceride molecule is monosaturated if it contains one double bond and polysaturated if it contains more than one double bond as illustrated in Figure 2.7. The structure of a typical triacylglyceride molecule containing stearic acid, oleic acid and palmitic acid bound to a glycerol backbone is shown in Figures 2.8.

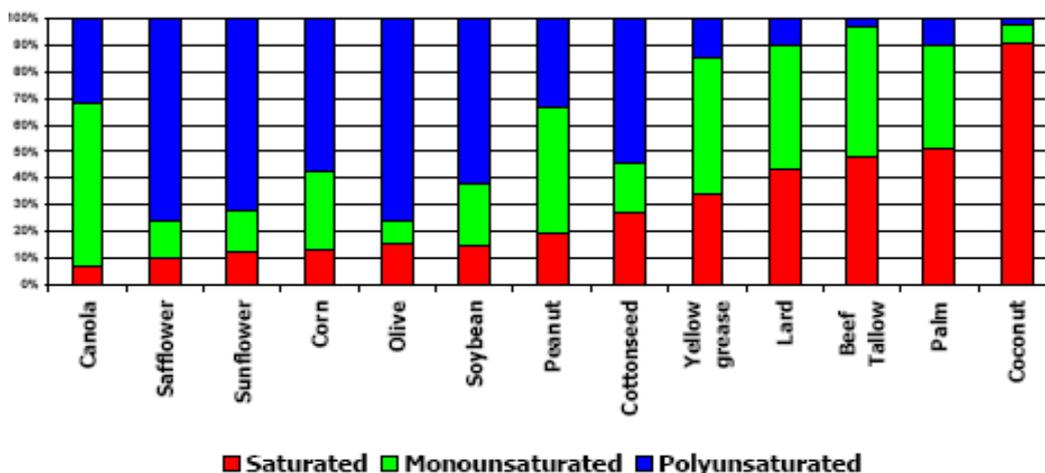


Figure 2.6: Fatty acid profile of different feedstock (Tyson &McCormick, 2006; IEE, 2006)

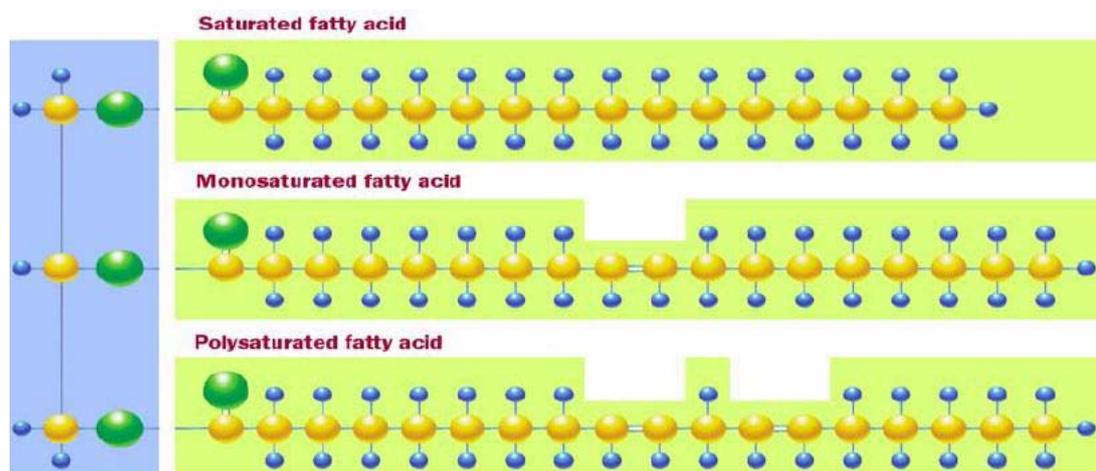


Figure 2.7: Exemplary composition of a triglyceride (UFOP, 2006)

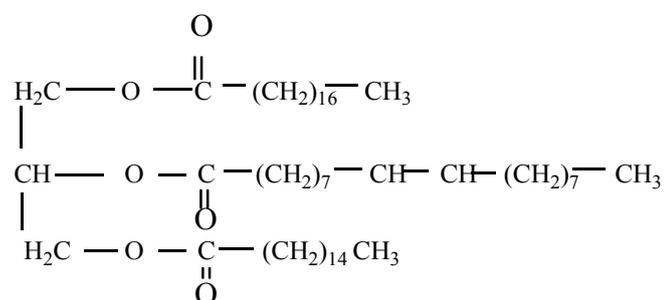


Figure 2.8: Structure of a typical triacylglyceride molecule with different fatty acids bound to the glycerol backbone.

The chemical features of fatty acids are collectively described by their carbon number and degree of unsaturation. These features affect the reactivity toward the transesterification and as a result the properties of produced biodiesel (FAME). This is important, since the FFA content affects the yield potential and thereby has a major impact on the economic feasibility of the feedstock (Mattingly et al., 2004). High FFA content in combination with conventional base catalysed transesterification lowers the yield of biodiesel and produces by products like soap stock and water as shown in Figure 2.9a. The selection of the catalyst which is central to the biodiesel conversion process is also dependent on the free fatty acid (FFA) present in the oil (Helwani et al., 2009). For triglyceride stock having lower amount of FFAs, base catalysed reaction gives a better conversion in a relatively short time while for higher FFAs containing stock, acid catalysed esterification followed by transesterification is suitable (Schuchardt et al., 1998) to avoid hydrolysis of the final ester product (confer Figure 2.9b).

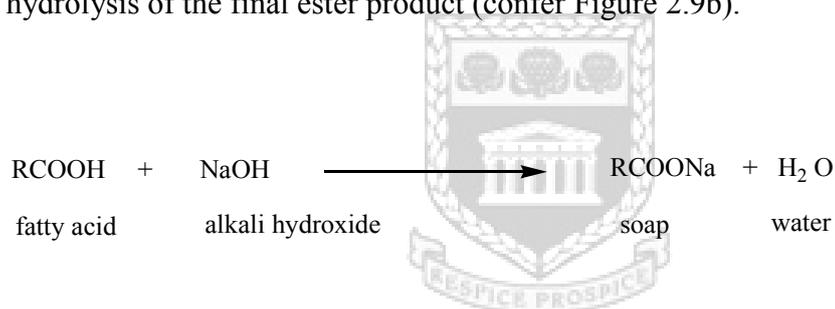


Figure 2.9a: Formation of soap with high FFA content feedstock

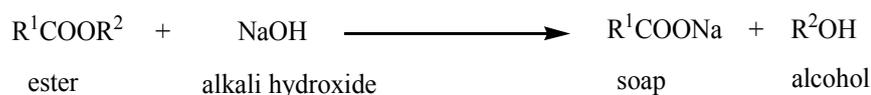


Figure 2.9b: Formation of soap by the hydrolysis of esters

2.3.5 Biodiesel feedstock costs

A major barrier in the commercialization of biodiesel production from vegetable oil is its high manufacturing cost, which is due to the higher cost of virgin vegetable oil. The cost of vegetable oil has a crucial role in the economics of the biodiesel. The significant and most crucial variables that affect the cost of

biodiesel are feedstock cost (cost of the raw materials), plant size and value of the glycerol by product (Gerpen, 2005; Ayhau, 2009; Al-Zuhair et al., 2007; Nelson and Schrock, 2006). Biodiesel feedstock are classified by the amount of free fatty acids they contain; refined vegetable oils <0.05%, crude vegetable oils 0.5-5%, used cooking oils 2-7%, animal fat 10-30 % (Maa and Hanna, 1999).

The production of biodiesel from waste cooking oil is one of the better ways to utilize it efficiently and economically (Gerpen, 2005; Wang et al., 2006; Zhang et al., 2003). The data on the requirements of diesel fuel and availability of waste cooking oil in any country indicate that the biodiesel obtained from waste cooking oil may not replace diesel fuel completely. However, a substantial amount of diesel fuel can be prepared from waste cooking oil, which would partly decrease the dependency on petroleum-based fuel. The amount of waste cooking oil generated in each country varies, depending on the use of vegetable oil.

Many developed countries have set policies that penalize the disposal of waste oil through water drainage. With respect to South Africa by-product disposal may present difficulties and environmental considerations may preclude production in sensitive areas (Meciarova et al., 2000). An estimate of the potential amount of waste cooking oil collected in South Africa is about 1.5 million litres per month and a total of 18million litres per year (Nieuwoudt, 2010).

2.4 World biodiesel production

Biodiesel currently accounts for only 10 % of the world bio fuels production with ethanol making up the rest. Global biodiesel production has expanded nearly fourfold in the last decade (Thurmond, 2010) with top producers being Germany, France, USA, Italy and Austria. Many governments wish to support their own farmers by creating new markets for agricultural products and to realize these non technical objectives, governments around the world have set up tax exemption systems, tax incentives and other energy credit systems making start ups in biodiesel production feasible and economically sustainable. Biodiesel for transport energy is an opportunity from a technical point of view, moreover high

performance biodiesel with outstanding cetane numbers and flow characteristics can generate new flexibility when blended with fossil diesel. According to Hou and Zheng, (2009) years of heavy investments in biodiesel production has resulted in a worldwide market. Recently published estimates predict that annual demand for biodiesel will grow within the next few years from six to nine million tonnes in the USA and from five to fourteen million tonnes in the EU (Thurmond, 2010).

2.5 Biodiesel production

Biodiesel can be prepared from a variety of sources including vegetable oils such as oilseeds (rapeseed, soya bean, canola oil, sunflower oil), animal fats, waste oils and greases (Gerpen, 2005) and most recently potentially from algae which have much higher yields and therefore poses less of a threat to food and water security (Chisti, 2007). There are five primary ways for making biodiesel: direct use and blending of vegetable oil (Maa et al., 2004), use of micro emulsions with short chain alcohols (Nimcevic, 2000), (iii) thermal cracking (pyrolysis) of vegetable oils (Alcantra et al., 2000) (iv) transesterification of triglycerides catalysed by bases or esterification of fatty acids with alcohols using acid catalysts (H_2SO_4) or solid acid catalysts (Kim et al., 2004; Bournay et al., 2005; Ondrey, 2004) and use of enzymes (Mittelbach, 1990; Shah et al., 2004; Hsu et al., 2004; Saka and Kusdiana, 2001) (v) catalyst free processes.

2.5.1 Direct use and blending

Vegetable oils may be used as fuels or blended with fossil diesel for use in diesel engines. However several obstacles need to be overcome, as these oils typically show viscosities ten to twenty times higher than the viscosity of fossil fuel diesel. This quality leads to poor fuel atomisation and results in incomplete combustion and the tendency for thermal and oxidative polymerisation leading to the formation of deposits on the injector nozzles. This can only be solved by the adapting the fuel to the engine and vice versa (Srivastava and Prasad, 2000).

Moreover blending diesel fuel with vegetable oil would require vegetable oil from 0 % to 34 % if proper atomisation is to be achieved (Mittelbach and Remschmidt, 2006).

Biodiesel can be used in its pure form, also known as neat biodiesel or B100. This is the approach that provides the most reduction in exhaust particulates, unburned hydrocarbons, and carbon monoxide. It is also the best way to use biodiesel when its non-toxicity and bio-degradability are important. Although neat biodiesel would not be expected to cause any operational problems, its solvent properties are at the highest intensity and may cause problems in loosening of varnish deposits in fuel tanks and degradation of fuel lines because some elastomers are not compatible with biodiesel (such as BUNA rubbers). It may cause paint removal near fuel fill ports (Biodiesel Education, 2006).

2.5.2 Microemulsion

Different derivatives such as microemulsions or blends of various vegetable oils with conventional fuel have been proposed as alternative fuels for diesel engines. As the formation of micro emulsion (co-solvency) is one of the four potential solutions for solving the problem of vegetable oil viscosity and various investigators have studied micro emulsification of vegetable oils with different alcohols and arrived at the conclusion that microemulsions of vegetable oils and alcohols cannot be recommended for long term use in diesel engines for similar reasons as applied to neat vegetable oils. The fuels are prone to incomplete combustion, the formation of carbon deposits and an increase in the viscosity of the lubricating oil (Mittelbach and Remschmidt, 2006).

2.5.3 Pyrolysis (thermal cracking)

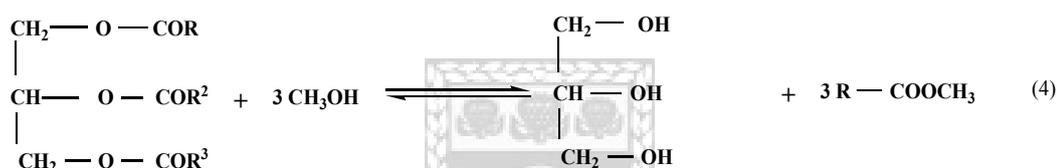
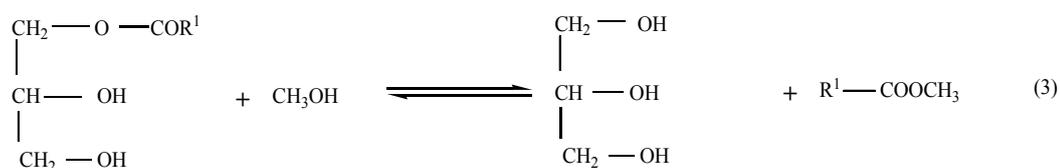
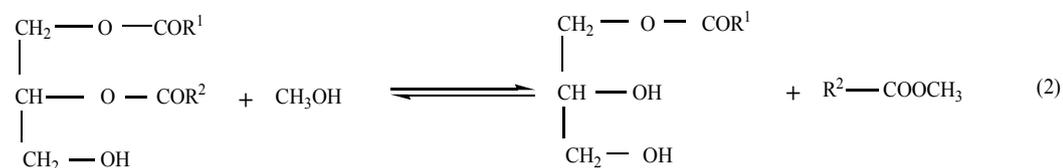
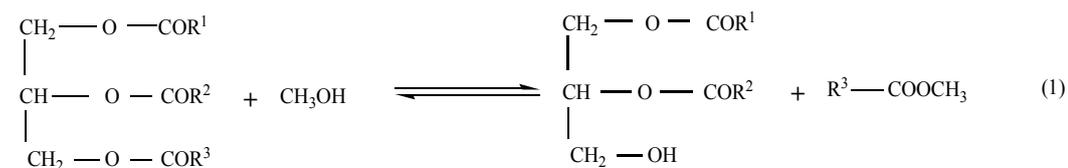
Pyrolysis of fats has a history of more than a century and has been used especially in areas of the world where there was no fossil fuel (Maa and Hanna, 1999). Pyrolysis denotes thermal decomposition reactions, usually in the absence of oxygen. This treatment results in a mixture of alkanes, alkenes, alkadienes, aromatics, and carboxylic acids; similar to the hydrocarbon –based diesel fuel in

many respects but the cetane number of the oils used is increased and the concentrations of sulphur, water and sediment for the resulting products are acceptable. However according to modern standards, the viscosity of the fuels is considered as too high, ash and carbon residues far exceed the values for fossil diesel and the cold flow properties of the resulting fuel is poor (Knothe and Steidley, 2005). It has also been argued that the removal of oxygen during this process eliminates one of the main ecological benefits of oxygenated fuels.

2.5.4 Transesterification of triglycerides

Biodiesel can be produced by the transesterification of triglycerides (TG) with alcohol, commonly methanol, in the presence of a base or acid catalyst, into fatty acid methyl esters (FAME). It can also be produced under a number of different processes highlighted subsequently.

There are three stepwise reactions that occur with the formation of the diglycerides (DG) and monoglycerides (MG) intermediates from the parent triglyceride under the transesterification reactions resulting in production of 3 mol of FAME and 1 mol of glycerol (GL) from 1 mol of TG as shown in the steps 1-4 of Figure 2.10 (Darnoko and Cheryan, 2000).



Triglycerides (TG)

Glycerol

Methyl ester

Figure 2.10: Reaction scheme showing the transesterification of triglycerides with methanol (Maa & Hanna, 1999).

2.5.4.1 Base catalysed process

Biodiesel is produced mostly by the transesterification of triglycerides of refined/edible type oils using methanol and alkaline catalyst but it has several disadvantages. The alkaline catalyst is corrosive to equipment and also reacts with free fatty acids (FFA) to form unwanted soap by products thus requiring extensive and expensive separation. On the other hand, the base catalysis in the homogeneous state is fast and need less of methanol.

The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification, an excess of the alcohol is needed to shift the equilibrium to favour fatty esters production. Salt waste streams are caused by the use of

homogenous catalysts and require neutralization. Alcohol provides the alkyl group that substitutes the fatty fraction of triglyceride. Methanol is most frequently used, mainly because the reaction rate is higher and the price is cheaper than any other commercial alcohol. The fuel qualities of alkyl esters have received varying evaluations in terms of alcohol used. Huber et al. (2006) and Saraf & Thomas, (2007) reported that a higher or branched alcohol can produce biodiesel with better fuel characteristics. In contrast, Tyson et al. (2006) reported that a methyl ester and ethyl ester are similar in heat content but that the former is slightly less viscous than the later. Knothe et al. (2005) also concluded that methyl ester was better than ethyl ester from the standpoint of engine performance: higher power torque was achieved from the engine when methyl ester was used as fuel. Narasimharao et al. (2007) reported that high alkyl esters caused more injector clogging than methyl ester and that their industrial uses were hindered by some technological problems. With regards to this study, methanol was the alcohol of choice based on these reports.

An alternative multistep process allows the use of feedstock having high FFA concentrations by carrying out the acid-catalyzed pre-esterification of the FFAs prior to the base-catalyzed TG transesterification first. The most widely used method, especially for commercial biodiesel production, and most economical, is the base-catalysed (alkali-catalysed) process for the transesterification of the oil (with a low content of free fatty acids) with methanol, typically referred to as the “methyl ester process”. This is illustrated in Figure 2.11. The reaction mechanism of base catalysed transesterification is detailed under homogenous catalysts under section 2.6.

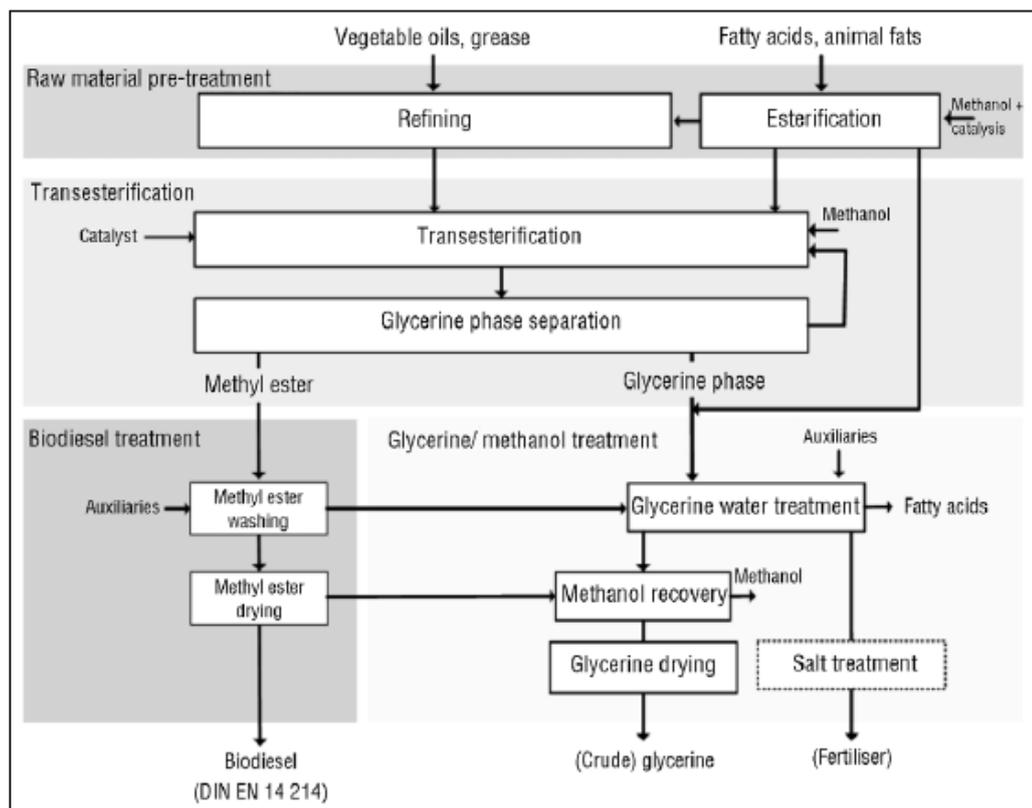


Figure 2.11: General scheme of biofuel production (IEE, 2006)

The combination of acid-catalyzed FFA pre-esterification followed by base-catalyzed transesterification is commonly called the integrated process; the integrated process despite the added cost of production is being increasingly applied to produce biodiesel from low-cost and high-FFA feedstock with good fuel qualities. A basic technology of the flow diagram of the process is shown in Fig. 2.12. Due to the limitations of the base catalysed transesterification reaction, the use of solid acid catalysts is an attractive solution to solve the problems associated with this conventional process as the catalysts could be separated more easily from reaction products and the reaction conditions could be less drastic. Additionally, the glycerol co-product arising from biodiesel production appears to be of higher quality when compared to the conventional homogeneous catalysis method (Bournay et al., 2005).

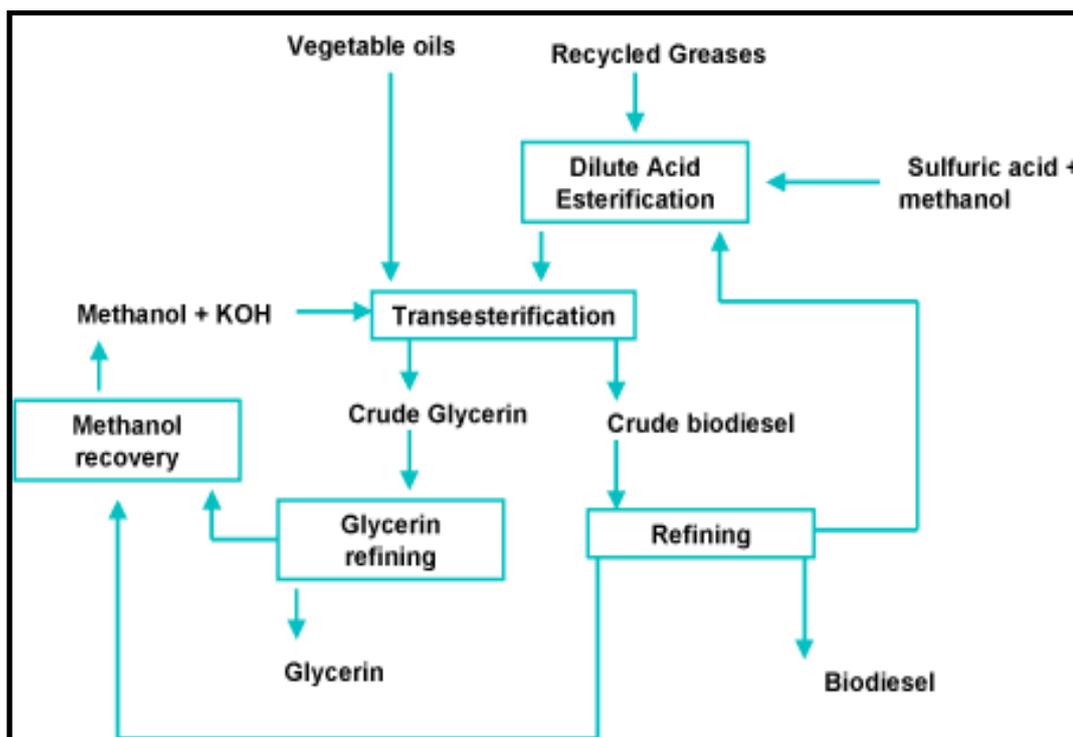


Figure 2.12: Basic technology involved in an integrated biodiesel process (USDOE, 2011)



2.5.4.2 Acid catalysed process

Acid catalysed transesterifications are usually far slower than alkali catalysed reactions and require higher temperatures and pressures as well as higher amounts of alcohol but offer the advantage of esterifying free fatty acids contained in the fats and oils. This route is therefore especially suited for the transesterification of highly acidic fatty materials such as waste edible oil. Moreover it enables the production of long and branched chain esters, which poses considerable difficulty in alkaline catalysis (Nimcevic et al., 2000) but the presence of water in the reaction mixture proves absolutely detrimental for acid catalysis (Canacki and Gerpen 1999). The transesterification process is usually catalyzed by Bronsted acids, preferably by sulfonic (Anton et al., 2006) and sulfuric acids (Kulkarni and Dalai 2006; Canacki and Gerpen 2003). These catalysts give very high yields in alkyl esters, but the reactions are slow, typically requiring temperatures above 100 °C and more than 3

hrs to reach complete conversion (Kim et al., 2004). Figure 2.13 shows the mechanism of the acid catalysed transesterification of vegetable oil.

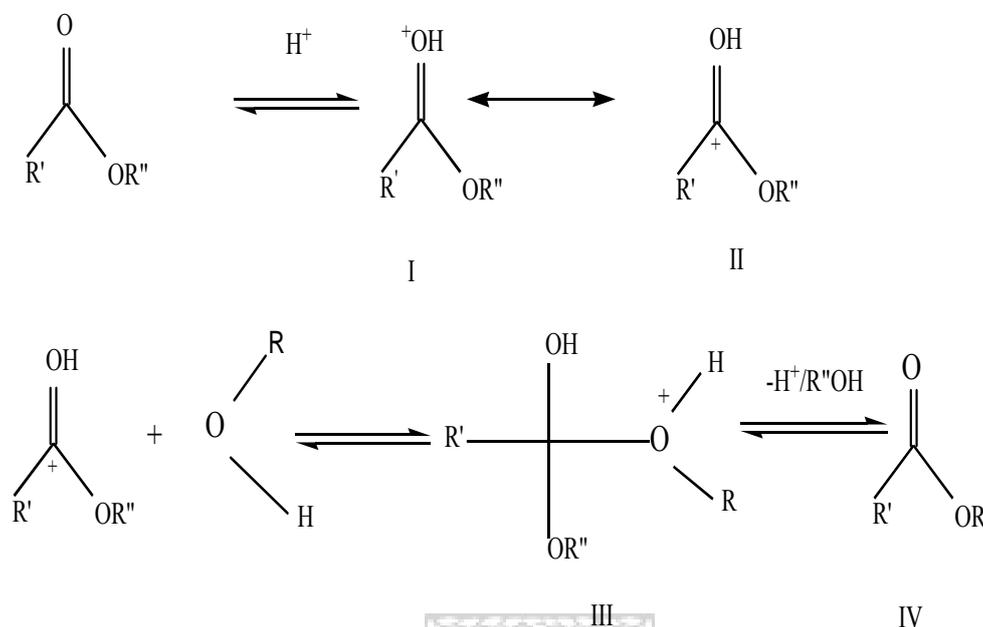
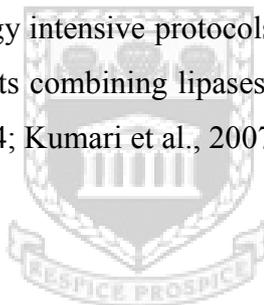


Figure 2.13: Mechanism of the acid catalysed transesterification of vegetable oil

It should be noted that acid catalysed transesterification reactions are seldom used as the sole reactions in industrial biodiesel production; they frequently serve as preliminary steps for the de-acidification of fatty materials followed by conventional alkaline operation. The main drawback of the pre-esterification method consists again in the necessity to remove the homogeneous acid catalyst from the oil after pre-esterification. So to improve the process, the need of a heterogeneous acid catalyst is inevitable. The introduction of a solid catalyst in biodiesel production could solve these problems and eliminate the washing process. There are numerous review papers recently published that focus on the solid catalysts related to biodiesel production processes (Janaun and Ellis, 2010; Hara, 2009; Zabeti et al., 2009; Arzamendi et al., 2007; Di Serio et al., 2008; Loreto et al., 2005).

2.5.4.3 Enzyme-catalyzed processes

Enzyme (such as lipase)-catalysed reactions have advantages over the previously mentioned methods which include: the generation of no by-products, easy product recovery, mild reaction conditions, and catalyst recycling, insensitivity to FFA and water content in waste cooking oil (Wu et al., 1999., Hsu et al., 2004). Enzyme-based transesterification is carried out at moderate temperatures with high yields, but this method cannot be used in industry today due to high enzyme costs, and the problems related to its deactivation caused by feed impurities. The enzyme can be immobilized on a support to obtain a heterogeneous catalyst however the use will only be possible if the enzyme costs are reduced as in the case of enzymes used in detergents, dairy products, textile, and leather processing. The enzymatic alcoholysis of pure triglycerides with or without solvent has been well-documented in literature (Shah et al., 2004; Du et al., 2003; Mittlebach, 1990). Efficient and low energy intensive protocols of the production of biodiesel from waste oils and animal fats combining lipases with alkali catalysts have also been reported (Shah et al., 2004; Kumari et al., 2007).



2.5.5 Catalyst free processes

One of the other methods of transesterification without any catalyst is the use of alcohols in the supercritical state, i.e., heated above the critical temperature.

Saka et al. (2009) demonstrated that preheating to a temperature of 350°C and treatment for 40 minutes in supercritical methanol was sufficient to convert the rapeseed oil to methyl esters and the properties of the methyl esters prepared by this method were similar to those prepared by the common method with a basic catalyst, the yield of methyl ester obtained by the supercritical method was higher.

The disadvantages that result from the use of a catalyst and its removal from the products are eliminated if a non catalytic transesterification reaction of vegetable oils with alcohol is realized. Although the use of supercritical alcohol for the transesterification of pure vegetable oil is well reported in literature, the application of this technique for the transesterification of waste cooking oil is not

well-documented, however the supercritical methanol method is reported to be more water-tolerant than the conventional method using an alkaline catalyst and proves that crude vegetable oils as well as their wastes could be readily used for biodiesel production by this same method (Kumari et al., 2007; Devanesan et al., 2007).

Despite having all these advantages, the supercritical methanol method has some serious disadvantages which include the requirement of high temperature, high pressure and a large amount of methanol (1:42 molar ratio of oil to alcohol). Therefore to apply this method on an industrial scale, further investigations of the production process, such as continuous operation and scaling up, as well as economic evaluations are needed. Interestingly van Kasteren and Nisworo (2007) in recent publication refuted previous claims however and reports that the supercritical transesterification process of biodiesel production can comparatively compete with the alkali and acid catalysed processes.

2.5.6 Application of ultrasound in biodiesel production

For more than two decades, sonochemistry (the chemical reaction during ultrasound homogenization) has developed as an expanding research area. The ultrasonic field is known to produce chemical and physical effects that arise from the collapse of cavitation bubbles. Low frequency sonication can be used to produce emulsions from immiscible liquids and this effect could be employed for biodiesel preparation as the mixing intensity or agitation is a very important parameter that must be considered during the production of biodiesel because of the fact that oil and alcohol are immiscible. The use of ultrasonication also provides a promising alternative to the use of conventional transesterification.

Previous research has indicated that the use of the ultrasound provides the mechanical energy for mixing and the required energy for initiating the transesterification reaction. One major problem in the transesterification of oils using methanol is the fact that the alcohol is a poor solvent for fatty materials thus the need for homogenization of the reaction mixture. Since this reaction can only

occur in the interfacial region between the liquids and also due to the fact that fats and alcohols are not totally miscible, transesterification is a relatively slow process. As a result, a vigorous mixing is required to increase the area of contact between the two immiscible phases, and thus to produce an emulsion. Vigorous mixing of the components is one method of homogenization which has been found successful for both batch processes and continuous operation. The application of low frequency ultrasonication to form emulsions of oils and alcohols has been reported extensively in literature (Gogate and Pandit, 2005; Ji et al., 2006; Stavarache et al., 2007; Babajide et al., 2010).

Research reports show that low frequency ultrasound is an efficient, time saving and economically functional, offering a lot of advantages over the conventional process. Reaction time is reduced dramatically; the static separation time is reduced remarkably, and yields are generally higher (Hsiao et al., 2010; Refaat and El Sheltawy, 2008; Stavarache et al., 2007). Lifka et al. (2004) and Ji et al. (2006) both studied the effect of mechanical stirring, ultrasonication, and hydrodynamic cavitations on methyl ester yields in the alkaline (KOH) transesterification of soybean oil using methanol (alcohol/oil molar ratio of 6:1) at a temperature of 45 °C and reported that ultrasonication gave the shortest reaction time and highest yield, while mechanical stirring gave the shortest reaction time and the lowest yield. Thanh et al. (2010) also studied the alkaline transesterification using KOH for a series of vegetable oils via mechanical stirring and ultrasonication processes and concluded that yields in both cases were identical. In a recent study by Kumar et al. (2010), it was shown that the combination of an ultrasound process and the use of a solid catalyst reduced the reaction time compared to the conventional batch processes with 98.53 % biodiesel yield. Production of biodiesel under the ultrasonic processing possess the following advantages, reduction in processing time, amount of alcohol, catalyst amount, separation time and reaction temperature as revealed in studies conducted in this research work.

2.5.7 Application of Jet –mixing in biodiesel production

The majority of commercial biodiesel is made by transesterification of vegetable oils and animal fats with methanol or ethanol in stirred tank reactors in the presence of base or acids catalysts. There is however some challenges related to this process as follows: (a) the reaction rate can be limited by mass transfer between the oils and alcohol because they are immiscible (b) transesterification itself is a reversible reaction and therefore there is an upper limit to conversion in the absence of product removal; (c) most commercial processes are run in a batch mode and thus do not gain some of the advantages of continuous operation. In order to overcome these problems, current conventional techniques involve long reaction times, high molar ratio of alcohol to oil and catalyst concentration. High operating cost and energy consumption are required to purify biodiesel and recover excess amount of alcohol and catalysts during downstream processing. Significant amounts of toxic waste water may also be produced during downstream purification. Long residence times and downstream processing time incur low production efficiency. Hence, some process intensification technologies have been developed and applied to improve mixing and mass/heat transfer between the two liquid phases in recent years (Qiu et al., 2010). These technologies either utilize novel reactors or coupled reaction/separation processes. Reaction rate is greatly enhanced and thus residence time may be reduced. Some of the technologies have been applied successfully in commercial production.

Impinging jets have been used in a variety of practical engineering applications to enhance heat transfer due to the high local heat transfer coefficient. Examples include quenching of metals and glass, cooling of turbine-blades, cooling and drying of paper and other materials, and more recently cooling of electronic equipment and a great number of studies have dealt with the heat transfer enhancement due to impinging jets and extensive reviews have also been provided (Martin, 1977; Jambunathan et al., 1992; Viskanta, 1993, Beitelmal et al., 2000).

Jet reactors are reactors based on the impinging jet technology. This system avails of a very intense mixing under pressure with different nozzle sizes which were

specially developed for steel cutting (with water) and further developed for the mining sector especially in the goldmine sector of South Africa.

Research conducted at the of the University of Stellenbosch identified the use of these jet reactors for biodiesel production and Nieuwoudt (2010) then improved on this discovery and technique to develop a continuous process reactor mainly for the production of biodiesel. This process will be optimised in the present study using a Jet system developed by Nieuwoudt (2010).

2.5.8 Comparison of the different biodiesel processes

A comparison of the different technologies used to produce biodiesel is presented in Table 2.2.

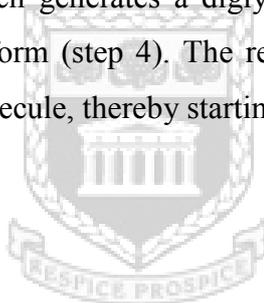
Table 2.2: A Comparison of the different technologies for biodiesel production processes

Variable	Alkali catalysis	Enzyme catalysis	Supercritical	Acid catalysis
Temp (°C)	55–80	60–70	30–40	239–385
High FFA Content	Saponified methyl ester	Esters	Esters	Unwanted products
Presence of water	Interference with reaction	No influence with reaction	Interference with reaction	Inhibits reaction
FAME yield	Normal	Higher	Good	Normal
Glycerol Recovery	Easy	Difficult	Difficult	Difficult
Cost of Production	Cheap	Relatively expensive	Medium	Cheap
FAME purification	Repeated washing	None	Repeated washing	Repeated washing

2.6 Homogeneous catalysts in biodiesel production

Conventional biodiesel production is done via base catalysed transesterification using homogeneous alkaline catalysts. This is the most commonly used technique as it is considered to be the most economical process (Singh et al, 2006).

Usually, the alkoxide anion required for the transesterification reaction is obtained by directly dissolving the pure alkali metal in the alcohol by adding an alkali hydroxide (Schuchardta et al., 1998; Lotero et al., 2005). As shown in Figure 2.14, the initial step of the catalytic process involves the production of an alkoxide ion through proton abstraction from the alcohol by base catalyst (step 1). The alkoxide ion attacks a carbonyl carbon of the triglyceride molecule and forms a tetrahedral intermediate ion (step 2), which is rearranged to generate a diglyceride ion and alkyl ester molecule (step 3). Finally, the diglyceride ion reacts with the protonated base catalyst, which generates a diglyceride molecule and turns the base catalyst into the initial form (step 4). The resulting diglyceride is ready to react with another alcohol molecule, thereby starting the next catalytic cycle.



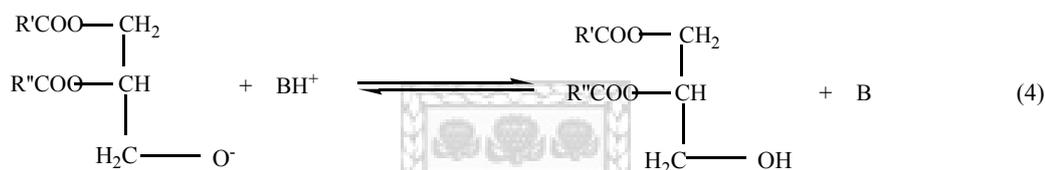
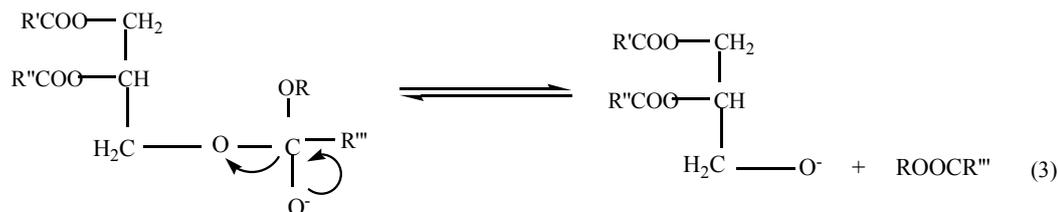
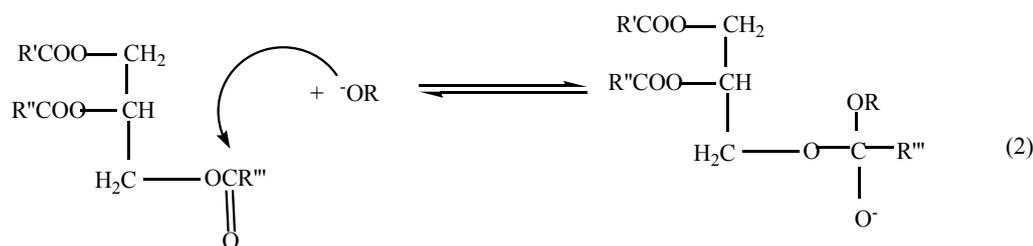


Figure 2.14: Mechanism of the base catalysed transesterification of vegetable oil (Lee et al., 2009)

Though alcoholates and alkali metals give rise to high conversion their high costs and safety risks make them unattractive for commercial biodiesel production. However it has been revealed that alkali hydroxides are more promising because they are cheaper and easier to handle. If KOH or NaOH are dissolved in an alcohol, the resulting solution would contain hydroxide and alkoxide ions in equilibrium (Caldin and Long 1954). The concentration of the alkoxide ions formed depends on the catalyst concentration, the pK_s value of the respective alcohol and the water content of the reaction mixture. These authors also showed that for a 0.1 molar solution of NaOH in 99 % ethanol, 96 % of the total base is present in the form of the ethoxide ion and they predicted similar results for anhydrous methanol. Thus alkali catalysed hydrolysis and soap formation only plays a minor role in water free alcohols (Caldin and Long, 1954).

Using KOH as catalyst as compared to NaOH also reduces the amount of methyl esters dissolved in the glycerol phase after transesterification reactions. This phenomenon decreases the tendency for soap formation thus reducing ester losses. Studies by Vicente et al., (2004) showed only 3 mol % of methyl ester dissolution in the glycerol phase after KOH catalysed methanolysis of sunflower oil, as opposed to more than 6 mol % methyl esters in the lower phase for NaOH catalysed reactions.

A major advantage is the fast separation of the glycerol phase in this process when most of the catalyst from the reaction mixture is removed easily as the produced esters will hardly get in touch with the hydroxide in the first instance. This favourable behaviour is particularly pronounced if KOH is used as the catalyst instead of NaOH as it accelerates phase separation by increasing the density of the glycerol layer due to a higher molecular weight (Mittlebach, 1989).

Another advantage is that phosphoric acid can be added to the alkaline glycerol phase obtained to derive potassium dihydrogen phosphate which can be used as a fertilizer. The use of the fertilizer adds extra value to the reaction products whereas the sodium salt obtained from the use of NaOH as catalyst is considered a waste product (Mittlebach and Remschmidt, 2006). Finally, stating the advantage of using NaOH as a catalyst over KOH is that sodium hydroxide catalysed transesterifications tend to be completed faster and its cost is cheaper. The resulting raw product obtained from the reactions utilising homogeneous alkaline catalysts to obtain biodiesel which has to be centrifuged and washed with water to cleanse it of impurities, which is a major drawback. Table 2.3 gives an overview of homogeneous alkaline catalysts which are frequently applied in alcoholysis reactions.

Table 2.3: Overview of homogeneous alkaline catalysts used for transesterification (Mittelbach and Remschmidt, 2006)

Catalyst	Examples	Reaction conditions	Feedstock	Alcohol	Ester yield
Alkali metals	Metallic sodium	alcohol :oil=2-4:1 (mol/mol) T= 65-70 °C	Pre-esterified waste oils Linseed oil	methanol 2-propanol 1-butanol	87 % 96 %
Alkali metal alcoholates and hydroxides	CH ₃ ONa, CH ₃ OK, KOH, NaOH, LiOH	alcohol :oil = 3-5:1 (mol/mol) T = 30-100 °C	Vegetable oils, recycled frying oil and animal fats	methanol abs. ethanol	98%
Aqueous alkali metal hydroxide solutions	40 - 55 % NaOH or KOH	alcohol: oil = 3-9:1 (mol/mol) ambient temp. and pressure	Oils and waste oils with 20 % FFA	methanol 90% ethanol	-
Strong organic bases	TBD TCG	alcohol :oil = 2.3:1 (mol/mol) T=70 °C, t=1hr 5 mol % of catalyst	Rapeseed oil	methanol	>99% >97%

2.7 Heterogeneous catalysts in biodiesel production

As previously enumerated, conventional homogeneous catalysis offers a series of advantages, a major shortcoming is the fact that homogeneous catalysts cannot be reused. Moreover the catalyst residues have to be removed from the ester product, requiring numerous washing steps and the amount of waste water produced is excessively massive. These factors are related to increased production costs in this process. Heterogeneous (solid) catalysts have the general advantage of easy separation from the reaction medium and reusability. Heterogeneous catalysis is thus considered to be a green process. The process requires neither catalyst recovery nor aqueous treatment steps. The heterogeneous transesterification of oils is an interesting alternative to reduce the costs associated with the purification and separation of reaction products. Purification steps of products are much more simplified with high yields of methyl esters being achieved (Cao et al., 2008).

Heterogeneously catalysed transesterification reactions generally require more severe operating conditions (relatively elevated temperatures and pressures), and the performance of heterogeneous catalysts have been reported to be generally lower than that of commonly used homogeneous catalysts (Refaat, 2010). A major problem also with heterogeneous catalysts is their deactivation with time owing to many possible phenomena, such as poisoning, coking, sintering, and leaching (Sivasamy *et al.*, 2009). Figure 2.15 shows a simplified flow sheet of a heterogeneous transesterification process. The use of solid catalysts to produce biodiesel however, requires a better understanding of the factors that govern their reactivity. Overall, the selected catalysts must have several qualities i.e., catalyze transesterification and esterification, be und deactivated by water, be stable, do not give rise to leaching, be active at low temperature, and have high selectivity (Di Serio *et al.*, 2008). To improve the performance of these catalysts, it is essential to understand the correlations between acid and base strength and catalytic activity they possess. It is also clear that the surface of these heterogeneous materials should exhibit some hydrophobic character to promote the favoured adsorption of triglycerides and to avoid deactivation of catalytic sites by strong adsorption of polar by-products such as glycerol and water (Lotero et al., 2005).

An overview of different heterogeneous catalysts types with regards to this study is discussed in the next section 2.7.1.

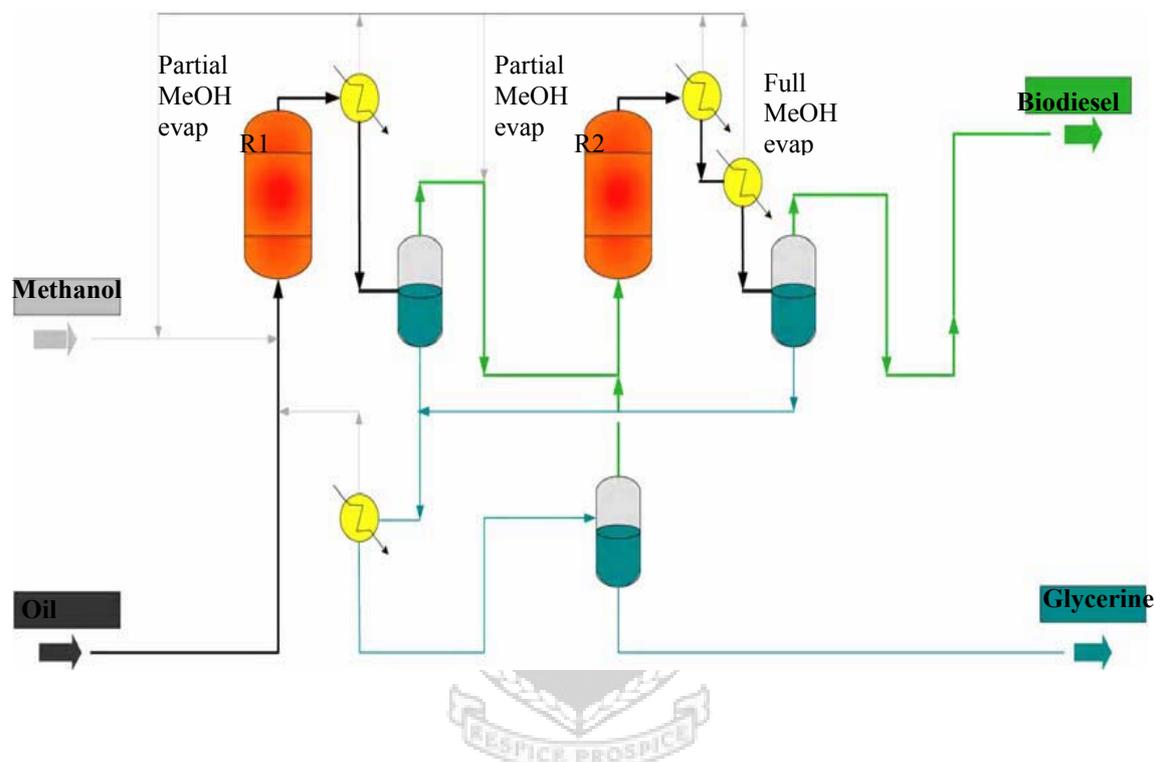


Figure 2.15: Flow sheet of heterogeneous transesterification process (Bournay *et al.*, 2005).

2.7.1 Metal Oxides

Many metal oxides have been studied for the transesterification process of oils; these include alkali earth metal oxides, transition metal oxides, mixed metal oxides and supported metal oxides. Zirconium oxide, titanium oxide and zinc oxide are among the transition metal oxides that have attracted attention for biodiesel production due to their acidic/basic properties (Zabeti *et al.*, 2009). These catalysts have shown good catalytic activities and good stability when used to catalyze esterification and transesterification simultaneously. However, they have not been generally used in the industrial production

process, mainly because of the high catalyst cost and difficulty in filtering the small catalyst particles respectively. Calcium oxide possesses relatively high basic strength and less environmental impacts due to its low solubility in methanol. As compared to KOH or NaOH, calcium oxide will probably bring about similar productivity with added advantages of easy product recovery, easier handling and an environmentally benign process (Refaat, 2010). Kouzu et al. (2008) reported that transesterification of soybean oil with methanol was carried out in the presence of calcium oxide (CaO), and also via homogeneous catalysis using sodium hydroxide. Results obtained revealed an absolute conversion into FAME in both cases. Sakai et al. (2009) reports economic feasibility studies on four batch processes for the production of biodiesel using a homogeneous KOH catalyst and a heterogeneous CaO catalyst via hot water purification and vacuum FAME distillation processes. Among the four processes, the manufacturing costs involved in the CaO catalyst with hot water purification process proved to be the lowest. Conclusively, calcium oxide can be widely applied for biodiesel synthesis owing to its cheap price, minor toxicity and high availability.

Recent reviews on this topic can be found in the following references (Refaat, 2010, Einloft, 2007; Yang, 2007; Kim, 2004).

2.7.2. Zeolites

Zeolite is the broad term used to describe a family of minerals called tectosilicates. They are constructed of tetrahedral AlO_4^{-5} and SiO_4^{-4} molecules bound by oxygen atoms (Fig 2.16a) and having a general formula of $\text{M}_x/n[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot z\text{H}_2\text{O}$, where the extra frame work cation that balances the anion charge of the framework (Jacobs 1977). These minerals contain small pores which provide a generous surface area. (Fig 2.16b) Zeolites can be custom made by manipulating the structure, silica-alumina ratio, pore size, and density. Other metals can also be incorporated into zeolites to obtain specific catalytic properties. Large uniform zeolite crystals are highly desired for many uses that range from crystal structure analysis, adsorption and diffusion studies to zeolite functional materials because of their unique crystal structure, the micro porous characteristics, and their high chemical and thermal stability (Lee et al., 2007).

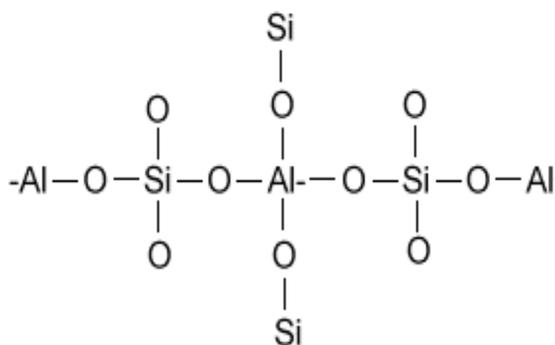


Figure 2.16a: Basic zeolite structure

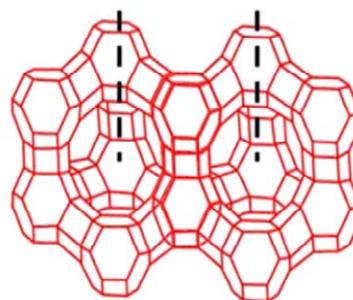
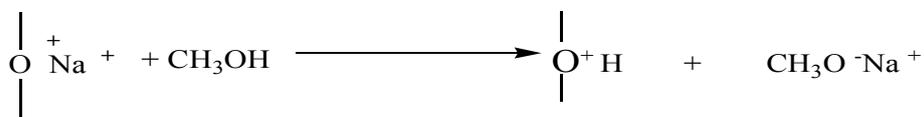


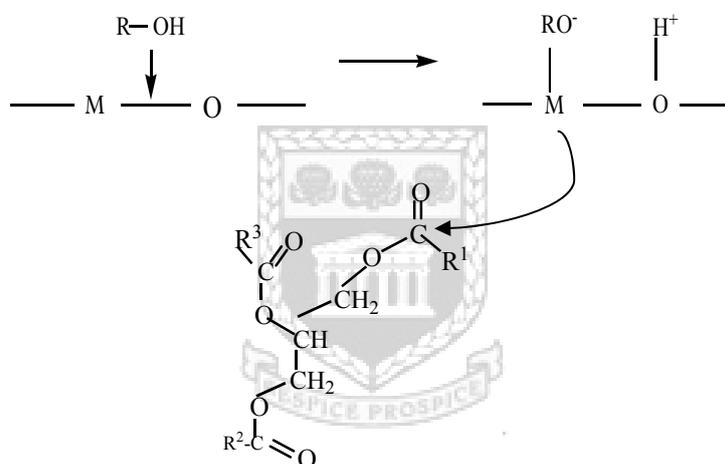
Figure 2.16b: Zeolite Na-X (ensemble of cages joined by hexagonal prisms)

Zeolite catalysts have also been studied for transesterification reactions (Georgogianni et al., 2009; Xie and Huang, 2007) and have attracted much attention in the preparation of solid base catalysts. The conventional zeolites suffer mass transfer limitation due to their microporous structures while zeolite-X has attracted attention for biodiesel synthesis among the zeolite family and is generally accepted as one of the most basic zeolites. The basicity and catalytic activity of these zeolites can be modulated through ion exchange of alkali and the occlusion of alkali metal oxides in zeolite cages (shown in Fig. 2.16b) by decomposition. The ion exchange of Na-X with larger monovalent cations such as K and inclusions of alkali oxides into pore cavities is reported to increase its basicity noticeably (Lee et al, 2009). The versatile catalytic ability of zeolites results from their chemical composition, pore size distribution and ion-exchange abilities. The acid-base properties of zeolites are controlled by the kinds and quantities of ion-exchanged cations, and by the Si/Al ratio of the main zeolite framework. To control the basicity of zeolite, two approaches are generally undertaken: ion exchange with alkali metal ions and the impregnation of basic components on the inner surface of the zeolite pores (Hattori, 2001). It has been reported that the former produces relatively weak basic sites, and the latter strong basic sites (Kim et al., 2004). Brønsted basic catalysts (NaOH or KOH) as mentioned previously, when mixed with methanol in transesterification reactions, the actual catalyst (the alkoxide group) is formed which

attacks the carbonyl carbon atom of the triglyceride molecule to convert triglycerides to their respective methyl esters.



A related mechanism is operational in the case of solid basic Bronsted catalyst such as a basic zeolite for transesterification reactions (Loreto, 2006). The mechanism is based on the Eley-Rideal (ER) mechanism where the alcohol is adsorbed on the catalyst site and the formed catalytic specie is a homogeneous alkoxides ion on the surface which attacks the positively polarised carbon triglyceride in the liquid phase as shown in Figure 2.17.



Where M is the alkali metal (Na or K) and R is alkyl group.

Figure 2.17: Eley-Rideal (ER) mechanism of Brønsted base catalysis (Endalew et al., 2011).

According to a study by Suppes et al. (2004), the ion exchange with potassium was more effective than with Caesium, in terms of the basicity and transesterification activity, because the large size of the Cs ions limits the exchange capacity compared to that for the smaller potassium, which affects the basicity associated with the framework oxygen. The challenge of using ion exchanged zeolites with lower methanol values comparable to the homogeneous counterpart therefore still exists; hence the search for a

catalyst with stable activity which could yield products under mild reaction conditions would be significant for industrial applications.

Table 2.4: Review of zeolite catalysts in biodiesel synthesis (Di Serio et al., 2008)

Catalyst	Methanol/oil molar ratio	Temp (°C)	Reaction time (h)	Cat conc (% w/w)	FAME yield (%)
NaX	6:1	60	24	10	6.8
NaX	10:1	65	8	3	2
KX	6:1	60	24	10	10.3
CsX	6:1	60	24	10	7.3
NaOx/NaX	6:1	60	24	10	82
4 %KOH/NaX	10:1	65	8	3	28
10% KOH/NaX	10:1	65	8	3	85

Fly ash can also be used to make zeolite; the chemical, mineralogical, and textural features make fly ash a highly suitable starting material for zeolite synthesis. Several studies have successfully prepared zeolites from fly ash under different reaction conditions (Table 2.4). Formation of different zeolite mineralogies and cation exchange properties depends on the composition of the initial fly ash, concentration of reacting alkali, temperature, pressure, time, and ratio of solid/liquid used (Inada et al. 2005; Querol et al., 2002). Zeolites have been found useful for their superior control of reaction selectivity at mild temperatures and pressures consequently lowering operating costs. The motivations for using zeolite catalysts are primarily for compliance to environmental regulation, to save on feed costs and treatment costs while reducing waste streams (Marcus and Cormier, 1999). The conversion of fly ash into zeolite also eliminates the disposal problem and turns an otherwise waste material into a useful raw material. Various potential applications for synthesized fly ash zeolites exist (Hui et al., 2009; Ojha et al., 2004) and zeolites modified by alkali ion exchange have also emerged as appealing solid bases (Suppes et al., 2004; Hattori, 2005) in biodiesel synthesis as mentioned previously. The application of zeolite Na-X synthesised from South African

Class F AFA as a heterogeneous catalyst in biodiesel synthesis will be investigated in this study.

2.7.3 Fly ash

The recent energy crisis, largely driven by factors of economic growth and social integration has led to the construction of new coal power plants in South Africa. Increasing demand for energy throughout the world has led to an increase in the utilization of coal and subsequently, in the production of large quantities of fly ash as a waste product (Hui et al., 2005). Despite the mounting interest surrounding the renewable sector, coal-fired power stations still account for a large percentage of South Africa's electricity generating capacity. Specifically, South Africa generates 93 % of its electricity from coal combustion. Eskom's coal-fired power stations consume approximately 109 million tons of coal per annum to supply the bulk of South Africa's electricity, producing around 25 million tons of ash, (Eskom fact sheet, 2009). Almost 90 % of the ash produced in the generation process is called fly ash or pulverised fuel ash (a waste by-product of burning coal to generate electricity). This is because, the coal is pulverised into a very fine dust before being fed into the boilers to ensure efficient combustion. It is estimated that around 300 billion tonnes per year of fly ash is produced worldwide and the amount is expected to increase in future due to the pressing need for generation of sufficient energy and only about 20–30% of the generated fly ash in the world is used (Ciccu et al., 1999).

Fly ash, an inorganic residue arising from the coal combustion processes consists essentially of SiO_2 and Al_2O_3 with many minor and trace elements as contaminants and thus being an environmental pollutant. Constant generation of fly ash in huge quantities is a matter of concern. In view of its important economical and environmental implications, the disposal or utilization of fly ash represents a significant challenge; therefore the development of environmentally safe applications for the utilization of coal fly ash is very important. Although fly ash is mainly used as building materials and in other civil engineering work (cement and dry wall board manufacturing), there is still

a large proportion which is being disposed in ponds or landfills. Products made from fly ash use refined fly ash which has been cleaned of contaminants (Murithi, 2009; Alvarez-Ayuso et al., 2008). Fly ash can either be considered to be an ecological nuisance due to the environmental and economic concerns during disposal or can be treated as a valuable raw material when it is utilized in an economical and beneficial way. Ciccu et al., (1999) are quoted thus “the value of fly ash as a resource is probably still under estimated”. The characteristics of fly ash such as type of particles, particle size distribution and chemical composition are of paramount importance with a view to their potential applications. Fly ash can also be used to make zeolite. Fly ash is an agglomerate of microspheres, which are mainly composed of Si and Al with minor amounts of Fe, Na, K, Ca, P, Ti, and S. The major mineral compound is amorphous aluminosilicate (glass) but other crystalline minerals are also present, such as mullite, quartz, hematite, magnetite, lime, anhydrites, and feldspar (Querol et al. 1995). These chemical, mineralogical, and textural features make fly ash a highly suitable starting material for zeolite synthesis. The conversion of fly ash into zeolite not only eliminates the disposal problem but also turns an otherwise waste material into a useful one. Several studies have successfully prepared zeolites from fly ash under different reaction conditions. Formation of different zeolite mineralogies and cation exchange properties depends on the composition of the initial fly ash, concentration of reacting alkali, temperature, pressure, time, and ratio of solid/liquid used (Lee and Jo, 2010).

The qualities of fly ash may be dictated by its chemical composition, and this may differ widely depending on the coal type (Murphy et al., 1984). Based on the ASTM standards (ASTM C 618 – 95), fly ash is classified according to the content of its major elements (Si, Al, Fe and Ca) (see Table 2.5).

Table 2.5: Fly ash classification according to chemical composition (Scheetz and Earle, 1998)

Chemical components	Class F	Class C
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , min. %	70	50
Sulphur trioxide (SiO ₃), max. %	5	5
Moisture content, max. %	3	3
Loss of Ignition, max, %	6	6
Available alkali (as Na ₂ O), max %	1.5	1.5

Class F fly ashes are produced from anthracite or bituminous coal combustion while Class C is from lignite or sub-bituminous coal combustion (Adriano et al, 1980). In addition to the above table, an interesting observation is noted where Class F fly ashes have been reported to contain > 5 % CaO (Koukouzas et al., 2007). See section 2.7.1 where the importance of the metal oxide CaO use as a catalyst is enumerated. South African AFA is mainly Class F with high CaO component which is unlike most other countries fly ash which is Class C with less CaO component.

Supported alkali/alkaline earth metal catalyst are a classical approach for application of base catalyst in the synthesis of biodiesel. The choice of precursor for the alkali/alkaline earth metal is important for the basic activity of the catalyst. Various supported catalysts have been examined for activity with use of supports like alkali and alkali earth oxides, alkali and alkali earth carbonates (Yang and Xie, 2007; Xie and Huang 2006). Some other heterogeneous basic catalysts such as Na/NaOH/g-Al₂O₃ (Kima et al., 2004), KNO₃/Al₂O₃ (Narasimharao et al., 2007), ZnO-La₂O₃ (Yan et al., 2009) have been studied. Most of the reported heterogeneous catalysts show a much lower activity than traditional homogeneous base catalysts. Of these reported the Na/NaOH/g-Al₂O₃ and KNO₃/Al₂O₃ catalysts suffered from the leaching of base catalyst components.

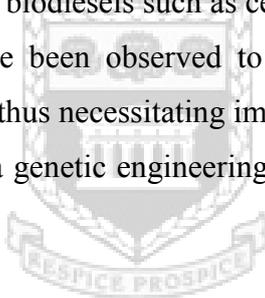
In the work published by Kotwal et al (2009), the authors produced different solid fly ash based base catalysts prepared from Class C fly ash with a low CaO content of 1.72 %, collected from Parli Thermal Power station of Ambajogai District, Maharashtra,

India which was used as a catalytic support in transesterification reactions. The catalytic performance of the different solid fly ash based catalysts prepared in transesterification reactions was conducted only on sunflower oil. The tools of catalyst characterisation in their study only included powder XRD and BET analysis and the properties of the methyl ester product obtained were not determined. The effect of a high FFA content on the catalytic activity of this catalyst in waste or unrefined oil was not reported. Results from the study also show that a reaction time of 8 h was required to obtain a conversion of 87.5 % with the most active fly ash based catalyst.

The gaps discovered in the study by Kotwal et al. (2009) stimulated a motivation for the use of South African Class F AFA as a catalytic support material in the transesterification reactions in this study. To address the issue of “cost of raw materials”, a further approach was to ascertain if the use of a fly ash base catalyst would be effective in converting unrefined oils and higher free fatty acids (FFA) raw material such as waste cooking oil to biodiesel which was not addressed in the study by Kotwal et al. (2009). The characterisation of the South African Arnot class F AFA used as catalytic support in this study (in chapter 5) was determined as it is considerably different in composition to the Class C fly ash used in India. Reaction parameters used in this study were identical to Kotwal et al. (2009) for comparative purposes are hereby acknowledged.

2.8 Biodiesel fuel properties

Fuels that are to be used in any form of engine must generally pass a number of tests and conform to specified guidelines to control their quality. Biodiesel and petroleum diesel vastly differ in their chemical composition. Fossil diesel typically consists of about 30-35 % aromatic carbons and 65-70 % paraffin and traces of olefins most of which are in the C₁₀ to C₁₆ range (Chang et al., 1996) and virtually oxygen free while biodiesel derived from rapeseed, soybean or sunflower seed oil primarily contains C₁₆-C₁₈ fatty acids methyl esters with one to three double bonds per molecule and its oxygen content amounts to about 11 % (m/m) (Schafer, 1998). These differences give biodiesel different physical and chemical properties. The composition and properties of the biodiesel also depend largely on the feedstock used in the manufacturing process. Some of the parameters based within current biodiesel standards are hereby highlighted and discussed. The fuel properties for biodiesels such as cetane number, heat of combustion, melting point and viscosity have been observed to increase with increasing carbon number and unsaturation degree, thus necessitating improvement by enriching parent oil plants with specific fatty acid via genetic engineering to improve the fuel properties of biodiesel (Lee et al., 2009).



2.9 Biodiesel fuel standards

Quality standards are prerequisites for the commercial use of any fuel product. They serve as guide lines for the production process, guarantee customers of high quality fuel and provide authorities with approved tools for the assessment of safety risks and environmental pollution (Mittelbach, 2006). Thus regular tests need to be done on biodiesel to ensure that it meets and maintains a consistently high level of quality in line with industry standards. Due to the relative recent appearance on the market of biodiesel, there are currently no accepted international standards. In 1997, the European committee for standardization was mandated to develop a uniform standard for fatty acid methyl ester fuels and come up with respective measurement procedures. The resulting norm EN14214 (European Union quality standard for biodiesel fuels) which

has come into force in 2004 is valid for all member states of the European Union. This standard includes 26 parameters: some of which are regulated in order to control the production process and ensure the good conversion of the fatty acid into FAME. Other parameters depend on the feedstock characteristics such as iodine value that depends on the fatty acid profile of the oil. As EN14214 is very restrictive in its limits, some oil crops that would have been suitable for biodiesel production are eliminated from the selection because they exceed these limits of importance such as the iodine value, stability and cold filter plugging point (CFPP) for winter period. However, some of the EU standard such as CFPP will not be relevant in some parts of the Southern region due to their different climatic conditions. The US norm however, for FAME fuels follows the ASTM D 6571 (American standards testing and methods) (see Table 2.6).

Most Southern African countries do not have any standard on biodiesel, in South Africa the standard for automotive fuel for diesel engines is SANS 1935:2004. This standard specifies the requirements and test methods to be used for marketed and delivered biodiesel either as automotive fuel for diesel engines at 100 % concentration, or as an extender for automotive fuel for diesel engines. At 100 % concentration, fuel for use in diesel engine vehicles are designed or subsequently adapted to run on 100 % biodiesel.

Table 2.6 Selection of international quality standards on neat biodiesel blends fuels

Country	Region/Standard	Date	Applicable to
Australia	Australian Standard	2003	FAME
European Union	EN14214	2003	FAME
USA	ASTM D 6751	2003	FAME

Tables showing the standard requirements for automotive biodiesel in the USA, European Union and South Africa and other countries can be found in the appendixes 1, 2 and 3. The relevance of this table will be seen in Chapter 4.

2.9.1 Cetane number

The cetane number is an indication of fuel readiness to auto-ignite when it has been injected into the diesel engine. Diesel fuels are required to have a cetane number higher than 40 and most refineries produce diesel with cetane numbers between 40 and 45. Biodiesel has a higher cetane number between 46 and 60 (depending on the feedstock used) which shortens the ignition delay in the engine and improves the combustion characteristics (Meher et al., 2006b).

2.9.2 Flash point

The flashpoint of a fuel is the temperature at which the vapour above the fuel becomes flammable. Petroleum-based diesels have flashpoints of 50 °C to 80 °C which makes them intrinsically safe. Biodiesel has a flashpoint of over 160 °C which means that the fire hazard associated with transportation, storage and usage of biodiesel is much less than with other commonly used fuels (Biodiesel Education, 2009).

2.9.3 Viscosity

Plants and waste oils have higher viscosities compared to diesel fuel; transesterification of these oils reduces the viscosity to a large extent in converting to biodiesels. Viscosity measurement is a basic parameter reflecting the extent of the reaction, since it is directly related with the fatty acid methyl ester (FAME) content of the transesterified product and is one of the specifications to comply with when producing biodiesel (it is as an indicator to measure the effectiveness and completeness of the ester conversion process).

2.9.4 Sulphur content

The sulphur content of fossil diesel has to be below 50ppm since the beginning of 2005 (SAPIA, 2006) as high sulphur contents in fuels have been associated with negative health effects and an increased service frequency on vehicles. Biodiesel is essentially seen as sulphur free when made from fresh vegetable oil. Biodiesel made from waste

vegetable oil (WVO) might contain traces of sulphur and would have to be tested to fall into regulatory limits (Mittelbach and Remschmidt, 2006).

2.9.5 Cold-filter plugging point (CFPP)

Cold temperature properties are measures of the behaviour of the fuel under low ambient temperatures. The cold filters plugging point is especially important in countries where the temperatures drop below 50°C. The cloud point is the lowest temperature at which the sample may be cooled while still retaining its fluidity. The cold-filter plugging point (CFPP) is considered a good indicator of operability limits of the fuel (Mittelbach and Remschmidt, 2006).

2.9.6 Heat of combustion

The heating value, also known as the heat of combustion, of biodiesel depends on the oil source. On a mass basis fossil diesel has a higher heating value; about 13% higher than that of biodiesel, but due the higher density of biodiesel, the disadvantage of biodiesel is only about 8% lower on a volumetric basis. This means that for the same injection volumes, engines burning biodiesel have slightly lower power and torque. If injection volumes are changed for biodiesel, the same power and torque can be achieved. Flexi-fuel vehicles use intelligent motors which can detect the type of fuel being used (biodiesel, petroleum diesel or a blend) and automatically adjust the injection parameters (Mittelbach and Remschmidt, 2006). An increase of the injection volumes leads to a slightly higher specific fuel consumption when using biodiesel. It is important to keep in mind that the above properties are those of pure biodiesel. If biodiesel is blended into fossil at 5% or 10%, the properties of the fossil diesel would not be affected to a noticeable extent. It is only the 'lubricity' property of the biodiesel that has an effect even if used in very low blends; this property makes biodiesel an ideal additive for fossil diesel.

2.10 Summary

In light of the discussions and reviews presented in this chapter, it is critical for the biodiesel industry to continuously improve on aspects that will strengthen its prospects of better market penetration and production technologies. The review supplies a brief synopsis of the different catalysts used in the process of transesterification of oils for the production of biodiesel. There are numerous review papers recently published focusing on specific issues related to production processes, feedstock, engine testing and emission and social, economy and policy (Januan and Ellis, 2010) which are beyond the scope of this study.

In this research study, the main goal is the search for efficient processes of producing biodiesel that will strengthen its prospect as the next generation green fuel via the ultrasound and continuous jet loop process technologies by the use of homogeneous base catalysts.

Moreover this study will also compare the process using homogeneous with that using heterogeneous catalyst. The onus thereafter lies in the selection and investigation of appropriate solid catalysts which can compare or improve on the conventional process. These would be of great significance for biodiesel production especially in the case of feedstock with high water and free fatty acids (FFA) content, strongly affecting the behaviour of conventional homogeneous base catalysts. Consequently, this study screened various heterogeneous catalysts that include fly ash based catalyst and AFA based zeolite catalysts for the transesterification reactions in the production of biodiesel that could used directly with refined or with waste oils.

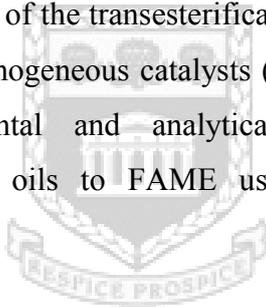
The experimental methods employed in achieving the research aims and objectives in this study follow in the next chapter.

Chapter 3

Experimental Methods

3. Introduction

The previous chapter of this study (chapter 2) focused on the review of literature. This chapter describes the chemicals, sample preparation, experimental and analytical methods used in this study. The sequence employed in the methodology in solving the research problem is highlighted in section 3.1 while the description of the chemicals used and their preparation are presented in section 3.2. This chapter consists of the three major parts which include (i) section 3.3 that describes the experimental methods for the determination of properties and fatty acid composition of oil samples (ii) section 3.4 that deals with the optimization study of the transesterification of vegetable oils to fatty acid methyl esters (FAME) using homogeneous catalysts (iii) section 3.5 that deals with the sample preparation, experimental and analytical methods used in studying transesterification of vegetable oils to FAME using the prepared KNO_3/FA as heterogeneous catalyst.



3.1 Overview

An overview of the chapter layout includes the following:

- i. Sample preparation and pretreatment
- ii. Transesterification reactions: This involves the reaction between the oil, catalyst, and methanol under different reaction conditions. Further steps (separation of phases, washing, purification and drying of the upper phase (methyl esters) are carried out in order to obtain a pure product sample.

- iii. FAME analysis: Analytical methods such as Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC) and Thin Layer Chromatography (TLC) were used at different stages to obtain relevant data towards the determination of the conversion, yield and purity of the methyl esters obtained from the transesterification reactions via the different catalytic systems.
- iv. Standard testing of FAME samples: This entails laboratory tests conducted to confirm and establish the properties and quality of the methyl esters (biodiesel) obtained under optimal conditions (under the different catalytic processes). The results are compared to biodiesel fuel standards based on European Union quality standard (*EN 14214, 2003*), American standard tests and measurements (*ASTM D 6751*) specifications.
- v. Catalyst preparations: This section sets out the protocols for catalyst preparation of the different catalytic systems. The use of potassium hydroxide (KOH) and sodium hydroxide (NaOH) as catalysts did not require any preparation in the homogeneous system however the heterogeneous catalysts (KNO_3/FA and $\text{FA}/\text{Na-X}$) were prepared using the wet impregnation method and conventional hydrothermal synthesis procedure respectively.
- vi. Catalyst characterization: Catalysts were characterised using different techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy-energy dispersion spectroscopy (SEM-EDS), Fourier transform infrared spectroscopy (FTIR), and temperature programme desorption (TPD).

3.2 Materials

Pulverized fly ash was collected from the ash collection systems at Arnot Eskom coal fired power stations (see legend 1 in Figure 3.1) in South Africa and used as raw material in the preparation of the KNO_3/FA catalyst.

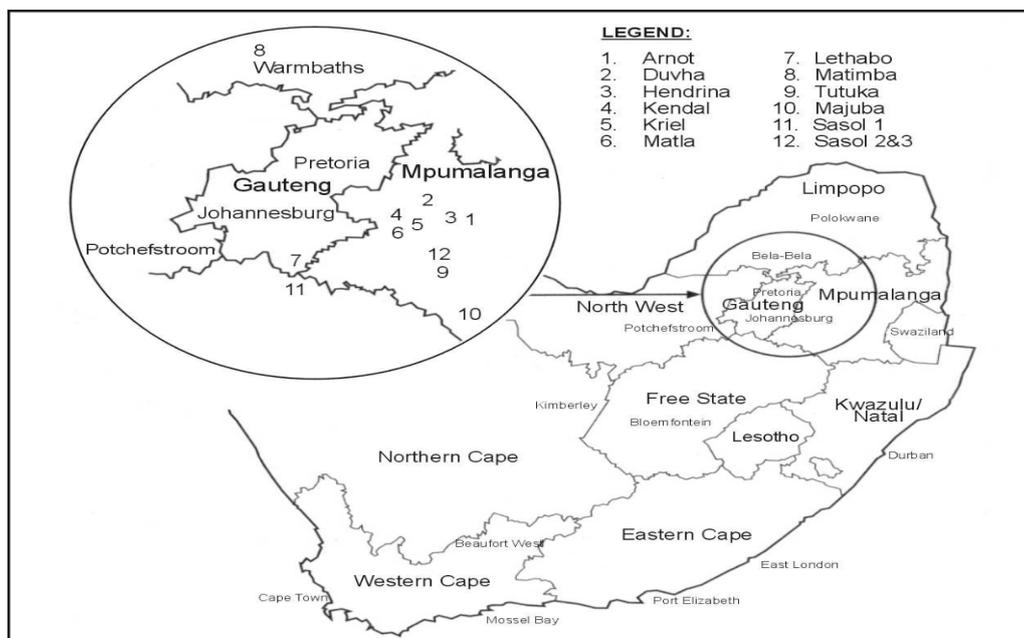


Figure 3.1: Location of important pulverised coal-fired thermal power stations in the Republic of South Africa (Krüger, 2003).

The list of the feedstock used in the study is given in Table 3.1. All reagents used in the procedures were of analytical grade and a list of the chemicals, solvents and acids used in this work is presented in the Table 3.2.

Table 3.1: Feedstock supply

Material	Source
*Sunflower (SFO)	Sun-foil Oils (Cape Town)
*Soybean (SBO)	Sun-foil Oils (Cape Town)
*Waste cooking oil	Mac Donalds (Stellenbosch)

Table 3.2: List of chemicals, solvents and acids used in the study

Chemicals/Solvents	Source	Grade/purity
Potassium Hydroxide pellets	Kimix Chemicals	99.9 %
Sodium Hydroxide pellets	Kimix Chemicals	99.9 %
Sodium sulphate	Kimix Chemicals	99.0%
Potassium Nitrate (KNO ₃)	Merck Chemicals	99.0%
Commercial zeolite Na-X	CWK, Bad Köstritz	
Potassium acetate	Kimix Chemicals	98%
Ethyl acetate	Kimix Chemicals	88%
Methanol	Sigma Aldrich	99.9%
Ethanol	Sigma Aldrich	99.9%
Acetone	Sigma Aldrich	99.9 %
Hexane	Sigma Aldrich	99.9 %
Acetic acid	Merck	30%
Hydrochloric acid	Merck	32%
10% Phosmolybdic acid	Sigma Aldrich	
Phenolphthalein indicator	Merck	
Bromo-phenol blue indicator	Merck	
G.C Internal standards:	Sigma Aldrich	44893-U
<ul style="list-style-type: none"> ▪ Glycerin 5000 µg/mL in pyridine ▪ Monoolein 5000 µg/mL in pyridine ▪ Diolein in pyridine, 1 x 2 mL ▪ Butanetriol 1 x 5 mL in pyridine ▪ Tricaprin, 8000 µg/mL in pyridine ▪ n- heptane-reagent grade 		

3.3 Experimental methods

3.3.1 Oil sample preparation

The fresh/refined oils (SFO and SBO) were used as purchased, while the used oil (WCO) had to be pre-treated to remove the dirt and other inert materials from the oil. The WCO was first filtered under vacuum to remove the dirt and other inert materials, then dehydrated using anhydrous sodium sulphate and again filtered under vacuum, prior to use.

3.3.2 Properties and fatty acid composition of oil samples

3.3.2.1 Density

Density is the mass per unit volume of any liquid at given temperature. Specific gravity is the ratio of the density of a liquid to the density of water. This property is important because it influences the efficiency of atomisation of the fuel and also very relevant in the determination of the cetane index of an oil sample (Srivastava and Prasad 2000). The density of the oil sample at 15 °C was determined following the ASTM standard D1298.

3.3.2.2 Acid value

Acid value (or "acid number" or "acidity") is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. The acid number is used to quantify the amount of acid present, for example in a sample of biodiesel. It is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in 1 g of sample. The oil samples were analysed in order to ascertain their acidity index necessary to carry out the transesterification reaction. The acidity

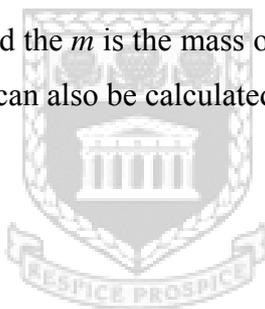
index of the raw oils was analysed following a well established experimental titration procedure according to ISO 1242:1999.

Procedure

In a typical procedure, a known amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a colour indicator. Each titration was repeated four times and the standard deviation calculated. The value is defined as equation:

$$Y = \frac{C_x V \times 56.1}{m} \quad (3.1)$$

Where Y is the acid value, V is the consumed volume of KOH (ml), C is the concentration of KOH (mol/l), and the m is the mass of the tested sample (g) and 56.1 is the molecular weight of KOH. It can also be calculated as $1.99 \times \text{FFA} \%$



3.3.2.3 Saponification value

Saponification value represents the number of milligrams of potassium hydroxide or sodium hydroxide required to saponify 1g of fat under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. As most of the mass of a fat/triester is in the 3 fatty acids, it allows for comparison of the average fatty acid chain length. The long chain fatty acids found in fats have low saponification value because they have a relatively fewer number of carboxylic functional groups per unit mass of the fat as compared to short chain fatty acids. If more moles of base are required to saponify N grams of fat then there are more moles of the fat and the chain lengths are relatively small, given the following relation:

$$\text{Number of moles} = \frac{\text{mass of oil}}{\text{relative atomic mass}} \quad (3.2)$$

The calculated molar mass is not applicable to fats and oils containing high amounts of unsaponifiable material with free fatty acids less than 0.1 %.

Procedure

Measurement of saponification value was performed according to the official test methods. A sample of fatty acid is first saponified by adding 0.5 mol/L potassium hydroxide ethanol, and then the excessive potassium hydroxide is titrated with 0.5 mol/L hydrochloric acid until the endpoint is reached.

$$\text{Saponification value} = \frac{(V_1 - V_2) \times 56.1 \times c}{m} \quad (3.3)$$

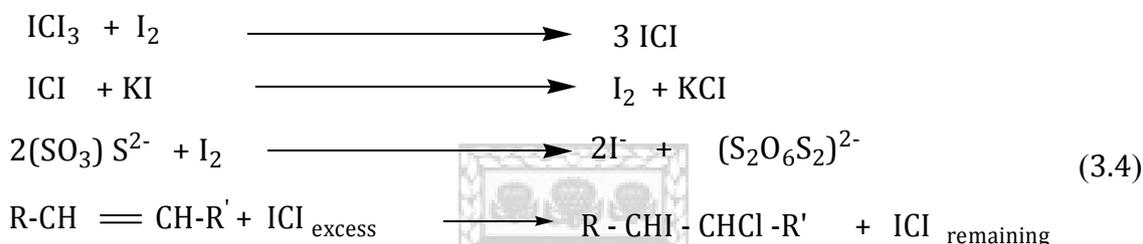
Where, V_1 is the volume, in millilitres, of specification hydrochloric acid solution required for the blank; V_2 is the volume, in millilitres, of specification hydrochloric acid solution required for the fat; c is the concentration of the specification hydrochloric acid solution, in moles per litre; m is the mass, in grams of sample taken.

3.3.2.4 Iodine value

Iodine value is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. An iodine solution is yellow/brown in colour and any chemical group in the substance that reacts with iodine will make the colour disappear at a precise concentration. The amount of iodine solution thus required to keep the solution yellow/brown is a measure of the amount of iodine sensitive reactive groups. The iodine value gives a measure of the average degree of unsaturation contained in fatty acids. This unsaturation is in the form of double bonds which react with iodine compounds. The higher the iodine number, the more unsaturated fatty acid bonds (C=C double bonds) are present in a fat (Mittelbach and Remschmidt, 2006).

Procedure

In a typical procedure, the fatty acid is treated with an excess of Wijs solutions, which is a solution of iodine monochloride (ICl) in glacial acetic acid. Unreacted iodine monobromide (or monochloride) is reacted with potassium iodide, converting it to iodine, whose concentration can be determined by titration with sodium thiosulfate. A scheme of the reactions, as shown in equations 3.4. The concentration of C=C in the original sample can therefore be calculated by measuring the amount of sodium thiosulfate needed to complete the titration. Therefore, the higher the degree of unsaturation, the more iodine absorbed and the higher the iodine value.



For a simple analysis, 0.2 grams of the fat was mixed with 20 ml Wijs solution and 10 ml 1,1,1-trichloroethane. It was then left in the dark for 30 minutes. Next, 15 ml of 10% potassium iodide solution and 10 ml of deionized water was added. This is then titrated against 0.1 M sodium thiosulfate (VI) solution. 1 ml of 0.1 M sodium thiosulfate solution = 0.01269 g of iodine. The difference between a control titration and the titration with the fat present multiplied by this factor gives the mass of iodine absorbed by the oil. Standard methods for analysis are for example ASTM D5768-02 (2006).

3.3.2.5 Viscosity

Viscosity can also be considered as a measure of the friction of fluids, as it also describes the internal resistance of the flow of fluid. There are two ways to report or measure a fluid's viscosity. It can either be expressed as dynamic viscosity, or kinematic viscosity. Dynamic viscosity (μ) which is also referred to as absolute

viscosity, or just viscosity, is the quantitative expression of a fluid's resistance to flow (shear), its SI unit is in pascal-second (Pa.s) which is mainly used in ASTM standards. Kinematic viscosity, on the other hand, is a ratio of the viscous force to the inertial force. Inertial force is characterized by fluid density (ρ). Kinematic viscosity (ν) is mathematically defined as

$$\nu = \mu/\rho \quad (3.5)$$

Viscosity is closely related with the fatty acid composition of a given oil sample, it increases with increasing length of the fatty acid chain that also relates to the rate of transesterification reaction of a given oil sample. The major aim of these reactions are to reduce the viscosity values of the triglycerides (before transesterification) and FAME(s) produced (after reaction) since the major drawback of using neat vegetable oils as fuels are due to the high viscosity values they possess. This viscosity difference between forms the basis of an analytical method (viscometry) applied to determine the conversion of vegetable oils to methyl esters. The viscosity difference between the component triglycerides and their corresponding methyl esters resulting from transesterification is approximately one digit (Knothe, 2001).

Procedure

The dynamic viscosity of the oil samples (SFO, SBO and WCO) was determined using the Anton Parr Physica Rheometer, Rheoplus /32 V 2.81 MCR 501 operating on a rolling ball principle at a temperature of 40 °C. One replicate for each sample was done as the instrumentation gave consistent results.

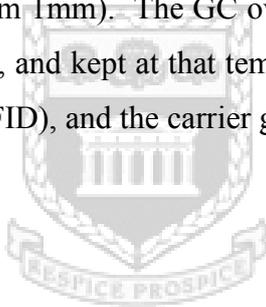
3.3.2.6 Water content

During the transesterification reaction, the presence of water causes the loss of yield of methyl ester due to the formation of soaps. In the biodiesel product, water can promote biological growth and hydrolytic reactions which are linked with automotive filter blockage. The water content in the waste cooking and the vegetable oils was measured

using a Thermo Orion AF7LC Coulometric Karl following EN ISO 12937 norm. The same method was used in the determination of the water content of the biodiesel obtained from the reactions.

3.3.2.7 Chemical composition

Fatty acid composition and the average molecular mass of the oil samples were identified by Gas Chromatography (GC). The fatty acid compositions of these fats and oils were determined by a well established GC procedure (Alacantra et al., 2000; Kemp, 1967). A standard mixture of these esters was injected in the GC for identification and quantification purposes. 0.050 g of standards and samples was dissolved in 10 ml of n-hexane and injected (1 ml) in a Varian CP-3380 GC, equipped with a carbowax capillary column (15 m x 0.53 mm 1mm). The GC oven was kept at 100 °C for 2 min, heated at 10 °C/min up to 220 °C, and kept at that temperature for 10 min. The detector was a flame ionization detector (FID), and the carrier gas helium (30 mL/min).



3.3.3 Preparation of reagents

The preparation of the chemicals used in the acidity titration tests are described below; 4g of NaOH was accurately measured and added into 1 L volumetric flask containing ultrapure water. The solution was made up to the 1 L mark with ultrapure water.

3.4 Transesterification reactions (homogeneous catalyst)

This section describes the experimental set up and procedure used for the transesterification reactions conducted with the three different oil samples using the homogeneous catalysts (KOH and NaOH) to convert the oil into fatty acid methyl esters (FAME) under the preliminary batch reaction tests. The use of KOH as homogeneous catalyst was applied under the main batch reaction tests, as well as for optimising the

conditions of the ultrasound reactor/mixer and the jet reaction tests. A number of transesterification experimental runs were carried out over the duration of the study and recorded. The process conditions such as the reaction time, temperature, and catalyst amount and methanol: oil ratio was varied. This was done to determine the optimal reaction conditions for each set of experiments. The procedure used for the transesterification reactions under each process system is explained in sections 3.4.1 and 3.4.2 in detail.

3.4.1 Experimental procedure (batch reaction tests)

The transesterification reactions under the batch tests were carried out with 100 g of each oil sample weighed and placed in a 500 ml three necked flask in a fume cupboard. The appropriate catalyst (KOH/NaOH) was dissolved in methanol and the resulting solution was added to the oil in the reactor. The oil sample was heated by placing on a hot plate equipped with a mechanical stirrer (Heidolph MR 3001K) which was capable of maintaining the required reaction temperature of 30 - 80 °C to within $\pm 0.1^\circ\text{C}$. The reaction was timed as soon as the catalyst /methanol solution was added to the reactor and it continued for the required reaction time range of 30 min to 2 h. The reaction was carried out under reflux equipped with a magnetic stirrer for mixing the oil methanol and catalyst at a stirring speed of 600rpm. After that the reaction had to be stopped by cooling the reactor to room temperature and the product mixture by using a suction flask. The mixture was placed in the separating funnel and allowed to stand overnight to ensure that the separation of the methyl esters and the glycerol phase occurred completely. The glycerol phase (bottom) was removed and left in a separate container. After the glycerol layer has been eliminated, the methyl ester layer was washed with two volumes of water to remove methanol, catalyst and the glycerol residuals until clear. Finally the methyl esters (biodiesel) were dried with sodium sulphate (25 wt% Na_2SO_4) based on the weight of oil. The methyl ester samples are then placed in an ice bath until required for analysis. Experiments were undertaken in duplicate to ensure that erroneous results were quickly identified within a series of samples. The experimental set up as shown in Figure 3.2 and Figure 3.3 shows the samples of products obtained

from the sunflower, soybean and waste cooking oil feedstock from different experiments conducted in the study.



Figure 3.2: Experimental set up of the mechanical agitation process



Figure 3.3: Samples of products obtained from the sunflower, soybean and waste cooking oil samples from experiments conducted in this study

3.4.2 Experimental procedure (ultrasound reaction tests)

Sonication experiments were carried out using an Omni ultrasound homogenizer (Figure 3.4a) with a 20 kHz frequency and a power output of 400 Watts. The experiments were performed at a controlled temperature of 30 °C using a water bath placed on the hot plate as shown in Figure 3.4b. The reaction mixture consisted of 100 g of SFO/WCO oil and 21.70 g of methanol. In order to determine the effect of the amount of catalyst needed to convert the waste cooking oil triglycerides to its respective FAMES via the ultrasound, reactions were conducted with catalyst amounts of 0.5 wt%, 0.75 wt%, 1.0 wt%, 1.25 wt%, 1.5 wt% based on a pre weighed sample of waste cooking oil used typically. The reaction time was varied from 10 min to 50 min at an interval of 10 min and samples after each interval. The reaction vessel containing the catalyst and the oil was placed under the ultrasonic homogenizer with the ultrasound macro tip immersed into the oil and kept in place about 5 cm away from the bottom of the reaction vessel. After a complete conversion, the reaction mixture was allowed to stand for at least 8 h for phase separation. The esters mixture formed the upper layer and the glycerol, the lower layer after separation by gravity, the upper layer (methyl esters, some methanol and traces of the catalyst) was placed in a rotary evaporator to distil off the excess methanol as the case may be and then passed through a column packed with macroporous polymer resins (GF 202) to eliminate traces of methanol and water.



Figure 3.4a: Ultrasound homogenizer

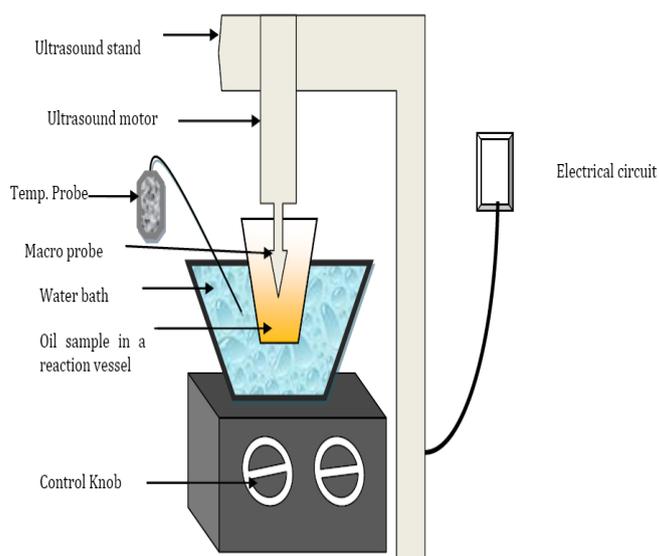


Figure 3.4b: Schematic diagram of the ultrasound transesterification system

3.4.3 Jet loop reactor test using homogeneous catalyst (KOH) at pilot scale

Biodiesel production can be enhanced by process intensification technologies such as the jet loop reactor as indicated in Figure 3.5a and b. The technology has the potential to improve production efficiency and thus reduce operating cost of the transesterification

process. Oil and methanol does not mix, which is why a catalyst, heat and a mixing unit is necessary for transesterification reactions to proceed. The use of a jet reactor can force the kinetics involved in these reactions to proceed much faster to completion.



Figure 3.5 (a): Jet loop reactor

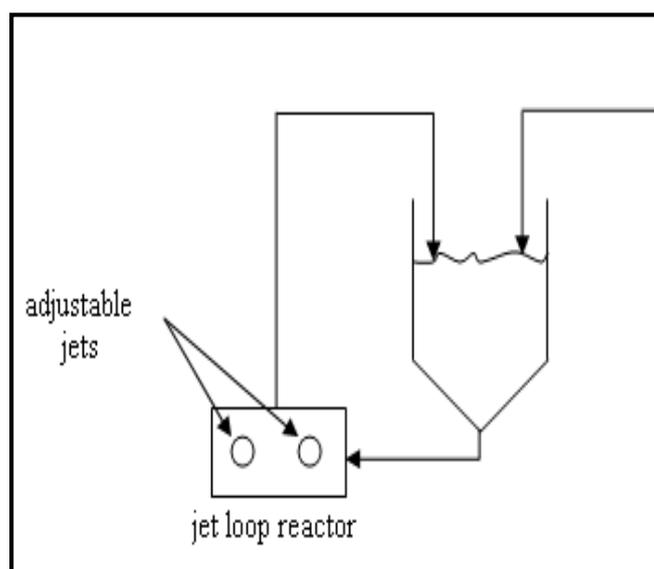


Figure 3.5 (b): Schematic diagram of the jet loop reactor.

Procedure

The jet loop reactor was first loaded with 5000 cm³ in volume of the waste cooking oil. Recirculation pumps were switched on and the oil heated by the jet loop via hydraulic friction up to 30 °C when a mixture of with a ratio of 4:1 methanol: oil (1100 cm³ of methanol) and 1 % in weight of KOH (45.4 g) in relation to the oil as catalyst was added to the reactor. The jet loop mixing regime was maintained for 1 h while samples of 100 cm³ were taken from a port situated at the bottom of the reactor at 5, 10, 15, 20, 30, 45 and 60 min. To each sample taken, five drops of water were added in order to stop the methanolysis reaction. Once the sampling sequence was finished, each sample was weighed to obtain the total mixture weight. After carefully covering to avoid excess methanol evaporation, the samples were set to rest for 8 h allowing maximum glycerol gravimetric separation from methyl esters formed and from the reacted oil mixture. Following the gravimetric separation process, the samples were cooled to temperatures of 5 to 9 °C for a period of 1 h period to permit the solidification of the lower layer comprising glycerol and facilitate its separation from the methyl esters. The solidified glycerol was then easily separated from the methyl esters and both phases independently weighed. Finally both the glycerol and the methyl ester mixture were heated in a thermo regulated bath at 70 °C for 30 min to eliminate any excess of dissolved methanol, followed by weight measurement of the remaining glycerol and biodiesel fraction separately.

3.5 Transesterification reactions (heterogeneous catalysts)

This section details the procedure employed during application of the heterogeneous catalysts; (KNO₃/FA AFA based and the AFA based zeolite FA/K-X) to conduct the transesterification reactions.

3.5.1 KNO₃/FA fly-ash based catalyst

The transesterification reactions were carried out with 100 g of sunflower oil weighed and placed in a 500 ml three necked flask. The oil was heated to 60 °C and then the

140– 165 ml of methanol and 5-20 g of AFA based catalyst were weighed and added into the oil. The reaction was carried out under reflux at a stirring speed of 600rpm with a magnetic stirrer for mixing the oil methanol and catalyst. An electronic temperature controller was used to vary the reaction temperature in the range of 180 - 260 °C and a reaction time range of 2 - 24 h was explored.

3.5.2 Zeolite FA/K-X catalyst

20 grams of sunflower oil was weighed and placed in a 100 ml two-necked flask. The oil sample was heated to 60°C by placing on a hot plate equipped with a mechanical stirrer (Heidolph MR 3001K). 5 ml of methanol and 0.6 g of zeolite catalysts were weighed and added into the reactor. The reaction was carried out under reflux; magnetic stirring was used for mixing the constituents at a stirring speed of 600 rpm. The reaction mixture was heated up to 60 -65 °C while continuously stirring until the completion of the reaction (8 h and 24 h).

Afterwards, in both procedures mentioned above, the reactions were stopped by cooling the reactor to room temperature and the product mixtures were then placed in the separating funnel and allowed to stand overnight. This was to enable adequate separation of the methyl esters and the glycerol phase. The glycerol phase (bottom) was removed and left in a separate container. Finally the methyl esters (biodiesel) fraction was dried by adding 25 weight percent of sodium sulphate (Na_2SO_4) based on the weights of the oil samples. The methyl ester samples were thereafter withdrawn from the dried bulk methyl ester product with glass capillary tubes and diluted with hexane to perform thin layer chromatographic (TLC) studies (section 3.6.5).

3.6 FAME analysis

Monitoring the extent of the transesterification reactions and FAME analysis involved a procedure that is used routinely for fat analysis in which non volatile fatty acids are chemically converted to the corresponding volatile methyl esters. The resulting volatile

mixture was analysed by a series of analytical methods which are going to be described in this section.

3.6.1 FAME composition

Fatty acids and methyl esters composition of the synthesised biodiesel samples obtained in this study were determined and identified by Gas Chromatography (Varian CP-3380 GC using Software: Delta 5.0) with a Column specification (Zebron ZB-WAX, 30m x 0.32mm x 250um) according to EN 14013 (2003) and ASTM 6584 (2003). These methods are suitable for analysis of samples containing methyl esters between C₁₄ and C₂₄.

Gas chromatography analyses were carried out to quantitatively and qualitatively determine the methyl esters produced. Helium was used as the carrier gas in the GC with the initial oven temperature set at 110 °C held for 0.5 min and subsequently increased to 220 °C (hold 8 min) at 10 °C/min. Temperatures of the injector and detector were set at 220 °C and 250 °C respectively. In each run, 1µL of sample was injected into the column. Methyl heptadecanoate was used as internal standard. The yield of the transesterification reaction was calculated by using Equation 3.6.

$$FAME\ Yield\ (\%) = \frac{\text{total weight of methyl esters}}{\text{total weight of oil in sample}} \times 100 \quad (3.6)$$

The yields of FAME in each experiment were calculated from the weight of FAME in the FAME phase and the theoretical material balance of the transesterification reaction, as shown in Equation 3.7.

$$FAME \text{ yield } \% = \frac{W_{FAME}/M_{FAME}}{3W_{oil}/M_{oil}} \times 100 \quad (3.7)$$

Where W_{FAME} represents the weight of FAME in the FAME phase and W_{oil} represents the weight of FAME in the weight of oil used. M_{FAME} and M_{oil} are the mean of molecular weight of the FAME and the oil, respectively. The factor 3 in the equation above indicates that one mole of triglyceride yields three moles of FAME.

The concentrations of the components such as triglycerides (TG), diglycerides (DG), monoglycerides (MG), and FAME were calculated by Equation 3.8.

$$C_i(\text{mol L}^{-1}) = \frac{\frac{W_i}{M_i}}{V} \quad (3.8)$$

Where W_i and M_i are the weight and the mean of molecular weight of the components in the FAME phase respectively and V is the volume of the FAME phase.

The FAME conversion was calculated using Equation 3.9.

$$Conversion(\%) = \frac{\frac{M_{biodiesel} \cdot \text{biodiesel content}}{MW_{biodiesel}}}{3 \frac{M_{oil}}{MW_{oil}}} \times 100 \quad (3.9)$$

The factor three appears in this formula since each triglyceride molecule yields three methyl ester molecules.

$$MW = \sum MW_i \cdot w_i \quad (3.10)$$

Where, MW is the mean molecular weight of biodiesel/oil. The mean molecular weight (equation 3.10) of biodiesel was calculated averaging the individual molecular weights (MW_i) of each constituent methyl ester, according to the biodiesel fatty acid methyl ester analysis (w_i).

The amount of the glycerol phase obtained from phase separation was determined by the gravity method and was calculated by Equation 3.11

$$GL(\text{wt}\%) = \frac{W_{GI}}{W_m} \times 100 \quad (3.11)$$

Where, W_{GI} is the weight of the glycerol phase and W_m is the weight of the reaction mixture, respectively. The weight of the reaction mixture was the sum of the weights of the raw materials (as the case may be), methanol and catalyst used for the transesterification.

The purity of FAME means the total fatty acid methyl ester concentration (wt %) in the FAME phase and the FAME yield (wt %) after the post treatment relative to the amount of vegetable oil poured into the reactor. The purity was calculated from the methyl ester and vegetable oil weights respectively.

3.6.2 Determination of free and total glycerol in biodiesel

A column injection Gas Chromatograph (DANI Instrument, USA) was used for the determination of MG, DG and TG and free glycerol in accordance with ASTM Standards (D6584). A fused silica capillary GC column was used in the GC apparatus with an internal diameter of 0.32mm and length of 30m. The temperature of the flame ionization detector was 250°C and the carrier gas pressure was 80Kpa. Triglycerides possess large molecules, free and bound glycerol as well; and contain hydroxyl groups which make them polar. It is therefore necessary to derivatize the large molecules by the use of silylation using N- methyl- N-trimethylsilyltrifluoroacetamide (MSTFA) to reduce polarity and improve thermal stability. Trimethylisation converts any hydroxyl groups into trimethylsilyl ether groups $-\text{OSi}(\text{CH}_3)_3$ which are more volatile and do not interact with the stationary phase of the fused silica capillary column.

Procedure for stock and standard solutions

Commercially prepared stock standards purchased from Sigma Aldrich containing glycerol, monoolein, diolein, triolein, butanetriol (internal standard 1) and tricaprins (internal standard 2) at concentrations specified in the ASTM methods (ASTM D6584, 2003) were used for these analyses. A list of these standards and reagents used in the

analysis are shown in Table 3.2. The calibration standards were prepared by mixing aliquots of the stock standards in ratios specified by ASTM method. 100 μ L of MSTFA was added to each calibration standard and then left to react for 20 min, after which 8ml of n-heptane was added to each calibration standard. The final reaction mixtures were directly injected into the gas chromatograph. The analysis for each biodiesel sample was carried out by dissolving 100 mg of the biodiesel sample in 8ml of heptane and injecting 1 μ l of the solution into the GC. n -heptane (a suitable organic solvent) is effective in transforming hydrocarbons such as polar glycerol and glycerides with high boiling point into a homogeneous state to improve volatility before injection into the GC. Please see ASTM D 6584 test method for determination of free and total glycerine in B100 in list of references. An analytical service was provided by an authorized analysis organization (Bio-services cc) and some chromatographs can be seen in appendices.

3.6.3 Soap and catalyst measurement

Production of biodiesel using an alkali catalyst always produces some amount of soap (Ma and Hanna, 1999). There will be more soap with waste oils than with refined vegetable oils as discussed in section 2.3.4 of the literature review. After the transesterification reaction is complete, the left over catalyst and soap tends to concentrate in the glycerol phase; however some soap and a small amount of catalyst may be left in the biodiesel phase. During the process development, it can be useful to know the amount of soap formed, where the catalyst resides and how effective the washing process was in removing these two compounds.

Procedure

A simple titration procedure is used to measure the amount of soap and catalyst American oil Chemical Society (AOCS) method Cc 17-79.

A gram of the biodisel sample was dissolved in 100 ml of acetone containing 2 % distilled water, then 2 ml of 1 % phenolphthalein indicator was added and titrated with

0.01M HCL until the phenolphthalein colour change (red to clear) was observed. This titre is designated as A.

1 ml of bromophenol blue indicator (0.4% in water) was added to the mixture. This indicator changes colour at about a pH of 4.5 and a titration was done until the bromophenol indicator changed from blue to yellow. This indicates that the pH is low enough and that all of the soap present should have been split into FFA and salt. This quantity of solution is designated as B.

The amount of HCL added during the first titration determines how much free basic catalyst is in the sample and the amount added during the second titration determines the amount of soap.

$$\text{grams of catalyst per gram of sample} = \frac{A \times 0.1 \times 56.1}{1000 \times W} \quad (3.12)$$

Equation 3.12 gives the amount of free catalyst in the sample where the catalyst is KOH and Equation 3.13 gives the amount of soap

$$\text{grams of soap per gram of sample} = \frac{B \times 0.1 \times 320.56}{1000 \times W} \quad (3.13)$$

3.6.4 Viscosity measurements

Viscosity of the FAMEs produced from the different oil samples were determined using the Anton Parr Physica Rheometer, Rheoplus/32 V 2.81 MCR 501 operating on a rolling ball principle at the test temperature of 40 °C.

One replicate for each sample was done as the instrumentation gave consistent results. The conversion efficiency of the oils obtained from the viscosity results was calculated using the Equation 3.14.

$$C = \frac{V(\text{tri}) - V(\text{me})}{V(\text{tri})} \% \quad (3.14)$$

Where, C is oil conversion (%), V (tri) is viscosity of triglyceride and V (me) is the viscosity of the converted methyl ester. The difference in viscosity between the pre-transesterified oils and the FAME derivatives can also be used to monitor biodiesel production in all the experiments and therefore catalyst activity. This type of relationship has been reported in the literature (Ramos et al., 2008) thus allowing the total concentration of methyl ester to be obtained from only the viscosity measurement.

3.6.5 Thin Layer Chromatography (TLC) measurements

TLC is generally used to separate and determine the concentration of different types of lipid groups in foods, *e.g.* triacylglycerols, diacylglycerols, monoacylglycerols, cholesterol, cholesterol oxides and phospholipids (Damyanova, 2004). A TLC plate is typically coated with a suitable absorbing material and placed into an appropriate solvent. A small amount of the lipid sample to be analyzed is spotted onto the TLC plate. With time the solvent moves up the plate due to capillary forces and separates different lipid fractions on the basis of their affinity for the absorbing material. At the end of the separation the plate is sprayed with a dye so as to make the spots visible. By comparing the distance that the spots move with standards of known composition it is possible to identify the lipids present.

The TLC was chosen because it is a rapid analytical method that gives quite accurate indication of oil and methyl esters content in the mixture.

Procedure

The primary characterization of the FAME product obtained after the completion of the reaction and in the experiments conducted using the KNO_3/FA as heterogeneous catalyst was analysed by silica gel TLC technique to check the conversion of the triglycerides into methyl esters according to the method described by Damyanova (2004). Silica gel TLC plates (Sigma Aldrich) were used for the various methyl ester samples from both the fly ash and zeolite catalysts were analysed on each plate shown

in Figures 3.6; **a**- 5 % KNO₃/FA at 5 h, **b**-5 % KNO₃/FA at 8hr, **c**- 10 % KNO₃/FA at 5 h, **d**-10 % KNO₃/FA at 8 h and **e**-5 % KNO₃/FA at 12 h; and Figure 3.7; **a**- CM/Na-X at 24 h, **b** - FA/ Na-X at 8 h, **c**- FA/KX at 8 h, **d**- FA/ Na-X at 24 h and **e**-5 FA/KX at 24 h. A mixture of hexane/ethyl acetate/acetic acid (80:20:2 v/v/v) was used as the mobile phase and silica gel as the stationary phase. Detection was obtained by spraying the plate with 10% ethanolic phosphomolybdate acid solution and heating the plates for 10 min at 180°C in an air circulating oven. Biodiesel shows a higher mobility than vegetable oil with the selected solvent system and complete conversion of vegetable oil to biodiesel was supported by the disappearance of the vegetable oil spot on the TLC plate. The ester content of biodiesel samples was later determined by GC as described previously in section 3.6.1.

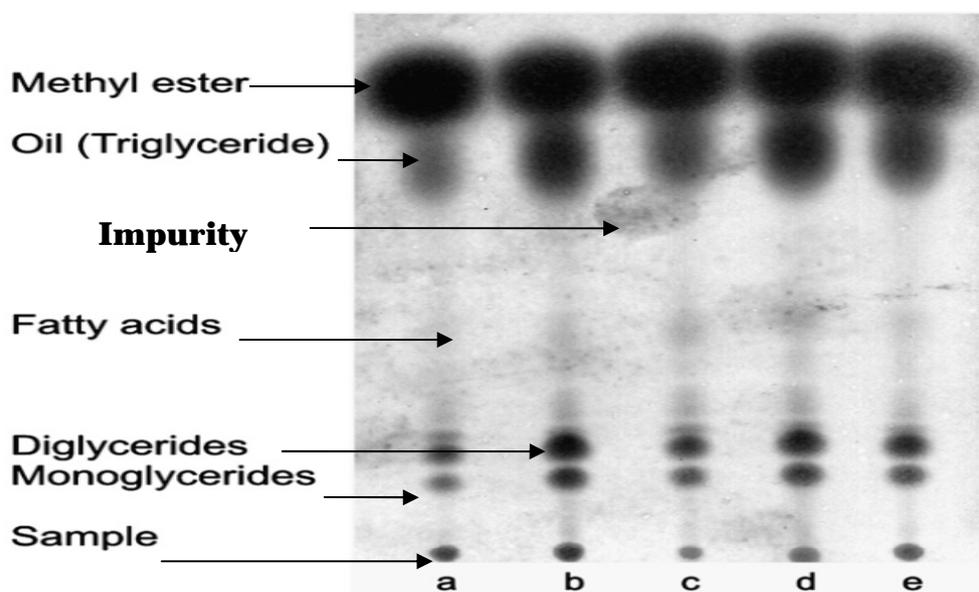


Figure 3.6: TLC plate showing the separation of FAME constituents (KNO₃/FA catalysts): **a**-5 % KNO₃/FA at 5 h, **b**-5 % KNO₃/FA at 8hr, **c**- 10 % KNO₃/FA at 5 h, **d**-10 % KNO₃/FA at 8 h and **e**-5 % KNO₃/FA at 12 h

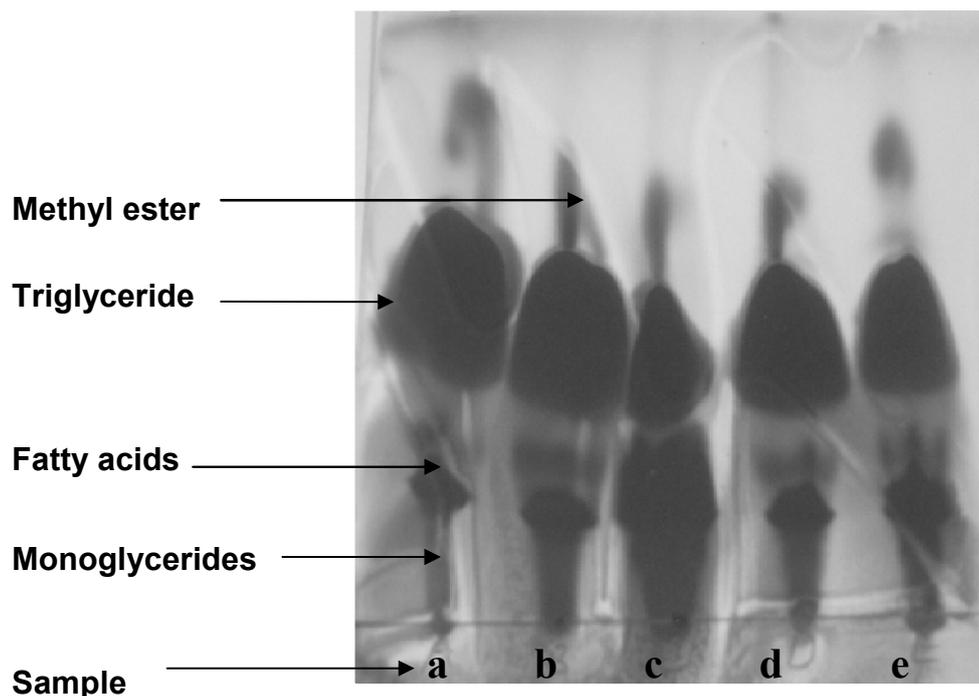
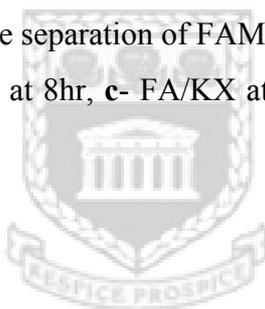


Figure 3.7: TLC plate showing the separation of FAME constituents (zeolite catalysts) a-CM/Na-X at 24 h, b- FA/Na-X at 8hr, c- FA/KX at 8 h, d-FA/Na-X at 24 h and e-5 FA/KX at 24 h.



3.7 Heterogeneous catalysts

Pulverized fly ash that was sampled from the ash collection systems at Arnot Thermal Power station in the Mpumalanga District of South Africa was used as a support in preparing the KNO_3/FA catalysts used in this study. The elemental chemical composition of the fly ash (on dry basis) was determined by various analytical methods as described in section 3.8.2 and characterisation results presented in section 5.3.2.2a/b found in chapter 5. The class of the fly ash was determined by the ATSM method C 618.

3.7.1 Sample handling and storage

Before its use, the Arnot fly ash material was ground to a fine powder and dried at 110 °C for 2 h and samples were sealed in a plastic container with an airtight lid. The containers were kept in a dark cool room away from sources of moisture, out of direct sunlight and away from fluctuating temperature. This is because upon exposure to the atmosphere many of the metastable assemblies of mineral phases in fly ash that were initially formed at high temperatures during coal combustion will alter to form thermodynamically stable minerals which might alter the overall initial phase composition of fly ash (Musyoka, 2009)

3.7.2 Catalyst preparation

Preparation of Arnot fly ash based (KNO₃/FA) catalysts

The KNO₃/FA catalysts were prepared using wet impregnation method as reported by Kotwal et al. (2009). To prepare the different loadings of the neutral salt on the AFA, 10.2, 20.4, 30.6, 40.8 and 60 ml of 1M KNO₃ aqueous stock solution mixed into 10 g of dried fly ash in each case to obtain the 5 %, 10 %, 15 %, 20 % and 25 % KNO₃/FA respectively. These samples were then constantly stirred continuously until homogeneous mixtures were obtained after about 30 min. The removal of water was accomplished by using rotary evaporator then drying at 100 °C for 2 h, and then calcined at 500 °C for 5 h in air. These were then characterised to determine the effect of the KNO₃ loading on the structural characteristics and its catalytic effect was calculated for the transesterification reactions. Calcination temperatures were not optimised in this study.

Preparation of zeolite catalysts

The main raw material, waste coal fly ash samples were collected from Arnot coal power plant (South Africa) to synthesize the AFA derived zeolite FA/Na-X catalyst. The AFA derived zeolite FA/Na-X catalyst was prepared by and according to the conventional hydrothermal synthesis process procedure (Musyoka et al., 2011).

This as-received zeolite FA/Na-X was then modified by an ion exchange with an alkali metal (K) using potassium acetate as a precursor. The FA/Na-X was dried in the oven at 110 °C for 2 h to remove any absorbed water on its surface, and then dispersed in 1.0 M solution of potassium acetate. The volume ratio of zeolite powder to the solution used was 1:10. The suspension was maintained at 60-70 °C for 24 h. The slurry was repeatedly washed with distilled water and then dried again in air at 120 °C for 2 h and then calcined at 500 °C for 2 h to obtain the ion exchanged zeolite FA/ KX. Calcination at temperatures above 300 °C removes most of the organic additives (acac) and impurities (Lee and Jo, 2010). Commercial zeolite Na-X used as a baseline for investigative studies was obtained from CWK, Bad Köstritz.

3.8 Characterization techniques

3.8.1 Surface area and pore size determination

An important physical analysis of the heterogeneous catalysts prepared as specified was conducted by the application of gravimetric nitrogen Brunauer-Emmett-Teller (N₂-BET) surface analysis technique. The catalyst samples (0.35 – 0.5g) were out-gassed at 110 °C on the Micrometrics Flow Prep 060 using helium gas. The Micromeritics Tristar instrument was used with nitrogen as the analysis gas and surface area based on a 5 point with 30 adsorption and 30 desorption points, together with a total pore size measurement.

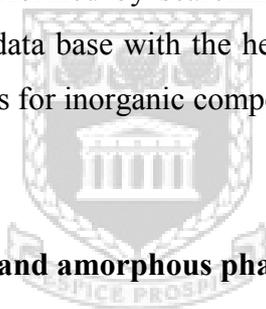
3.8.2. Qualitative XRD analysis

The qualitative analysis of the mineral and amorphous phases in the catalyst samples were done by XRD. Samples were prepared for XRD analysis using a back loading preparation method. The samples (after being ground to a fine powder) were placed in a sample holder and the crystalline phases were characterised using a Philips X-ray diffractometer with Cu-K α radiation. The XRD instrument operating conditions were as given in Table 3.3.

Table 3.3: XRD operating parameters

Radiation source	Cu-K α
Radiation wavelength (λ)	1.542 Å
Range	104
Time constant	1 s
Preset	1000 counts/s
Voltage	40 kV
Current	25 mA
2 θ range	4° < 2 θ < 60°
2 θ /step	0.1°
Anti-scatter slit	1°

The phase identification was performed by searching and matching obtained spectra with the powder diffraction file data base with the help of JCPDS (Joint committee of powder diffraction standards) files for inorganic compounds.



3.8.3 Quantification of mineral and amorphous phases

After addition of 20 % Si (Aldrich 99 % pure) for determination of amorphous content and milling in a McCrone micronizing mill, the samples were prepared for quantitative XRD analysis using a back loading preparation method. Samples were analysed with a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-K α radiation. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weight %) was estimated using the Rietveld method (Autoquan Program).

3.8.4 X-ray fluorescence (XRF)

XRF spectroscopy is widely used for the qualitative and quantitative elemental analysis of solid environmental, geological, biological, industrial and other samples. XRF has

the advantage of being non-destructive, multi-elemental, fast and cost-effective. Furthermore, it provides a fairly uniform detection limit across a large portion of the periodic table and is applicable to a wide range of concentrations, from a 100 % to few parts per million (ppm). Its main disadvantage is that analyses are generally restricted to elements heavier than fluorine and that a large sample is required (Kalnicky and Singhvi, 2001).

Fresh fly ash was analysed for elemental composition using X-ray fluorescence (XRF), and a Philips 1404 Wavelength Dispersive Spectrometer fitted with a Rh tube was used. The samples were oven-dried at 50 °C for 12 h to remove the water content prior to analysis. The XRF technique reports in % oxides for major elements and ppm for minor elements. The elements reported as % oxides (in the case of batch reaction tests' solid residues) were converted to ppm elements using element conversion software accessed at <http://www.mariscigrp.org/oxtol.html>.

3.8.5 Scanning Electron Microscopy (SEM)

SEM is found useful in obtaining rapid qualitative elemental analysis of an unknown sample. The morphology of the fly ash and zeolite synthesised in this investigation was examined using a Hitachi X-650 scanning Electron Microanalyser equipped with a CDU lead detector at 25 kV. Samples were mounted on aluminum pegs and coated with a thin film of gold to make them conductive.

3.8.6 Energy Dispersive Spectroscopy (EDS)

Also called Energy Dispersive X-ray Spectroscopy (EDX), is a technique based on the collection and energy dispersion of X-rays created when high energy electrons bombard a sample. This method detects all elements from boron to uranium and is usually non-destructive. Two methods are used to determine the x-rays that are produced: (1) energy-dispersive analysis, which separates and detects x-rays of specific energy and displays them as histograms, whereas (2) wavelength-dispersive analysis uses the reflection of x-rays of a crystal at a characteristic angle to detect x-rays of specific

wavelengths (Goldstein et al., 2003). The EDS is attached to the Scanning Electron Microscope (SEM) and the two techniques are often used together. The X-rays have energies that are characteristic of the elements in the sample. The instrument's electronics process the signals to give histograms of energy vs. signal strength, the latter being related to relative elemental concentration. The method detects all elements from boron to uranium and is usually non-destructive. Detection limits range from 0.05-2 % for high to low Z elements, respectively. EDS is particularly good for relating elemental composition to topographical features but it is only qualitative and should be supported by other techniques such as XRF for quantitative elemental composition.

The fresh Arnot fly ash, the KNO_3/FA catalyst sample and the zeolite based catalysts were oven-dried at 105 °C for 12 h in preparation for the SEM-EDS analysis. The dried samples were sprinkled on special glue mixed with carbon graphite and mounted on aluminium stubs. The morphology of the samples was established by secondary electron mode. The “photo” imaging was used to identify regions of relative homogeneity and thereafter EDS analysis was done on some spots for qualitative elemental composition.

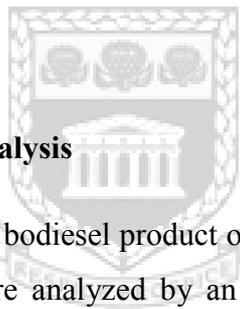
3.8.7 Fourier Transform Infra Red (FTIR)

Fourier Transform Infrared spectroscopy (FT-IR) was used to monitor changes and also provide information about the molecular structure of the fly ash based catalysts. FT-IR requires virtually no sample preparation so in this case, approximately 15 mg of the catalyst samples in each case was placed on the Attenuated Total Reflectance (ATR) sample holder of a Perkin Elmer spectrum 100 FT-IR spectrometer. The sample was recorded in the range of $4000\text{-}250\text{ cm}^{-1}$, baseline was corrected and the spectra smoothed. The use of diamond cells with beam condenser or microscope allowed adjustment of the thickness of a sample by squeezing which enables analysis of microgram samples to be performed.

Fourier Transform Infrared spectroscopy (JASCO FT/IR-4100 spectrometer) was used to provide information about molecular structure of the commercial zeolite and AFA based zeolite material. The samples were scanned from $400\text{ to }4000\text{ cm}^{-1}$.

3.8.8 CO₂-Temperature–Programmed Desorption (CO₂-TPD)

The basicity of both the AFA based catalysts was measured by CO₂ temperature–programmed desorption (CO₂-TPD). A 0.10g sample was pre-treated at 500 °C for one hour in dry He flow (30ml/min) and cooled to room temperature then exposed to pure CO₂ for 30 min in order to absorb CO₂ species. After purging the catalyst with helium to remove physisorbed species, the CO₂-TPD profile was obtained at a heating rate of 10 °C/min from room temperature to 500 °C. The TPD signal and temperature corresponding to CO₂ desorbed were recorded simultaneously and the CO₂-TPD data is acquired. The amount and temperature of the desorbed CO₂ qualitatively corresponds with the amount and strength of the basic sites. The temperature of desorption and the maximum desorbed CO₂ are illustrative of the strength and amount of basic sites, respectively. The basic site density was obtained by integration of the area under the curve.



3.9 Biodiesel characterisation analysis

To confirm the quality of the final biodiesel product obtained under the different optimal conditions, biodiesel samples were analyzed by an authority certified to analyze the characteristics of commercial biodiesel fuels (Bio-services laboratory, Johannesburg, South Africa). The following parameters were analysed using certified procedures; (i) density at 15 °C, (ii) kinematic viscosity at 40 °C, (iii) iodine value (iv) acid value (v) water content (vii) total ester content (viii) flash point. The testing results of the FAME products in the present study are shown in chapter 4. Industrial standards specifications that were used for evaluating the properties of the biodiesel samples were; EN 14214, ASTM D6751 and SANS 1935:200 and are listed at the appendices.

The next chapter (chapter 4) will present and discuss the results of the characterization of the fresh and used oil samples. The result of the transesterification experiments in the batch reaction tests, ultrasound tests and jet reactor tests carried out on the oil samples with KOH as catalyst will also be presented and discussed.

Chapter 4

Biodiesel Synthesis via Homogeneous Catalysis

4. Introduction

This chapter firstly presents the major physical and chemical properties of the feedstock used in this study (sunflower, soybean and used cooking oils). The chapter also highlights the reaction parameter optimisation results for the production of the fatty acid methyl esters (FAME) obtained in both the conventional batch reaction process and the continuous operation system used whilst employing low frequency ultrasonic technology or the jet reactor.

In order to optimize the production of these FAMES or biodiesel (as the case may be), the effect of relevant process parameters which include: temperature, residence time, and methanol to oil ratio and catalyst amount on the FAME yield and rates of conversions using the different oil samples, are reported. The results discussed in this chapter stem from the experimental procedures outlined in the experimental methods (sections 3.3).

4.1 Overview

Fatty acid methyl ester (FAME) commonly known as biodiesel has been perceived as a potential source of renewable and environmental-friendly energy in the future, replacing exhaustible petroleum-derived diesel. A significant amount of research has been carried out worldwide to produce biodiesel due to its advantages compared to conventional diesel. For instance, biodiesel is superior to diesel in terms of sulfur content, flash point, aromatic content and biodegradability (Murugesan et al., 2009; Demirbas, 2003; 2006). Apart from that, the feedstock for biodiesel production is derived from renewable sources such as edible/non-edible oils and waste animal fats, which are abundant and

inexhaustible. Hence, production of biodiesel will ensure the sustainability of human development and energy source in the future. Despite the bright prospect of biodiesel as a sustainable source of energy, its commercialization efforts have been very limited throughout the world. One of the major obstacles is the high cost of refined vegetable oil as feedstock, which consists of nearly 70 % of the total production costs (Phan and Phan, 2008; Bautista et al., 2009; Chung et al., 2009; Meng et al., 2008). Hence, in order to reduce the cost of biodiesel and not to compromise feedstock for humans, waste or low-quality oils/fats which are inexpensive and readily available can be utilized as feedstock. However, the challenge of employing these cheap feedstocks is the presence of impurities such as water and free fatty acids (FFA) which are common components in waste oils/fats (Peng et al., 2008; Felizardo et al., 2006; Rosa et al., 2008; Chen et al., 2009). The characterization of the oil samples used in this study and the effect of the process variables on the transesterification process in determining yields and conversion of triglycerides to FAME via different reaction processes is expected to give an insight into the physicochemical compositions of these triglycerides and ascertain their overall effects on the different process operations and impacts on the optimization of the whole biodiesel production.

The objectives of this chapter are; (1) to discuss results of the physical, chemical compositions of the fresh and used oil samples, (2) to do an evaluation of the effects of the different reaction parameters on the yield and conversion rates of the different feedstock to their corresponding FAME(s), (3) to maximize and evaluate the process optimization of the different reaction systems used in producing the FAME, (4) to determine whether the FAME(s) produced with each of the oil samples under different process conditions meet industrial specification, as the product cannot be regarded as “Biodiesel” if industrial specifications are not met.

4.2 Materials and methods

The detailed descriptions of the fresh and used/waste oil samples used in the section of the study are presented in chapter 3 sections 3.2. The oil sample preparation procedure

is outlined in section 3.3.1. The analytical procedures involved in determining the physical and chemical properties of the oil samples are also presented under section 3.3.2.

In this section, KOH was used as the main homogenous catalyst and the methods and procedure employed for the transesterification reactions conducted under this section are described in section 3.4, while the experimental procedure of the homogeneous transesterification reactions and pictorial representations of the respective experimental set-ups under each process system (batch reaction, ultrasound and the jet reactor) are presented in sections 3.4.1, 3.4.2 and 3.4.3 respectively.

4.3 Results and discussion

The results and discussion presented in this chapter of the thesis are in the following sequence; Section 4.3.1 presents and discusses the fresh and used oil samples characterization results. Section 4.3.2 presents the properties and fatty acid composition of the fresh and used oil samples.

Section 4.3.3 discusses the results of the preliminary studies to determine the influence of process parameters on FAME yield via the batch reactions tests. Section 4.3.4 presents and discusses the results of the influence of process parameters on FAME yield via the main batch reaction experiments. Section 4.3.5 presents and discusses the results of the effects of the process parameters on FAME yield and rates of conversions via the ultrasound reaction test using the different oil samples. Section 4.3.5 presents and discusses the results of the effects of the process parameters on FAME yield and rates of conversions via the jet reactor system and section 4.3.6 presents the test results of the influence of process variables on FAME conversion via the jet- mixing process. Finally, in section 4.4 the characterisation results of fatty acid methyl esters produced under the different reaction systems are presented and then compared with standard specifications.

4.3.1 Oil characterization

The characterization of the feedstock materials; sunfloweroil (SFO), soybean oil (SBO) and waste cooking oil (WCO) used for further experiments is presented in this section (4.3.1). The main rationale for the characterization of the fresh oil samples used in this study was to determine the fatty acid composition of the triglycerides present in the oil samples, as the chain length and number of double bonds determines to a large extent the physical characteristics of both fatty acids and triglycerides. The characterisation is also necessary in order to measure the following baseline values; density, viscosity, saponification, water content and acid. Viscosity is closely related to the fatty acid composition of a given oil sample, it increases with increasing length of the fatty acid chain and also relates to the rate of transesterification reaction of a given oil sample. The major aim of these reactions are to reduce the viscosity values of the triglyceride (before transesterification) and FAME(s) produced, since the major drawback of using neat vegetable oils as fuels is due to the high viscosity values they possess. The acid value of the oil samples is determined to a large extent by the type of feedstock and the respective degree of refinement, while the water content plays a very important role in the transesterification process as high water contents are associated with hydrolytic reactions. The type of fatty acids present in the oil samples also determines the saponification value (section 4.3.2.2). The characteristics of the fresh and used oil samples determine the yields and conversions of the different triglycerides present in the samples to their corresponding FAME(s) and are also expected to give an insight into the extent to which the FAME(s) produced met laid down quality specifications of biodiesel.

4.3.2 Properties and fatty acid composition of oil samples

It is pertinent before conducting the transesterification reactions on any oil sample to determine the physical and chemical properties to establish whether the oil sample would need pre-treatment. The type of catalyst to be used in conducting the transesterification or esterification reactions would be chosen on the basis of the oil

sample characteristics. This has been discussed in detail in the literature review (section 2.3.2).

4.3.2.1 Physical and chemical properties of oil samples

Physical and chemical properties of the raw materials such as density, acid value (AV), iodine value (IV), saponification value (SV), viscosity and moisture content were determined by methods described previously in chapter 3 (section 3.3.2). The physical and chemical properties of the different oil samples used in this study are presented in Table 4.1.

Table 4.1: Physical and chemical properties of the different feedstock used in this study (n=3).

Property (Unit)	SFO	SBO	WCO	Typical values (Literature)
Density (g cm ⁻³)	0.882	0.891	0.925	0.80-0.94
Acid value (mg KOH/g oil)	0.1	0.3	1.37	NA
Iodine value (g I ₂ /100 g oil)	125	130	102.5	100-160
Saponification value (mg KOH/g)	176.6	181.3	184.2	170-200
Viscosity (m Pas at 40°C)	29.4	29.3	37	27-48
Water Content (wt %)	ND	ND	0.65	NA

*N.D Not Detected, *N.A Not Applicable

The density values of the different oil samples ranged from 0.882 to 0.925 which fell with the ranges reported in literature (Mittelbach and Remschmidt, 2006). Density is the mass per unit volume of any liquid at a given temperature. Specific gravity is the ratio of the density of a liquid to the density of water. This parameter is important in engine performance since fuel injection operates on a volume metering system and density is also very relevant in the determination of the cetane index (Srivastava and Prasad 2000).

The acid values of SBO and SFO were very low (0.1 and 0.3 respectively) compared to the acid value of WCO (1.37); these low acid values allowed for the use of a basic catalyst in the transesterification process (Alacantha et al., 2000).

The saponification value (SV) of the oil samples ranged from 176.6 to 184.2. Saponification value is inversely related to mean molecular mass and by measuring saponification value, mean molecular mass can be obtained. The measured results of the oil sample parameters shows favourable repeatability with less than 0.3% relative standard deviation, based on three replicates.

The iodine values of the oil samples, WCO, SFO and SBO were 102.5, 125 and 130 respectively. The iodine value is a measure of the degree of unsaturation of oil which gives an indication of the presence of double or bonds; the higher the iodine value, the more reactive, less stable, softer, and more susceptible to oxidation and rancidification the oil would be. According to literature (Mittelbach and Remschmidt, 2006), triglycerides iodine values in the range of 50-100 may result in decreased engine life, and in particular to decreased fuel pump and injector life, however these must be balanced against greatly decreased fuel costs (if using cheap, surplus oil) and it may be found that even with increased maintenance costs this is economically viable.

The dynamic viscosity value of the different oil samples varied from 29.4 to 37. Viscosity is closely related to the fatty acid composition of a given biodiesel sample (Refaat et al., 2008). It increases with increasing length of the fatty acid chain thus explaining the high viscosity value for the waste oil.

The moisture content values of the fresh oils (SBO and SFO) were below 0.1 wt% while the value for WCO (0.65 %) revealed a higher moisture content, thus making it necessary to heat up the oil sample to 60 °C to eliminate moisture before the main transesterification reactions in order to prevent side reactions during the transesterification reactions. During the transesterification reaction, the presence of water causes a reduced yield of methyl ester due to the formation of soaps (Meng et al., 2008).

4.3.2.2 Fatty acid profile of oil samples

The oil samples used for producing the FAME in this work were analysed to determine the fatty acid composition according to the analytical methods discussed in the previous chapter in section 3.6 and findings are summarized in Table 4.2. The values are measured in triplicate.

Table 4.2: Fatty acid composition of the different feedstock samples used in this study (n=3).

Fatty Acid % wt	SFO	SBO	WCO
Palmitic Acid (C16:0)	14	11.75	6.08
Stearic acid (C18:0)	6.02	3.15	3.26
Oleic Acid (C18:1)	35.60	23.26	16.93
Linoleic Acid (C18:2)	44.78	55.53	73.73
Linolenic Acid (C18:3)	0.6	6.31	N.D
Mean molecular weight (g mol ⁻¹)	845.34±12.03	867.21±17.56	884.16± 15.76

*N.D Not detected

Natural oils have varying composition of various fatty acids and thus may result in different activities for the transesterification reactions (Mittelbach and Remschmidt, 2006). The fatty acid composition of the oil samples show that the oil samples were composed mainly of four types of fatty acid triglycerides including palmitic acid, stearic acid, linoleic acid and oleic acid triglycerides. The oils show a high degree of unsaturation i.e. oleic and linoleic acids (~80%w/w) which favours the use of basic catalyst (Freedman et al., 1984) to produce unsaturated fatty acid methyl esters.

The waste cooking oil sample had the highest amount of short carbon chains of fatty acids (C16:0) in comparison to sunflower oil and soybean oil. These short carbon chains

of fatty acids have less steric hindrance in comparison to long carbon chains of fatty acids which would result in mutually activating effect (Stavinoha and Howell, 2000).

4.3.2.3 Summary

The characterisation of the different oil samples used in this study by various analytical methods revealed their physical, chemical properties as well as their fatty acid composition. In the light of previous discussion on the requirements for the feedstock in chapter 2, four oil crops including sunflower seed oil and soybean oil dominate the feedstock sources used for world-wide biodiesel production. The high content of linolenic acid present in the feedstock limits their use as fuel production without prior conversions to methyl ester through transesterification reactions. They both display iodine values of 121-130g I₂/100 g.

The use of waste cooking oils obtained from households and restaurants for use as feedstock in biodiesel production makes sense from an economic point of view; however waste oils typically contain high amounts of water and free fatty acids (Table 4.1) limiting their use in base catalysed transesterification reactions.

The results showed that all the oil samples tested can be adequately used as raw materials in the transesterification reactions experiments as acid values reported are within low limits (less than 2 mg KOH/g) which is suitable for use with a basic catalyst (in this case KOH).

4.3.3 Preliminary studies on the influence of process variables on FAME yield (batch process)

The preliminary batch transesterification reaction tests on the different feedstock oil samples was carried out to gain an insight into the effects of using different types of basic catalyst (NaOH and KOH) and varying the methanol to oil ratio and reaction time or temperature on the yields of the FAME(s) produced during the reactions (see section 3.4.1. for experimental details). The findings of the preliminary tests were used as the

basis for choosing the parameters to be applied in the main batch reaction tests. The preliminary study was carried out by reacting measured volumes of the different oil samples, (details in section 3.4.1) with the methanol at different ratios (1:1 to 9:1) at different contact times (30 - 90 min) and temperature (30-70 °C). In this section, transesterification reactions were conducted at a stirring speed of 600 rpm.

4.3.3.1 Effect of Type of catalyst

The SFO, SBO and WCO oil samples having acid values of 0.1, 0.3 and 1.37 respectively were transesterified with methanol at different molar ratio of methanol to oil (6:1) at temperatures of 30 °C and 60 °C. The upper temperature level was determined by the boiling point of methanol (65 °C). The lower level was 30 °C since lower temperatures than that could require a cooling system which would increase production costs. The results of the effect of the type of catalyst on the transesterification reactions involving the different oil samples are presented in Table 4.3.

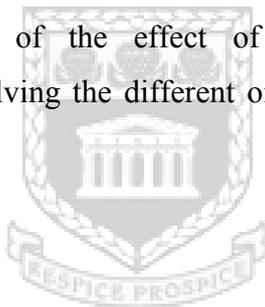


Table 4.3: Comparison of two catalysts for the preparation of FAME from SBO, SFO and WCO at methanol: oil ratio (6:1). (n = 3)

Catalyst (%wt/wt)	Temperature	Time	FAME yield (wt%)		
			SFO	SBO	WCO
0.5% KOH	30 °C	60 min	78	75.6	63
		90 min	78	80.3	60.5
1% KOH	30 °C	60 min	78	80	64
		90 min	87	84	74
0.5% KOH	60 °C	60 min	94	83	77
		90 min	92	90	75
1% KOH	60 °C	60 min	92	94	80
		90 min	95	96	90
0.5% NaOH	30 °C	60 min	76	74	57
		90 min	72	76	67
1% NaOH	30 °C	60 min	74	69	66
		90 min	72	70	68
0.5% NaOH	60 °C	60 min	81	85	67
		90 min	93	92	88
1% NaOH	60 °C	60 min	96	94	88
		90 min	92	96	87

From the study, the NaOH catalysed transesterification proceeded quicker than the KOH catalysed reaction, where FAME yields (96, 94 and 88 %) were observed at a reaction time of 60 min for the SFO, SBO and WCO respectively and FAME yields (95, 96 and 90 %) were observed at a reaction time of 90 min for the SFO, SBO and WCO respectively.

This observation agrees with studies conducted by Vicente et al. (2006) where the authors stated that sodium hydroxide catalysed transesterification tends to be completed

faster. However as shown in Table 4.3, higher FAME yields were observed with the use of KOH as catalyst, hence its use in the main reaction batch experiments reported in the next section (4.3.4). This favourable behaviour is particularly pronounced if KOH is used as catalyst instead of NaOH as it accelerates phase separation by increasing the density of the glycerol layer due to its molecular weight (Mittelbach, 1989). The decreased tendency for soap formation when using KOH as a catalyst compared to NaOH also reduces the amount of methyl esters dissolved in the glycerol phase after the reaction and thus reduces ester losses according to previous studies (Vincente et al., 2004; Mittelbach and Remschmidt, 2006).

It is also worthy of mention that another advantage of the use of KOH as catalyst is that potassium dihydrogen phosphate can be obtained from the addition of phosphoric acid to the glycerol phase derived from the alkaline transesterification reactions which can be used as a fertilizer thus adding extra value to the reaction products, whereas the respective sodium salt is considered as a waste product (Zhang et al., 2003).

Finally, higher yields were observed from the transesterification of the different oil samples conducted under a higher temperature of 60 °C (Table 4.3) which is the temperature used for the conventional biodiesel process, this can be attributed to the fact that a higher initial temperature helps in faster settlement of glycerol (Gupta et al., 2007).

It is evident from Table 4.3, that of the two catalysts used, 1 wt%KOH gave the best FAME yields for the transesterification conducted on the different oil samples and that the use of KOH had a significant impact on the yield of the methyl esters, It was also observed that lower FAME yields were recorded for WCO using either of the alkaline catalysts. This is due to the presence of a higher acid value which promotes soap formation and which prevents glycerol separation, drastically reducing ester yield (Kulkarni and Dalai, 2006). The relatively high water content of the WCO sample (0.65 %) could also contribute to this as it might affect the FAME yield by favouring a saponification reaction.

The optimum concentration for both homogeneous alkaline catalysts tested in this section appeared to be 1 wt% for all the types of oil sampled. Further experiments were however carried out to determine the optimum catalyst dosage using only KOH and results are presented under the main batch reaction tests.

4.3.3.2 Effect of methanol to oil ratio

The effect of the methanol: oil ratio on the yield of methyl esters produced from a series of experiments conducted with the different oil samples using KOH as catalyst as a sequel to the experiments conducted in section 4.3.3.1, is presented in Figure 4.1.

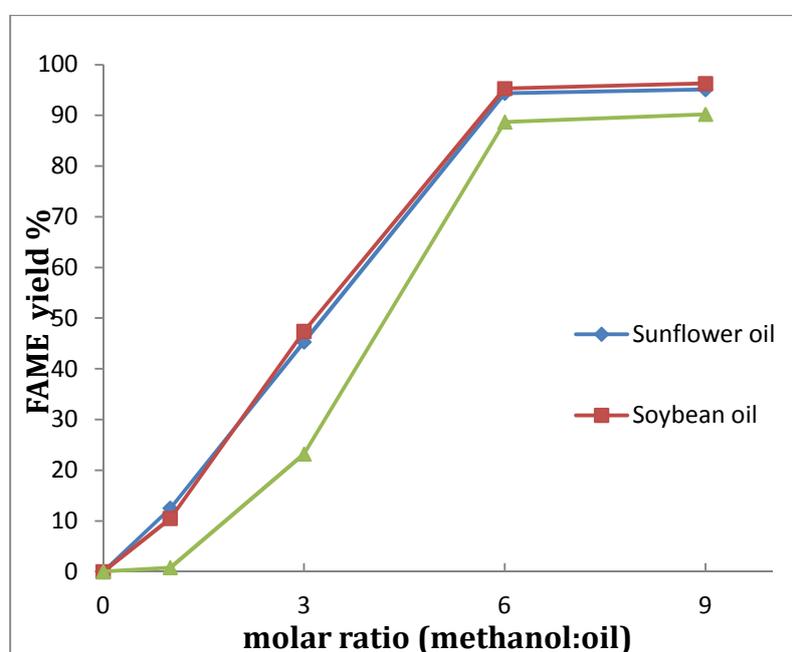
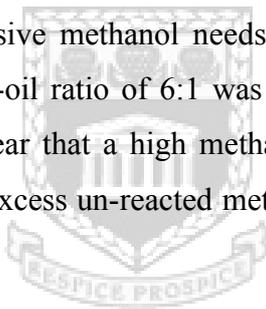


Figure 4.1: Effect of molar ratio of methanol to oil on the FAME yields for the different oil samples at a reaction condition of 60 °C, 90 min and catalyst amount of 1 wt % KOH.

The effect of methanol: oil ratio on the different oil samples was investigated from a molar ratio of 1:1 to 9:1 at an interval of 3:1 under the optimum reaction parameters obtained from the preliminary batch reaction tests. As can be seen from Figure 4.1, the transesterification did not proceed at a methanol: oil ratio of 1:1. At a methanol: oil

ratio less or equal to 3:1, transesterification progressed with FAME yield (45.3 % and 47.4 %) for the SFO and SBO respectively but a foamy layer was observed during the phase separation, with the lower layer being gelatinous and the upper layer being opaque. This was most probably due to the presence of unreacted triglycerides indicating that the methanol at a 3:1 ratio was insufficient to perform a complete reaction due to the stoichiometric requirement of three mols of alcohol to form one mol of glycerol and three mols of the respective methyl esters. However at 6:1 methanol-to-oil ratio, a product yield of 94.4 % and 95.3 % for SFO and SBO samples respectively was recorded. On observation of the WCO results, it was found that the increase in methanol/oil molar ratio to 9:1 gave the best results; with an increase in the molar ratio, the FAME yield of the WCO correspondingly increased. The highest yield (90.2 %) was achieved at a methanol-to-oil ratio of 9:1 and the results obtained by methanol-to-oil ratio of 9:1 were similar to results obtained by methanol-to-oil ratio of 6:1 (88.7 %). Thus considering that the excessive methanol needs to be removed via the use of a rotary evaporator, a methanol-to-oil ratio of 6:1 was deemed to be more suitable in a practical process. It was thus clear that a high methanol to oil ratio would favour an increase in FAME yield and an excess un-reacted methanol could be recycled easily by vaporisation after reaction.



The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification reaction, an excess of the alcohol favours the formation of the products and salt waste streams caused by the use of homogeneous catalysts that require neutralization (Meher et al., 2006). Usually a high methanol/oil ratio improves the oil dispersion under agitation, thus the transesterification can be performed easily.

The viscosities of the FAME products obtained from the different oil samples used in these experiments reduced on an increase in the amount of methanol used and also showed a visible difference from the original values as shown (Table 4.4).

Table 4.4 compares the viscosity values of the oil samples before and after the transesterification reactions at a methanol: oil ratio of 6:1. The products after the reaction had a much lower viscosity than the feedstock oils. Consequently, the

methanol-to-oil ratio of 6:1 was further studied in the transesterification of the oil samples under consistent reaction conditions.

Table 4.4: Comparison of viscosity values before and after transesterification reaction

Sample	Viscosity Value(s) at 40 ⁰ C (mPa.s)	
	before T. R	after T.R
Sunflower	29.4	3.48
Soybean	29.3	3.50
Waste Cooking oil	37	3.85

*T.R-Transesterification Reaction

4.3.3.3 Summary

The aim of the preliminary study of the transesterification using the different oil feedstock was to gain an insight into the effect that the type of catalyst and process variables such as methanol: oil ratio, reaction time and temperature would have on the methyl esters yield.

The preliminary study showed that the use of KOH rather than NaOH as catalyst did have a significant effect on the methyl esters yield. It was also observed that the methanol to oil ratio did significantly affect the yield of methyl esters prepared from the different oil samples used. The significant effect of the amount of methanol used in the transesterification reactions indicated that a higher amount of methanol was needed for the completion of the reactions and this factor was consistent with the results obtained for the different oil samples used in this study. Thus a methanol oil ratio of 6:1 was chosen in the subsequent main batch reaction tests.

The effect of reaction temperature and time on the transesterification reactions was shown to play a significant role in achieving high yield of the methyl esters. These preliminary tests gave an indication of the reaction times and temperature ranges in which the main batch reactions tests were to be conducted; reaction time (60 - 120 min)

and reaction temperatures (30 - 70 °C). The results and discussion of the main batch reaction tests are presented in the next section (section 4.3.4).

4.3.4 Influence of process variables on FAME yield: batch process

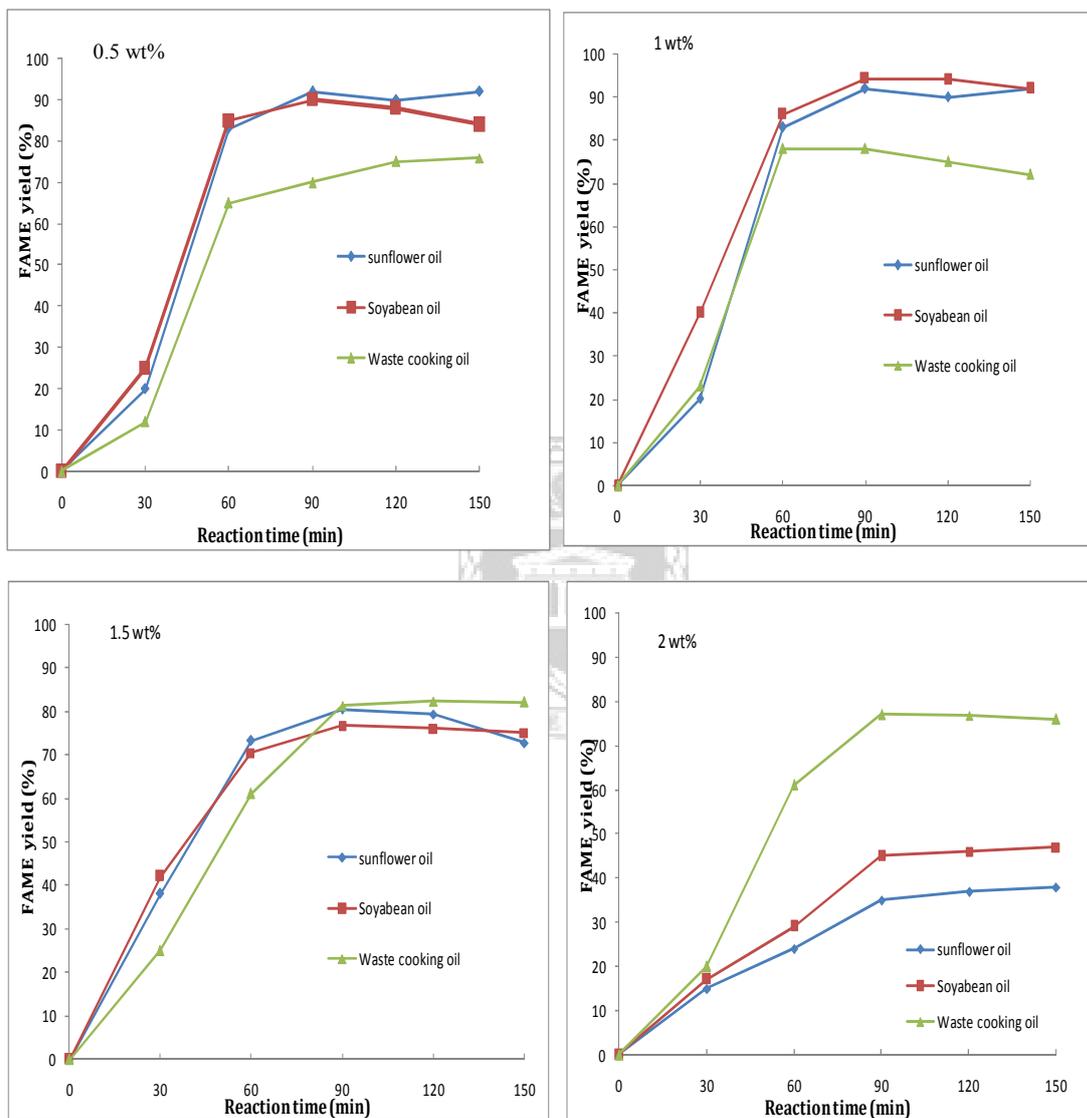
This section presents and discusses the results of the main batch reaction tests (see section 3.4.1.1 for experimental details) of the transesterification reactions involving the different feedstock, methanol and KOH used as catalyst. The preliminary batch reaction tests presented in the previous section (4.3.3) gave an insight into the effect of the type of basic catalyst, the methanol to oil ratio and the reaction time on the yields and conversions of the oil samples to FAME(s). The profiles clearly showed the effect of these parameters thereby giving an indication of what majorly influences the forward reaction in the transesterification process.

Having determined the effects of the type of catalyst (NaOH vs. KOH), methanol to oil ratio and the contact time on the FAME yield and conversion during the preliminary batch reaction tests, the main batch reaction tests were carried out using KOH as catalyst (at different concentrations), contact times between 30 to 120 min, temperatures between 30 to 70 °C at a constant methanol to oil ratio of 6:1.

This section evaluates and discusses the effects of catalyst concentration, contact time, temperature and free fatty acid content (FFA) on the FAME yield during the batch transesterification reaction tests. Thereafter, the influence of each process variable was established under the ultrasound and jet mixing reaction systems and will be presented and discussed in section 4.3.5 and 4.3.6 respectively. An evaluation of the quality of the FAME from the different reaction systems would then be compared to standard specifications in section 4.4.

4.3.4.1 Effect of catalyst concentration

The effect of catalyst concentration (KOH) ranging from 0.5 to 2 wt% on the transesterification reactions involving the different oil samples is presented in Figure 4.2.



Figures 4.2: Reaction profiles of the effect of catalyst amount under different reaction times and reaction conditions of 6:1methanol: oil ratio and reaction temperature of 60°C.

The reaction profiles as shown in Figures 4.2 indicate that the transesterification reaction was strongly dependent upon the amount of catalyst applied. Without the addition of catalyst, the transesterification reaction did not occur. The presence of the catalyst increased the reaction rate, as is evidently shown in the figure. When the amount of catalyst increased from 0.5 wt% to 1.0 wt% at a constant molar ratio of 6:1, conversion to methyl esters increased gradually. The best yields of FAME (94.2 and 93 %) for SFO and SBO oil samples respectively, were reached at a catalyst concentration of 1.0 wt% and a further increase in the catalyst concentration to 1.5 wt% did not lead to an increase the conversion but led to extra effort as it was necessary to remove the base catalyst from the product by washing at the end of the reaction. These results were qualitatively confirmed as similar trends were observed in other studies (Encinar et al., 1999, 2002, 2005). However, with a further increase in the catalyst amount (2 wt%) a decrease in the product yield was observed for the SBO and SFO oil samples, which may be as a result of the formation of an emulsion which led to the formation of gels possibly owing to an increase in soap content, which increased the viscosity of the FAME formed. These factors hindered the glycerol separation and hence reduced the apparent ester yield. A higher catalyst concentration of 1.5 to 2 wt% however favoured the transesterification reaction of the WCO. According to Freedman et al.(1984) and Kulkarni et al. (2006), when FFA levels are above 1% in an oil sample, it is necessary to add extra alkali as this allows for a portion of the catalyst to be devoted to neutralizing the FFAs by forming soap while still leaving enough to act as the catalyst.

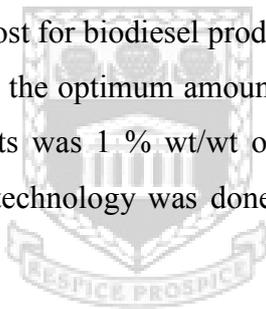
In transesterification, the active catalyst species is the methoxide radical (CH_3O^-), and the activity of a particular catalyst depends upon the amount of methoxide radicals that are available for the reaction as each mol of triglyceride reacts with 3 mol of a primary alcohol and yields 3 mol of alkyl esters (biodiesel) and 1 mol of glycerol (by-product). Dissolving potassium in methanol produces the methoxide ion according to the reaction:



Because potassium hydroxide is a strong base, its dissociation constant is very large: therefore the amount of methoxide ions depends only on the catalyst concentration; as a result, the higher the amount of catalyst, the faster the reaction proceeds (Thanh et al., 2010)

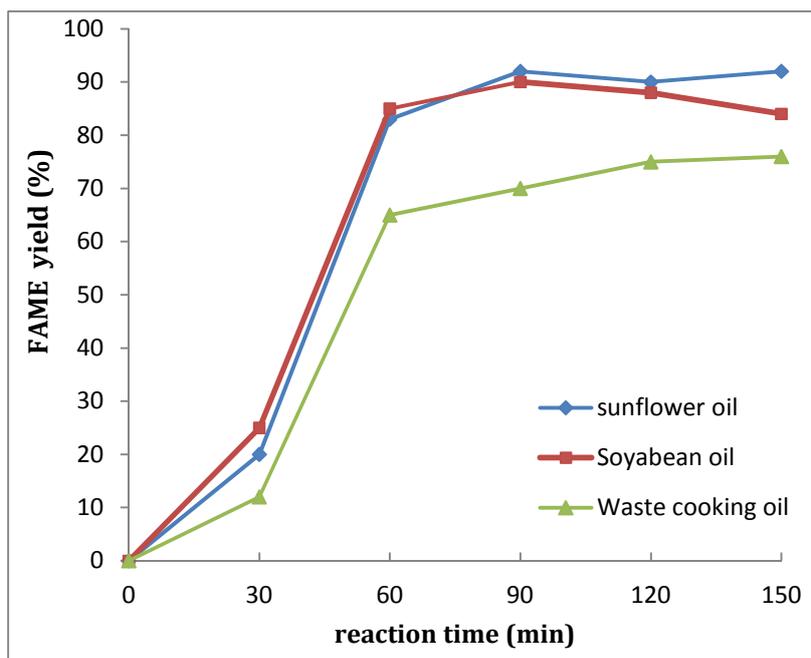
In the case of alkaline catalysis, the literature presents many studies (Evera et al., 2009; Vincete et al., 2004; Lang et al., 2001; Nouredini et al., 1998; Freedman et al., 1984) relating to these processes. In each case, the most suitable amount of catalyst depended on the type of oil utilised and the best suited concentrations reported are typically between 0.5 and 1 wt%.

From the view-point of the reaction kinetics, a larger amount of catalyst leads to a higher yield of FAME in a shorter reaction time. On the other hand, it also allows an increased soap formation, and thus results in difficulties in washing and purifying FAME, as well as increases the cost for biodiesel production due to the need to purchase more catalyst. As a consequence, the optimum amount of potassium hydroxide deemed acceptable based on these aspects was 1 % wt/wt of oil. An attempt to improve the process by applying ultrasound technology was done and results will be presented in section 4.3.5.1.



4.3.4.2 Effect of reaction time

To determine the optimum reaction time for the production of FAME from the different oil samples, the reactions were conducted at varying reaction time (30 to 150 min), at a fixed catalyst concentration of 1 % (wt/wt of oil) , 60 °C and a 6:1 methanol-to-oil ratio. The influence of the reaction time on the transesterification reactions conducted on the different oil samples is presented in Figure 4.3.

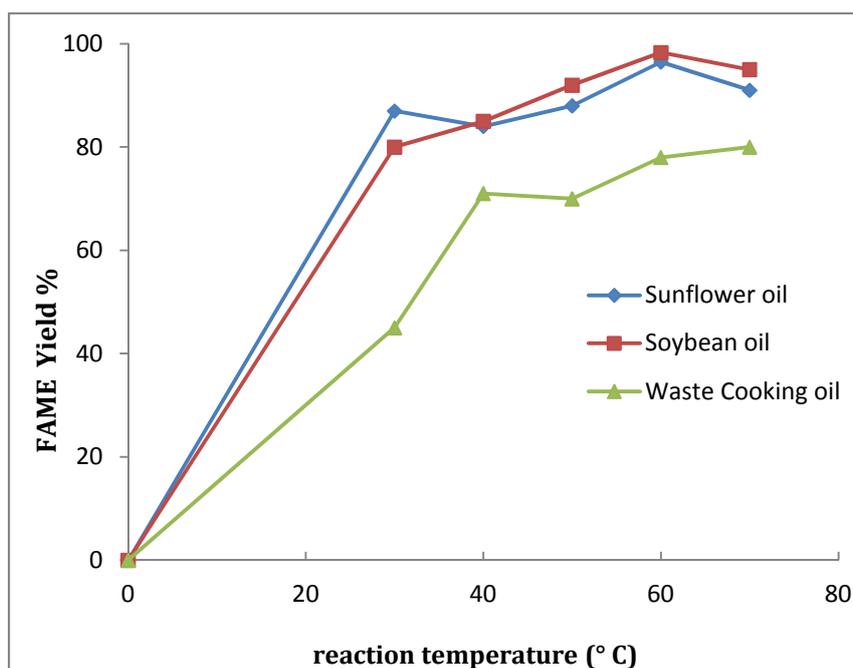


Figures 4.3: Effect of reaction time on FAME yield at a catalyst concentration of 1.1% (wt/wt of oil), 60 °C and a 6:1 methanol-to-oil ratio.

The study of the influence of the reaction time upon the transesterification reaction conducted at 60 °C (Figure 4.3) was optimized with the highest achievable mixing degree, an excess amount of alcohol (6:1 methanol: oil ratio) and optimum potassium hydroxide concentration of 1.0 wt% for all the feedstock oils. When the reaction time reached 90 min, no triglyceride was left in the product mixture, indicating complete conversion as was monitored by TLC (see section 3.6.5). In this experiment, glycerol started to separate within 15 min, after the experiments were completed. The ester content increased with reaction time from 15 min onwards and reached a maximum at a reaction time of 90 min, and then remained relatively constant with increased reaction time. The results indicated that an extension of the reaction time from 90 to 150 min had no significant effect on the conversion of triglycerides but led to a reduction in the product yield in the case of soybean oil. This is because longer reaction time enhanced the hydrolysis of esters (reverse reaction of transesterification), resulting in a loss of esters as well as encouraging soap formation (Sivaprakasam and Saravanan, 2007). Considering the economics involved, 60 min was selected as the optimum reaction time for the remainder of the transesterification reactions conducted.

4.3.4.3 Effect of reaction temperature

In order to study the effect of reaction temperature on FAME formation, the transesterification reaction was carried out under the optimal conditions obtained in the previous sections (i.e. at a methanol: oil ratio of 6:1, 1 % KOH (wt/wt of oil) and reaction time of 60 min). The experiments were conducted at temperature ranging from 30 to 70 °C at 10 °C intervals. The effect of reaction temperature is shown in Figure 4.4.



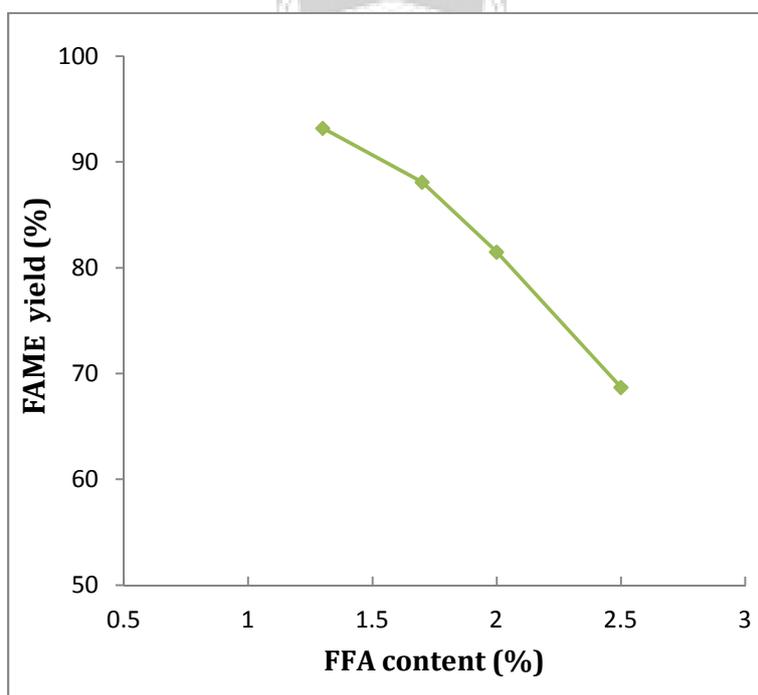
Figures 4.4: Effect of reaction temperature on FAME yield at a catalyst concentration of 1 % (wt/wt of oil), 60 min and a 6:1 methanol-to-oil ratio.

Experimental results (Figure 4.4) showed that the transesterification reaction could proceed within the temperature range studied but the reaction time to complete the reaction varied significantly with reaction temperature. It can be seen that high product yields were achieved for the respective oil samples at a maximum of 60 °C. With the temperature increased above 60 °C, the product yield started to decrease with respect to all the oil samples used in the study, the reason for this is that higher temperature accelerates the side saponification reaction of triglycerides (Eevera et al., 2009) and although a reflux condenser was used in the experimental set up to avoid methanol

losses when the reaction temperature approaches or exceeds the boiling point of methanol (65 °C), the methanol molecules would vaporise and form a large number of bubbles that then inhibits the reaction (Meng et al., 2008). Refaat et al. (2008) reported a similar yield (95.74 %) for WCO at a slightly higher temperature of 65 °C although the work was done with a higher methanol: oil ratio of 9:1, while Felizardo et al. (2006) reports similar yields at the same temperature (65 °C) used in this study but at a lower methanol: oil ratio of 4.8.

4.3.4.4 Effect of FFA content

The effect of FFA content of the different feedstock oils on FAME yield with different waste cooking oil samples (with FFA content value ranging between 1.2-2.5) at optimum reaction conditions obtained for the waste cooking oil in previous experiments. Results are presented in Figure 4.5.



Figures 4.5: Effect of FFA on the waste cooking oil FAME yield at a catalyst concentration of 1 % (wt/wt of oil), 60 min, 6:1 methanol-to-oil ratio and reaction temperature of 65 °C.

The FAME yield values recorded varied from 53.24 to 94.27 % (Figure 4.5) while the soap values in the FAME product varied from 1.69 to 37.09 mol/mol oil (determination of soap content can be perused in section 3.5.3). The amount of soap produced included the soap formed from the neutralization of the free fatty acids and from triglyceride saponification in both the biodiesel product obtained and glycerol (by product). The experiments revealed that the presence of water and FFA in the WCO sample has a significant effect on the yield of methyl esters. In previous sections, lower FAME yields were observed from the waste cooking oil sample used in this study having an acid value of 1.37.

In order to reduce the cost of biodiesel, waste or low-quality oils which are inexpensive and readily available can be utilized as feedstock, the challenge of employing this cheap feedstock however is the presence of impurities such as water and free fatty acids (FFA) which are common components in waste oil (Penget al., 2008; Felizardo et al., 2006; Chen et al., 2009; Rosa et al., 2008). In light of the recent discussions and debate on food security viz “food versus fuel”, it is vital to investigate the feasibility of utilizing cheap waste oils as feedstock for use in biodiesel production. The use waste oils could also offer an advantage in order to decrease the cost of production and this is a major objective of this research work. However, as shown in this section that the FFA content of WCO would limit the biodiesel yield.

4.3.4.5 Summary

The study on the process optimization of the various feedstock oils used in this study showed that the quantity of catalyst, amount of methanol, reaction temperature and reaction time and FFA content are the main factors affecting the production of methyl esters. The optimum values of these parameters for achieving maximum conversion of oil to esters depended on the chemical and physical properties of these oils. The following conclusions were drawn from the study: (i) addition of excess catalyst causes more triglycerides' participation in the saponification reaction leading to a marked reduction in the ester yield; (ii) biodiesel production process is incomplete when the

methanol amount is less than the optimal value (iii) operating beyond the optimum amount of methanol, the ester yield would not be increased but will result in additional cost for methanol recovery (iv) higher reaction temperature decreases the viscosities of the oils and resulted in increased rate of transesterification and shortening of the reaction time. When the temperature increases beyond the optimum level it induces a negative impact on the ester yield due to acceleration of the saponification of triglyceride and evaporation of methanol molecules crucial for the transesterification reaction (v) sufficient reaction time is necessary to ensure complete conversion of triglycerides into esters. However, excess reaction time did not promote the conversion but favoured the reverse reaction of transesterification which resulted in a reduction in the methy ester yield and a high FFA content in feedstock could also limit the methy ester yields.

The optimum reaction conditions for production of methyl esters from the fresh oil samples (SFO and SBO) using KOH catalyst and magnetic stirring were established as follows: the reaction time of 60 min at 60 °C with a methanol: oil ratio of 6:1 (180 ml of methanol for 1000 ml of oil) and 1 % of KOH catalyst (wt/wt of oil). However, the optimum reaction conditions for the used oil (WCO) includes a reaction time of 90 min at 60 °C, methanol: oil ratio of 6:1 and 1.5 wt% of KOH catalyst.

4.3.5 Influence of process variables on FAME yield: ultrasound process

As a sequel to the experiments conducted previously in sections 4.3, the influence of the process variables on the FAME yields with respect to experiments conducted using the ultrasonic homogeniser were investigated and the experimental results presented. The experimental set up of the transesterification reactions via the Omni ultrasound homogenizer (20 KHz frequency) equipped with a probe is highlighted in the previous chapter in sections 3.4.1.2. The experiments were done at a bench scale.

In the conventional biodiesel process, the use of mechanical agitation is predominant and is very important in the transesterification reaction as oils are immiscible with the

catalyst (KOH) and methanol solution, thus motivating investigation of the use of the ultrasound reactor in order to improve the yield of biodiesel and/or to shorten the reaction time of the process.

This section studies the influence of the process parameters on the transesterification of the different oil samples (SFO, SBO and WCO) via the ultrasound technology. It also makes a comparison in the conversion efficiency of both the mechanical agitation process (batch reaction tests) and the low frequency ultrasonic homogenizer reaction tests conducted involving the various oil samples.

4.3.5.1 Effect of catalyst concentration

The effect of catalyst concentration on FAME yield from the transesterification reactions carried out on the different oil samples under the following reaction conditions: a reaction time of 30 min, 30 °C and a methanol: oil ratio of 6:1 via the ultrasonic process is presented in Table 4.5.

Table 4.5: Effect of catalyst concentration on FAME yield via the ultrasonic process (n = 3).

Catalyst	FAME yield (wt %) 24 kHz		
	WCO	SFO	SBO
0.5	78.2 ± 0.06	95.30 ± 0.8	98.23 ± 0.2
0.75	96.8 ± 0.08	98.32 ± 0.4	97.65 ± 0.04
1.0	95.98 ± 0.7	91.78 ± 0.3	93.67 ± 0.56
1.25	93.4 ± 0.67	90.64 ± 0.5	90.03 ± 0.78
1.5	94.8 ± 0.03	88.78 ± 0.3	86.4 ± 0.45

Table 4.5 highlights the results of the transesterification reactions carried out on the different oil samples via the ultrasonic process while Figure 4.6 compares mechanical stirring vs ultrasound assisted conversion of WCO and SFO. The table shows that the addition of a large amount of catalyst did not lead to an increase in the biodiesel yield in the ultrasound process. Excess catalyst reacted with the oil, leading to the formation of soap, thus as the catalyst concentration increased, the separation of esters became difficult. A minimal catalyst amount of 0.5 wt% was adequate in propelling the transesterification reaction using the ultrasonic homogenizer. However as shown in Figure 4.6, a concentration of 0.75 wt% gave the best yields for sunflower oil but 1.5% for WCO.

A plot of the catalyst concentration versus the conversion efficiency for the reactions conducted under the ultrasound tests and the batch mechanically stirred reaction tests is illustrated in Figure 4.6 under the following reaction conditions: a reaction time of 90 min, temperature of 30 °C and a reaction time of 30 min, temperature of 60 °C, respectively.

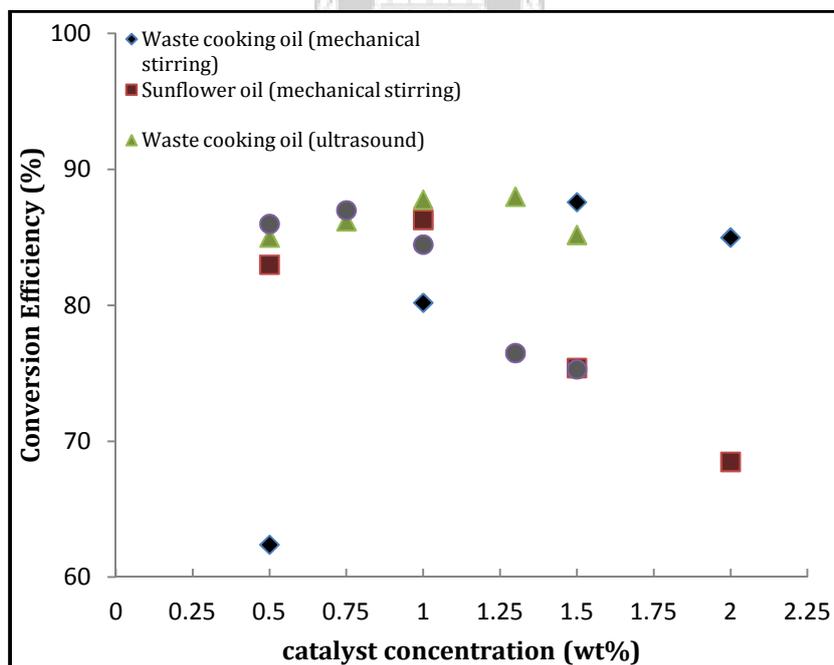


Figure 4.6: Effect of catalyst concentration on conversion efficiency of the oil samples under a 6:1 methanol/oil ratio at 30 °C and reaction time of 30 min.

The conversion efficiency of the waste cooking oil (WCO) with ultrasound mixing was highest at a catalyst concentration of 1 wt%, slightly higher than at a catalyst concentration of 0.75 wt% during the ultrasonication, while the maximum conversion efficiency for the waste cooking oil under mechanical and ultrasound stirring was observed in both cases at a catalyst concentration of 1.5 wt%. The high values observed can be attributed to the acid value of the waste oil. The presence of polymerized and oxidized material in waste oil is thought to affect the efficiency of catalysts in the transesterification reaction, and thus may be causing the difference between the conversion efficiencies of the WCO and SFO oil samples (Finnegan, 2008). When compared to the percentage catalyst required for the conventional stirring method, there was a reduction of about 25 % of the amount of catalyst needed for the transesterification reaction when using ultrasound mixing. As mentioned previously, high concentrations of alkaline catalyst form soaps in the presence of large residues of fatty acids resulting in emulsion formation between soaps and water molecules, thus leading to low yields of methyl esters. Lifka and Ondruscka (2004) studied the effect of ultrasonication versus mechanical stirring on the alkaline transesterification of rapeseed using NaOH at a concentration of 0.5wt% at 45 °C and reported conversions of between 80 to 85 % obtained for both the ultrasound assisted and mechanically stirred reactions after 30 min. Georgogianni et al. (2008) also reported a yield of 81 % with regards to using a catalyst concentration of 1.5 wt% KOH to convert sunflower seed oil which was somewhat lower than the value reported here (88.78 %). This could be attributed to the fact that the sunflower seed oil used in their study was unrefined and therefore possessed a higher FFA content.

In a report by Thanh et al. (2010) the optimum amount of potassium hydroxide recorded in the pilot studies they conducted, via a two step continuous ultrasound process, was 1.0 wt%. Another study carried out with low concentrations of catalyst ranging between 0.2 to 0.6 wt% on soybean oil done by Santos et al. (2009) to verify the efficiency of the ultrasonic process also showed that the yield of biodiesel decreased when too high concentrations of catalyst were applied, due to soap formation.

4.3.5.2 Effect of contact time

The relationship between the FAME yield and contact time during the transesterification reactions via the ultrasonic process is presented in Figure 4.7. This experiment was carried out on the different oil samples under the following reaction conditions: methanol: oil ratio of 6:1, 30 °C and catalyst concentration of 0.75 % (wt/wt of oil). The reaction time was varied between 10-60 min.

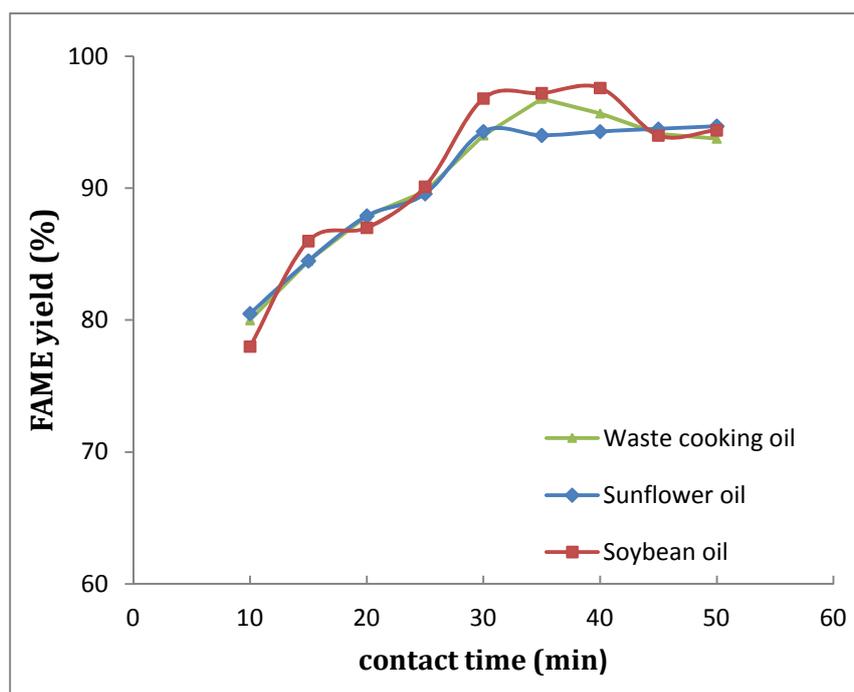


Figure 4.7: Effect of reaction time on FAME yield during ultrasound mixing using a 6:1 methanol/oil ratio at 30 °C and catalyst concentration of 0.75 % (wt/wt of oil).

A FAME yield of 96.78 % was recorded in the case of the WCO using ultrasound mixing, which was higher than the yield of 87.30 % obtained using the mechanical mixing at 30 mins (Fig. 4.6). This higher yield was obtained at a lower temperature (30 °C) and shorter time (30 min); this can be attributed to the fact that the sonochemical effect induced by the acoustic cavitations was stimulated by the ultrasonic irradiation of the oil and methanol molecules to form microscopic fine emulsions causing them to mix with each other easily. It is also postulated that an increase in the interfacial area of

droplets strongly accelerates the reaction rate, which agrees with studies done by Ramachandran et al. (2009).

Methyl ester yields of 98.32 % and 93.70 % were observed from the SFO sample under the ultrasonic and batch reaction tests respectively, while yields of 96.32 % and 90.07 % respectively were recorded for the SBO oil sample. These values agree with reports from a comparison of ultrasonic irradiation with mechanical stirring for transesterification of neat vegetable oil and methanol with base-catalyst that was made by Georgogianni et al. (2007; 2008). In a recent study by Thanh et al. (2010) the transesterification of canola oil containing 0.4 wt% of FFA with methanol was assisted by ultrasound irradiation in a circulation process, the optimal FAME yield was observed at a KOH concentration of 0.7 wt% and a reaction time of 50 min, although at a reduced methanol to oil molar ratio of 5:1.

During the transesterification of waste cooking oil containing 1.7 wt% of FFA by Thanh et al. (2008), the best yield of FAME was attained when the amount of KOH catalyst was 1.0 wt.% at the same reaction time reported in this study. As conversion rate increased with time, it was observed that the initial rate of transesterification reaction of the SFO was slow, so that its yield was lower than WCO before 20 min reaction time, thereafter the WCO gave a higher yield than sunflower oil up to 40 min after this time yield values became identical.

Although natural oils contain different amounts of triglycerides, their transesterification are by and large, similar to a single compound, triolein. The WCO used had the highest amount of short carbon chains of fatty acids (C16:0) in comparison to sunflower oil. These short carbon chains of fatty acids have less steric hindrance in comparison to long carbon chains of fatty acids, therefore have more possibility of contact with catalyst (Lucena et al., 2008) consequently contributing to the reduced conversion time and corresponding increased biodiesel yield. It is considered that the emulsion between triglycerides and alcohols occurs more rapidly during ultrasound compared to the batch reaction tests (mechanical agitation) because of smaller size of emulsion droplets that would be formed with the use of the ultrasound. As droplets are formed the contact

surface area of the immiscible solution increases, resulting in the higher rate of the transesterification reaction, in other words, the effective mass transfer caused by the ultrasonic field resulted in the higher rate of transesterification reaction.

4.3.5.3 Effect of temperature

The effect of temperature on FAME yield from the transesterification reactions was carried out on the sunflower and waste cooking oil samples under the following reaction conditions via the ultrasonic process at the reaction conditions: catalyst amount 0.75 wt%, methanol: oil molar ratio of 6:1 and a reaction time of 30 min. The temperature was varied between 30-70 °C and mechanically stirred results are compared to ultrasound mixing as is shown in Figure 4.8.

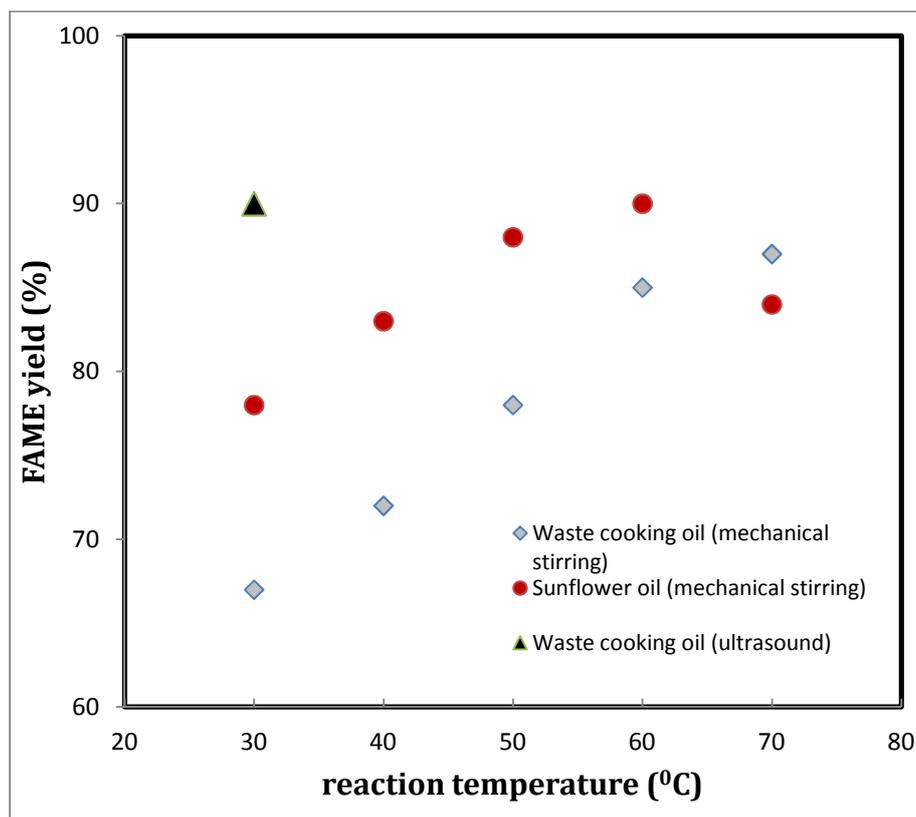


Figure 4.8: Comparison of the effect of mechanical stirring and ultrasound stirring at different reaction temperature on FAME yields via ultrasound mixing (6:1 methanol/oil ratio and catalyst concentration of 0.75 %wt/wt of oil).

In this work, the conversion efficiency of the waste oil under the ultrasonication was as high as 98 % even at low temperature of 30 °C compared to the conversion efficiency obtained under the mechanical stirring process, the reason for low conversion with mechanical stirring is ascribed to a high viscosity obtained (5.8 mPas), most probably due to the evaporation of methanol when the reaction temperature exceeds its boiling point of 65 °C, consequently resulting in an incomplete reaction.

Please note that the transesterification reaction experiments under the ultrasound process were conducted at 30 °C and the temperature was controlled with a thermostated water bath (section 3.4.1.2 for experimental set up). Figure 4.8 shows that FAME yield of 90 % was obtained at 30 °C with the ultrasound hence other temperatures were not explored in the case of the ultrasound. Transesterification can proceed at ambient temperature using ultrasound mixing depending on the feedstock used. The ultrasonic field causes cavitation bubbles near the phase boundary between the alcohol and oil phases, and this result in microfine bubbles being formed. The cavitations may also lead to a localized increase in temperature at the phase boundary enhancing the transesterification reaction. Due to formation of micro jets and localized temperature increases neither agitation nor heating is required to produce biodiesel via the ultrasound technology (Santos et al., 2009). A methyl ester yield of 90 % was obtained in the transesterification of the WCO, this result corresponds to similar studies done by Ji et al.(2006), where a similar result was reported (biodiesel yields from 90 % to 97 %).

4.3.5.4 Summary

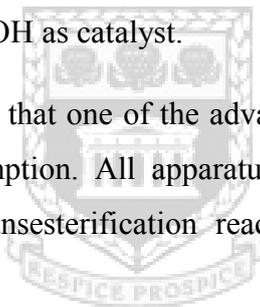
This study demonstrates that the ultrasound assisted transesterification reactions of all the oil samples used (SBO, SFO and WCO) and methanol with potassium hydroxide homogeneous catalyst is very efficient. The optimal reaction conditions for production of fatty acid methyl esters obtained from the transesterification of the WCO via the ultrasound technology with regards to this study were established as follows: a reaction time of 30 min, 30 °C, 6:1 methanol/oil ratio and a 0.75 wt% (KOH) catalyst

concentration. The ultrasound assisted transesterification reactions at optimum conditions on the different oil samples led to higher yields of methyl esters (96.8, 98.32 and 97.65 % for WCO, SFO and SBO respectively) compared to methyl esters yields (90, 95 and 96 % for WCO, SFO and SBO respectively)

Under the mechanical agitation process at optimum conditions of 1.0 wt%, 90 min, 60 °C and a 6:1 methanol/oil ratio in the batch reaction tests conducted. Considerable increases in yield of the methyl esters were obtained at room temperature, in a remarkably short time span (completed in 30 min) and a lesser amount of catalyst (0.75 wt %) was needed to complete the transesterification reactions.

A FAME yield of 96.8 % from the waste cooking oil was achieved showing that waste cooking oil has the potential to be used as a low cost feedstock in the production of biodiesel. The cost of the process can be significantly reduced with the use of the ultrasound mixing when using KOH as catalyst.

The study has been able to show that one of the advantages of ultrasonic processing is the reduction of energy consumption. All apparatuses used in the pilot plant were electrically operated, as the transesterification reactions were carried out at room temperature.



4.4 Scale up of processing using jet- loop reactor

This section aims presents results on the influence of the reaction parameters on the transesterification reactions of only the waste cooking oil sample (WCO) using the jet-loop reactor. The experimental set up of the transesterification reactions using the jet loop reactor is highlighted in section 3.4.1.3 of chapter 3. In order to make an adequate comparison of the experimental results conducted previously in sections 4.3.4 and 4.3.5, the influence of the reaction parameters viz; catalyst amount, reaction time, methanol to oil ratio, and temperature on FAME yield was investigated and the experimental results are presented.

4.4.1 Effect of reaction time and catalyst amount

The influence of catalyst amount on FAME yield from the transesterification reactions carried out on waste cooking oil sample using the jet loop reactor under the following reaction conditions: methanol: oil molar ratio of 4:1, reaction time of 30 min was investigated and results presented in table 4.6. To minimise the use of methanol, the ratio of 4:1 was used. These experimental results represent the best performances of triplicate experiments carried out.

Table 4.6: Effect of reaction parameters on FAME yield via the jet loop process

Run	KOH (% wt)	Reaction time	FAME yield (%)
1	0.5	25 min	99.6
2	0.5	30min	96.9
3	0.5	40 min	72.10
4	0.5	50 min	76.9
5	0.75	25 min	92.10
6	0.75	30 min	95.5
7	0.75	40 min	85.8
8	1.0	25 min	86.8
9	1.0	30 min	86.9
10	1.0	40 min	76.8

Extensive preliminary experiments with the WCO samples previously (section 4.3) indicated that the major variables in the transesterification reaction were methanol to oil ratio, catalyst amount, reaction time and reaction temperature. Based on preliminary experiments, experimental tests were designed to determine the optimum conditions for the transesterification process of the WCO via the use of the jet loop reactor. The

optimum experimental conditions which were obtained were methanol to oil ratio 4:1 with 0.5 wt % KOH results at 25 min (Table 4.6).

An increase in temperature has been shown to significantly increase the rate of side reactions thus consuming catalysts and producing unwanted by-products (Dorado et al., 2003). Temperature also has a significant effect on capital expenditure. Methanol boils at approximately 65°C at atmospheric pressure. As temperature increases the pressure required to maintain the methanol as a liquid rapidly increases thus doubling the temperature results in more than an 8 fold increase in the pressure capacity of the vessel – increasing capital expenditure and hazards associated with operating the plant. In this experiment, the effect of temperature was not investigated as it was difficult controlling and maintaining the temperature of the jet loop, the temperature of the reaction however was monitored to range between 45°C - 55 °C. It is necessary to point out that the majority of production on a larger scale occurs between 60 and 65°C. This prevents the need for the use of pressure vessels while providing high reaction rates and high solubility. Since pressure vessels were not an issue, increasing temperature beyond this point may provide increased reaction rates but saponification and hydrolysis will also increase thus reducing yield (Oui et al., 2009).

4.4.2 Summary

An increase in the rate of reaction by the intense agitation and mixing process between alcohol and oil was observed when the jet reactor was employed in the production of biodiesel using waste cooking oil as feedstock. Rates of transesterification were intensified due to uniform mixing by the use of the jet loop reactor. A high FAME yield of 99.6 % was obtained at an initial reaction time of 12 min. It took less reaction time to reach equilibrium for the complete conversion of the waste cooking oil and high selectivity due to less side reactions. The total amount of methanol needed was reduced by 16 wt% with respect to the volume of the oil. The results show that after the optimum condition of 25 min of reaction time with a methanol: oil ratio of 4:1 and a catalyst amount of 0.5 wt%, a FAME yield of 99. 6% was recorded. This process also

allows for an efficient separation and purification of the methyl esters phase (Table 4.7). Advantages posed by the use of the jet reactor in the transesterification reaction include; lower temperature, less side reactions, use of pressure vessels unnecessary, easily upgradable to normal systems, enhancement of mass transfer and its functionality in a continuous system.

4.5 Fatty acid methyl ester characterization

To ascertain the quality of the methyl esters produced under the different process conditions (mechanical agitation, ultrasound and jet process), the quality of the final biodiesel products obtained from the optimal conditions were further characterised using the services of an authorized biodiesel analysis organization. The comparison of the characterisation results of the FAME products obtained from the different oil samples under the different process systems are given in Table 4.7. This table gives the certified quality of the methyl ester product as analytical methods used are specified under international standards (refer to appendices).

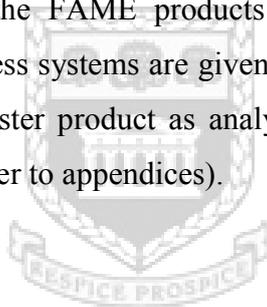


Table 4.7: Properties of biodiesel produced from SFO, SBO and WCO oil samples under optimal conditions via the mechanical process, the SFO and WCO via the ultrasound process and WCO under the Jet reactor process systems.

Test parameter	Unit	SANS 1935:2004	Test method	Mechanical Process			Ultrasound Process		Jet reactor
				WCO	SFO	SBO	WCO	SFO	WCO
Appearance				not clear	clear	clear	clear	clear	clear
Density (15 °C)	kg m ⁻¹	860-900	ISO 3675	874	882	885	881	883	891.1
Viscosity	(mm ² /s at 40°C)	1.9–6.0	ASTM D 445	5.81	4.51	4.08	4.98	4.02	2.58
Iodine value	I ₂ g/100 g	140 max	ASTM D 5768	146	124	130	134	120	130
Acid value	mg KOH/g	0.5 max	ASTM D 974	0.47	NA	NA	0.25	NA	0.12
Water content	ppm	0.05 max	EN ISO 12937	0.03	NA	NA	0.03	NA	0.02
Cetane number	nil	51 min	ASTM D 613	50	50	52	50	53	51.5
Total ester	mass %	96.5 min	EN 14103	94.3	96.3	95.2	98.2	98.7	96.7
Total glycerol	mass %	0.25 max	ASTM 6584	0.21	0.01	0.02	0.20	0.03	0.23
Free glycerol	mass %	0.02 max	ASTM 6584	0.02	0.01	0.13	0.02	0.01	0.021
Mono-glyceride	mass %	0.8 max	ASTM 6584	0.1	0.018	0.01	0.11	0.03	0.5
Di-glyceride	mass %	0.2 max	ASTM 6584	0.5	0.02	0.01	0.13	0.17	0.15
Triglyceride	mass %	0.2 max	ASTM 6584	0.25	0.01	0.03	0.11	0.23	0.15
Methanol content	mass %	0.2 max	EN 14110	0.23	0.05	0.05	0.2	0.01	0.02
Flash point	°C (open cup)	120 min	ISO 3679	180	160	164	184	178	182
Sulphated ash	(%wt/wt)	0.02 max	EN 14113	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02
Total of Na and K	mg/kg	5.0max	EN 14538	<1.0	-	-	<1.0	-	<1.0

4.5.1 Density at 15 °C

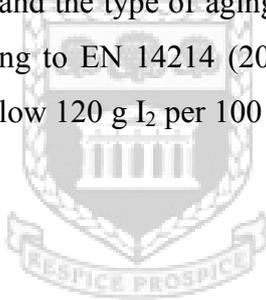
The density results obtained in this study (Table 4.7) showed that for all the conditions studied with regards to the biodiesel produced under the mechanical process, the ultrasound process and the jet reactor process systems had a density in the range of 0.864–0.900 g/cm³. The standard for biodiesel states that the fuel should have a density between 0.860 and 0.900 g/cm³. This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel (Ryan et al., 1984).

4.5.2 Kinematic viscosity at 40 °C

The kinematic viscosity of the biodiesel samples produced from the optimum conditions under the different process systems ranged from 4.1 to 6.3 mm²/s (Table 4.7).. The low viscosity value of 2.58 was obtained for the biodiesel under the jet reactor method while a very high value of 5.81 was obtained for the mechanically stirred waste cooking oil sample (Table 4.7). This indicates the significance of the process systems employed in both cases, with the low value of 2.58 most probably as a result of the intense agitation enhanced by the jet reactor system and a high value of 5.81 most probably as a result of an incomplete transesterification reaction (Knothe and Steidley, 2005). Even more than density, the kinematic viscosity is an important property regarding fuel atomization, as well as fuel distribution. For biodiesel to be used in diesel engines, the kinematic viscosity must be between 3.5 and 5.0 mm²/s. Different viscosities are due to the incomplete reaction of the waste cooking oils or to the inefficient biodiesel purification, leaving conjugated or free glycerol in the methyl esters phase. In fact, the presence of glycerides changes the apparent viscosity of the methyl esters, revealing the extent of the transesterification reaction and the methyl esters phase purity (De Filippis et al., 1995). It is worth mentioning that the extent of the reaction, as well as the experimental conditions used in the different biodiesel production processes, greatly influenced the fuel properties and especially its apparent viscosity.

4.5.3 Iodine value

The iodine values (Table 4.7). of the produced methyl ester (biodiesel) from SFO and SBO revealed values ≤ 130 while the analyses of several samples of the produced methyl ester (biodiesel) from the waste cooking oil under the different reaction processes revealed iodine values between 130 and 146. These high values were expected since most of the waste cooking oils used in South Africa are derived from sunflower seeds and are characterized by iodine values between 120 and 140. Furthermore, the iodine value rises during the later stages of oil degradation and especially if the oil is exposed to temperatures higher than 180 °C, due to elimination reactions of the oxidized triglyceride molecules and during frying the formation of C18:2 and C18:3 were enhanced (Supple et al., 2002). The iodine value is an important measure that allows determination of the unsaturation degree of the fuel. This property greatly influences fuel oxidation and the type of aging products and deposits formed in diesel engines injectors. According to EN 14214 (2003), methyl esters used as diesel fuel must have an iodine value below 120 g I₂ per 100 g of sample.



4.5.4 Acid value

The maximum acid value found for the biodiesel produced from the waste cooking oil under the different reaction processes in this study was 0.47 (recorded for the batch reaction test under the mechanical agitation process), while the lowest value of 0.12 was obtained from the jet reactor process system (Table 4.7).. Although for about 70 % of the samples analyzed, this parameter ranged between 0.15–0.2 which is well below the required value. The acid value measures the content of free fatty acids in biodiesel. This value was not applicable to the refined oil samples used as they contained negligible amounts of free fatty acids. Considering that the presence of free fatty acids influences fuel aging, the European Standard specifies a maximum value of 0.5 mg of KOH/g of sample.

4.5.5 Water content

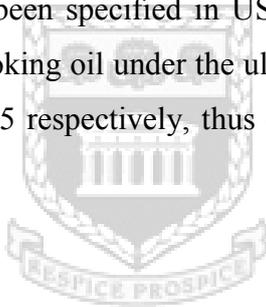
Fuel contaminated with water can cause engine corrosion or react with the glycerides to produce soaps and glycerol. Therefore, EN 14214 (2003) imposes a maximum content of 0.05 % of water in fuels. In this study, the produced methyl ester samples from the waste cooking oil samples under the different reaction processes were routinely dried over anhydrous magnesium sulphate. This technique although used in laboratory practice, is very efficient and the water content in several samples of the product was consequently low, ranging from 0.01 % to 0.03 % (Table 4.7). On an industrial scale, drying is usually carried out by distillation under vacuum (0.05 bars) at temperatures of between 30 - 40 °C. This was done for the production of methyl esters with the jet-loop reactor, thus for a moisture content value of only 0.02 was recorded for the FAME produced with this reactor.

4.5.6. Total ester content

As shown in Table 4.7, total ester content values of 94.3, 98.2, and 96.7 % were recorded for the methyl ester produced from the waste cooking oil sample under the mechanical, ultrasound and the jet-loop reactor respectively, the influence of the transesterification process system and feedstock (type of oil sample) on the total ester content of the biodiesel produced is significant. From the results, it proved that the ultrasound assisted process and the high intensification enhanced by the jet loop process gave total ester content values that meet the EN 14214 specifications. According to EN 14214 (2003), the minimum acceptable purity for biodiesel is 96.5 % in methyl esters which is equivalent to the SANS 1935:2004, however the acceptable purity for biodiesel according to the ASTM D 6751 has no limit (Table 3 of the appendix). The increase of the purity of the biodiesel product is the net result of an efficient removal of glycerol and sufficient reaction extent associated with the use of the ultrasound and jet loop reactor (Freedman et al., 1984; Tomasevic and Siler-Marinkovic, 2003).

4.5.7 Cetane number

The results of (Table 4.7) cetane numbers for all the different methyl esters in the studies conducted on the waste cooking oil via the different process systems have CN value of higher than 51 except methyl esters obtained from the mechanical agitation batch reaction test (49.91). Better ignition quality of the fuel is always associated with higher cetane number value (CN). This is one of the important parameter, which is considered during the selection of methyl esters for use as biodiesel. For this different countries/organization have specified different minimum values. Biodiesel standards of USA (ASTM D 6751) and European Organization (EN 14214) have set this value as 47 and 51, respectively (Biodiesel Standards 2006 in the appendix). Generally, methyl esters with higher CN are favoured for use as biodiesel; however, an increase in CN will lead to the solidification of methyl esters at higher temperature. To avoid this situation, the upper limit of CN (65) has been specified in US biodiesel standards. The methyl ester obtained from the waste cooking oil under the ultrasound and jet reactor processes both show values of 50 and 51.5 respectively, thus can be used both in cold and hot climates.



4.5.8 Methanol content

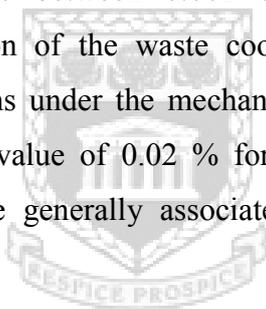
Methanol is another possible contaminant of the methyl esters phase responsible for metal corrosion, particularly of aluminium, and for the decreasing of the fuel flash point. EN 14214 (2003) specifies a maximum content of 0.2 % of methanol in biodiesel. The alcohol was easily removed from the esters phase during the washing step, the methanol content varied from 0.02 % to 0.11 % under the different reaction processes; the methanol content was within the specifications (Table 4.7).

4.5.9 Flash point

The flash point results (Table 4.7) show that the samples of methyl ester obtained from the SFO and SBO samples under the mechanical agitation had a flash point of 160 and 164 °C respectively. However, for the methyl esters produced from the waste cooking oil samples under the mechanical, ultrasound and the jet-loop reactor; values of 180 °C, 184 °C and 182 °C were recorded respectively. These values were well within specification and were higher than those required as EN 14214 (2003) specifies that biodiesel must have a flash point higher than 120 °C.

4.5.10 Sulphated ash

The values for sulphated ash (Table 4.7) obtained for the several productions under the different reaction systems were between 0.002 % and 0.006 %, meeting fuel specifications with the exception of the waste cooking oil methyl ester (0.05 %) obtained from the batch reactions under the mechanical agitation process. EN 14214 (2003) establishes a maximum value of 0.02 % for sulphated ash. This property is important since high values are generally associated with injector and fuel filters clogging.



4.5.11 Sodium and Potassium content

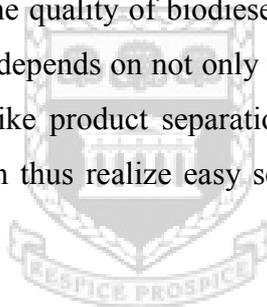
The total sodium and potassium content of several biodiesel samples produced under the mechanical, ultrasound and the jet-loop reactor respectively was in the range of 2.3–5.3 mg/kg of fuel (Table 4.7) and only two productions were out of specification. These results indicate that the washing procedure and the purification method used were efficient in the removal of potassium from the methyl ester phase. Because the presence of high amounts of sodium and potassium in biodiesel induces metal corrosion as well as saponification of the methyl esters phase, EN 14214 (2003) specifies a maximum value of 5 mg/kg. It is well known that the content of sodium or potassium (as a result of catalyst residue) in biodiesel is mainly determined by the efficiency of the washing step.

4.5.12 Summary

The production of biodiesel from waste cooking oils (WCO) is feasible by basic catalyzed transesterification (KOH) and the biodiesel fuels produced under the different reaction systems (ultrasound homogeniser and jet loop reactor) have the quality required to be a diesel substitute. The jet loop reactor technology for biodiesel production studied focused on reaction or/and product separation. The jet loop reactor achieved low total glycerol amount <0.24 wt% (see Table 4.7) in shorter residence times because the reaction is intensified by improving mass and heat transfer rate and mixing intensity.

The values of density, viscosity were similar to those of automotive and heavy duty engine fuel. The flash point which is higher than that of diesel fuel constituted a safety guarantee from the view of handling and storage.

It is worthy of mention that as the quality of biodiesel is a crucial issue in commercial production, the biodiesel quality depends on not only upon the reaction process but also on the downstream processing like product separation, water washing, and methanol recovery. These technologies can thus realize easy scale-up and commercialization of biodiesel production.



Chapter 5

Biodiesel Synthesis via Heterogeneous Catalysis

5. Introduction

This chapter deals with the transesterification reaction studies involving heterogeneous catalysis. The chapter presents and discusses the results of the physical and chemical characterization of South African (class F) AFA, AFA based catalyst (KNO_3/FA) and AFA based zeolite (Na-X) samples. The South African (class F) AFA used in this study is distinctly different from the class C fly ash collected from India. The problem analysis and the justification for this study based on previous studies can be looked up in section 2.7.3 of the literature review.

Several analytical and instrumental techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy-energy dispersion spectroscopy (SEM-EDS) were used to characterize the fresh AFA and the heterogeneous catalysts. The details of these procedures and the results discussed in this chapter stem from the experimental procedures outlined under materials and methods in Chapter 3.

In this chapter, AFA ash collected from Arnot coal power plant (South Africa) loaded with KNO_3 and a new zeolite, FA/Na-X derived from the AFA were used as heterogeneous catalysts in biodiesel synthesis. The influence of various reactions parameters such as the loading amount of active components, methanol: oil ratio, reaction time, temperature and catalyst deactivation were investigated. The results of the catalytic activity of these catalysts and the effect of the reaction parameters on catalytic performance are presented.

The results and discussion of this chapter are divided into four major sections (5.3, 5.4, 5.5 and 5.6). Section 5.3 gives the results of the physical and chemical characterization of the fresh AFA sample and the AFA based catalyst denoted as KNO_3/FA . Section 5.4 presents and discusses the physical and chemical characterization of the zeolite based catalyst synthesized from South African (class F) AFA by Musyoka. (2011), while sections 5.5 and 5.6 present the results of the transesterification reactions involving the AFA/ KNO_3 based catalysts and the AFA-zeolite based catalysts respectively. A brief summary of findings is presented at the end of the section.

5.1 Overview

South Africa's coal is high in ash content, and as such, the use and development of environmentally safe applications in the utilization of the waste coal fly ash is considered an environmentally important issue. The disposal and management of the huge quantities of fly ash generated by thermal and power stations in the country has been a concern to policy advisers, industrial and the scientific communities. Apart from fly ash from pulverized coal power plants, another primary source of fly ash is from municipal waste incineration plants.

Most of the approaches taken previously to face this challenge were either geared to utilize the ash beneficially in order to reduce the cost of disposal, or to minimize its environmental impact. The utilization of fly ash as a suitable feedstock for use as heterogeneous catalyst for the transesterification would allow beneficiation of fly ash in an environmentally friendly way which would also make the transesterification process more economically viable.

The problems associated with homogeneous catalysts as mentioned in the literature review provided an impetus for the search of a stable and more environmental friendly solid base catalyst. While searching for promising solid base catalysts by various researchers recently, several attempts have been made using basic zeolites, alkali and

alkali earth oxides, alkali and alkali earth carbonates, supported guanidine and basic hydrotalcites to conduct the transesterification reactions (Georgogianni et al., 2009). Moreover, various supported catalysts have been examined for their activity with use of supports like zinc oxide (Yang and Xie, 2007; Xie and Huang 2006), NaX zeolite (Xie and Huang, 2007) and mesoporous silica (Albuquerque et al., 2008). The challenge of a cheaper process still exists however because there is a constant need to develop an improved cost-effective and eco-friendly processing for manufacturing of biodiesel. Improved processing could potentially lead to easier refining of the produced biodiesel and glycerol, recycling of the catalysts and hence, lower production costs (Bournay et al., 2005).

As previously stated, solid strong bases are extremely desirable for developing environmentally benign processes to catalyze various reactions under mild conditions and to minimize the production of pollutants (Son et al., 2009). Solid bases derived from KNO_3 supported on porous materials have been reported recently (Xie et al., 2006, 2007; Xu et al., 2007; Alonso et al., 2007; Salinas et al., 2010). Zeolite X is also generally accepted as one of the most basic zeolites and the ion exchange of zeolite Na-X with larger monovalent cations such as K and Cs increases the basicity markedly. The chemical composition, pore size distribution, ion exchange abilities of zeolites is responsible for their versatile catalysis abilities (Lee et al., 2009). The use of structure promoters or catalyst supports which can provide more specific surface area and pores for the active species where they can anchor and react with large triglyceride molecules is desirable in order to promote mass transfer associated with heterogeneous catalysts.

Considering the importance of developing environmentally safe applications for the utilization of coal fly ash, an attempt was made in this study to develop an efficient, inexpensive and environmental friendly fly ash-based heterogeneous catalyst for use in the transesterification reactions for the production of biodiesel (FAME). The application of a new Na-X zeolite prepared from the South African Class F, AFA denoted as FA/NaX and ion exchanged with K^+ (FA/KX) for use as heterogeneous catalysts in the production of biodiesel is hence reported.

This chapter provides results of (1) the physical and chemical compositions of the fresh and used oil feedstock samples, (2) The physical and chemical composition of the fresh AFA & prepared AFA based catalysts and AFA -zeolite based catalysts (3) the influence of the different reaction parameters on the yield and conversion rates of oil triglycerides to their corresponding FAME(s) using these heterogeneous catalysts, (4) the optimisation of the reaction process using the AFA based catalysts and comparison of the results obtained when KOH was used as a homogenous catalyst (5) the quality and suitability of the FAME(s) produced under the above set of conditions using the AFA based catalysts in comparison with standard specifications.

5.2 Materials and methods

The description of the source materials and procedures employed for the preparation and characterisation of the heterogeneous catalysts used in the study are presented in chapter 3, sections 3.7.2 and 3.8 respectively. The various analytical procedures such as XRD and SEM-EDS are presented under sections 3.8.2 and 3.8.3 while the experimental procedure of the transesterification reactions (conducted using the batch set up) is presented in sections 3.5. The analysis of the methyl ester product obtained under the set of experiments conducted in this chapter was done by applying these of TLC and GC (see sections 3.6). Analytical tests to check conformity of selected samples to international standards are set out in Table 3 in the appendix.

5.2.1 Oil characterisation

The characterization of the feedstock materials (fresh and used oil samples) used for all experiments are presented in Table 4.1 of section 4.3.1. As can be observed from those results, three different oil samples were used for testing, however in this section, Sunflower oil was used as feedstock to perform the transesterification reactions to determine the catalytic activity of the fresh AFA and prepared KNO_3/FA catalyst. All the physical, chemical properties and chemical composition of the oil used in this

section can be previewed in the previous chapter (section 4.3.2.1). Recent characterisation done on the feedstock used in the transesterification reactions with the commercial and AFA -zeolite catalysts can be perused in section 5.6

5.3.Results and discussion: Arnot fly ash based catalysts

5.3.1 Catalyst characterisation (KNO₃/FA)

The characterization of the catalysts fresh AFA and AFA based catalyst (KNO₃/FA) used for further experiments are presented in this section 5.3.2a and 5.3.2b respectively. The main reason for the characterization of the AFA and the KNO₃/FA catalysts used in this study was to determine and compare the morphological transformation before and after preparing the catalyst and to also be able to do mass balances in a controlled environment. The objective of this section is to understand the physical, chemical and mineralogical compositions of the AFA and the AFA based catalyst-KNO₃/FA and thereafter to determine the catalytic activity and performance of the above-mentioned on the transesterification reactions and the conversion/yields of sunflower oil to its respective methyl esters. The characterization of the AFA based catalyst-KNO₃/FA and its use in the transesterification of sunflower oil is expected to give an insight into its chemical composition and catalytic performance in this regard.

5.3.2a Physical composition of fresh Arnot fly ash: (SEM-EDS)

The morphology of the fresh AFA obtained by SEM is shown in Figure 5.1 below, while Table 5.1 shows the elements present in the area analyzed (determined by 4 replicates of EDS) on each sample.

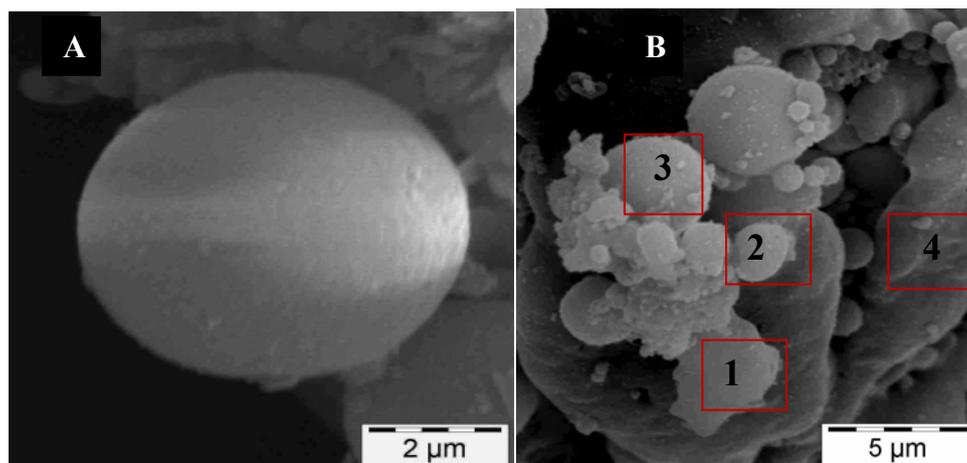


Figure 5.1: SEM-EDS micrograph of (A) the Arnot fresh ash (AFA) and (B) showing the areas chosen for EDS analysis at different magnifications.

Table 5.1: EDS analysis of the chosen areas (weight %) of fresh AFA.

Element	1	2	3	4	Average
O	45.67	37.18	53.05	47.56	45.87
Mg	1.59	ND	ND	ND	1.59
Al	17.43	21.68	10.04	16.55	16.47
Si	25.48	30.76	33.59	22.89	28.18
S	ND	1.06	ND	ND	1.06
K	1.49	1.14	ND	ND	1.32
Ca	8.34	7.2	3.32	13	7.97

The surface morphology of AFA is shown in Figure 5.1a & b while Table 5.1 showed the EDS based qualitative compositional analysis of a selected area of the SEM micrographs. The micrographs show that the particles of the AFA were generally spherical in shape. The surface of the fresh AFA particles was observed to be relatively smooth and spherical because the glass phase covers the particle (Musyoka, 2009). Micro spheres, typically between 30 and 100 μm in diameter, can be described as hollow cenosphere or non crystalline glass beads (Shao et al., 1997). The morphology of AFA grains is largely determined by the heating and cooling regimes in the pulverised coal boiler. The EDS is qualitative but confirms the matrix of ash is composed mainly of Si and Al with minor Ca, Mg and K oxides present.

5.3.2b Physical composition of the prepared Arnot fly ash based catalysts KNO_3/FA : (SEM-EDS)

The morphology of the AFA based catalysts (5 % KNO_3/FA & 10 % KNO_3/FA) prepared according to procedure adapted from Kotwal et al. (2009) specified in section 3. 7.2 are shown in Figure 5.2 below while Table 5.2 shows the elements present in the area analyzed (determined by EDS) on each sample.

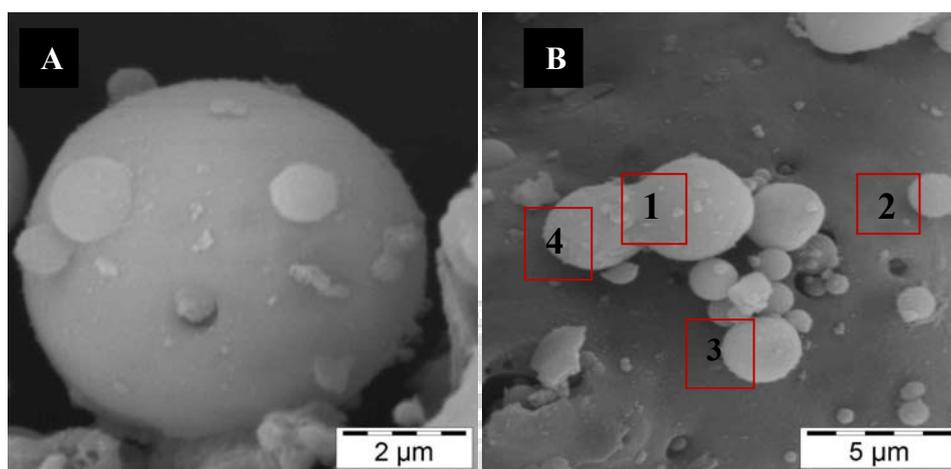


Figure 5.2: SEM-EDS micrograph of the (A) prepared Arnot fly ash based catalysts (5 % KNO_3/FA) and (B) showing the area chosen for EDS analysis.

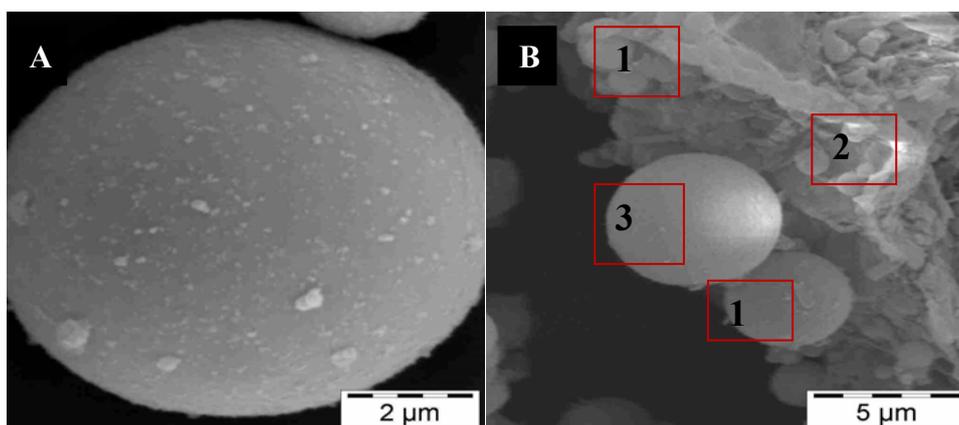


Figure 5.3: SEM-EDS micrograph of the (A) prepared Arnot fly ash based catalyst (10 % KNO_3/FA) and (B) showing the area chosen for EDS analysis.

Table 5.2: EDS analysis of the chosen areas (weight %) of the prepared AFA based catalyst.

Element	5 % KNO ₃ / FA					10 % KNO ₃ / FA				
	1	2	3	4	Ave	1	2	3	4	Ave
O	45.67	37.18	53.05	47.56	45.85	54.67	45.80	63.15	59.78	55.85
Mg	1.59	ND	ND	ND	1.59	1.59	ND	ND	ND	1.59
Al	17.43	21.68	10.04	16.55	16.52	17.43	21.68	10.04	16.55	16.52
Si	25.48	30.76	33.59	22.89	28.18	25.48	30.76	33.59	22.89	28.18
S	ND	1.06	ND	ND	1.06	ND	1.06	ND	ND	1.06
K	2.56	3.56	1.45	1.67	2.31	3.45	6.56	3.15	2.35	3.88
Ca	8.34	7.2	3.32	13	7.97	8.34	7.2	3.32	13	7.97

The surface morphology of the prepared AFA based catalyst are shown in Figures 5.2 and 5.3 while Table 5.2 shows the elements present in the area analyzed (determined 4 replicate analyses by EDS) on each sample. It was observed that the loading of potassium nitrate on the AFA did not show any disruption in the structural morphology of the AFA which was used as support. It also revealed an adequate impregnation of the potassium on the AFA which was visible in the increased values of K obtained from the EDS analysis. These results should be treated with caution as EDS is not quantitative. To quantify the composition of the catalyst, XRF analysis was conducted on the prepared AFA samples and the 5 % KNO₃/ FA and 10 % KNO₃/ FA catalyst samples.

5.3.3a Elemental composition of the Arnot fly ash

The result of the elemental composition of the AFA determined by XRF (see section 3.8.4) is reported in the Table 5.3 below. The information obtained was fundamental since it provided data for major elemental composition of the matrix of the AFA. The analysis was done in triplicate.

Table 5.3: XRF of fresh Arnot fly ash

Major oxides (mass %)	run 1	run - 2	run - 3	Ave	StdDv.
SiO ₂	50.93	51.08	50.73	50.91	0.1782
Al ₂ O ₃	31.03	30.75	30.94	30.91	0.1438
Fe ₂ O ₃	3.47	3.48	3.43	3.46	0.0314
MnO	0.02	0.02	0.01	0.02	0.0029
MgO	1.46	1.49	1.49	1.48	0.0198
CaO	6.23	6.19	6.18	6.2	0.0242
Na ₂ O	0.10	0.10	0.11	0.10	0.0061
K ₂ O	0.620	0.60	0.60	0.60	0.0094
P ₂ O ₅	0.58	0.55	0.57	0.56	0.0156
TiO ₂	1.66	1.65	1.65	1.65	0.0095
SO ₃	0.24	0.25	0.25	0.24	0.0037
Loss on ignition	3.67	3.85	4.04	3.85	0.185
Sum (%)	100	99.99	99.99	99.99	0.0008
SiO ₂ /Al ₂ O ₃	1.64	1.66	1.64	1.65	0.012

The elemental chemical compositions of AFA (on dry basis) obtained was SiO₂ 50.91 %, Al₂O₃ 30.91 %, Na₂O 0.10 %, CaO 6.2 %, Fe₂O₃ 3.46 %, MgO 1.48 %, TiO₂ 1.65 %, MnO 0.02 %, K₂O 0.60 % and P₂O₅ 0.56 %. Before its use as support, the material was ground to a fine powder. The average SiO₂/Al₂O₃ ratio of Arnot fly ash was found to be 1.65. The major elemental chemistry of the AFA is consistent with SiO₂ + Al₂O₃ + Fe₂O₃ ≥ 70 % meaning that it is “class F” fly ash (ASTM C 618 method). This is a typical composition of fly ash from combustion of bituminous coal from South Africa (Gitari et al., 2005). This composition is completely different from the fly ash collected from India especially with respect to the calcium oxide (CaO) content. The South African class F- AFA gave a value of 6.2 % for CaO content in comparison to a value of 1.72 % from the fly ash collected from Parli Thermal Power station of Ambajogai District, Maharashtra, India in Kotwal et al (2009) study.

5.3.3b XRF Analysis of the Arnot fly ash based catalyst (KNO₃/FA)

XRF was used to determine the potassium (K) composition of the different 5 % KNO₃/FA and 10 % KNO₃/FA loadings of the prepared AFA based catalyst as prepared in section 3.7.2 before and after transesterification reactions according to the procedure outlined in section 3.8.4 and results are presented in Table 5.4.

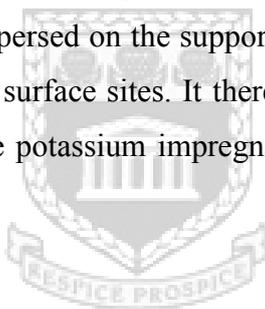
Table 5.4: Potassium content of the prepared catalysts before and after transesterification reactions (XRF analysis)

Catalyst	K (wt%)
Fresh Arnot fly ash	1.5
5 % KNO ₃ wt/wt (fresh)	7.56
5 % KNO ₃ wt/wt (spent)	4.25
10 % KNO ₃ wt/wt (fresh)	10.78
10 % KNO ₃ wt/wt (spent)	5.26

*Fresh-before use in transesterification reaction, Spent-After use as a catalyst in the transesterification reaction.

XRF was used to determine the potassium content in the 5 % KNO₃/FA and 10 % KNO₃/FA before use in the transesterification reaction (fresh) and after use as a catalyst in the transesterification reaction (spent). The spent catalyst was analysed to check the amount of the active species remaining for reuse in the reaction (Table 5.4). The results show that 43 % of the potassium of 5 % KNO₃/FA was leached from the surface during transesterification while 51 % of the potassium of 10 % KNO₃/FA was leached from the surface. This corresponds to the BET results (Table 5.5) obtained from the spent 10 % KNO₃/FA catalyst, having lower surface area than that of the fresh Arno catalyst, 10 % KNO₃/FA because part of the K initially deposited on the catalyst surface was leached from the solid during use, which reveals a lack of chemical stability of the catalyst under reaction conditions (Arzamendi et al., 2007). Therefore, the leached potassium in both cases could catalyze the transesterification a homogeneous catalyst.

In a heterogeneous catalyst, it is important to ensure that the active species are not leached from the solid support of the catalyst. If the leaching of the active species on the catalyst is high the active species could act as a homogeneous catalyst and the process advantages of the heterogeneous catalysts can be partially lost (Macleod et al., 2008; Alonso et al., 2007). Studies conducted by Xie et al. 2006 revealed that strong basic sites are formed on the composites of Al_2O_3 (used as a support) resulting from the decomposition of loaded KNO_3 retaining a high efficiency in the catalytic reactions conducted with soybean oil. Recent studies have shown that potassium based salts loaded on a series of support strongly affects the activity of the heterogeneous catalyst for the transesterification reactions (Xie et al. 2007; Sun et al., 2007; Alonso et al. 2007). It is very likely that dispersion of KNO_3 on fly ash support weakens the combination of K^+ and NO_3^- ions due to the interaction between KNO_3 and the surface of support, which is beneficial for the decomposition of KNO_3 . At low loading of KNO_3 , the active base sites are more dispersed on the support surface and strong adsorption of reactant may occur at unreactive surface sites. It therefore implies that the fly ash may act as an adequate support as the potassium impregnated on the AFA is only partially lost during the reaction.



5.3.4a Mineral composition of fresh Arnot fly ash: (XRD)

The qualitative and quantitative X-ray diffraction spectra XRD patterns of the fresh AFA used in this study are shown in Figures 5.4 and 5.5.

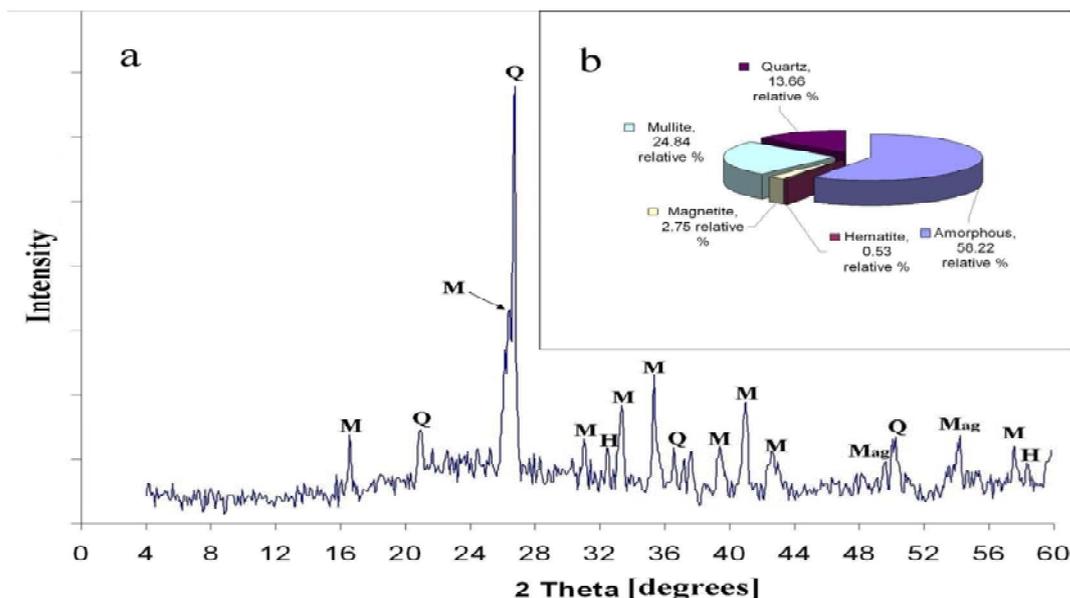


Figure 5.4: XRD Spectra of Arnot fly ash (Q = Quartz, M = Mullite, H = Hematite, Mag = Magnetite) where (a) Qualitative analysis (b) Quantitative analysis.

The XRD pattern of the AFA exhibited the characteristic peaks of crystalline phases viz. α -Quartz, Hematite, Magnetite and Mullite. From the XRD pattern of Arnot fly ash presented in Figure 5.4, it was found that the predominant phases were quartz (SiO_2) with major peak at $26.9^\circ 2\theta$ and less intense peaks also identified, mullite ($3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), major peaks at $26.4^\circ 2\theta$ (i.e as a shoulder on the quartz peak), magnetite, and hematite. The presence of amorphous phases are identified as a broad diffraction ‘hump’ in the region between 18 to 32 degrees 2θ (Inada et al., 2005; Murayama et al., 2002; Hui et al., 2005). Quantitative XRD analysis (b) shows that the quantity of the mineral phases identified were in the following order; Amorphous (58.22 %) > Mullite (24.84 %) > Quartz (13.66 %) > Magnetite (2.75 %) > Hematite (0.53 %) (See Fig. 5.4).

5.3.4b XRD Analysis of the prepared Arnot fly ash based catalysts KNO_3/FA

The XRD patterns of the fresh AFA (Fig 5.4) can be compared to the prepared AFA based catalyst (KNO_3/FA) with various wt% loadings (5-25) of potassium nitrate (KNO_3) (Figure 5.5).

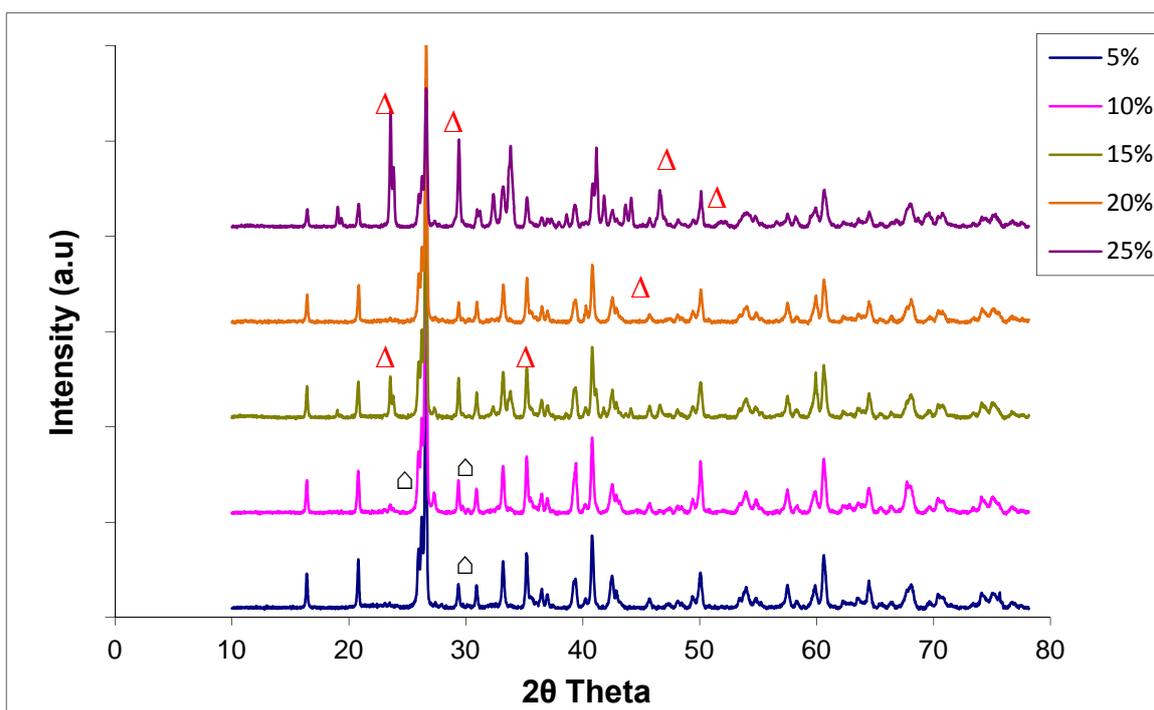


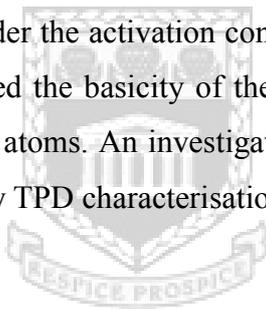
Figure 5.5: XRD patterns of the prepared Arnot fly ash based catalyst with characteristic peaks due to KNO_3 (\triangle) and K_2O (\square).

The XRD patterns of the AFA based catalyst KNO_3/FA , exhibited the characteristic peaks of fresh fly ash crystalline phases viz. α -Quartz, Hematite, Magnetite and Mullite at $2\theta = 20^\circ, 32^\circ, 37^\circ, 46^\circ,$ and 67° . When the loading of the KNO_3 on the AFA was increased from 5 to 10 wt%, the XRD patterns were almost the same as the typical XRD pattern of the AFA itself indicating a good dispersion of KNO_3 on the fly ash support. This also suggests that a good dispersion occurs as KNO_3 can be well dispersed on the fly ash support (rich in SiO_2 and Al_2O_3) in the form of a monolayer at a low loading (Li et al., 2008). When the loading of KNO_3 was further increased to 15 wt%, characteristic peaks associated with KNO_3 and K_2O species were observed at $23^\circ, 29.5^\circ$ and 31.08° respectively (Zhu et al., 1998; Jiang et al., 2000; Xie et al., 2006; Ma et al., 2004). A new phase of K_2O can be observed when the loading was increased to 25 % at $2\theta = 31^\circ, 39^\circ, 51^\circ$ and 55° . These results agree well with results reported in literature (Kotwal et al., 2009; Xie et al. 2006). The supported species is typically introduced through wet impregnation of a solution containing the solvated precursor into the pores and

calcination at 500 °C decomposes the occluded compounds thus creating the supported alkali metal oxides (Robert, 2003).

The XRD result of $\text{KNO}_3/\text{Al}_2\text{O}_3$ reported by Xie et al. (2006) showed that at low K loading, the XRD patterns were identical to that of Al_2O_3 because of the good dispersion of K on Al_2O_3 . The extent of decomposition of KNO_3 varied with the initial amount of loading. Beyond 5 % wt loading, the XRD of the catalysts were shown to have the characteristics peaks of KNO_3 as well as of K_2O but it seems that, once the amount of KNO_3 loading exceeds 5 wt%, not all, but only a part of the loaded KNO_3 might have decomposed to K_2O . This was attributed to the uneven dispersion or clustering of KNO_3 on the fly ash support (Kotwal et al., 2009). Moreover, the intensity of KNO_3 peaks was found to increase with the increase in amount of loading.

Thus, the literature suggests that good dispersion of KNO_3 occurred up to 10 % (wt/wt) loading on the AFA substrate under the activation condition employed and occlusion of potassium metal clusters enhanced the basicity of the AFA by increasing the negative charge of the framework oxygen atoms. An investigation into the basicity of the active species was further determined by TPD characterisation (section 5.3.7).



5.3.5 BET Analysis of fresh Arnot fly ash and prepared fly ash based catalyst

The results obtained for N_2 -BET surface area, pore diameter and volume of the fresh AFA and the prepared AFA based catalyst under the specified conditions (see section 3.8.1) are presented in Table 5.5. The pore size distribution of the micro pores present in the fresh Arnot fly ash and the AFA based catalyst (5 % KNO_3 / FA) are also presented in Figures 5.6 and 5.7 respectively.

The surface areas of the various KNO₃/FA samples were determined by N₂-BET measurements done in duplicate (Table 5.5).

Table 5.5: BET surface area of the different AFA based materials.

Material	Surface area (m ² /g)
Fresh AFA	2.787 ± 0.017
5% KNO ₃ wt/wt (fresh)	1.1704 ± 0.013
10% KNO ₃ wt/wt (fresh)	0.5511 ± 0.001
5% KNO ₃ wt/wt (spent)	0.11 ± 0.001
10% KNO ₃ wt/wt (spent)	0.18 ± 0.001

The results show the surface areas of fresh AFA, the 5 % KNO₃/FA and the 10 % KNO₃/FA were 2.79, 1.17, 0.55 m²/g respectively. The spent 5 % and 10 wt% KNO₃/FA had a lower surface area than the fresh AFA. This trend also show that the surface areas of the KNO₃/FA catalyst decreased as the loading amounts of KNO₃ increased. A low surface area value (0.38 m²/g) was reported by Kotwal et al. (2009) for the 5 % loading fly ash catalyst calcined at 773K for 5 h. It is suggested that the low BET value recorded might probably be due to a clog-up of the fly ash support pores with other undesirable materials.

In this study, the lower surface area observed with regards to the spent 5 wt% KNO₃/FA than the fresh catalyst might probably be due to the leaching of the active species (K) from the pores structure when used in the transesterification reaction. However, the loss of surface area in the catalyst has lesser impact than the loss of active species on the catalyst. In both cases the spent catalyst surface areas were lower than fresh AFA.

The pore size distribution of the micro pores present in the fresh AFA and the AFA based catalyst (5 % KNO_3/FA) are presented in Figures 5.6 and 5.7 respectively.

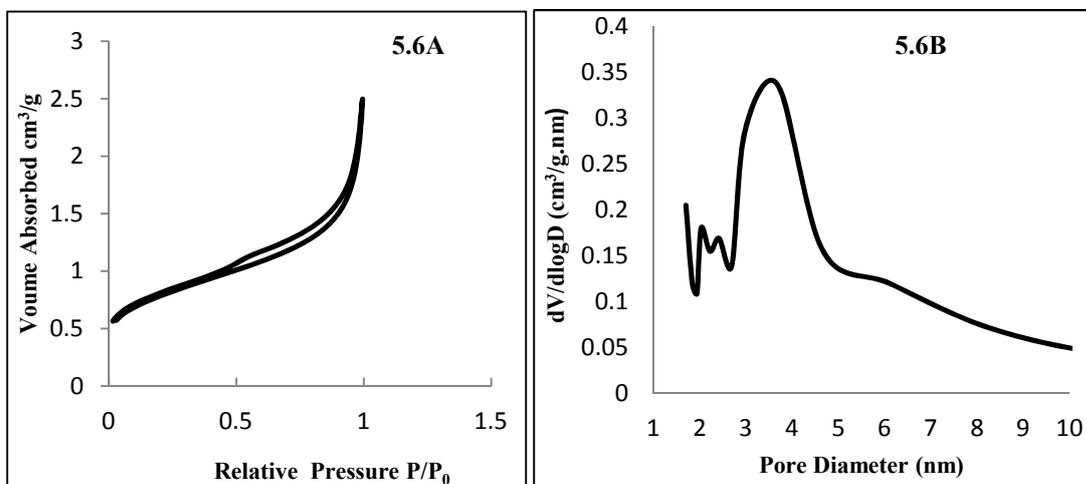


Figure 5.6: (A) N_2 adsorption-desorption isotherms of AFA (B) Pore size distribution of AFA.

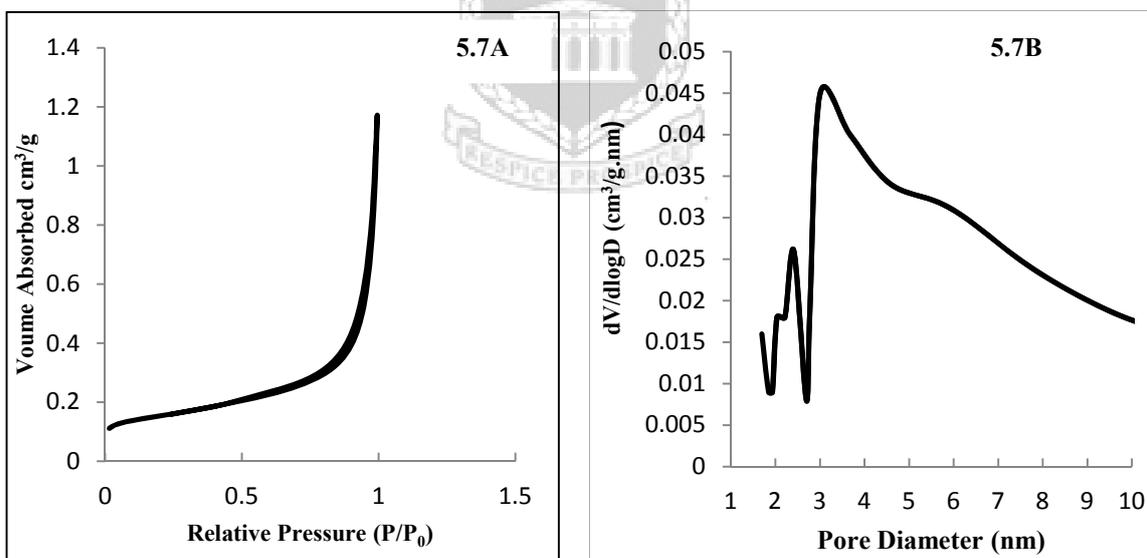
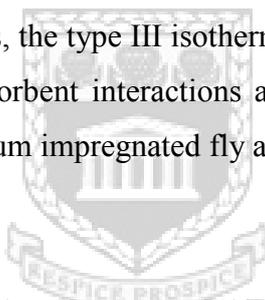


Figure 5.7: (A) N_2 adsorption-desorption isotherms and (B) Pore size distribution of the 5 % KNO_3 impregnated fly ash

The N_2 adsorption and desorption isotherms obtained in Figure 5.6 and 5.7 also showed that mesopores were formed and that the micropore volume of the samples decreased with the agglomeration process, after addition of KNO_3 . The mesopore diameter of the fresh AFA particles was centred at 3 to 5 nm while the pore size distribution of the KNO_3/FA was broad. There was a decrease in the surface area when the fresh AFA used as a support was modified by the wet impregnation of KNO_3 species on the AFA followed by calcination at 500 °C. The N_2 adsorption and desorption isotherms obtained showed that larger mesopores were formed after formed after KNO_3 loading and that the smaller mesopore and micropore volume of the samples decreased as the loading of KNO_3 increased. The micropore volume of the AFA decreased monotonously with the potassium oxide loading even for high loadings. The decrease in surface area and micropore volume with increasing potassium loading could be assigned to a decrease of the available void volume (Lowell, 2006). From the nitrogen adsorption-desorption isotherms presented in the figures, the type III isotherm convex to the axis indicates that the P/P_0 attractive adsorbate-adsorbent interactions are relatively weak and the lower adsorption volume on the potassium impregnated fly ash indicates a low surface area.



5.3.6 FTIR analysis of fresh AFA and prepared AFA based catalyst

The FT-IR vibration bands of the fresh AFA as well as the prepared AFA based catalyst (KNO_3/FA) are presented in Figure 5.8. This information/data was determined according to the procedure highlighted in section 3.8.7 and the bands are assigned according to standard practice.

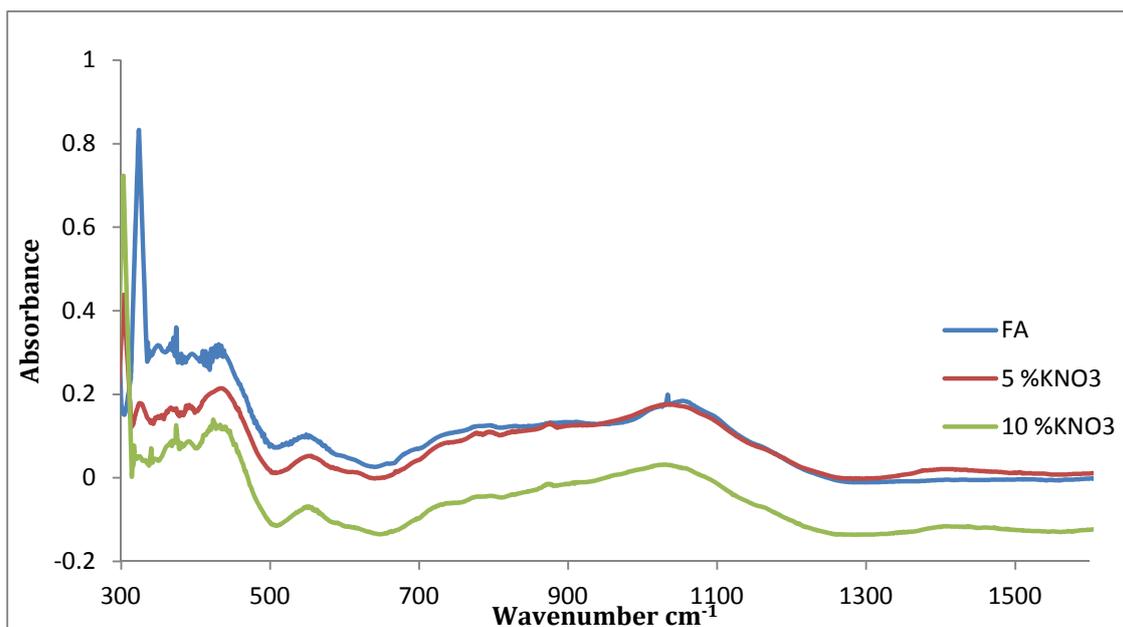


Figure 5.8: IR spectra of fresh AFA, 5% KNO₃/FA and 10 % KNO₃/FA catalyst.

Further investigation of the fresh AFA and the KNO₃/FA catalysts was conducted via IR spectroscopy as shown in Figure 5.8. The samples showed three wide bands characteristic of aluminosilicates: the band at 460 cm⁻¹ was associated with T–O bending vibrations [*] the bands appearing at around 704, 780 and 800 cm⁻¹, associated with T–O (T = Al, Si) symmetric stretching vibrations that correspond to quartz present in the original fly ash; the band appearing at 1053 cm⁻¹ was associated with T–O (T = Al, Si) asymmetric stretching vibrations (Musyoka, 2009). The shoulder at around 950 cm⁻¹ is probably due to the presence of a glassy phase while the bands at 1135 and 700 cm⁻¹ are likely to be from the asymmetrical stretching vibration and symmetrical vibration of the Al–O–Si groups, respectively (Colthup et al., 1964). The bands found at 700 cm⁻¹ are likely to be from mullite (Farmer, 1988). Fernandez-Jimenez and Palomo (2005) reported that bands around 550 and 560 cm⁻¹ (Fig.5.8) are associated with octahedral aluminium present in the mullite phase. Silicate bands between 900-1200 are found to be broad and diffuse because of the overlapping of different types of silicate molecular vibration resulting from various silicate minerals (Mollah et al., 1999). A broad adsorption peak observed at 1380-1400 cm⁻¹ for all the potassium impregnated fly ash catalysts is assigned to weak aliphatic bonds associated with N-O bond of KNO₃.

identifying the presence of occluded nitrates within the AFA pores (Nakamoto, 1970). Similar observations were made by Choi et al., (2007) and Piantone et al., (2003). These observations are also in agreement with other reports from literature (Nadkarni et al., 2009).

5.3.7 Basicity of prepared KNO_3/FA catalysts (TPD Characterisation)

CO_2 -Temperature programmed desorption (CO_2 -TPD) under conditions as specified in section 3.8.8 was carried out to study the basic properties of the prepared KNO_3/FA catalysts. The TPD profiles of desorbed CO_2 on the different loadings of the prepared KNO_3/FA catalysts are shown in Figure 5.9.

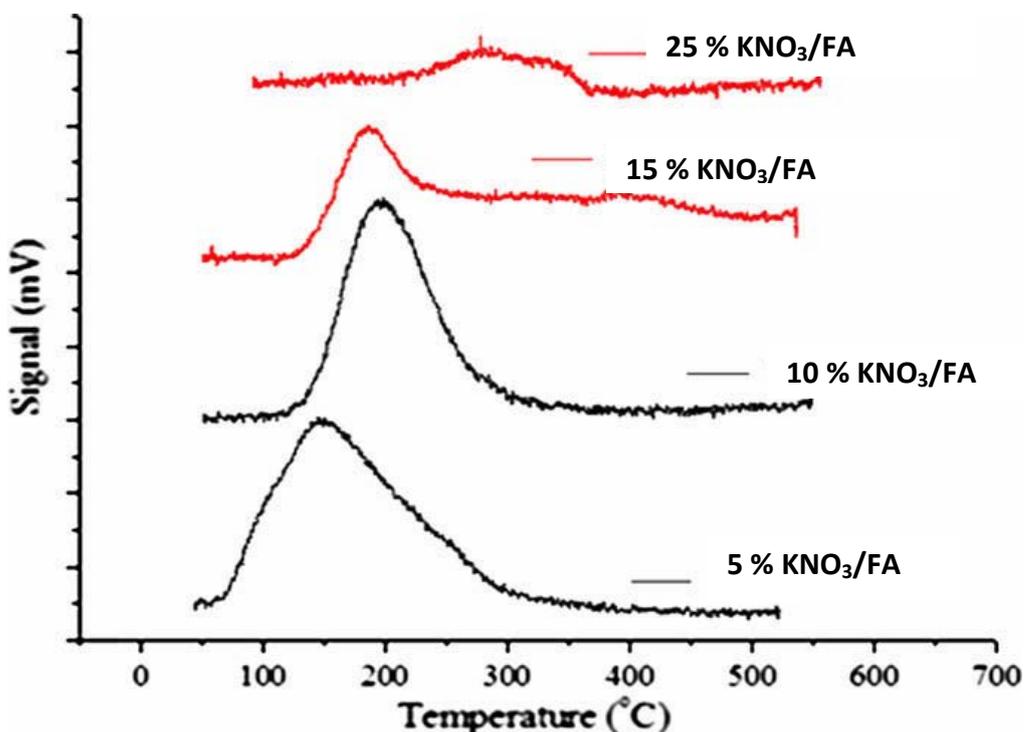


Figure 5.9: CO_2 -TPD profile of the different loadings of the prepared KNO_3/FA catalysts.

The TPD curve for the different loadings of the prepared AFA based catalyst (5 % KNO_3/FA and 10 % KNO_3/FA) consists of peaks at 155 and 195 °C, respectively

(Figure 5.9). The results show that the desorption peak at a temperature of 155 °C can be attributed to the interaction of CO₂ with sites of weak basic strength (Yin et al., 2004) and also can be attributed to basic sites of medium strength, related to the activity of that catalyst as shown in section 5.5.1 (Xie et al., 2006). It has been proposed that these CO₂ adsorption sites correspond to the NO₃²⁻ groups on the surface. Similarly, the results show desorption peaks for 15 % KNO₃/FA and 25 % KNO₃/FA catalysts at 200 and 285 °C, respectively. The peak at a temperature of 200 °C can be attributed to the interaction of CO₂ with sites of intermediate basic strength which correspond to the K₂O groups loaded on the surface of the AFA used as support (XRD analysis). It is clearly observed that the basic strength increases as the KNO₃ loading increases especially in the case of the 25 % KNO₃/FA sample at ~300 °C. The increase in temperature for CO₂ desorption corresponds to an increase in the strength of basicity of catalysts (Pathak et al., 2010). From literature, it is seen that there are three ranges for the desorption of CO₂, which include 20–200, 200–350 and 350–550 °C, and they correspond to weak, intermediate and strong basic centres respectively (Anderson et al., 1979). Although CO₂ could not be quantitatively measured in these experiments, if the desorption peak intensity is high then the number of basic sites is large and vice versa. From the results, there is a strong indication that the number of weak basic sites was greater than intermediate basic centres in the lower KNO₃ loadings of the prepared catalyst (5 % KNO₃/FA and 10 % KNO₃/FA) (Katikaneni et al., 1998; Lewandowski and Sarbak, 2000). This CO₂-TPD analysis suggests that the prepared AFA based catalyst possessed the relevant and necessary basic sites to sustain the transesterification reactions with sunflower oil.

Taking into account all the information obtained from the catalyst characterisations, K₂O derived from KNO₃ was most probably the main active site responsible for the basicity of the catalyst. This conclusion spurred the decision to investigate the catalytic activity of the 5 % KNO₃/FA and 10 % KNO₃/FA catalysts in the heterogeneous transesterification reactions.

5.4 Results and discussion: zeolite catalyst characterisation

In this section, the characterization results of the AFA- zeolite based catalysts are presented. Commercial zeolite Na-X (see Table 3.2) was used as a baseline for comparison of the catalytic activity of the Arnot fly ash derived zeolite Na-X catalysts. The as- received AFA based zeolite Na-X was ion exchanged with potassium using potassium acetate as precursor to obtain the FA/K-X following the procedure highlighted in section 3.6. This was done in order to increase the basic strength required for improved transesterification reactions as reported in literature (Suppes et al., 2009), as potassium-acetate exchanged commercial Na-X zeolite has shown superlative performance in transesterification reactions (Broges et al., 2010). The characterization results of the AFA -zeolite Na-X catalysts are discussed in the sub-sections 5.4.1 -5.4.5.

5.4.1 X-ray powder diffraction (XRD)

The XRD patterns of the commercial zeolite catalyst (CM /NaX) as a baseline and the AFA- zeolite Na-X catalysts (FA/NaX) are shown in Figure 5.10.

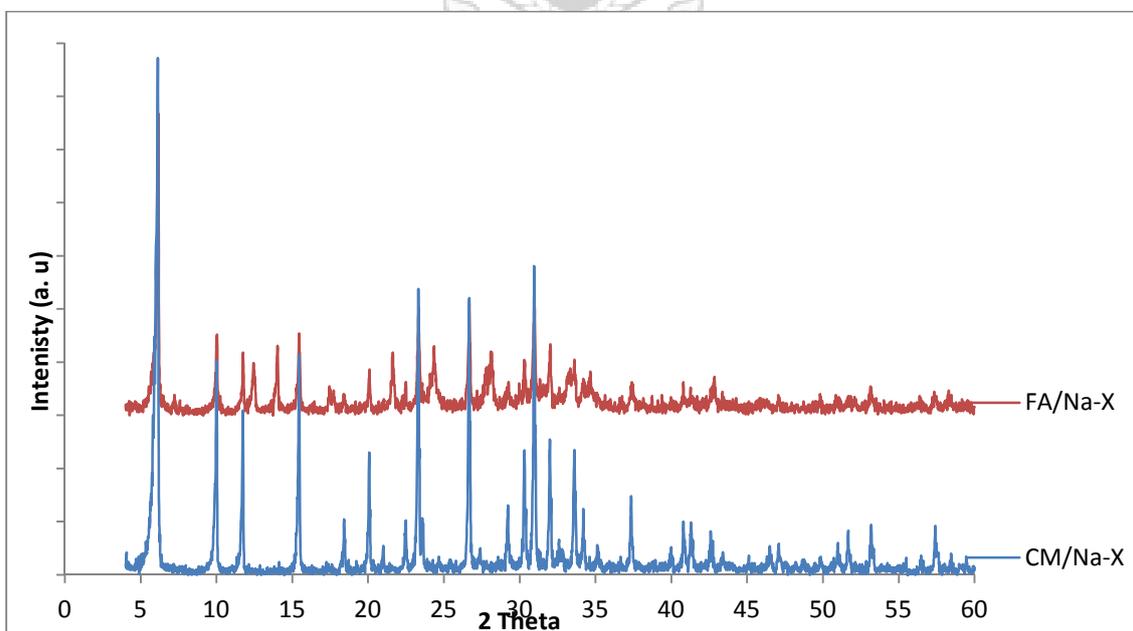
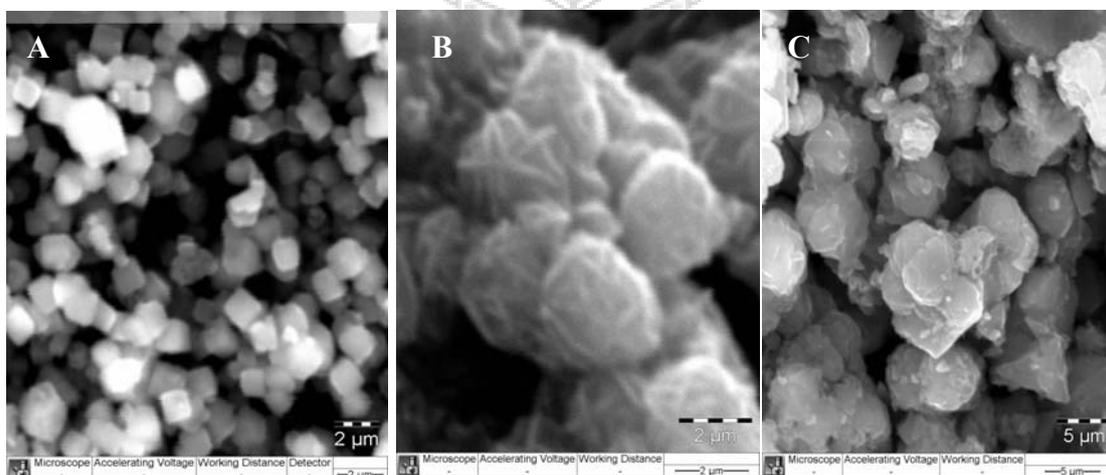


Figure 5.10: XRD patterns of the commercial zeolite catalyst (CM /Na-X) and the as received AFA- zeolite catalyst (FA/Na-X)

XRD results for the as received AFA -zeolite showed typical diffraction peaks of zeolites Na-X. Normally zeolite X which is classified under the faujasite group of zeolites has the ratio of Si/Al ranging from 2 to 4 (Lee et al., 1996). Using fly ash as the feed stock to synthesize these zeolites, one can obtain different types of zeolites depending on the composition of the synthesis mixture (Querol et al., 2002). In the case of the synthesis of AFA -zeolite Na-X, the low Si/Al ratio in this ash source had been found to preferentially give the zeolite Na-X phase (Musyoka, 2011). The XRD patterns of the commercial zeolite Na-X (CM/Na-X) and AFA -zeolite Na-X (FA/Na-X) presented in Figure 5.10 show similar diffraction peaks except a contaminant phase whose peaks can be seen to appear at $2\theta = 12^\circ$, 14° and 24° . Reports from literature state that faujasite family of zeolites (X and Y) are thermally stable (Lee et al., 2007) hence making them attractive for transesterification reactions requiring moderate to elevated temperatures.

5.4.2 Scanning electron microscopy (SEM)

Morphologies of the commercial zeolite Na-X and AFA -zeolite FA/Na-X catalysts are shown in Figures 5.11.



Figures 5.11: SEM-EDS micrograph of (a) commercial zeolite catalyst (CM /NaX) (b) as-received AFA- zeolite catalyst (FA/NaX) and (c) as-received AFA -zeolite catalyst after K^+ exchange (FA/KX).

Scanning Electron Microscopy (SEM) was used to determine the particle size and the morphology of all the zeolite crystals. The morphology of the commercial Na-X was

found to contain the typical octahedral crystal formation of faujasite zeolites (Lee et al., 2007) as shown in Fig.5.11a. The SEM micrograph of the fresh AFA (Fig. 5.1) shows the initial morphology of the starting material before zeolitization. After the conventional hydrothermal synthesis process to obtain the zeolite FA/Na-X (Fig. 5.11b) the unique morphology with nano platelets was observed. This is different from the well known pyramidal octahedral shaped crystals as observed in the commercial zeolite Na-X (Katsuki and Komarneni, 2009). This phenomenon however confirms and shows an evidence of the faujasite phase complimented also by XRD analysis. The morphology of AFA -zeolite FA/Na-X after ion exchange with K^+ (Fig. 5. 11c) as expected did not show any significant difference.

5.4.3 BET surface area

The surface areas of the commercial zeolite catalyst (CM /Na-X), AFA -zeolite catalyst (FA/Na-X) and ion exchanged AFA-zeolite catalyst (FA/K-X) as determined by BET measurements (section 3.8.1) are shown in Table 5.6.

Table 5.6: BET surface area measurements of the zeolite catalysts

Sample	BET area m^2/g	Pore volume cm^3/g
CM /Na-X	802	3.62
FA/Na-X	320.7	1.40
FA/K-X	257	1.28

The BET surface area and the pore volume of the commercial and AFA - zeolite Na-X were determined. The surface areas values of the commercial zeolite used as baseline in this study was found to be higher than that of the AFA -zeolite as shown in Table 5.6. The difference can be attributed to the degree of phase purity as highlighted by the XRD analysis reported in section (5.4.3). Comparing the surface area of the FA/Na-X with its K^+ ion exchanged counterpart, it can be seen that the AFA -zeolite Na-X exhibited a higher surface area value of $320.7 m^2/g$. On the other hand, the ion exchanged FA/K-X gave a lower surface area value of $257 m^2/g$. This gives an indication that the ion

exchange with K^+ had a significant pore blocking effect as a result of the relative bigger size of the K cation compared to the Na cation. The relatively high surface area for both the FA/NaX and FA/KX compared to the AFA and KNO_3/FA catalysts presented previously presents an advantage for the use of these AFA -zeolitic materials, which presumably would anchor and enable catalytic reactions of the large triglyceride molecules (Endalew et al., 2011). This is desirable to promote conversion of triglycerides into methyl esters during the transesterification reactions in biodiesel synthesis. A higher surface area of the AFA -zeolite FA/Na-X is reported in this study in comparison to the surface area values reported in literature (Tanaka et al., 2002; Querol et al., 2002). It is expected that these characteristics would project a higher potential in increased catalytic efficiency subsequently during the transesterification studies.

5.4.4 Fourier transformed infrared (FTIR) spectroscopy

The FT-IR curves of the commercial zeolite catalyst (CM /Na-X) and the AFA- zeolite catalyst (FA/Na-X) are shown in Figure 5.12.

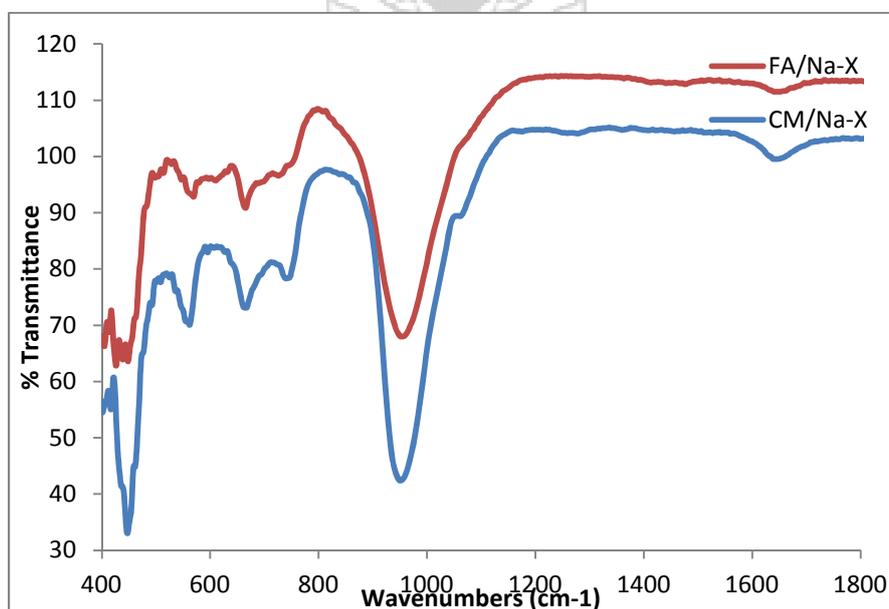


Figure 5.12: IR spectra of the commercial zeolite catalyst (CM /Na-X) and AFA-zeolite catalyst (FA/Na-X)

IR analysis of the AFA -zeolite catalyst (FA/Na-X), obtained through the conventional hydrothermal synthesis process shows all the characteristic bands for zeolite Na-X and compares well with the bands obtained from its commercial counterpart (Fig 5.12). A summary of vibration bands of zeolites was reported by (Breck, 1974). The strongest vibration at 950 cm^{-1} is assigned to a T–O stretch and the stretching modes involving mainly the tetrahedral atoms are assigned in the region of 740 and 620 cm^{-1} . Generally, stretching modes are sensitive to the Si–Al composition of the framework which may shift to a lower frequency with increasing number of tetrahedral aluminium atoms, resulting in the occurrence of the second group of frequencies that are sensitive to the linkages (Flanigien, 1991). The vibration bands of secondary building units of zeolite Na-X are reported to occur in the regions of 600 – 500 and 430 – 300 cm^{-1} (Lee et al., 1996). The band in the 600 – 500 cm^{-1} region can be related to the presence of a double ring in the framework structures and is observed in all the zeolite structures that contain the double 4 and double 6-rings (Flanigien, 1991). The IR analysis of the AFA -zeolite catalyst (FA/K-X) is not shown as no difference is expected from the bands exhibited for AFA -zeolite Na-X.

Putting into consideration, the information and the insight obtained from the various characterisations done on the AFA-zeolite materials, a subsequent application using these zeolitic materials as heterogeneous catalysts were done and results presented in section 5.6.

5.5 Transesterification reactions: KNO_3/FA catalysts

The prepared KNO_3/FA catalysts were studied in the heterogeneous transesterification firstly using refined sunflower oil sample (earlier characterised) as feedstock. The influence of the occluded potassium oxide species on the catalytic performance of the fly ash based catalyst for the transesterification of sunflower oil was studied at two different nominal loadings (5 % KNO_3/FA and 10 % KNO_3/FA). With the aim of maximizing the conversion of oil and yield of product, a systematic study was also carried out in relation to the optimization of reaction parameters such as catalyst loading

(wt/wt), methanol to oil molar ratio, reaction time, temperature and reusability of catalyst on the conversion of sunflower oil to its methyl esters.

5.5.1 Influence of wt% of KNO_3 loading on the methyl ester yield

The effect of wt% KNO_3 loading on the methyl ester yield was firstly studied. The KNO_3/FA catalysts were prepared by varying the loading amount of KNO_3 from 5 to 25 wt% and were used to catalyse the transesterification reactions. Reaction conditions for the transesterification reactions (100 g of sunflower oil) conducted using these catalysts include a reaction time of 5 h, 15:1 methanol to oil molar ratio, 15 g of the catalyst, 600 rpm stirrer speed at a reaction temperature of 160 °C. The results obtained are presented in Figure 5.13.



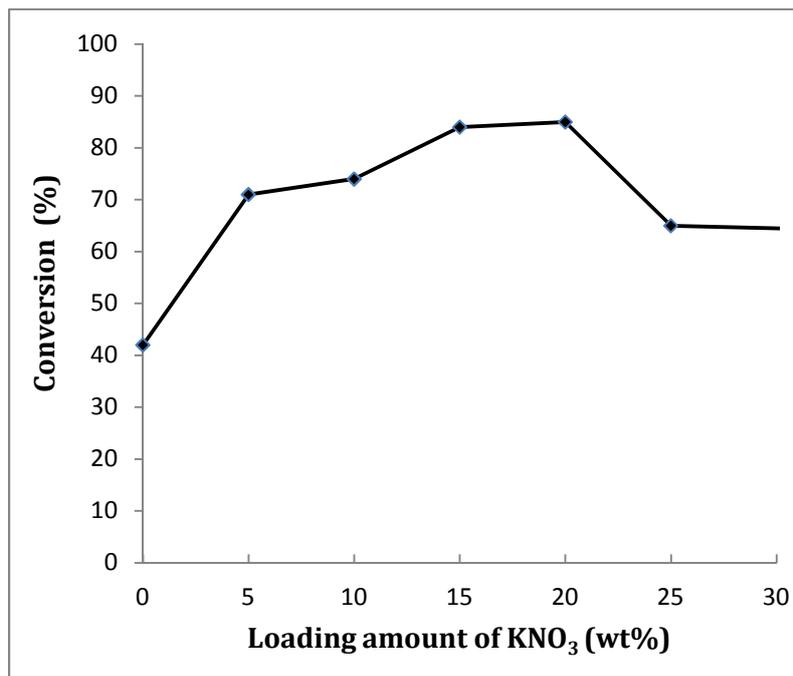


Figure 5.13: Influence of loading of KNO₃ (wt %) on methyl ester conversion. Reaction conditions: methanol/oil molar ratio 15:1, reaction time 5 h, catalyst amount 15 g and temperature of 160 °C at a stirrer speed 600 rpm.

The results shown in Figure 5.13 reveal that at zero loading of KNO₃, the fly ash by itself could catalyse the transesterification reaction and achieved a 40 % conversion without additional modification. As the loading of KNO₃ was increased from 5 to 25 wt% of the mass of catalyst, the feedstock oil conversion increased, and the highest conversion (85.07 %) was obtained at a KNO₃ loading of 15-20 wt%. However, when the amount of loaded KNO₃ was over 25 wt%, the biodiesel yield decreased and remained below 65 % conversion. It is believed that the agglomeration of the active KNO₃ phase or the covering of the basic sites by the excess KNO₃ occurred, and hence a lowering of the surface area of the catalyst was caused which resulted in lower activity, even though it is unclear how the KNO₃ impregnated on the surface of the support is responsible for this. It was postulated that the new phase of K₂O was the cause of the high catalytic activity and basicity of the catalyst, since when increasing the KNO₃ loading to 15–25 wt%, the biodiesel yield was increased (Xie et al., 2007).

Further increasing the KNO_3 loading to over 25 wt% however, the biodiesel yield decreased. In comparison, however to reports in Kotwal et al (2009), a conversion value of 87.5 % was obtained for the 5 % KNO_3 loading possibly due to a higher reaction time of 8 h and reaction temperature of 170 °C.

Clearly, the result in this study shows a correlation of the effect of loaded KNO_3 content on the catalyst basicity. It is very likely that dispersion of KNO_3 on fly ash support weakens the combination of K^+ and NO_3^- ions due to the interaction between KNO_3 and the surface of the support, which is beneficial for the decomposition of KNO_3 . At low loading of KNO_3 , the active base sites are more dispersed on the surface of the support and a strong adsorption of reactants may occur at unreactive surface sites, whereas, if too much KNO_3 is loaded on the support, it cannot be well dispersed, consequently only part of the loaded KNO_3 could be decomposed on the support.

More significantly, coinciding with the results of XRD as mentioned above (section 5.3.2.3b), the excess KNO_3 could cover the basic sites on the surface of the Arnot fly ash composite and cause a lowered catalytic activity or could leach into solution becoming available as homogeneous catalyst. Therefore these results indicate that the catalytic activity was proportional to the amount of decomposed KNO_3 instead of the total loading of KNO_3 .

5.5.2 Influence of amount of catalyst

The influence of the amount of catalyst used of the 5 % KNO_3/FA and 10 % KNO_3/FA catalyst, on the methyl ester yield from the transesterification reactions carried out on sunflower oil sample were performed under the following reaction conditions: reaction time of 5 h, 160 °C, methanol: oil ratio of 15:1 and a stirrer speed of 600 rpm. Catalysts were varied between 5 and 20 g per 100 g of oil. Results are presented in Figure 5.14.

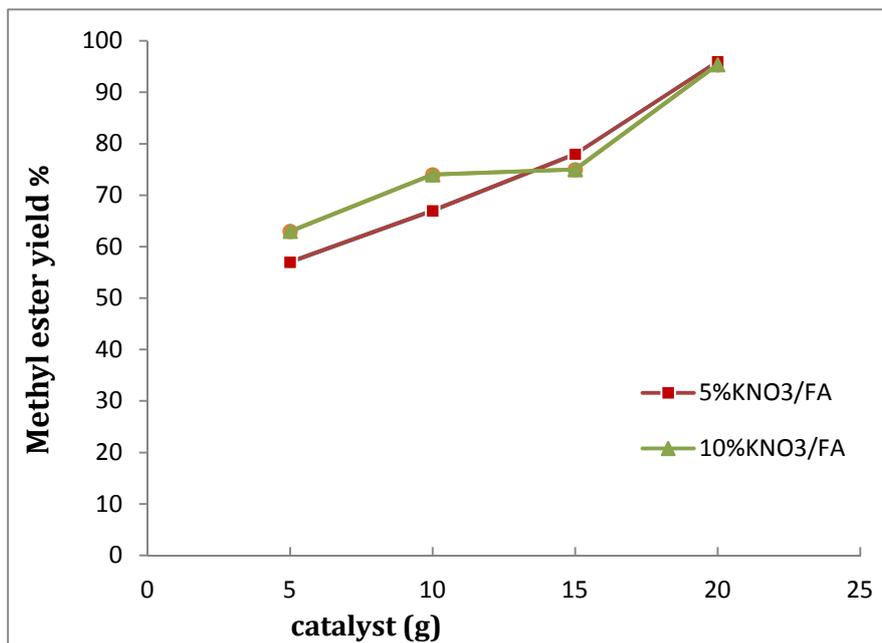
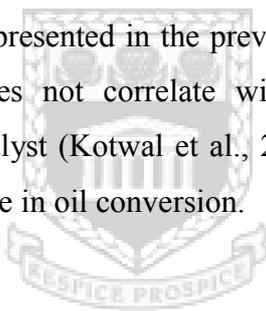


Figure 5.14: Methyl ester yield as a function of amount of catalyst used, at reaction conditions: reaction temperature of 160 °C, reaction time of 5 h and a methanol: oil ratio of 15:1 at a stirrer speed 600 rpm.

To determine the influence of the amount of catalyst used per unit volume on the methyl ester yield, the catalyst amount was varied within the range from 5 to 20 wt%. The reaction was carried out with 5 % KNO₃/FA and 10 % KNO₃/FA at a methanol to oil ratio of 15:1, a temperature of 160 °C catalysts for 5 h. As shown in Figure 5.15, it was observed that the methyl ester yield correlated directly with an increase in the amount of catalyst added.

The results showed that when the amount of catalyst per unit volume of methanol and oil mixture was not sufficient (5 g), the methyl ester yields were relatively low (<75 %) and as the amount of the catalyst increased there was a corresponding increase in yield. The highest methyl ester yields of 96 % and 95.45 % were obtained for the 5 % KNO₃/FA and 10 % KNO₃/FA respectively at a catalyst amount of 20g. From the view of point of the reaction kinetics, a larger amount of catalyst leads to a higher yield of methyl esters in a shorter reaction time. However with a further increase in the amount

of catalyst to over 15 g, the mixture of reactants and catalyst became viscous, leading to a problem of mixing and a demand of higher power consumption for adequate stirring (bench scale at 600 rpm). On the other hand, when the catalyst loading amount per unit volume was not enough, maximum production yield could not be reached. To avoid this kind of problem, an optimum amount of catalyst loading per reaction volume had to be investigated. The challenge that is posed by the three phase reaction system is that the initial mass transfer control is inhibited due to heterogeneous kinetics. This is because of the fact that the solid catalyzed process is an immiscible liquid/liquid/solid 3 phase system (corresponding to oil, methanol and catalyst) that is highly mass transfer limited (Lee et al., 2009). Due to these reasons, an optimum catalyst amount was established to be 15 g per 100 g of oil in this system as it was sufficient in catalyzing the transesterification reaction. The maximum methyl ester yield reached 94%, which was a little higher than the methyl ester yield value obtained in the conventional homogeneous KOH catalyst system (92 %) as presented in the previous chapter (Table 4.3 in section 4.3.3.1). The result obtained does not correlate with the reports obtained for the heterogeneous fly ash based catalyst (Kotwal et al., 2009) where a catalyst loading of above 15 %wt/wt led to a decrease in oil conversion.



5.5.3 Influence of methanol: oil ratio

The influence of methanol: oil ratio on the methyl ester yield from the transesterification reactions carried out with the 5 % KNO_3/FA and 10 % KNO_3/FA on the sunflower oil sample were performed under the following conditions: catalyst amount of 15 g per 100 g of oil, reaction temperature of 160°C, reaction time 5 h and a stirrer speed of 600 rpm. Results are shown in Figure 5.15.

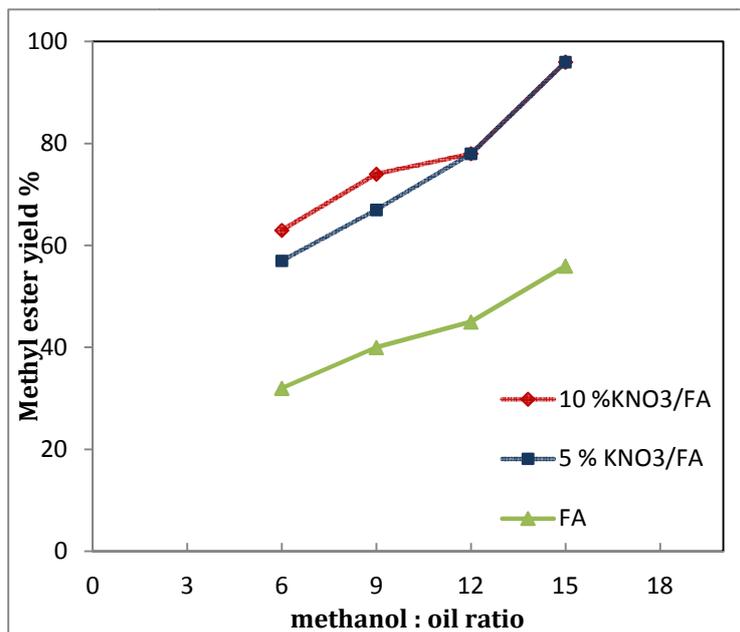


Figure 5.15: Effect of methanol to oil ratio on methyl ester yield at reaction conditions: reaction temperature of 160 °C, reaction time 5 h, catalyst amount (15 g) at a stirrer speed of 600 rpm.

The effect of changing the methanol to oil ratio on the methyl ester yield was examined by varying the amount of methanol with a fixed amount of oil (100 g) during the transesterification reactions. The initial amounts of methanol were set and amounts of oil corresponding to the methanol: oil ratios of 6:1, 9:1, 12:1, 15:1 were used as illustrated in Figure 5.16. The stoichiometric molar ratio of methanol to oil for transesterification is 3:1, and typically a ratio of 6 is used for homogeneous catalysis. In Figure 5.16, when the molar ratio of methanol to oil was 6:1 the methyl ester yield was only 57 % and 63 % for the 5 % KNO₃ /FA and 10 % KNO₃ /FA respectively after 5 h of reaction. In the case of the fresh AFA, an increase in yield corresponded to an increase in methanol content, the presence of silicate (SiO₂) and alumina (Al₂O₃) in the AFA may contribute to the increase observed. According to studies carried out by Hoang et al (1992) and Stern et al. (1998), ester yields (50-88 %) at a very high alcohol

to oil ratio (14:1-54:1) were recorded with the use of silicates and layered clay minerals as catalysts in biodiesel production.

The results (Fig. 5.15) also indicate that a higher molar ratio of methanol to oil (15:1) gave a high methyl ester yield (95.4 % and 96 %) for both the 5 % KNO_3 /FA and 10 % KNO_3 /FA catalysts. Thereafter no significant increase in the methyl yield was observed at a methanol to oil ratio of 20:1. A methanol to oil molar ratio of 15:1 was also recorded as optimum for all catalytic tests conducted for the heterogeneous fly ash based catalyst in Kotwal et al. (2009). It is noteworthy however that the AFA used in this study gave better results most probably due to the difference in composition of the South African Class F- AFA and Indian Class C fly ash used in previous study. The excess methanol promotes the transesterification reaction and extracts products from the catalyst surface to renew catalytic sites (Yan et al., 2008; Helwani et al., 2009). Thus, high ratio of methanol to oil is beneficial in this case. It has however been reported that a limitation exists to the use of a greater amount of methanol needed to propel the forward reaction, which is an occurrence of flooding of the active sites by the methanol molecules rather than triglyceride molecules. This flooding might hinder the completion of the triglyceride conversion to methyl esters, as conversion at methanol oil ratios higher than 15 appeared to decline (Shu et al., 2009). Also, feeding too much alcohol adversely affects the transesterification process by rendering the product separation difficult as glycerol; the co-product specie of methyl ester is highly soluble in methanol, which reverses the transesterification progress according to the Le Chatelier's principle (Lee et al., 2009). Another important variable affecting methyl ester yield and conversion is the type of alcohol to triglyceride. In general, short chain alcohols such as methanol, as well as ethanol, propanol, and butanol can be used in the transesterification reaction to obtain high methyl ester yields (Hanh et al., 2008). Other forms of alcohol apart from methanol however were not considered in this study.

5.5.4 Influence of reaction time

The influence of the reaction time (between 2-24 h) on the methyl ester yield from the transesterification reactions carried out with the 5 % KNO_3 /FA and 10 % KNO_3 /FA

prepared catalyst on the sunflower oil sample were performed under the following reaction conditions: a methanol: oil ratio of 15:1, 160 °C and 15 g. Results are shown in Figure 5.16.

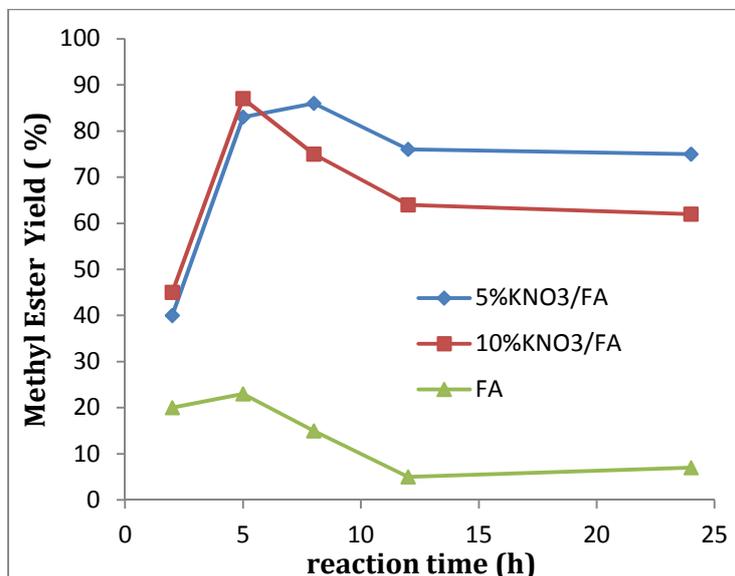


Figure 5.16: Influence of reaction time on oil methyl ester yield under reaction conditions: reaction temperature of 160 °C, catalyst amount 15 g and methanol: oil ratio of 15:1 at a stirrer speed 600 rpm.

The effect of reaction time on the yield of the methyl esters was studied using the fresh AFA, 5 % KNO₃/FA and 10 % KNO₃/FA catalyst. The set of experiments were carried out at different times (2, 5, 8, 12 and 24 h). It could be observed that the methyl ester yield increased slightly (max 23 %) in the case of the fresh AFA from 2 to 5 h where after it decreased steadily with an increase in the reaction time. As can be seen from Figure 5.17, for the 5 % KNO₃/FA, the methyl ester yield increased to above 80 % in the initial 2 h and afterwards remained relatively constant at 78 % as a result of near-equilibrium conversion. The yields recorded were about 81.96 and 86 % at reaction times of 5 and 8 h respectively, whereas for the 10 % KNO₃/FA catalyst, the yield increased from 2 to 5 h, recording a maximum yield of 87.5 % at 5 h. A decline in yield was observed afterwards, remaining nearly constant below 70 % from 12 h onwards. These results show that the reaction equilibrium was reached after 5 h with the 10 %

KNO_3/FA , when the reaction temperature was 160 °C. The study by Kotwal et al. (2009) showed that longer than 8 h reaction time had a negative impact on the oil conversion, which may be partly associated with the transformation of glycerol co-product after an extended period of time causing a loss in methyl ester yield. It was however established in this study that a shorter reaction time of 5 h in comparison to Kotwal's study could enhance the transesterification reactions using the class F -AFA based catalysts.

5.5.5 Influence of reaction temperature

Figure 5.17 shows the influence of reaction temperature on the methyl ester yield from the transesterification reactions carried with the fresh AFA, 5 % KNO_3/FA and 10 % KNO_3/FA prepared catalysts on the sunflower oil sample under reaction time of 5 h, a catalyst amount of 15 g and a methanol: oil ratio of 15:1.

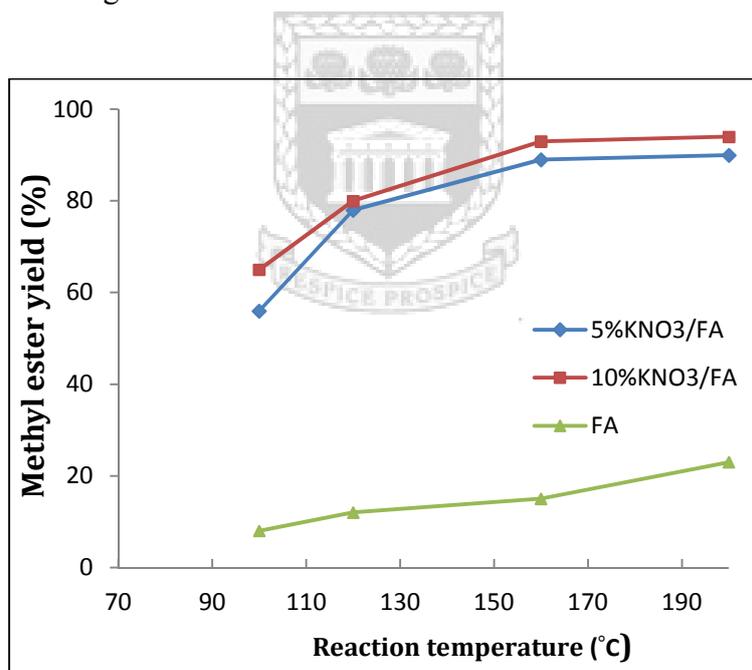


Figure 5.17: Influence of reaction temperature on methyl ester yield under a reaction time of 5 h, catalyst amount 15 g, and methanol: oil ratio 15:1 at a stirrer speed 600 rpm.

The influence of reaction temperature on the yield of the methyl esters was studied using the fresh AFA, 5 % KNO_3/FA and 10 % KNO_3/FA catalyst. It was observed from the results shown in Figure 5.18 that as reaction temperature increased, there was a

corresponding increase in the conversion of the triglycerides to methyl esters, resulting in high methyl ester yields (93.10 % and 89 %) at temperatures of 160 °C for the 10 % KNO₃/FA and 5 % KNO₃/FA respectively. The highest yields (95.1 wt% and 89.34 %) were however observed at a reaction temperature of 200 °C. Published activity data (Kotwal et al., 2009) also shows that an increase in oil conversion corresponds to an increase in temperature. In the case of the fresh Arnot fly ash class F fly ash, a steady and slight increase in methyl ester yield was observed as the temperature increased. This may be attributed to the presence of metal oxides e.g. CaO, and Fe₂O₃ in the fly ash material (XRF analysis). CaO is known to be effective in catalysing transesterification reactions (Refaat, 2011). According to studies carried out by Hofmann, (1986) on the use of Fe₂O₃ on Al₂O₃ as catalyst, the metal oxide is capable of initiating transesterification although ester yields of > 95 % were reported at a higher temperature (210-280 °C). Reports from literature also showed that comparative methyl ester yield values could be obtained during the transesterification of sunflower oil over zeolite X catalyst at lower temperature of 60 °C (Ramos et al., 2008). Studies done by Artkla et al. (2008) reports a high methyl ester yield on transesterification of palm oil with methanol at a temperature range of 60-150 °C in the presence of K₂O loaded on MCM-41 synthesized from rice husk at a temperature of 100 °C.

It is worthy of mention that preliminary transesterification reactions were conducted at the methanol reflux temperature (65 °C) with KOH (see section 4.3.3) but the conversion of the triglyceride into methyl esters did not proceed. The reason for this is unknown, but it is believed that this temperature was too low for the interaction of the weak basic sites and the heavy triglyceride molecules to take place. From extensive literature review, some recent studies on the use of heterogeneous base catalysts have shown reaction temperatures in excess of 200 °C to achieve > 90 % conversion in transesterification reactions of different feedstocks within the timescale of the experiments (Bayense et al., 1996 ; Suppes et al., 2001; Georgogianni et al., 2009). However, if oil is exposed to higher temperature (around 250 °C) the degradation of triglycerides and unsaturated fatty acids leads to the formation of undesirable polymeric products (Kulkarni et al., 2006). It is therefore, concluded from this study that a

temperature of 160 °C required to obtain high yields of methyl ester using the AFA based catalyst is quite acceptable. Further research, however still needs to be carried out to determine the possibility of achieving a lower reaction temperature required for the transesterification reactions.

5.5.6 Effect of water and FFA

The prepared KNO_3/FA catalysts were studied in the heterogeneous transesterification lastly using waste cooking oil with varying amounts of water and FFA in order to examine their effects on the catalytic activity of the 5 % and 10 % KNO_3/FA catalyst for the transesterification reactions. Since water and FFA are usually considered as poisons to both homogeneous acid and base catalysts in traditional biodiesel production processes, the catalytic performance of the fly ash based 5 % KNO_3/FA and 10 % KNO_3/FA catalysts were studied in these scenarios.

Some experiments were carried out with varied percentage of water content from 0.5 % to 2.0 wt% with respect to oil (w.r.t) and a varied percentage of FFA content (0.5 %, 1.0 %, 2.0 %, 2.5 % and 5.0 %) in the reaction mixtures were investigated to determine the effect of water and FFA on the catalytic activity of the KNO_3/FA catalysts. The result of these effects on methyl ester yields under were performed reaction conditions; reaction time of 5 h, catalyst amount of 15 g, methanol: oil ratio of 15:1 and reaction temperature of 160 °C and results are shown in Table 5.7.

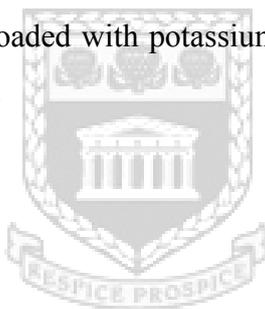
Table 5.7: Effect of water and FFA content on methyl ester yield

Water Content (%)	Methyl ester yield (%)		FFA Content (%)	Methyl ester yield (%)	
	5% KNO ₃ /FA	10% KNO ₃ /FA		5% KNO ₃ /FA	10% KNO ₃ /FA
0	91	94.3	0.5	88	92
0.5 %	75	78	1.0	85	85.3
1.0 %	73.3	65	2.0	45	48.2
1.5 %	50	61.3	2.5	16.2	20.5
2.0 %	32.3	35	5.0	-	-

From the results shown in Table 5.7, with the use of both KNO₃/FA catalysts the addition of water significantly decreased the yield of methyl esters. For example, in the absence of water, a 94.3 % methyl ester yield was obtained while for the oil with 2.0 % water; a 35 % methyl ester yield was obtained with the use of the 10 % KNO₃/FA. This signifies that the methyl ester yield was affected by the presence of water in the waste cooking oil feedstock as the yield decreased steadily with increasing amounts of water content, showing that the KNO₃/FA catalysts possessed a low tolerance to water present in the waste cooking oil feedstock. Water content in oil is a major concern which adversely affects the yield of biodiesel. This occurrence is a major disadvantage as low cost feedstock e.g. waste cooking oils (except if moisture is eliminated) cannot be used to produce biodiesel with the 5 % and 10 % KNO₃/FA catalyst. This observation can be best explained by two step processes; hydrolysis and esterification which hinders the favourable yield of esters (see section 2. 3.4)

In the study, it was also found that the FFA content in the waste cooking oil sample (Table 5.7) up to an amount of 1.0 % offered FAME yields of 85 and 85.3 % when the 5 % and 10 % KNO₃/FA catalysts were used respectively. However a further increase in

FFA above 1 % resulted in a decrease in FAME yield in both cases. For the KOH catalyzed process (section 4.3.4.4), FFA content showed a considerable negative effect on the FAME yield. It is a known fact that the FFA content in oils is a major nuisance in biodiesel production due to the side reaction between FFA and base catalysts to produce saponified products. Thus, FFA in oil feedstock is usually limited to 0.5 % or less in traditional processes (Freedman et al., 1984; Maa et al., 1998) however for the 10 % KNO_3/FA catalyst, its use can be extended in a feedstock with a FFA content of up to 1.0 %, allowing the use of this catalyst for some high FFA content feed stocks. The remarkable tolerance to a high content of FFA poses a great advantage for the use of the 10 % KNO_3/FA catalyst prepared from South African Arnot class F fly ash. This phenomenon presents a clear difference between this study and Kotwal's, as catalytic investigations using their fly ash based catalyst with waste cooking oil or sunflower oil with a high FFA content was not done. In this study, Class F- AFA has proven its use as an effective base catalyst when loaded with potassium for use in the transesterification reactions of refined and waste oil.



5.5.7 Effect of mixing

Methanol and oil are known to be immiscible, as the reactants initially form a three-phase system: oil/methanol/catalyst. The difference in properties between methanol and triglycerides initially creates a heterogeneous biphasic system causing a mass transfer limitation. This makes methanolysis reactions diffusion-controlled, as poor diffusion between the phase's results in a slow reaction rate, while a faster stirring speed causes better contact among the reactants and solid catalyst resulting in an increase of the reaction rate (Noureddini and Zhu, 1997).

The transesterification reactions were thus carried out at two randomly chosen stirring speeds (300 and 600 rpm). At a lower stirring speed, oil conversion reached 46.5 % after 5 h of reaction, whereas at 600 rpm the oil conversion reached 87.4% at the same reaction conditions (reaction time of 5 h, catalyst amount of 15 g, methanol: oil ratio of 15:1 and reaction temperature of 160 °C). This showed that an efficient mixing of the

reagents was essential to reach desired conversions rate. To overcome this mass transfer limitation, good mixing is essential (Zhou and Boocock, 2006) as insufficient mixing would not allow the reactions to proceed as required.

5.5.8 Catalyst Stability and Reusability test

In order to assess the stability of the fly ash based catalyst (10 % KNO_3/FA) the re-use of the prepared catalyst was investigated in the production of biodiesel from sunflower oil to its methyl ester via the transesterification reaction. The reactions were repeated three times under the same reaction conditions described previously (section 3.5). After each cycle of use in the transesterification reactions, the catalyst was recovered by filtration before re-use. The relative activity of the catalyst employed for the first batch was defined as 100 %. Figure 5.18 describes the de-activity profile of the catalytic runs for the 10 % KNO_3/FA .

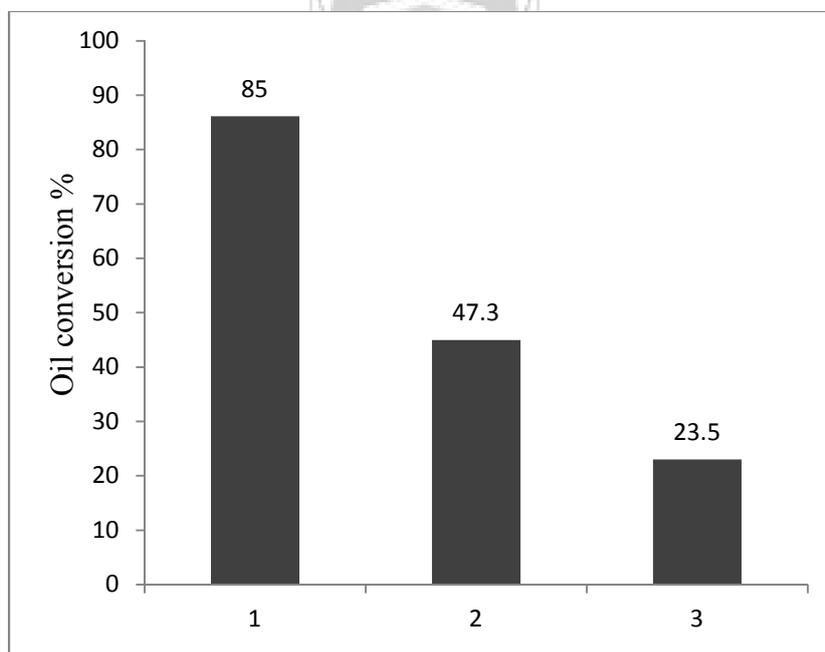


Figure 5.18: The de-activation profile of 10 % KNO_3/FA catalyst after reuse.

Figure 5.18 describes the de-activation profile of the catalyst upon reuse, where 1, 2 and 3 denotes the number of runs. Sunflower oil conversion values of 85, 47.34 and 23.56 %

were observed respectively. A decline in oil conversion was observed after each reuse of the catalyst and could be attributed to the leaching and loss of active species from the composite catalyst into the product in the course of the reaction. The product was removed after each run hence any leached KNO_3 would have been lost.

5.5.9 Biodiesel Characterisation

The quality of the final biodiesel was characterised. The product was obtained under the best optimised conditions of the transesterification reactions (methanol to oil ratio of 15:1, reaction temperature of 160 °C, catalyst amount of 15 g and reaction time of 5 h at a stirrer speed of 600 rpm) as obtained using the heterogeneous Arnot fly ash 10 % KNO_3 /FA catalyst. The physical properties and chemical composition of the methyl ester samples were tested and analysed to determine their characteristics and compared with standard specifications. The results are given in Table 5.8. A comparison can be made with biodiesel fuel standards; SANS 1935:2003, ASTM D6751 & EN 14103 (refer to appendix). The analysis of the biodiesel product was performed by a certified laboratory using certified analytical methodologies.

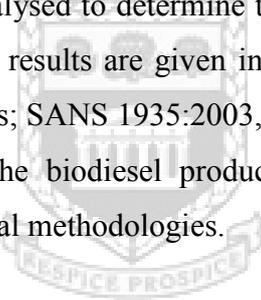


Table 5.8: Properties of methyl esters produced from sunflower oil via the use of 10 % KNO₃/FA catalyst under the optimum reaction conditions (molar ratio of 15:1, 160 °C, 15 g catalyst and reaction time of 5 h)

Test parameter	Unit	Value range	SANS 1935:2003	
			Test method	Product
Appearance			observation	clear
Density (15 °C)	kg m ⁻¹	860-900	EN ISO 3675	883
Viscosity	(mPa at 40°C)	1.9–6.0	ASTM D 445	4.08
Iodine value	I ₂ g/100 g	140 max	ASTM D 5768	132
Acid value	mg KOH/g	0.5 max	ASTM D 974	0.55
Water content	ppm	0.05 max	EN ISO 12937	<0.05
Cetane number	nil	51 min	EN D 345	52
Total ester	mass %	96.5 min	EN 14103	94.3
Total glycerol	mass %	0.25 max	ASTM 6584	0.02
Free glycerol	mass %	0.02 max	AOCS Ca14-56	0.13
Mono-glyceride	mass %	0.8 max	AOCS Ca14-56	0.01
Di-glyceride	mass %	0.2 max	ASTM D 6584	0.5
Triglyceride	mass %	0.2 max	ASTM D 6584	0.25
Methanol content	mass %	0.2 max	EN 14110	0.23
Flash point	°C (open cup)	120 min	EN ISO 3679	164
Total of K	mg/kg	5.0max	EN 14538	4.52

*Notes: this table gives the certified quality of the methyl ester product as analyzed by an authorized analysis organization. The analytical methods used are specified under SANS: South African Standard for biodiesel and testing method. EN: European Standard for testing method. ISO: International standard. ASTM: American standard tests and measurements. AOCS: American oil chemical society

Only the major properties of the testing results showing the properties of the methyl ester obtained in this study will be discussed (Table 5.8).

The sunflower oil sample exhibited an initial high viscosity value of 29.0 mPas (table 4.1) before transesterification and after transesterification the dynamic viscosity of the methyl ester product sampled recorded a dynamic viscosity value of 4.08 mPas, which was in the range of the standard ASTM D6751 for biodiesel. Analyses of iodine content

revealed an iodine value of 132 g/100 g which was also within specification while the maximum acid value obtained was 0.55 mg KOH/g. The total ester content of 94.3 % was recorded and was just below the specified value. The methanol content of the tested sample was 0.23 %; this value was just outside the specifications of a maximum of 0.2. The low methanol content achieved was pleasant considering the amount of methanol consumed in the transesterification reactions. The excess alcohol was easily removed from the methyl ester phase after transesterification using a rotary evaporator during the washing step. The total potassium content of the methyl ester product tested had a value of 4.53 mg/kg which was within specification. The presence of high potassium content in biodiesel induces metal corrosion as well as saponification of the methyl esters phase. Although this value was on the high side, it still met the EN standard which specifies a maximum value of 5 mg/kg.

5.5.10 Summary (Arnot fly ash based catalysts)

South African Class F - AFA loaded with KNO_3 was used as a heterogeneous solid-base catalyst in the transesterification of sunflower oil and waste cooking oil to methyl esters. The catalysts with different loadings of KNO_3 (5-25 %) were prepared by a wet impregnation method followed by calcination at 500 °C. A number of characterisations were carried out to determine the physical and chemical composition of the prepared fly ash based catalysts. The elemental chemical composition of the South African Class F, AFA contains relatively high concentrations of SiO_2 , Al_2O_3 and CaO . The composition of SiO_2 50.91 %, Al_2O_3 30.91 %, Na_2O 0.10 %, CaO 6.2%, Fe_2O_3 3.46 %, MgO 1.48 %, TiO_2 1.65 %, MnO 0.02 %, K_2O 0.60 % and P_2O_5 0.56 % was completely different from the fly ash collected from India especially with respect to the calcium oxide (CaO) content. The South African Class F- AFA gave a value of 6.2 % for CaO in comparison to a value of 1.72 % given for the CaO content present in the fly ash collected from India. This observation was considered to account for the relatively higher basic strength exhibited to enhance the catalytic activity of the AFA based catalysts in the transesterification reactions conducted in this study.

The results from the XRD showed that the intensity of KNO_3 peaks increased with the increase in amount of loading suggesting that good dispersion of KNO_3 occurs up to 10 % (wt/wt) loading. The N_2 -BET revealed surface area values of 2.78, 1.17, and 0.55 for the AFA, 5 and 10 wt% KNO_3/FA catalysts respectively. The presence of occluded pores within the fly ash based catalyst as a result of the impregnation of K species is suggested to be responsible for the decrease in surface area values. The catalytic activities of the prepared heterogeneous base catalysts show a striking correlation with their basic properties and transformation determined through the TPD and XRD respectively, as was observed from the influence of % loading of active component (KNO_3) on the AFA support upon the conversion of sunflower oil to methyl esters. The decomposition products of the loaded K_2O species in the composite were probably responsible for the activity of the basic sites observed. K_2O derived from KNO_3 might be an essential component in the catalyst for its efficiency. It is interesting also to note that at zero loading; the AFA by itself could catalyse the transesterification reaction without additional modification even though only a low conversion was recorded.

The results of the study were further extended to optimize the reaction parameters viz; catalyst amount (g), reaction time, methanol to oil ratio and reaction temperature using the 5 and 10 wt% KNO_3/FA catalysts. The best reaction conditions were established to be as follows; ratio of methanol to oil of 15:1, 15 g of catalyst, reaction temperature of $160\text{ }^\circ\text{C}$, reaction time of 5 h at a stirring speed of 600 rpm. The result obtained in this study demonstrates a yield of 89 % and 93.10 % for both the 5 wt % and 10 wt % KNO_3/FA catalysts respectively at reduced reaction time of 5 h and a lower temperature of $160\text{ }^\circ\text{C}$ as opposed to reports in literature. The catalytic activity of the prepared catalysts for conversion of waste cooking oil (to reduce the cost of raw material) with controlled water and FFA content was investigated in order to determine their effect on the transesterification reactions. Results show that the 10 % KNO_3/FA catalyst can be applied as a catalyst for a feedstock with a FFA content of up to 1.0 %. The high tolerance of the 10 % KNO_3/FA to a high content of FFA in the low quality waste cooking oil feedstock is a great advantage for the use of this catalyst. It was found that

the methyl ester yield was affected by the content of water in the waste cooking oil as the yield decreased steadily with an increase in the amount of water in the feedstock oil. This showed that the catalysts possessed a low tolerance to water. Although the 10 % KNO_3/FA catalyst showed a considerable initial activity for the biodiesel reaction, a decrease in catalytic activity was observed when the recovered catalyst was reused. South African AFA has thus demonstrated to be useful as a catalytic support and found effective as a solid base catalyst when impregnated with potassium for the transesterification of refined and waste oil with methanol. The catalyst prepared with 10 % KNO_3 loading on the AFA and after calcination was found to be the optimum catalyst, which gave the highest basicity and the best catalytic activity for the transesterification reactions conducted in this study. Finally, the overall properties of the methyl ester product made at the optimised conditions of methanol: oil molar ratio of 15:1, temp. of 160 °C, catalyst amount 15 g and reaction time of 5 h satisfy the SANS 1935:2003 and European Committee Standard (EN14214) with the exception of the sulphated ash and potassium content.

5.6 Transesterification reactions: zeolite catalysts

The catalytic activities of the commercial Na-X, AFA-zeolite Na-X (FA/Na-X) and the K^+ exchanged AFA-zeolite Na-X (FA/K-X) catalysts were studied in the transesterification reactions on sunflower oil with methanol. The properties of the sunflower oil include; acid value -0.89, density @ 15 °C -0.92 kg/l, and kinematic viscosity @ 15°C -31.3. The reactions were conducted at two different reaction conditions. Firstly, a reaction time of 8 h, methanol oil ratio 6:1, and temp of 65 °C and secondly, a reaction time of 24 h, methanol oil ratio 6:1, and 65 °C. The results are presented in Figures 5.19.

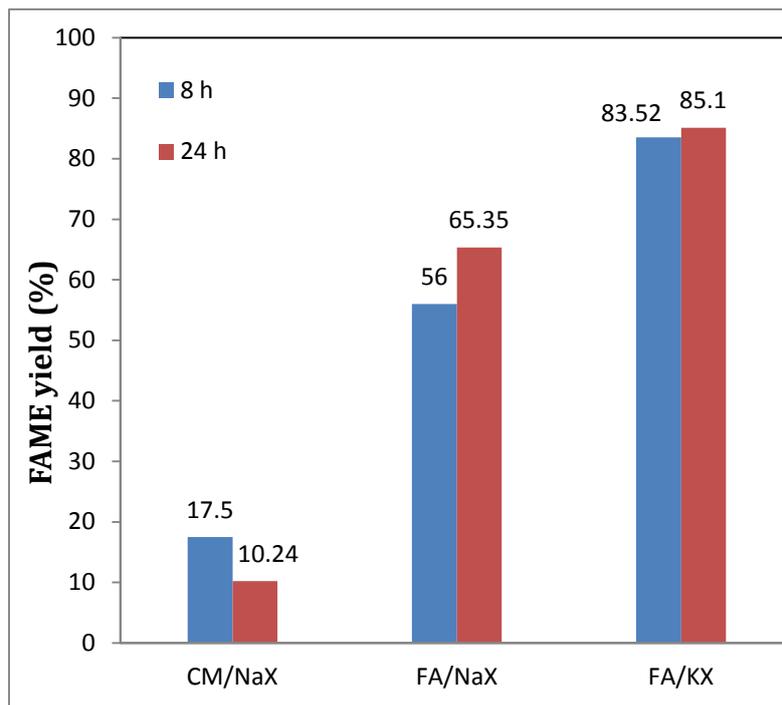


Figure 5.19: Catalytic activity of the zeolite catalysts under reaction conditions of 8 and 24 h, methanol oil ratio 6:1, catalyst (3 % wt/wt) and temperature of 65 °C.

The catalytic activities of all the catalysts used in the transesterification reactions is shown in Figure 5.19 and reveals ester yields of 17.5, 56 and 83.53 % for the CM /Na-X, FA/Na-X and FA/K-X zeolite catalysts were obtained respectively at a reaction time of 8 h. At a reaction time of 24 h, while other reaction conditions remained constant, ester yields of 10.24, 65.35 and 85.51 % were obtained with the use of the CM /Na-X, FA/Na-X and FA/K-X zeolite catalysts respectively. The results show slightly higher methyl ester yields at a reaction time of 24 h with the exception of the commercial zeolite (CM /Na-X) recording a lower FAME value of 10.2 %. The catalytic activity of the ion exchanged AFA-zeolite FA/K-X catalyst was clearly higher than the commercial CM /NaX and the AFA- zeolite FA/Na-X catalysts for both contact times (8 and 24 h). The basic strength of an alkali ion exchanged zeolite which increased correspondingly with the electropositive nature of the exchanged cation can be attributed to this observation. It has been shown that the conversion to methyl ester over commercial Na-X faujasite zeolite that was ion exchanged with more electropositive cations was higher than the parent zeolite (Xie et al., 2007; Suppes et al., 2004; Borges et al., 2011).

The transesterification activities of the AFA- zeolite catalysts FA/Na-X and FA/K- also followed the order of basic strength illustrating a correlation between the intermediate electro negativity of both catalysts with the yield of the methyl esters. The transesterification reaction based on the ER mechanism to explain this phenomenon can be perused in section 2.7.2.

According to reports in literature, the use of different types of faujasite zeolite catalysts used in transesterification reactions have reported low conversions (Suppes et al., 2004; Brito et al., 2007; Borges et al., 2011) in comparison to the value of reported in this work. Different zeolite forms for catalysis of transesterification reactions at different reaction conditions have also been reported (Endalew et al., 2011). The finding in this study presents superior activity to those previously results reported. The relatively higher FAME yields derived from the AFA zeolite Na-X in this study can be related to the AFA raw material used in the zeolite synthesis. The elemental composition of the Class F –AFA as previously mentioned was shown to be rich in SiO₂ and Al₂O₃ content and the high surface area (320.7 m²/g) observed for the zeolite made from this AFA feedstock from South Africa (section 5.4.4) might have contributed to this phenomenon.

Brogues et al., (2011) recently reported a 80.8 % FAME yield from a potassium acetate loaded zeolite Na-X at high reaction temperature and methanol amount while Noiroj et al. (2009) and Xie et al. (2007) also report the use of KOH/NaY and KOH-promoted Na-X zeolite catalysts to achieve a biodiesel yield of 91 % and 85 % conversion to methyl esters in 8 h at 66 °C respectively although at higher methanol: oil ratios of 10:1 whereas in this study, a methanol: oil ratio of 6: 1 was used and found sufficient to propel the transesterification reaction. If the methanol: oil ratio is high, a surplus of the methanol molecules would cause a flooding of available sites (Shu et al., 2009). In other transesterification studies conducted with basic zeolites, the incorporation of occluded NaOx species in zeolite-X significantly increased the basic strength and concentration, which ultimately enhanced the transesterification activity and increased the yield of methyl ester from soybean oil when NaOx/NaX replaced K–X as a catalyst. Another report required a long operation time (24 h) and a reaction temperature at 120 °C, obtained at a methanol/oil molar ratio of 6:1, which is the lowest recorded for

heterogeneous biodiesel synthesis (Di Serio et al., 2009). To the best of our knowledge, no report of a fly ash derived zeolite Na-X or K-X used as a catalyst in biodiesel synthesis has been found in literature. Reports in literature have however shown high FAME yields from sunflower oil using commercial zeolite based catalysts (Brigo et al., 2011)

The overall results indicated that a FAME yield of 83.53 and 85.5 % could be obtained from the transesterification reaction of sunflower oil at 8 and 24 h respectively using the ion exchanged Arnot fly ash zeolite Na-X catalyst (FA/K-X) at a reaction temperature of 65 °C. The reaction temperature employed in this study was found suitable for the transesterification reactions (Ramos et al., 2008). The activity of the FA/K-X catalyst give a slightly lower FAME yield of 85.5 % when compared to the FAME yield of 93.7 % obtained from the homogeneous KOH catalyst at similar reaction conditions optimised under the homogeneous system (section 4.3.4).

5.6.3 Summary of zeolite catalysts

Zeolite Na-X synthesized from South African Class F Arnot fly ash was ion exchanged with potassium using potassium acetate as precursor to obtain a new FA/K-X zeolite catalyst. The inclusion of potassium into the pore cavity of the AFA- zeolite Na-X through ion exchange was adopted to increase the basicity of the zeolite to promote the transesterification reactions. Different techniques including XRD, FTIR, SEM, and BET were employed in the characterisation of the AFA based zeolites. XRD results for the as received zeolite synthesized from AFA showed typical diffraction peaks of zeolites Na-X compared with the XRD patterns of the commercial zeolite Na-X (CM/Na-X). SEM images of the FA /Na-X zeolite showed the unique morphology with nano platelets which is different from the well known pyramidal octahedral shaped crystals as observed in the commercial zeolite Na-X. The morphology of the FA /K-X zeolite did not show any significant difference after K⁺ ion exchange. The AFA-zeolite Na-X (FA /NaX) exhibited a high surface area and pore volume of 320.7 m²/g and 1.40 cm³/g respectively. On the other hand, the ion exchanged FA/K-X had a lower surface area of

257 m²/g, probably as a result of the relative bigger size of the K⁺ cation compared to Na⁺ indicating that the ion exchange process had a pore blocking effect. Comparing the surface area value of the AFA-zeolite Na-X that was used in this study with that reported in literature, a higher surface area is reported in this work. This enhanced surface area improved the catalytic efficiency during the transesterification studies. The transesterification activities of the AFA -zeolite catalysts (FA/Na-X and FA/K-X) were also investigated and were found to be active in the transesterification reactions of sunflower oil and methanol to produce fatty acid methyl esters (biodiesel). Furthermore, the FA/K-X presented higher catalytic activity, than the Na form, FA/Na-X mostly as a result of the anchoring of the alkali metal (K) through ion exchange inside the zeolite pores, resulting in a higher basicity and conversion of methyl esters.

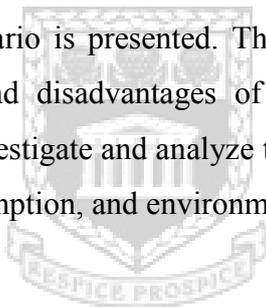
The overall results for the heterogeneous system indicated that a FAME yield of 83.53 and 85.5 % could be obtained over a new heterogeneous catalyst FA/K-X for transesterification reactions using sunflower oil as feedstock at reaction times of 8 and 24 h respectively at reaction conditions of methanol: oil ratio of 6:1, 3 % wt of catalyst and at a reaction temperature of 65 °C. These reaction conditions were chosen based on a review of literature. To the best of our knowledge, the use of a fly ash derived zeolite K-X and more specifically, South African Class F Arnot fly ash based zeolite used as a catalyst in biodiesel synthesis is hence firstly reported. These results show an improvement on the results obtained in the investigations conducted on the use of the AFA both as a catalyst and a catalyst support for KNO₃ since the ester products were obtained at a mild temperature of 65° C and at a comparative reaction time of 8 h. These applied operation conditions could be exploited as this could go a long way in reducing biodiesel production operating costs. A comparison of the different catalytic systems involved in the transesterification reactions conducted in this study and the benefits of one over the other will be discussed in the next chapter.

Chapter 6

A Comparative Study of the Transesterification Catalytic Processes

6. Introduction

This chapter presents a comparison of the transesterification reaction studies via the different catalytic processes involved in this study. It presents two study cases; the homogeneous and heterogeneous catalytic processes. A comparative study is carried out for the different catalytic processes involved in biodiesel production in this study and a technical analysis for each scenario is presented. The main differences between each process with the advantages and disadvantages of each of the processes are also presented. The objective is to investigate and analyze the different scenarios, to evaluate productivity, raw material consumption, and environmental impacts in each process.



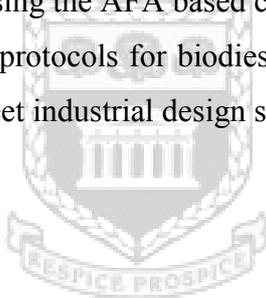
6.1 Overview

Biodiesel has become an attractive diesel fuel substitute due to its environmental benefits since it can be made from renewable resources. However, the high costs surrounding biodiesel production remains a main problem in making it competitive in the fuel market either as a blend or as a neat fuel. More than 80 % of the production cost is associated with the feedstock itself and consequently, efforts are focused on developing technologies capable of using lower-cost feedstocks, such as recycled/waste cooking oils (chapter 4). The main issue however with waste oils is the high level of free fatty acids found in the recycled materials.

The conventional technology employs sodium or potassium mixed in methanol to give the respective methoxide as a homogeneous base catalyst for the transesterification reaction in this study illustrates the drawbacks in working with feedstocks such as waste cooking oil that contains high levels of free fatty acids. On the other hand, in this study, research performed using heterogeneous catalysts based on fly ash feedstock is reported in chapter 5. These catalysts allow the use of vegetable oils that will permit biodiesel production at lower investment costs and will require less downstream process equipment since this step has been eliminated.

6.2 Study Cases

Two different processes were studied: 1) homogeneous alkaline catalyst using KOH and 2) heterogeneous basic catalyst using the AFA based catalyst (KNO_3/FA) and the AFA - zeolite FA/K-X catalyst. All the protocols for biodiesel production were proposed as a continuous process in order to meet industrial design scale of oil processing.



6.2.1 Study Case 1

In first case a base catalyzed process was studied. The flow diagram of the process is shown in Fig. 6.1. In this mechanically stirring process, the base catalyst (KOH) and the alcohol (methanol) were pre-mixed in a “catalysts preparation reactor” to be used in both transesterification stages later on. The oil and the catalyst mix were then fed to the first transesterification stage simultaneously. After the reaction, the product stream was passed through a decanter to separate the glycerol phase, which was later fed to a neutralizer reactor, from the oil phase which was fed to the second transesterification stage. After the second reactor, the product stream was passed through a column to separate the oils from the glycerol phase. The oil phase was washed with water to remove the catalyst and small amount of undesired compounds. The separation of water and FAME was done in a separating column and the excess alcohol was removed. After

this separation step, the FAME stream was dewatered by passing the stream through a distillation column.

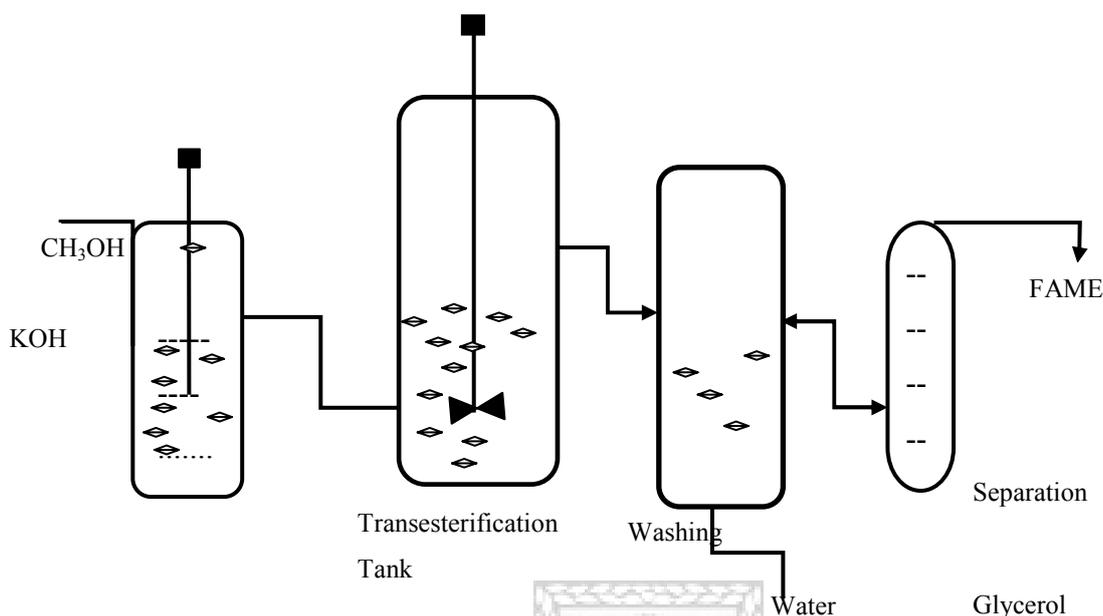


Figure 6.1: Case 1 process flow diagram



6.2.2 Study Case 2a (KNO_3/FA catalyst)

In the second case, a heterogeneous process scenario using KNO_3/FA as catalyst was simulated. A flow sheet of this process is shown in Fig. 6.2. In this process, the waste cooking oil was fed into the first transesterification reactor simultaneously with methanol and mechanically stirred. The reaction was carried out at a higher temperature ($160\text{ }^\circ\text{C}$) than the homogeneous case 1 technology and in consequence, at a higher pressure. After the first mixing step and the transesterification tank, the FAME product stream with methanol was separated from the glycerol. The biodiesel stream leaving the transesterification tank was fed to a separation tank to purify the biodiesel from the glycerol and other impurities. The biodiesel produced will exit from the bottom of the equipment. The methanol from the separation tank was recycled to the overall process to reduce the cost of alcohol used in the process.

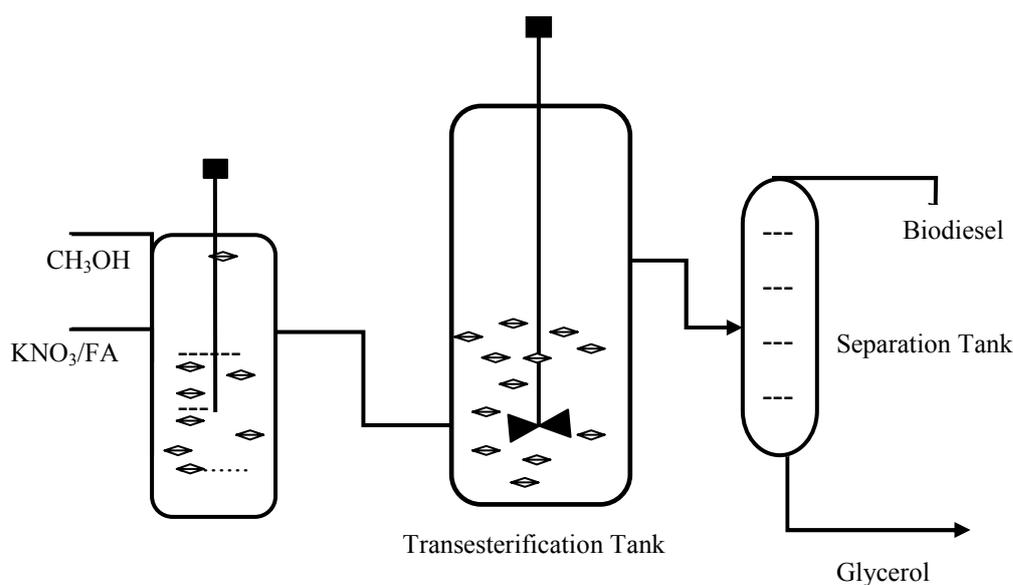


Figure 6.2: Case 2 process flow diagram

6.2.3 Study Case 2b (FA/K-X catalyst)

In the case scenario where the AFA zeolite catalyst FA/K-X was used, the flow sheet of the process followed is similar to Fig. 6.2 and the processes described in the section 6.2.2. The main difference between the two different heterogeneous catalysed processes was the reaction temperature at which the reaction was conducted. Using the FA/K-X catalyst in this case did not require elevated temperatures and pressure as the reactions were conducted at 65 °C at atmospheric pressure. It also did not require too much an excess of methanol as in the case of the Arnot fly ash based KNO_3/FA catalyst. These lower energy requirements presented the advantage of the biodiesel production process catalysed by the AFA based zeolite catalysts.

6.3 Results and discussion

This section presents the results and discussion of the comparison of the different process scenarios with the waste feedstock oil samples used and the FFA content.

Table 6.1 gives the details of the technical aspects of each scenario and a comparative analysis between them is then performed.

Table 6.1: Main technical aspects of the different catalytic processes

	Case 1	Case 2a	Case 2b
Operating temperature (°C)	60	160	65
Feed Streams			
Feedstock (waste oil) (g)	100	100	100
FFA content %	1	1	0.86
Methanol (mls)	21.7	145	20
Catalyst (g)	1	15	3
Outcoming streams (g)			
Biodiesel (conversion %)	97	98	98
Total glycerol performance	0.20	0.17	0.15

Table 6.1 compares process parameters and conversion achieved for each technology applied. All the reactions for each case were carried out in a batch mechanically stirred reactor. The reaction temperature was set at 60 °C in case 1 when KOH was used as a catalyst in the homogenous scenario. In the heterogeneous catalysed reactions however (2a), the reaction temperature was increased to 160 °C when the FA/KNO₃ catalyst was used, while in the case of the AFA -zeolite zeolite K-X catalyst (2b), the reaction temperature of 65 °C was able to achieve an adequate conversion of triglycerides into biodiesel. The amount of methanol and catalyst added, varied in all cases.

Both the homogeneous and the heterogeneous processes proved to be suitable possibilities for biodiesel production but the excess methanol needed to propel the AFA based catalysed reactions in case 2a makes the process quite undesirable. In the outcoming biodiesel stream in all cases, the FAME (biodiesel) is over 96 % of the stream concentration (w/w). For the processes described above, all cases also satisfied the total glycerol in the biodiesel. All process scenarios have final conversions of triglycerides to biodiesel of over 96.5 %.

6.4 Summary

From the two technologies applied in converting oils with a relative amount of about 1 % FFA, both homogeneous and the heterogeneous process technologies have proved suitable for biodiesel production.

The homogeneous process offers mild reaction conditions to obtain the biodiesel product but since the number of process units involved, due to the requirements for purification of the out coming stream, and effective disposal of the waste water effluent as shown in the flow process diagram would induce additional costs of production which is a limitation to the use of this process.

The heterogeneous alternative involving the AFA based catalysts does not present an environmentally benign process due to excessive reaction conditions involved, especially with regard to methanol requirement and catalyst amount needed for the production of biodiesel.

The use of the AFA based potassium exchanged zeolite catalysts however, appears to offer an environmentally benign process because of the moderate reaction conditions and the lower amount of methanol required in obtaining favourable biodiesel yields. Putting into consideration that the zeolite catalyst materials used in this study are derived from AFA, it thus proffers a safe application for the utilisation of waste coal fly ash. This added advantage would direct a possible future technology for biodiesel catalysis.

Chapter 7

Conclusions and Recommendations

7. Introduction

This chapter takes as its starting point an overview of the major issues addressed in the previous chapters and to what extent the stated objectives were achieved and research questions answered. It is then followed by a summary of the main contributions made and major findings. Considerations of possible directions and recommendations for further work are also given.

7.1 Overview

The aims and objectives of this study were to provide detailed insight into the optimisation of biodiesel production via different process intensification technologies such as the mechanical stirring, ultrasound assisted mixing and jet-loop mixing on a large scale in the conventional homogeneous catalysis using KOH as catalyst. The optimisation study determined the effects of the different reaction parameters on the yield and conversion rates of the different oil feedstock to their corresponding methyl esters. The methyl esters produced with each of the oil types under the different process conditions were characterised to determine the fuel properties of the final biodiesel product.

In addition to these, South African Class F Arnot fly ash loaded with KNO_3 and South African Class F Arnot fly ash based zeolite Na-X as well as K-X catalysts prepared for use in the transesterification of sunflower oil also formed a major part in this study. The use of these solid catalysts aimed to address the drawbacks of the conventional homogeneous base catalysis using NaOH or KOH. To achieve these main objectives, different experimental approaches were employed. The results obtained from the

different experimental tests, characterisations and analyses were integrated in order to give a conclusive statement on the findings in this study.

The study also addressed the research questions and an overview of findings is firstly presented.

- The optimum reaction parameters to process the fresh and used oil samples to biodiesel of high quality were determined for both conventional and ultrasound reactor systems.
- The optimum parameters for biodiesel production using the homogeneous and heterogeneous transesterification catalytic reactions systems were obtained by varying various reaction parameters in a batch process system.
- A continuous new scale up processes (ultrasound and jet loop reactor) improved FAME yield and fuel quality of used cooking oil used as feedstock in biodiesel production.
- The use of the scale up processes (ultrasound and jet loop reactor) resulted in a significant reduction of methanol and catalyst amount coupled with the savings on reaction time. Consequently, a significant improvement in the FAME yield and reduction in the optimum reaction conditions utilised as when compared to the mechanically agitated process system.
- South African class F Arnot fly ash could be used as a support in the preparation of a heterogeneous catalyst containing KNO_3 that could result in a favourable yield of methyl esters from sunflower oil and waste cooking oil with an easier refining of the produced biodiesel. It was envisaged that the use of this cheap catalyst will present a process that is environmentally benign for conversion of waste cooking oil.
- As received zeolite NaX synthesised from South African Arnot Class F fly ash and ion exchanged with an alkali metal (K) could be used as a solid zeolite catalyst in the transesterification reactions of vegetable oils with methanol.
- The biodiesel produced from these homogeneous and heterogeneous transesterification catalytic reactions involving the Arnot fly ash based catalyst

and process intensification systems were shown to meet standard quality specifications for FAME.

7.2 Summary of Findings

This section sets out the major findings resulting from this research.

7.2.1 Transesterification reactions: Homogeneous Catalysis

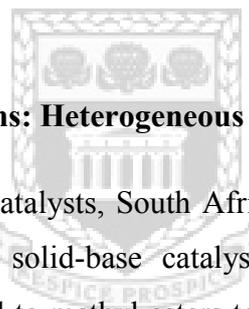
This study has shown that reaction parameters; such as the quantity of catalyst, the amount of methanol, the reaction temperature and the reaction time are the main factors affecting the production and yield of methyl esters significantly. The optimum values of these parameters for achieving maximum conversion of oil to esters also depended on the chemical and physical properties of the oils feedstock.

The following findings were also drawn from the study; (i) addition of excess catalyst causes more triglycerides' participation in the saponification reaction leading to a marked reduction in the ester yield; (ii) the biodiesel production process is incomplete when the methanol to oil ratio is less than the optimum value of 6 (iii) operating beyond the optimum value of methanol to oil, the ester yield would not be increased but would result in additional cost for methanol recovery; (iv) higher reaction temperatures such as decreased the viscosities of the oils and resulted in an increased rate of transesterification and shortening of the reaction time. However, when the temperature increased beyond the optimum level of 60 °C, it induced a negative impact on the ester yield due to acceleration of the saponification of triglyceride(v) sufficient reaction time was necessary to ensure complete conversion of triglycerides into esters. However, excess reaction time did not promote the conversion but favoured the reverse reaction of transesterification causing in a reduction in the ester yield.

This study also demonstrated that the ultrasound-assisted transesterification reaction of waste cooking oil and methanol with potassium hydroxide was very efficient in maximizing the FAME yield. The maximum FAME yield when waste cooking oil was

used as feedstock and ultrasound mixing was applied, the conversion was 96.8 % with optimum conditions of methanol/oil molar ratio of 6:1, 0.75 wt% potassium hydroxide catalyst in 100 ml of oil and 30 min contact time.

When applying the newly developed jet loop process reactor at a reaction temperature of 30 °C, it was found that significant processing gains were obtained and the optimum reaction conditions of 25 min contact time, methanol: oil ratio 4:1 and a catalyst amount of 0.5 wt% (wt /wt) in 100 mls of oil. The new processing approach using the jet loop reactor allowed the added advantage of an efficient and speedy separation of the methyl ester and glycerol phase (within 30 min). Finally, the properties of the products of the methyl esters obtained from the ultrasound-assisted transesterification reactions and the newly developed jet loop process reactor met the South African Standard (SANS 1935:2004) which is almost the same as EN14214 and ASTM D6751 standards.



7.2.2 Transesterification reactions: Heterogeneous catalysis

In preparation of heterogeneous catalysts, South African Class F Arnot fly ash loaded with potassium was used as a solid-base catalyst to do baseline studies in the transesterification of sunflower oil to methyl esters to make a meaningful utilization of waste coal fly ash in biodiesel catalysis. The Arnot fly ash based catalysts with different loadings of KNO_3 (5-25 %) were prepared by according to methods in literature. The 10 % KNO_3/FA was found to be the optimum fly ash catalyst, which gave the highest basicity and the best catalytic activity for the transesterification reactions conducted in the study. Further optimisation studies were extended to reaction parameters viz; catalyst amount used (g), reaction time, molar ratio of methanol to oil and reaction temperature on methyl ester yield using the 5 and 10 wt% KNO_3/FA catalysts. The results showed that the 10 wt% KNO_3/FA recorded a higher methyl ester yield (87.5%) at the optimum reaction conditions. The optimum reaction conditions were established as being; ratio of methanol to oil of 15:1, 15 g of catalyst, reaction temperature 160 °C, reaction time 5 h at a stirring speed of 600 rpm. The catalytic activity of the South African Class F Arnot fly ash / KNO_3 catalysts for conversion of waste cooking oil (to

reduce the cost of raw material) with controlled water and FFA content was also investigated. Results show that the 10 % KNO_3/FA catalyst can be applied as a catalyst for a feedstock with a FFA content of up to 1.0 %. The high tolerance of the 10 % KNO_3/FA to a high content of FFA in the low quality waste cooking oil feedstock is a great advantage for the use of this catalyst. The methyl ester product obtained from the transesterification reactions were tested and the overall properties of the methyl ester product were found to satisfy the SANS 1935:2003 and European Committee Standard (EN14214) with the exception of the sulphated ash and potassium content.

On the other hand, South African class F Arnot fly ash was converted to a zeolite; FA/Na-X material. The as-received zeolite was then ion exchanged with potassium to give the FA/KX. These catalyst materials were also utilized in the transesterification reactions. To the best of our knowledge, no report of a AFA derived zeolite Na-X or AFA derived zeolite K-X used as a catalysts in biodiesel synthesis has been found in literature. The inclusion of potassium into the pore cavity of the zeolite-NaX was adopted to increase its basicity. The high surface area observed and reported for both the AFA-zeolite Na-X and AFA -zeolite FA /KX presented an advantage for use as catalysts in this study. The use of the zeolite FA /KX catalyst was desirable in promoting the conversion of triglycerides into methyl esters during the transesterification reactions in the biodiesel synthesis as it was presumed to anchor and facilitate the catalytic reactions of the large triglyceride molecules. Overall results indicated that a FAME yield of 83.53 and 85.5 % could be obtained from the transesterification reaction of vegetable oil at 8 and 24 h respectively using the ion exchanged Arnot fly ash zeolite NaX catalyst (FA/KX) at a reaction temperature of 65 °C, catalyst amount 3 % (wt/wt) and methanol: oil ratio 6:1. The findings showed significant improvement on reports in literature as this catalyst can be produced cheaply. The ion exchanged zeolite FA/KX catalyst could resolve the limitations of the base-catalyzed process with respect to easy separation, recovery and regeneration of the catalyst material. The advantages that the ion exchanged zeolite FA/KX offers in the heterogeneous catalysis of biodiesel production could allow for the large scale industrial utilisation of waste coal fly ash converted into zeolite for biodiesel synthesis.

7.2.3 A Comparative study of the different catalytic processes

A comparison of the transesterification reaction studies via the different catalytic processes (homogeneous and heterogeneous) involved in the study was carried out. Both process technologies involved in the catalytic processes were found suitable for the production of biodiesel considering the various oil feedstock investigated with negligible or relatively low amount of FFA. The activity of the FA/KX catalyst gave a slightly lower yield (83 %) when compared to the yield obtained from the homogeneous KOH catalyst (98.32 %) at similar reaction conditions of methanol/oil molar ratio of 6:1, and a reaction temperature of 65 °C optimised under the homogeneous system.

In the case of the Arnot fly ash based catalysts, high temperature of 160 °C, catalyst amount of 15 g (15 % wt/wt to oil) and volumes of methanol (methanol to oil ratio of 15:1) were required in comparison to its conventional homogeneous counterpart to obtain an optimum yield of 87.5 %. The large amount of catalyst and use of excess methanol and was a demerit in the use of FA/KNO₃; the methanol was however recovered and reused in the system. The water washing step was eliminated in heterogeneous processes, reducing purification steps and waste water effluent. The application of the FA/KNO₃ catalysts or the zeolite FA /KX in a continuous processing unit led to easy separation of product phases and recovery of catalyst. This could lead to a substantial decrease in the cost of biodiesel production.

It is worthy of note that at this stage, considering cost and energy consumption, the homogeneous process using the ultrasound assisted and jet loop reactor technologies would be a better option to follow, however possible improvements on the heterogeneous system especially involving the South African class F Arnot fly ash based zeolite KX catalysts possess much potential.

7.3 Conclusion

In conclusion, the combination of the transesterification reaction experiments and FAME analysis tests employed in this study proved the significant effect of different reaction parameters (catalyst amount, methanol to oil ratio, reaction temperature, reaction time) on methyl ester/FAME yield. The ultrasound assisted transesterification reactions at optimum conditions and much reduced processing time on the different oil samples led to higher yields of methyl esters while the newly developed jet loop process system showed even better results with an optimum reaction condition of 25 min of reaction, a methanol: oil ratio of 4:1 and a catalyst amount of 0.5 wt%. These intensification processes allowed an added advantage for an efficient separation and purification of the methyl esters phase in comparison to the conventional process.

This study has shown that the use of South African class F -AFA -zeolite K-X and FA/KNO₃ catalyst can be used as heterogeneous catalysts in biodiesel synthesis. Furthermore, by anchoring alkali metal, potassium (in this study) in the pores of the AFA -zeolite Na-X catalysts through ion exchange promotes superior conversion of triglycerides into methyl ester at moderate operating reaction conditions.

The use of the solid base catalysts in this study possesses potential to new developments in the production of biodiesel; allowing process simplification and offering reduction in processing costs by improving the mass transfer limitation of the three phase reaction and simplifying the product purification processes as compared to what is required in conventional homogeneous catalysis.

7.4 Recommendations for future study

The broad scope of this thesis suggests there is a plethora of further work that can still be done as a breakthrough in heterogeneous catalysis and design of catalysts materials necessitates a downstream without further cleaning steps, preparation methods with less complex or refined steps, sustainable and environmentally benign precursors and/or

materials as well as reaction conditions, which are less severe to be competitive with conventional homogeneous reaction system.

Having investigated the catalytic activity of solid base catalysts derived from South African Class F fly ash (obtained from Arnot power station), more investigations are currently underway to determine the optimum reaction conditions for the FA/KX catalyst. Deactivation tests for the recovered FA/KX catalyst obtained in this study and the overall properties of the methyl ester product made at optimised conditions would also be subsequently determined.

Further studies on improving the catalyst morphology and investigating the catalytic activity of zeolite catalysts to serve as potential molecular sieves with respect to high water and FFA content oil feedstock should be the focus of future research directions.

The use of the ultrasound could also be investigated in the heterogeneous system using the prepared Arnot fly ash based catalyst and the Arnot fly ash zeolite catalysts to determine the possibility of reducing the time and temperature required for transesterification reaction to take place. This will enable reduction of cost of the biodiesel production especially when the continuous process is scaled up.

The exploration of economically useful applications for crude glycerol is expected to gain even more importance within biodiesel research in the near future, as increases in the world-wide FAME fuel production will necessarily entail increased formation of crude glycerol as well. Possible applications of the crude glycerol phase are limited, however to keep the cost of biodiesel fuel production competitive; ensuring the removal and resale of high purity product glycerol in its pure form is essential. This is seen to be a secondary product of the reaction and can be used for various applications including: catalytic conversions, biological conversion, fuel oxygenates, carbon source for bioreactors treating acid mine drainage and agricultural use.

Major efforts should be developed with regards to fuel specifications for biodiesel that will assure consistent quality and performance, but not tie the final fuel to any specific raw material, in view of significant variation in biodiesel properties based on the raw material and sometimes the process conditions.

In the light of emerging discussions on the environmental effects of biodiesel fuel, the negative impacts of biodiesel production, conversion and transport has to be considered as well, so life cycle assessment (LCA) studies could be done to compare the fuel energy input and the emissions of certain ecologically relevant compounds throughout the whole fuel cycles.



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Appendices

Appendices

Appendix 1:

Table 1: Requirements for Automotive Biodiesel in South Africa (SANS 1935:2004)

Property		Requirements
Ester content	methyl ester,% mass fraction	min 96,5
Linolenic acid	methyl esters % mass fraction	max 12
Polyunsaturated (> = 4 double bonds)	methyl esters % mass fraction	max 1
Methanol content	% mass fraction	max 0,2
Monoglyceride content	% mass fraction	max 0,8
Diglyceride content	% mass fraction	max 0,2
Triglyceride content	% mass fraction	max 0,2
Free glycerol	% mass fraction	max 0,02
Total glycerol	% mass fraction	max 0,25
Density	15 °C, kg/m ³	860 – 900
Kinematic viscosity	40 °C, mm ² /s	3,5 – 5,0
Flash point	°C	min 120
Sulphur content	mg/kg	max 10,0
Sulfated ash content	% mass fraction	max 0,02
Water content	% mass fraction	max 0,05
Total contamination	mg/kg	Max 24
Copper strip corrosion	(3 h at 50 °C), rating	Max Class 1
Oxidation stability	at 110 °C, h	Min 6
Acid value	mg KOH/g	max 0,5
Iodine value g of iodine/100 g of FAME		max 140
Carbon residue (on 10 % distillation residue)	% mass fraction	Max 0,3
Cetane Number		min 51,0
Group II metals (total of Ca and Mg),		max 5,0
Group I metals (total of Na and K),		max 5,0
Phosphorus content	mg/kg	max 10,0
Cold Filter Plugging Point (CFPP) winter, Summer	°C °C	max -4 max 3

Appendices

Appendix 2

Table 2: European Standard for testing method EN 14103

Property		Requirements
Ester content	Methyl ester % mass fraction	min 98.2
Linolenic acid	Methyl ester % mass fraction	max 12
Methanol content	% mass fraction	max 0.2
Monoglyceride content	% mass fraction	max 0.8
Diglyceride content	% mass fraction	max 0.2
Triglyceride content	% mass fraction	max 0.2
Free glycerol	% mass fraction	max 0.02
Total glycerol	% mass fraction	max 0.25
Density	15 °C g/cm ⁻¹	0.860 – 0.90
Kinematic viscosity	40 °C, mm ² /s	3,5 – 5,0
Flash point	°C	min 120
Sulphur content	mg/kg	max 10
Sulfated ash content	% mass fraction	max 0.02
Water content	mg/g	max 500
Particulate	mg/kg-1	max 24
Copper strip corrosion	(3 h at 50 °C), rating	1
Oxidation stability	at 110 °C, h	min 6
Acid value	mg KOH/g	max 0.5
Iodine value	1g of iodine /100 g of FAME	max 120
Carbon residue (on 10 % distillation residue)	% mass fraction	max 0,3
Cetane Number		min 51
Group II metals (total of Ca and Mg),	mg/kg	max 5
Group I metals (total of Na and K),	mg/kg	max 5
Phosphorus content	mg/kg	max 10.0
Cold Filter Plugging Point (CFPP) winter, Summer	°C °C	max -4 max 3

Appendices

Appendix 3: Biodiesel International Standards

Table 3: Biodiesel standard from different international countries (Journey to Forever, 2006)

	Europe	Austria	CzechRepublic	France	Germany	Italy	Sweden	USA	Australia
Standard/ Specification	EN 14214	ON C1191	CSN 65 6507	Journal Officiel	DIN V 51606	UNI 10635	SS 155436	ASTM D-6751	Fuel Standard (Biodiesel) Determination
Date	2003	July 1997	Sep 1998	Sep 1997	Sep 1997	April 1997	Nov 1996	Jan 2002	Sept 2003
Application	FAME	FAME	RME	VOME	FAME	VOME	VOME	FAMAE	-
Density 15°C g/cm	0.86 - 0.90	0.85 - 0.89	0.87 - 0.89	0.87 - 0.90	0.875 - 0.90	0.86 - 0.90	0.87 - 0.90	-	0.86 -0.89
Viscos. 40°C mm2/s	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0	3.5-5.0
Distillat. 95% °C	-	-	-	<360	-	<360	-	90% @ 360°C	<360
Flashpoint °C	>120	>100	>110	>100	>110	>100	>100	>130(150 av.)	>120
CFPP °C (cold filter plugging point)	*country specific	0/-15	-5	-	0/-10/-20	-	-	-	-
Pour point	-	-	-	<-10	-	<0/<-15	-	-	-
Sulfur % mass	<10 mg/kg	<0.02	-	<0.01	<0.01	<0.01	<0.001	<0.05	50 mg/kg (max) 10 mg/kg (max) (from 1 Feb 2006)
CCR 100% % mass	-	<0.05	<0.05	-	<0.05	-	-	-	-
10% dist. resid. % mass	<0.3	-	-	<0.3	-	<0.5	-	-	-
Sulfated ash % mass	<0.02	<0.02	-	<0.03	-	-	<0.02	<0.02	(Oxid) Ash % mass
(Oxid) Ash % mass	-	-	-	-	-	<0.01	<0.01	--	--

	<500	-	<500	<200	<300	<700	<300	<0.05%	<0.05% vol
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Water mg/kg								vol. (water & sediment)	(water & sediment)
Total contam. mg/kg	<24	-	<24	-	<20	-	<20	-	<24
Cu-Corros. 3h/50°C	1	-	1	-	1	-	-	<No.3	<10 mg/kg sulfur Class 1 (max) >10 mg/kg sulfur No. 3 (max)
Oxidation stability	6 h min	-	-	-	-	-	-	-	6 h min
Cetane No	>51	>49	>48	>49	>49	-	>48	>47	>51
Neural. No Acid value) mg KOH/g	<0.5	<0.8	<0.5	<0.5	<0.5	<0.5	<0.6	<0.8	<0.8
Methanol % mass	<0.20	<0.20	-	<0.1	<0.3	<0.2	<0.2	-	<0.2
Ester Content % mass	>95.5	-	-	>96.5	-	>98	>98	-	>96.5
Monoglyceride % mass	<0.8	-	-	<0.8	<0.8	<0.8	<0.8	-	-
Diglyceride % mass	<0.2	-	-	<0.2	<0.4	<0.2	<0.1	-	-
Triglyceride % mass	<0.2	-	-	<0.2	<0.4	<0.1	<0.1	-	-
Free glycerol % mass	<0.02	<0.02	<0.02	<0.02	<0.02	<0.05	<0.02	<0.02	<0.02
Total glycerol % mass	<0.25	<0.24	<0.24	<0.25	<0.25	-	-	<0.24	<0.25
Iodine No	<120	<120	-	<115	<115	-	<125	-	-
Linolenic acid ME % mass	<12	-	-	-	-	-	-	-	-
C18:3 and high unsaturated acids % mass	-	<15	-	-	-	-	-	-	-
Phosphous mg/Kg	<10	<20	<20	<10	<10	<10	<10	<0.001% mass	<10
Ramsbottom carbon residue, % mass	-	-	-	-	-	-	-	0.10	-
Carbon residue	-	-	-	-	-	-	-	<0.050% by mass	<0.30 % mass (10% distillation residue)
Gp 1 metals (Na, K) mg/kg	<5	-	-	-	-	-	-	-	<5
Gp 1 metals (Na, K) mg/kg	<5	-	-	-	-	-	-	-	<5
Alkalinity mg/kg	-	-	<10	<5	<5	-	<10	-	-

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Appendix 4: South African Diesel Consumption

Table 4: South African past and future diesel consumption (SAPIA, 2006)

Year	Fossil Diesel Million litres	1% Biodiesel Million litres	5 % Biodiesel Million litres	10 % Biodiesel Million litres
2000	6254			
2001	6488			
2002	6831			
2003	7263			
2004	7679			
2005	8115			
2006	8521			
2007	8947	89	447	895
2008	9394	94	470	939
2009	9864	99	493	986
2010	10357	104	518	1036
2011	10875	109	544	1087
2012	11419	114	571	1142
2013	11990	120	599	1199
2014	12589	126	629	1259
2015	13218	132	661	1322
2016	13879	139	694	1388
2017	14573	146	729	1457
2018	15302	153	765	1530
2019	16067	161	803	1607
2020	16871	169	844	1687

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Appendix 5: Feedstock Potential in Sub Saharan Africa

Table 5: Potential oil crops/ seeds in Southern Africa (Amigun & Musango, 2011)

Crop	Country grown	Area harvested (ha)	Production (tons)
Cashewnuts	Angola	2800	1100
	Mozambique	60000	85000
Sesame seeds	Angola	2700	1700
	Mozambique	16000	11000
Castor oil	Angola	13500	3500
	Mozambique	150000	52071
	South Africa	8000	4900
Pumpkin	Mozambique	330	600
	South Africa	11000	72900
Rapeseed	South Africa	35000	32000
Avocados	South Africa	17000	99650
	Swaziland	50	300
	Zimbabwe	170	1100
Coconut	Mozambique	70000	265000
Soybean	Malawi	70000	45000
	South Africa	174400	322995
	Zambia	10000	12000
	Zimbabwe	65000	105000
Cotton seed	Angola	2700	2700
	Botswana	1100	2500
	Malawi	69826	76761
	Mozambique	360000	240000
	Namibia	3800	5700
	South Africa	14000	26275
	Swaziland	14800	7200
	Zambia	127000	140000
	Zimbabwe	400000	240000
Sunflower	Angola	15000	11000
	Botswana	6200	7000
	Malawi	7575	5745
	Mozambique	12000	5128
	Namibia	135	50
	South Africa	564300	885560
	Zambia	15000	8000
	Zimbabwe	23000	23000
Maize	Angola	1115000	570000
	Botswana	56000	12000
	Lesotho	160000	105000
	Malawi	1596955	2634701
	Mozambique	1284930	1284930
	Namibia	18000	40000
	South Africa	2799000	11597000
	Swaziland	47409	26170
	Zambia	663990	1445655
	Zimbabwe	1730000	496000

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Appendix 6: Lists of oil producing crops in the globe (Faupe! and Al Kurki, 2002)

Plant	Latin Name	Kg Oil/ Hectare	Plant	Latin Name	Kg Oil/ Hectare
Corn	<i>Zea mays</i>	145	Tung oil tree	<i>Aleurites fordii</i>	790
cashew nut	<i>Anacardium occidentale</i>	148	Sunflower	<i>Helianthus annuus</i>	800
Oat	<i>Avena sativa</i>	183	Cocoa	<i>Theobroma cacao</i>	863
Palm	<i>Erythea salvadorensis</i>	189	Peanut	<i>Arachis hypogaea</i>	890
lupine	<i>Lupinus albus</i>	195	opium poppy	<i>Papaver somniferum</i>	978
rubber seed	<i>Hevea brasiliensis</i>	217	Rapeseed	<i>Brassica napus</i>	1000
Kenaf	<i>Hibiscus cannabinus L.</i>	230	olive tree	<i>Olea europaea</i>	1019
calendula	<i>Calendula officinalis</i>	256	Piassava	<i>Attalea funifera</i>	1112
Cotton	<i>Gossypium hirsutum</i>	273	gopher plant	<i>Euphorbia lathyris</i>	1119
Hemp	<i>Cannabis sativa</i>	305	castor bean	<i>Ricinus communis</i>	1188
soybean	<i>Glycine max</i>	375	Bacuri	<i>Platonia insignis</i>	1197
coffee	<i>Coffea Arabica</i>	386	Pacan	<i>Carya illinoensis</i>	1505
linseed	<i>Linum usitatissimum</i>	402	Jojoba	<i>Simmondsia chinensis</i>	1528
hazelnut	<i>Corylus avellana</i>	405	babassu palm	<i>Orbignya martiana</i>	1541
euphorbia	<i>Euphorbia lagascae</i>	440	Jatropha	<i>Jatropha curcas</i>	1590
pumpkin seed	<i>Cucurbita pepo</i>	449	macadamia nut	<i>Macsdamia terniflora</i>	1887
coriander	<i>Coriandrum sativum</i>	450	brazil nut	<i>Bertholltia excelsa</i>	2010
mustard	<i>Brassica alba</i>	481	Avocado	<i>Persea americana</i>	2217
camelina	<i>Camelina sativa</i>	490	Coconut	<i>Cocos nucifera</i>	2260
sesame	<i>Sesamum indicum</i>	585	Oiticia	<i>Licania rigida</i>	2520
crambe	<i>Crambe abyssinica</i>	589	buriti palm	<i>Mauritia flexuosa</i>	2743
safflower	<i>Carthamus tinctorius</i>	655	Pequi	<i>Caryocar brasiliense</i>	3142
buffalo gourd	<i>Cucurbita foetidissima</i>	665	macauba palm	<i>Acrocomia aculeata</i>	3775
Rice	<i>Oriza sativa</i>	696	oil palm	<i>Elaeis guineensis</i>	5000

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Appendix 7: Summary of Test methods

Relative Density (15 °C) EN ISO 3675: The relative density of a sample is determined with the use of a hydrometer. Biodiesel has a typical relative density of 0.88.

Kinematic Viscosity ASTM D 445: The kinematic viscosity of biodiesel and blends is determined by the time it takes for a sample to flow by gravity through a calibrated capillary tube. The viscosity is calculated by multiplying the time, in seconds, by a tube-specific constant. It is critical to have proper fuel viscosity to ensure optimal fuel performance.

Iodine Value ASTM D 5768: This test is used to determine the level of unsaturation of the fuel. As the number of unsaturated bonds in the ester chain increases, so does the iodine value.

Water and Sediment EN ISO 12937: A sample is centrifuged in a specific centrifuge tube to determine the presence of free water or sediment. Large amounts of either free water or sediment can lead to handling issues, filter plugging, and microbial growth.

Total Ester Content EN 14103: This is a European method which determines the amount of the fuel sample that is a fatty acid ester.

Cetane Number D 613: The cetane number is a measure of the ignition quality of the fuel. It is determined by running fuel in a specific engine with prescribed operating conditions.

***Free & Total Glycerin ASTM D 6584:** Free glycerin is the amount of actual glycerin (a by-product of transesterification) contained in the fuel. Total glycerin is a combination of the amount of free glycerin and glycerin related molecules (monoglycerides, diglycerides, and triglycerides). This test evaluates the glycerin content of the fuel from all sources, free or bound.

***Monoglyceride Content ASTM D 6584:** Through the process of transesterification, triglyceride molecules are converted into fatty acid methyl esters and glycerin. During an intermediate step in this process, monoglyceride molecules are formed. A high

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concentration of monoglyceride molecules can show an incomplete reaction and may cause engine deposits.

***Diglyceride Content ASTM D 6584:** Through the process of transesterification, triglyceride molecules are converted into fatty acid methyl esters and glycerin. An intermediate step in this process converts the triglyceride molecule into a diglyceride molecule. A high concentration of diglyceride molecules indicates an incomplete reaction and may cause engine deposits.

***Triglyceride Content ASTM D 6584:** The triglyceride content of biodiesel is determined by gas chromatography. High triglyceride content can lead to incomplete combustion and engine deposits. A high level of triglycerides shows that the transesterification reaction was not complete.

*ASTM 6584 could also be obtained with AOCS Ca14-56.

Methanol Content EN 14110: This test method uses gas chromatography to determine the methanol content of a sample. If not properly removed, a small amount of methanol can make the biodiesel sample flammable

Flash Point (open cup) EN ISO 3679: This test is used to determine if the methanol has been sufficiently removed in the biodiesel purification process.

Sulfated Ash ISO 3987: This test is used to determine the presence of abrasive solids, soluble metallic soaps, or unremoved catalysts.

Sodium and Potassium, Combined EN 14538: The presence of sodium or potassium in a biodiesel sample can be attributed to unremoved soaps or catalysts.

References:

Annual Book of ASTM Standards, copyright American Society for Testing and Materials, 100 Harbor Drive, West Conshohocken, PA 19428.

European Standard EN 14214, 2003: Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods. *CEN – European Committee for Standardization, Brussels, Belgium.*