Transesterification of Animal fat to Biodiesel over Solid Hydroxy Sodalite Catalyst in a Batch Reactor

Chabisha Precious Makgaba

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering

Supervisor: Prof. M.O. Daramola

September 2017

Declaration

I declare that this dissertation is my own unaided work. It is being submitted for the degree of Master of Science in Chemical Engineering at the school University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

…………………………………………………………………………………………………

(Signature of Candidate)

………………………day of………………………. year…………………….

day *month* *year*

Dedication

I dedicate this dissertation to my most loving family and friends who have shown support all through out, my mother, Anna, and my late dad, Mankweng. To my sisters Mangoetjana, Metja, Ramoraswi, Mamare, Rose and my brothers Madikela, Nkalebetša and the late Kaizer. My friends, Thabitha, Lebo, Laurah, Louisa, Emma and Makhensi. I appreciate all that you have done to ensure that I am able to complete my dissertation. Most importantly, I dedicate this dissertation to the Almighty God, if it was not for Him, this work would not have been possible.

Acknowledgements

I would like to thank Doctor Mbense and Bruce Mothibedi from the School of Chemical and Metallurgical Engineering for their efforts in assisting me with equipment for the experimental work. I would like to pass special gratitude to my supervisor, Professor M.O. Daramola, for his patience, guidance and for believing in me. I would also like to acknowledge Ms Sibongile Maswanganyi, as she assisted with the ordering of the chemicals which I required to carry out the experiments. I would like to achnowledge Thapelo Mbhele from the School of Chemistry (University of Witwatersrand) for assisting with the GC-MS methods. I am also grateful to the National Research Foundation (NRF), South Africa for funding this MSc degree program at the University of the Witwatersrand.

Abstract

Owing to the ongoing advancement in technology, escalating population sizes and urbanization rate, fossil fuels (coal, petroleum oil and natural gas) remain attractive as an energy source to run most of the daily operations. Consequent to heavy consumption of fossil fuels, the world faces detrimental challenges such as future energy security and environmental concerns. Combustion of fossil fuels results in emission of greenhouse gases such as CO_2 and SO_2 thereby contributing to global warming and acid rain problems. These alarming challenges drive the need for exploration of alternative energy sources to reduce dependence on fossil fuels.

Presented in this dissertation is a study of biodiesel, a biodegradable, non-toxic and environmentally benign energy source as an alternative to petroleum-based fuels. Chemically known as fatty acid alkyl ester (FAAE), biodiesel is commonly produced from vegetable oils or animal fats in addition to methanol by a catalysed transesterification reaction. Currently, biodiesel is more expensive than petroleum diesel due to high operation costs incurred during the production process. Despite the high prices, biodiesel production continues to grow on an industrial scale across the world as supported by policy measures and biofuel targets.

Researchers have identified two main factors that contribute to high costs of biodiesel production; 1) type of feedstock and 2) type of catalyst used in the production process. Conventional methods of production use edible oils as feedstock. This becomes unjustified due to the potential price hikes in the food market owing to the prospective competition between fuel and food industries. As a result, numerous researchers reported on the use of cheap and non- edible feedstock oils such as waste cooking oil and animal fat.

However, the challenge with the use of non-edible oils is their high content of free fatty acids (FFA) which is unattractive for a smooth transesterification process, more especially when homogeneous base catalysts are used. Homogeneous base catalysts are widely used in current industrial biodiesel production methods because they yield faster transesterification processes due to increased reaction rates. However, these types of catalysts are much sensitive to FFA, so when high FFA content feedstock is used, a saponification reaction occurs which consequently reduces the yield of biodiesel. An additional process unit is required to reduce the FFA content via esterification process prior to the main transesterification reaction.

Furthermore, since the reaction mixture is homogeneously combined with the product, an additional process unit for product separation is required to recover the resulting biodiesel from the mixture, translating into additional production costs.

Researchers are currently exploring the use of heterogeneous catalysts, which tend to avoid the saponification reaction and reduce the need for an esterification reaction used as oil pre-treatment step to reduce FFA content. This dissertation is therefore dedicated to attaining a economic and environmentally attractive process for biodiesel production using cheap non-edible beef tallow oil (BTO) and a heterogeneous hydroxy sodalite (H-SOD) catalyst.

Some industrial operations such as zeolite manufacturing processes produce a low grade H-SOD as by products, which is in turn disposed as chemical waste and therefore induces ground water contamination concerns. Exploration on the use of H-SOD as catalyst can largely contribute to the environmental protective measures as a waste management process among other benefits. The use of H-SOD is extensively reported in current research development on membrane separation; limited research reports on the use of H-SOD material to catalyse chemical processes are present in literature. For the first time in open literature, H-SOD is reported as the solid catalyst for biodiesel production in this dissertation.

The investigative study commenced with a preliminary study to gauge the feasibility of using H-SOD as a catalyst where a batch transesterification of waste cooking oil (WCO) was studied. The reaction was conducted at 60 ^{o}C for 12 h at a methanol-to-WCO ratio of 7.5:1 using 3 wt. % H-SOD catalyst with a particle size of just below 300 Å, the stirring intensity was kept at 1000 rpm to ensure uniform mixing throughout the reaction. The product obtained after the reaction was analysed using a pre-calibrated Chromatography-Mass Spectrometer (GC-MS) described in Chapter 5, and the results demonstrated the possibility of catalysing a transesterification reaction using solid H-SOD.

Under the same reaction conditions, the study was then extended to an investigation on the use of H-SOD to catalyze transesterification of BTO (4.53 % FFA) to FAME. The results showed that FAME was produced, at a yield of 39.6% and a conversion of 68.4%. Seeing that the yield and conversion obtained is relatively small compared to literature findings, the effect of some process conditions on the conversion and biodiesel yield were studied. The transesterification reaction was conducted with variations in the mixing intensity (700 – 1250 rpm), catalyst particle size (200 – 300 Å), reaction time (6 – 24 h) and reaction temperature (40-60 °C). The

maximum performance of H-SOD catalyst for a transesterification of BTO was achieved with a conversion of 78.3% and biodiesel yield of 62.9% obtained at optimum conditions: a stirrer speed of 1000 rpm, with the smallest catalyst particle size of 200 Å at maximum temperature of 60 °C and 24 h reaction time. The values of activation energy, reaction constants and frequency factor obtained from the kinetic study were 0.0011 min^{-1}, 5.52 $x10^{8}$ min^{-1} and 79.20 kJ/mol, respectively, and are within the range of the results reported in literature. As a result, solid H-SOD is recommended as a catalyst for the batch transesterification of BTO in a biodiesel production process.

Publications from the study

Below is a list of publications that have come out of this study, copies of published papers are provided in Appendix B:

Peer-reviewed Articles:

Makgaba, C.P., T. Aniokete, Daramola, M.O. (2017) Waste to energy: effect of reaction parameters on the transesterification of animal fat oil to biodiesel over a solid hydroxy sodalite (SOD) catalyst, Int. J. Environment and Sustainable Development (under review)

Makgaba, C.P., Sekoai, P.T., Daramola, M.O. (2017) Waste to energy: Conversion of animal fat to biodiesel over solid sodalite catalyst, In: Proceedings of the International Conference on Energy, Environment and Climate-ICEECC 2017, July 3-5, Mauritius, pp 143-150.

Makgaba, C.P. & Daramola, M.O. (2015) Transesterification of waste cooking oil to biodiesel over calcined hydroxy sodalite (HS) Catalyst: A preliminary investigation, In: Proceedings of the International Conference on Sustainable Energy and Environmental Engineering-SEEE 2015, October 25-26, Thailand, pp 52-56.

Oral presentations:

Makgaba, C.P. & Daramola, M.O. (2016) Investigation of the effect of mass transfer limitation on the transesterification of animal fat to biodiesel over solid hydroxy sodalite catalyst in a batch reactor, In: Proceedings of the Center of Renewable Energy and Water – CREW 2016, November 24-25, Vaal University of Technology, Johannesburg, South Africa.

Contents

List of Tables

List of Figures

Nomenclature

A = Pre-exponential Factor or Frequency factor

AV = Acid Value

BET = Brunauer, Emmett and Teller

BTO = Beef Tallow Oil

BTU = British Thermal Unit

$C_2H_4O_2$ = Acetic acid

CAA = Clean Air Act

CaO = Calcium oxide

CH_4 = Methane

CO_2 = Carbon Dioxide

DG = Diglyceride

E_A = Activation Energy

EPA = Environmental Protection Agency

EN 14103 = European standard

FAAE = Fatty acid alkyl ester

FAME = Fatty acid methyl ester

FFA = Free Fatty Acid

FTIR = Fourier transform infrared spectroscopy (FTIR)

FWHM = Line Broadening at Half the Maximum Intensity

GL = Glycerol

HCL = Hydrochloric acid

H-SOD = Hydroxy Sodalite

IEO = International Energy Outlook

IV = Iodine Value

IZA = International Zeolite Association

k = Overall Reaction Rate Constant

KOH = Potassium Hydroxide

LCA = Life Cycle Analysis

LTA = Linde Type A zeolite

MeOH = Methanol

MG = Monoglyceride

N_2O = Nitrous oxide

Na_2SiO_3 = Sodium metasilicate

$NaAlO_2$ = Sodium aluminate

NaOH = Sodium hydroxide

PFO = Pseudo First Order

PTFE = Polytetrafluoroethylene

R = Gas Constant

RDS = Rate determining step

SEM = Scanning Electron Microscope

Standard Biodiesel = F.A.M.E. Mix, C4 - C24

SV = Saponification Value

t = Reaction Time

T = Reaction Temperature

TG = Triglyceride

TGA = Thermal Gravimetric Analysis

WCO = Waste Cooking Oil

XRD = X-ray Powder Diffraction

CHAPTER 1: BACKGROUND OF THE STUDY

1.1. Introduction

In the recently released International Energy Outlook 2016, the US Energy Information Administration has estimated a significant growth in global energy demands in the next 24 years. The energy consumption was projected to escalate from 549 quadrillion Btu to 815 quadrillion Btu, a 48 % growth between 2012 and 2040 (U.S. Energy Information Administration 2016). The fast growth of economies in developing countries such as China and India continues to influence the energy consumption rate mainly because of industrialization and the increase in gross domestic product per capita (Chai et al. 2016; Hubacek et al. 2017). Other factors contributing to high energy consumptions are population size and urbanization rate (Nejat et al. 2015). Fossil fuels (natural gas, coal and oil) make up the largest portion of primary energy source amid a broader range of sources of energy, accounting for 86% of the total energy consumed on a global scale (*World Energy Outlook* 2008). Energy derived from fossil fuels made both economic and industrial sense upon discovery during the industrial revolution in the 18th century, thereby replacing biomass as source of energy. Coal was perceived inexhaustible and the fact that it could be used in its natural form made it much more attractive to the energy industry (U.S. Department of Energy 2013; Wrigley 2013).

However, modern research has demonstrated that fossil fuels reserves are potentially diminishing and therefore they are not as inexhaustible (Ayompe et al. 2011), as a result, the world faces a challenge with energy security. In the past decades, the discovery of detrimental effects of the continuous combustion of fossil fuels brought to attention the crucial need for researchers to explore alternative energy sources. Combustion of fossil fuels for energy generation results in emission of greenhouse gases; carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). The increased concentration of these gases in the atmosphere potentially results in global warming. Consequently, other ways of generating energy have become of great interest in current ongoing research. Extensive work under the search for alternative methods of energy generation have demonstrated the potential of the use of renewable energy sources including but not limited to solar energy, geothermal, wind power and the use of biofuels (Foleya et al. 2012; Zhou et al. 2010; Yang et al. 2007; Agarwal 2007; Heberle & Brüggemann 2010).

Renewable technologies are referred to as clean and sustainable energy sources for their ability to minimize environmental impacts by reducing greenhouse gas emissions and minimizing secondary wastes (Panwar et al. 2011). Explored in this study is a type of biofuel portfolio; biodiesel, which represents over 80% of biofuels production and accordingly, it is the main alternative to diesel fuel (Mata et al. 2010; Bozbas 2008). Biodiesel is chemically termed fatty acid alkyl ester (FAAE). The naming for the alkyl group depends on the type of alcohol used in the biodiesel production process, for example, methanol is most commonly used, and in such a case the naming of the resulting biodiesel product is fatty acid methyl ester (FAME). The transesterification reaction where methanol is used also referred to as methanolysis. Biodiesel is a biodegradable, non-toxic and environmentally benign diesel fuel and its study as an alternative fuel to reduce dependence on fossil fuels has become an attractive area of research (Makgaba & Daramola 2015; Marchetti et al. 2007; Ramadhas et al. 2005). It is a viable alternative fuel as it meets the strict fuel quality and engine performance, completed the health effects testing requirements according to the 1990 Clean Air Act (CAA) Amendments and is legally registered with the Environmental Protection Agency (EPA) for sale and distribution (Speight 2011; Makama 2012). Furthermore, biodiesel can be mixed at any proportion with diesel; hence it can be applied in diesel engines without much additional modification. A more realistic idea however, is not to replace petroleum diesel, but to use biodiesel as a blend; the Life Cycle Analysis (LCA) of biodiesel have demonstrated the possibility to reduce greenhouse gas emission by blending biodiesel with diesel in the transport sector (Beer et al. 2000).

Biodiesel is commonly produced from vegetable oils or animal fat using transesterification reaction. The reaction involves the use of short chained alcohol, usually methanol, as well as a catalytic material. The cost of biodiesel remains high compared to petroleum diesel, due to economical inefficiencies resulting from its production process. Conventional methods of biodiesel production involve the use of edible oils. Seeing that there is a potential for competition between the food and fuel industries, utilization of edible oils as feedstock in the biodiesel production becomes unjustified, as a result, researchers have opted for exploring of non-edible oils such as Jatropha oil, animal fat and waste cooking oil as alternative feedstock for biodiesel production (Guo et al. 2012; Aransiola et al. 2012; 2013; Daramola et al. 2016). Non-edible oils usually contain high content of Free Fatty acids which tends to be unfavorable for transesterification reaction, more especially when homogeneous base catalysts are used. Saponification reaction occurs in conjunction with the transesterification reaction thereby reducing the yield of biodiesel. Furthermore, an additional process unit for product separation is required to recover the resulting biodiesel from the mixture with the catalyst (Hemmat et al. 2013; Canakci & Sanli 2008).

The use of heterogeneous catalysts tends to overcome the effect of saponification reaction, reduces the need for an esterification reaction used as oil pre-treatment step to reduce content of the FFA (Islam et al. 2013) and potentially eliminates the need for high investments in the additional product separation step. The process of transesterification reaction is influenced by process variables such as reaction temperature, reaction time and type of catalyst amongst others (da Cunha et al. 2009; Jagadale & Jugulkar 2012; Kim et al. 2004). This study further explored the influence of some of reaction parameters on the performance of the transesterification reaction of waste beef tallow over solid hydroxy sodalite catalyst. The aim of this study was to investigate the viability of using cheap non-edible beef tallow oil for biodiesel production. This in turn paves a way for effective disposal of the waste (Belgharza, et al. 2014). Furthermore, this study assessed the feasibility of using a potentially economic catalyst (H-SOD) for the transesterification of waste oils to biodiesel.

1.2. Problem statement

While biodiesel fuel is appealing due to its environmental benefits, it is currently more expensive to produce on an industrial scale compared to petroleum diesel. The present study sought a more economically sustainable method for producing biodiesel. The high costs of production in conventional methods are mainly due to the costs of feedstock and type of catalyst used for biodiesel production (Musa, 2016; Narasimharao, Lee, & Wilson, 2007; Thanh, Okitsu, Van Boi, & Maeda, 2012). Extensive research was conducted on the exploration of cheap non-edible oil feedstock for the production of biodiesel such as waste cooking oil (WCO) and waste animal fat (Adewale, Dumont, & Ngadi, 2015; Alptekin, Canakci, & Sanli, 2014; Diasa J. M., et al., 2012; Chuah, Klemeš, Yusup, Bokhari, & Akbar, 2017; Hassani, Najafpour, & Mohammadi, 2016; Fatah, Mansour, & Fouad, 2016). WCO as an alternative feedstock is more cost effective but there is currently insufficient supply of waste cooking oil to meet the anticipated demand of biodiesel. For instance, in the United States, an estimated amount of 100 million gallons can be produced from used cooking oil per year, which is about 1 % of the US diesel fuel market (Tabak, 2009). While the application of waste cooking oil is limited to smaller scale projects, the availability of animal fat in large quantities from abattoirs makes animal fat appealing as a potential feedstock when thoroughly investigated (Atadashi et al. 2012). Therefore, in the present study, cheap and readily available waste beef tallow fat was used as feedstock. Biodiesel derived from animal fat oil proves to contain high cetane number and calorific value compared to vegetable oil derived biodiesel (Diasa et al. 2012). On the other hand, conventional methods for biodiesel production use homogeneous catalysts, which also contribute to high costs of production since an additional product separation process is required to separate the homogeneous catalyst from the product mixture (Dehkordi & Ghasemi 2012).

Furthermore, homogeneous base catalysts react with the FFA in the oil via saponification; an unwanted soap formation side reaction which use up a part of the triglyceride and results in lower product yields. Recent studies attract investigations on heterogeneous catalysts, which amongst others, are associated with an advantage of easy product separation as opposed to homogeneous catalysts. Accordingly, this study explored the use of a heterogeneous base catalyst; hydroxy sodalite, for the production of biodiesel. During heterogeneous catalytic reactions, catalysts are normally in solid form whereas the reactants are in gaseous or liquid form. Mass transfer or diffusion exists between the different phases; hence one finds that heterogeneously catalyzed reactions are more prone to mass transfer limitation than the homogeneous catalytic reactions. Despite the anticipated effect of mass transfer on the rate of the transesterification reaction, limited literature is available on the influence of mass transfer on the heterogeneously catalyzed transesterification reaction.

1.3. Research questions

To obtain the outcomes documented in this dissertation, the following questions were posed:

1.3.1. Can H-SOD crystals catalyze transesterification reaction for the conversion of animal fat oil into biodiesel?

1.3.2. What is the effect of operating variables such as reaction time, temperature, catalyst particle size and mixing intensity on the yield of biodiesel produced via transesterification of animal fat oil to biodiesel over hydroxy sodalite catalyst?

1.3.3. What is the kinetics of transesterification of animal fat oil into biodiesel over a H-SOD catalyst in a batch reactor?

1.4. Specific objectives

In order to answer the research questions, the study focused on the following objectives:

1.4.1. To investigate the process of transesterification reaction for the conversion of animal fat to biodiesel over H-SOD catalyst in a batch reactor and compare the property to an existing standard biodiesel.

1.4.2. To determine the kinetics of transesterification of animal fat oil into biodiesel over a H-SOD catalyst in a batch reactor.

1.4.3. To investigate the influence of reaction temperature, reaction time, catalyst particle size and mixing intensity on the biodiesel yield during the transesterification of animal fat oil to biodiesel over H-SOD catalyst in a batch reactor.

1.5. Scope of the study

The scope of research under the biodiesel production process is broad. Some researchers have focused on testing various types of catalysts, homogeneous and heterogeneous, others evaluated catalyst kinetics. Other researchers investigated the choice of suitable feedstock and, or type of reactors appropriate for biodiesel production. Biodiesel production processes such as pyrolysis and transesterifications make a part of the broader scope of research, as well as cost evaluation of existing and potential methods for biodiesel production. The scope of this study was narrowed to: (1) Investigating the feasibility of novel H-SOD particle as catalyst for biodiesel production, (2) evaluating effects of operating variables on the production process and (3) investigating the kinetics of the H-SOD catalyst during a heterogeneous batch transesterification of animal fat oil.

1.6. Expected outcome

Contribution to scientific research is in terms of enhanced understanding of kinetics and the influence of mass transfer during the conversion of animal fat to biodiesel using a solid hydroxy sodalite catalyst in a batch reactor. Numerous researchers have conducted studies on the use of H-SOD material in membrane separation technology. However, very little research has been reported on the use of this type of zeolite material for catalysis purposes. As far as it can be ascertained, no other literature has been reported on the use of hydroxy sodalite particles to catalyze transesterification of tallow oil to biodiesel. As such, this study serves as the first to ever report the use of H-SOD particles for biodiesel production.

1.7. Structure of the dissertation

This dissertation is organized in to 8 main chapters. Chapter 1 gives background information about the study, detailing the problem statement as well as the aim and expected outcome of the study, Furthermore, the scope of the study is specified in this chapter. Chapter 2 gives the comprehensive review of literature in relation to the present study, highlighting the essential contribution of variety of researchers and identifying possible gaps in this field of study. Chapter 3 gives details about determination of properties of the biodiesel, Chapter 4 expatiates on the methods for H-SOD catalyst synthesis as well as characterization.

A preliminary study was carried out to investigate the feasibility of using H-SOD particles to catalyze transesterification for biodiesel production; Chapter 5. Waste cooking oil feedstock was used for the purpose of preliminary investigation, for the reason that unlike animal fat, it does not require intense process conditions (such as longer reaction times). In Chapter 6, H-SOD catalyst was tested on animal fat oil feedstock, the resulting biodiesel was compared to the standard biodiesel. From the results obtained in Chapter 6, the reaction performance was relatively low, initiating a further study detailed in Chapter 7, where the influence of reaction parameters on the transesterification reaction performance was investigated. The results obtained in Chapter 7 allowed an estimation of optimum values of reaction parameters to achieve high transesterification reaction performance. The reaction kinetics was investigated in Chapter 8. Chapter 9 details the conclusion of the study and the recommendations for future work.

CHAPTER 2: LITERATURE REVIEW

2.1. What are biofuels?

Fuels, which are directly or indirectly derived from organic matter- plant and waste animal material, are termed biofuels (Demirbas, 2007). With the advancement of technology on biofuel production, materials such as sugar crops, oil crops, lignocellulose crops, algae, aquatic biomass and animal waste materials are continuously seeing their use in the biofuel industry (Stöcker 2008; Parikka 2004; Menon & Rao 2012; Hinchee et al. 2010; Alptekin et al. 2014). Types of biofuels include bioethanol, biodiesel and biogas and bio-ethers which are industrially produced worldwide. Biodiesel can be used in diesel engines with little or no modification to the engine mechanism, and is commonly produced by transesterification of vegetable oils or animal fats (Canakci & Sanli, 2008). Bioethanol fuels are used in gasoline engines and are derived from sugar, starch or lipids by fermentation process. With slight engine adaptations, biogas can be used in gasoline engines and it is derived from manure by anaerobic digestion (Naik et al. 2010; Ellabban et al. 2014).

Benefits of biodiesel:

Biodiesel is derived from renewable and domestic feedstock, hence potentially sustainable and reduces dependence on fossil fuels. Biodiesel has a flashpoint higher than that of petroleum diesel or gasoline; as a result, it is one of the safest fuels available (Aransiola et al. 2014). Other environmental benefits of biodiesel include its low toxicity, less polluting, reduces greenhouse gases. It generally lowers harmful emissions compared to petroleum diesel and is biodegradable. Production and use of biodiesel contribute significantly less emissions, about 78% less than petroleum diesel (Tri-State Biodiesel 2015). The emission profile of biodiesel contains lesser SO_2, CO_2, unburned hydrocarbons and particulate matter than petroleum diesel. Biodiesel does not contribute to acid rain formation due to its lack of sulphur or aromatics content. Pure biodiesel with no sulphur provides an operational advantage of extending the life of catalytic converters. Biodiesel also provides significant improvement in lubricity over petroleum diesel. It is miscible with diesel so can be used in its purest form; B100 i.e. 100% biodiesel or blended with petroleum diesel in any percentage; commonly B2, B5 or B20 which are 2%, 5% or 20% biodiesel, respectively. Even 1% blending of biodiesel with diesel can provide up to 30% increase in lubricity. The good lubricating properties of biodiesel are capable of lengthening the life of an engine. Furthermore, biodiesel can be distributed through the diesel fuel pumps that are already in existence, hence little or no modification of pumps will be required (Makgaba & Daramola 2015; Ramadhas et al. 2005; Atadashi et al. 2012; Tri-State Biodiesel 2015; Demirbas 2007; 2008; Gupta & Demirbas, 2010).

Drawbacks of biodiesel:

There are however some downsides of biodiesel. Compared with petroleum diesel, biodiesel is significantly more expensive; about one and half times more expensive (Mata et al. 2010; Galvez & Berge 2013; Goodstein 2008). High costs of producing biodiesel are primarily due to the cost of feedstock, which comprises 50-70% production costs. Vegetable oil feedstock such as soybean, only constitutes a small percentage; about 20 % of extractable oil, and energy used to manufacture fertilizers coupled with agricultural processes (cultivating, harvesting and transporting) for growing the vegetable crops play a significant role in escalating the biodiesel production costs (Ramadhas et al. 2005). In its purest form, biodiesel becomes problematic during cold temperatures; viscosity and cold flow properties such as cloud point and pour points are higher than those of petroleum diesel fuel. Solid wax crystal nuclei tend to form at low temperatures resulting in engine start-up problems, fuel filters may become clogged and have to be replaced from time to time. Biodiesel also act aggressively with rubbers hoses in some engines, making them susceptible to corrosion which may cause leakages (Gupta & Demirbas 2010; Galvez & Berge 2013). Biodiesel is associated with increased emissions of nitrogen oxide which can form smog, so to some extent, it can contribute to global warming and climate change. The other disadvantage is that the calorific value of biodiesel is generally lower than that of petroleum diesel (Ramadhas et al. 2005).

2.2. Generations of biofuels

Biofuels are classified in to different generations depending on their production technologies (Demirbas 2008), particularly the kind of feedstock from which the biofuel is produced. First generation biofuels are produced from sugar, starch and grains which are primarily useful for both food and livestock feed. The first generation biofuels are currently being produced in some countries; Brazil, USA, China and India. The future of biofuel production using current technologies however becomes questionable due to the issues of competition with the food market, the rising costs of some edible crops and food stuffs due to biofuel production, and the high production costs of biofuels among others (Padula et al. 2014). Second generation biofuels can be produced using non-food sources such as wood and industrial waste and can potentially solve the problem of competition with food market, but are currently not yet commercially produced in any country to date (Razzaque 2013). The third generation biofuels also known as *Oilgae* or *Algae fuel* is looking at algae as production feedstock (Demirbas 2008). The third generation biofuels are still applied only under research; considerable developments are required before they can contribute much in the energy generation market.

2.3. Biodiesel production process

The potential use of pure vegetable oils to power engines was documented over a century ago by Dr. Rudolf Diesel (1858-1913); the German inventor and a mechanical engineer who invented the diesel engine (Salameh 2014). Vegetable oils are non-toxic and are derived from renewable sources unlike diesel. The major challenge with the use of vegetable oils is that they are highly viscous and may cause mechanical problems when used directly in diesel engines (Kibbey et al. 2014). The high viscosity of vegetable oils prompted researchers to investigate several methods which could possibly reduce the viscosity of vegetable oils. Some of the methods explored are dilution, pyrolysis (or thermal cracking), micro-emulsion and transesterification (Kibbey et al. 2014).

2.3.1. Biodiesel production methods

Dilution is primarily a blending of vegetable oil with diesel fuel in an attempt to improve viscosity. In a review on biodiesel production, Ma and Hanna (1999) recognized other factors that attribute to the impracticability implementation of dilution or the use of raw vegetable oils in engines; acid composition, gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, and lubricating oil thickening.

Microemulsion generally describes a thermodynamically stable dispersion of two immiscible liquids stabilized by surfactants or co surfactants, the dispersion looks as clear as a homogeneous solution due to the small droplets size; diameter range 1-150 nm (Ma & Hanna 1999), In short, Microemulsions are clear, stable isotropic fluids with three components; oil phases, aqueous phase and a surfactant (Abbaszaadeh et al. 2012), and can be classified into ionic and non-ionic microemulsions as per type of surfactant used. In the case of biodiesel production, the immiscible liquids are oil and a solvent such as methanol, ethanol or 1-butanol (Agarwal 2007; Parawira 2010). This technique is used for its benefits including short production period, simple implementation, no heat energy requirement and no by-product formation due to non-involvement of chemical reactions which also results in lower production costs (Bora et al. 2015), and in addition increase in cetane number results in good spray characteristics in the biodiesel (Ma & Hanna 1999; Parawira 2010; Gashaw & Teshita 2014). Nonetheless, emulsified and microemulsified biofuel have been reported to provide inconsistent lube oil consumption and produce more deposits of carbon and lacquer on the engine components (e.g. injector tips, intake valves and tops of the cylinder liners) than diesel fuel (Melo-Espinosaa et al. 2015), furthermore, continuous use of micro-emulsified diesel in engines causes problems like injector needle sticking and incomplete combustion (Abbaszaadeh et al. 2012; Parawira 2010; Gashaw & Teshita 2014).

Pyrolysis (thermal cracking) is the process of converting one organic substance in to another using heat in the absence of air (or oxygen) or by heat with an aid of a catalyst (Abbaszaadeh et al. 2012; Gashaw & Teshita 2014). Studies have shown that the pyrolysis of vegetable oil to produce biofuels produces alkanes, alkenes, alkadienes, aromatics and carboxylic acids in various proportions (Gashaw & Teshita 2014). Pyrolysed vegetable oils tend to contain trace amount of contaminants such as sulphur, water and sediments which could lead to corrosion problems with in the engine (Kamaruddin et al. 2013). The combustion of vegetable oils with sulphur content has a negative environmental impact (Parawira 2010); it could lead to SO_2 emissions which contribute to acid rain formation. Also, thermal cracking is quite and expensive process owing to high maintenance costs of the distillation unit for various fractions separations, the removal of oxygen during the thermal processing limits the benefits of using oxygenated fuel and furthermore, the pyrolytic chemistry is difficult to characterize due to the presence of variety of reaction paths and products (Ma & Hanna 1999; Gashaw & Teshita 2014; Abbaszaadeh et al. 2012; Gashaw & Teshita 2014; Kamaruddin et al. 2013). Among these methods, transesterification seems to be best choice owing to simplicity of the process and the fact that the resulting fatty acid ester has characteristics much closer to that of diesel (Demirbas 2008).

2.3.2. Transesterification reaction for biodiesel production

Transesterification term primarily describes organic reactions involving transformation of one type of ester into the other by an interchange of alkoxy moiety (Schuchardt et al. 1998; Pathak 2015). When alcohol is used, the transesterification reaction is termed alcoholysis i.e. the organic group R″ of an ester is exchanged with the organic group R′ of an alcohol to form a different type of ester (FAAE)and a different alcohol in the presence of a catalyst. The alkyl group naming of the resulting ester varies with the type of the alcohol used, for example, if in the case of methanol, the term becomes FAME. Vegetable oils or animal fat are used as an ester source; triglyceride to be reacted with a short chained alcohol to form glycerol and the FAAE (Demirbas 2008). The transesterification reaction mechanism is composed of a sequence stepwise of reversible reactions as depicted in Figure 1. Triglycerides react with FFA to form Glyceride (GL) and the alkyl ester, the reactions of glycerol and alkyl ester form monoglyceride (MG) and diglyceride(DG) in subsequent stepwise reactions (Rachmanto et al. 2014).

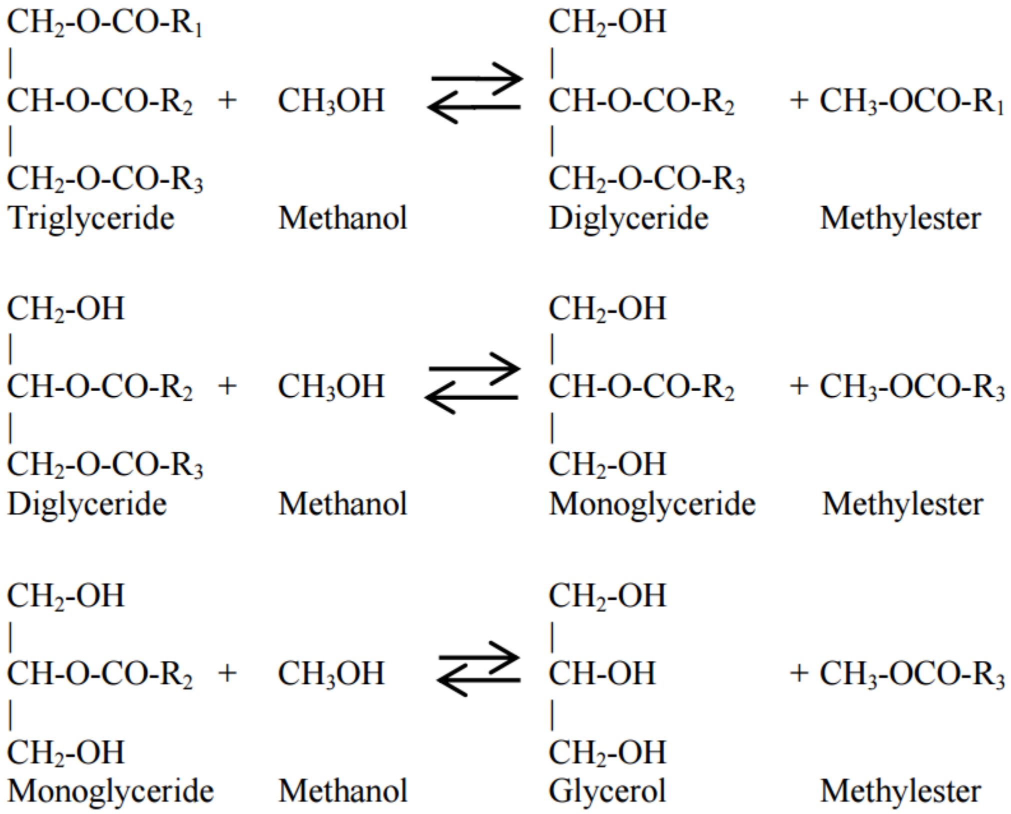

Figure 1: The transesterification reaction mechanism (Rachmanto et al. 2014).

2.3.3. Feedstock for biodiesel production

Biodiesel feedstock is generally classified into four main types which include vegetable oils, algae, waste animal fats and used cooking oil. There are many other alternative feedstock sources such as the *jatropha curcas* and *madhuca indica* which are normally preferred in regions with climate conditions which do not support the growth of the traditional sources (Moser 2009). Feedstock sources are initially tested for properties such as moisture content, free fatty acid, kinematic viscosity, saponification value, volatile matter, insoluble impurities, oxidation stability, sulphur and phosphorus, calcium and magnesium. It is desirable that feedstock sources for biodiesel production possess the following characteristics: adaptability to local growing conditions (rainfall, soil type, latitude, etc.), regional availability, high oil content, favorable fatty acid composition, compatibility with existing farm infrastructure, low agricultural inputs (water, fertilizer, pesticides), definable growth season, uniform seed maturation rates, potential markets for agricultural by-products, and the ability to grow in agriculturally undesirable lands and/or in the off-season from conventional commodity crops (Moser 2009).

Due to the issue of competition between fuel and food industries, and high costs affiliated with virgin oil, research on triglyceride source for biodiesel production narrowed to the use of waste cooking oil and waste animal fat as alternative resources. Animal fats that are currently studied include pork lard, BTO and mutton fat (Diasa et al. 2012; Ito et al. 2012; Mutreja et al. 2011). The use of waste material is not only beneficial due to low costs and availability (Canakci & Sanli 2008), but they also contribute to alleviation of environmental impacts that may be incurred when they are incorrectly managed (Diasa et al. 2012). Used animal fat unlike virgin oils constitute high content of free fatty acid. During the process of frying, the oil undergoes decomposition into different by-products, one of which is FFA. Decomposition is due to heat, moisture or foods being fried. For biodiesel production, homogeneous base catalysts such as sodium hydroxide and potassium hydroxide which are commercially used react with the FFA by a process of saponification; an unwanted soap formation side reaction (Pinto et al. 2005).

2.4. Catalysis in biodiesel production via transesterification reaction

The reaction for biodiesel product via transesterification depends largely on the presence of the catalyst, either homogeneous or heterogeneous catalyst (Atadashi et al. 2012). The difference between heterogeneously catalyzed reactions and homogeneously catalyzed reactions is on the basis of their phases; the former involves a reaction where catalyst is in the same reaction phase as the reactants and products and the former involves different phases, but the reactants and products may be in the same phase. Industrial methods for biodiesel production involve the use of homogeneous catalysts such as sodium hydroxide and potassium hydroxide, because they are highly selective to biodiesel product and they are associated with high activity (Atadashi et al. 2012; Sheldon et al. 2007). Homogeneous catalysts generally employed are either basic or acidic. Basic catalysts are normally preferred to acid catalysts since they yield faster reaction rates among other benefits. (Freedman et al. 1984).

The use of homogeneous catalysts becomes a problem when it comes to costs consideration of the industrial biodiesel production process. This is as a result of the operational costs incurred during the addition of the product separation process unit, furthermore, depending on the quality of the reaction process, a washing stage may also be required which implicates extra costs of washing water. More over basic homogeneous catalysts exhibit high level of sensitivity to water and free fatty acid contents in the oil feed, as a result, they tend to react with the free fatty acids to form soap. There will therefore be a need to add a pretreatment step, to reduce the content of free fatty acids prior the main transesterification step (Luque & Melero 2012).

Scientists therefore saw a need to investigate the use of heterogeneous catalysts as an attempt to reduce the current operational costs during biodiesel production. Product separation process is less intense when heterogeneous catalysts are used, for example, physical process such as filtration or decantation may be used to separate the solid catalyst from the liquid reaction mixture (Bhaduri & Mukesh 2001). Heterogeneous catalysts are generally less sensitive to the presence of free fatty acids in the oil, hence the oil pretreatment step can be avoided (Atadashi et al. 2012; Islam et al. 2013; Agarwal 2007) potentially reducing the operational costs.

2.5. Reactors for biodiesel production

One other way to investigate the transesterification reaction for biodiesel production is by using continuous flow reactors such as packed bed reactor/plug flow reactors and continuous stirred tank reactors. Continuously operated reactors are preferred to batch reactors because they are efficient during large scale commercial processes, as they result in consistent quality of the product at low capital and operating costs (He et al. 2005).

One of the simplest ways to investigate transesterification reaction for the production of biodiesel is by using laboratory batch stirred reactors (Banković-Ilić et al. 2014). Batch reactors are generally used for their advantage of high flexibility and good control of the amount of feedstock used in laboratories as well as commercial scales. Transesterification reactions conducted using batch reactors are associated with high product purities, however, the reaction residence times are usually long (Leevijit et al. 2004; Veny et al. 2014; Darnoko & Cheryan 2000). The other disadvantage of the use of batch reactors is that they are mostly suitable for plants that run on small scale.

2.6. Factors influencing biodiesel production via transesterification

One way to reduce the high costs of biodiesel is to reduce its operating costs by optimizing the operating parameters (Eloka-Eboka et al. 2014). A large portion of investigative research in biodiesel production was conducted on the effect of process variables on the performance of transesterification reaction. Most studies focused on the in-depth investigation of transesterification reaction mechanism (da Cunha et al. 2009; Jagadale & Jugulkar 2012; Kim et al. 2004; Odin et al. 2013) which directly links to the economy of the process. Generally, the efficiency of converting oil to biodiesel by transesterification depends largely on process variables such as reaction time, reaction temperature, extent of mixing, alcohol to oil molar ratio and the amount of catalyst (da Cunha et al. 2009; Jagadale & Jugulkar 2012), Kim et al. 2004; Eloka-Eboka et al. 2014; Abbah et al. 2016; Anastopoulos et al. 2009). Transesterification reaction is endothermic in nature; hence the reaction temperature influences the rate of transesterification reaction by improving the frequency of particle collision (Daramola et al. 2016; Farooq et al. 2016).

2.7. Effect of mass transport in biodiesel production via heterogeneous catalysis

The mixture of the polar alcohol and the non-polar triglyceride is inherently heterogeneous due to low mutual solubility. Thus, mass transfer limitation exists due to the thin film between the two phases thereby decreasing the reaction rates. However, research has reported on the possibility to force a homogeneous mixing between alcohol and triglycerides by optimizing reaction conditions such as temperature, pressures and molar ratio (Liu 2013). Some researchers have also demonstrated the effect of mixing speed on the homogeneity of the reactants in the transesterification process using variety of oil feedstock and catalysts (Noureddini & Zhu 1997; Bambase et al. 2007; Rashid et al. 2009; Berchmans et al. 2013). The results showed that for homogeneously catalysed transeterification process, the impact of agitation intensity is only observed during the initial stage of the transesterification reaction where mass transfer is dominant, as the reaction proceed, the agitation intensity tends to have minimal effect on the transesterification process. When transesterification is established at optimum agitation level,the reaction becomes kinetically controlled and primarily influenced by temperature (Berchmans et al. 2013).

Heterogeneous catalytic reactions consist of catalysts in a different phase with the reacting species. Catalyst material is normally in solid form whereas the reactants are in gaseous or liquid form. Mass transfer or diffusion occurs between the different phases; hence one will find that heterogeneously catalyzed reactions are more prone to mass transfer limitation than homogeneous catalytic reactions (Klaewkla et al. 2011). There exists a further thin film between reactant mixture and the catalyst pellet as shown in Figure 2. During the transesterification process, the alcohol-oil bulk phase diffuses through the thin film surrounding the solid catalyst particle; this is called an external transport phenomenon. The liquid phase then diffuses into the catalyst particle core area through the pores in the process of internal mass transfer. It can be observed that the concentration of the bulk phase decreases with the thickness of thin film depicted by the distance in Figure 2.

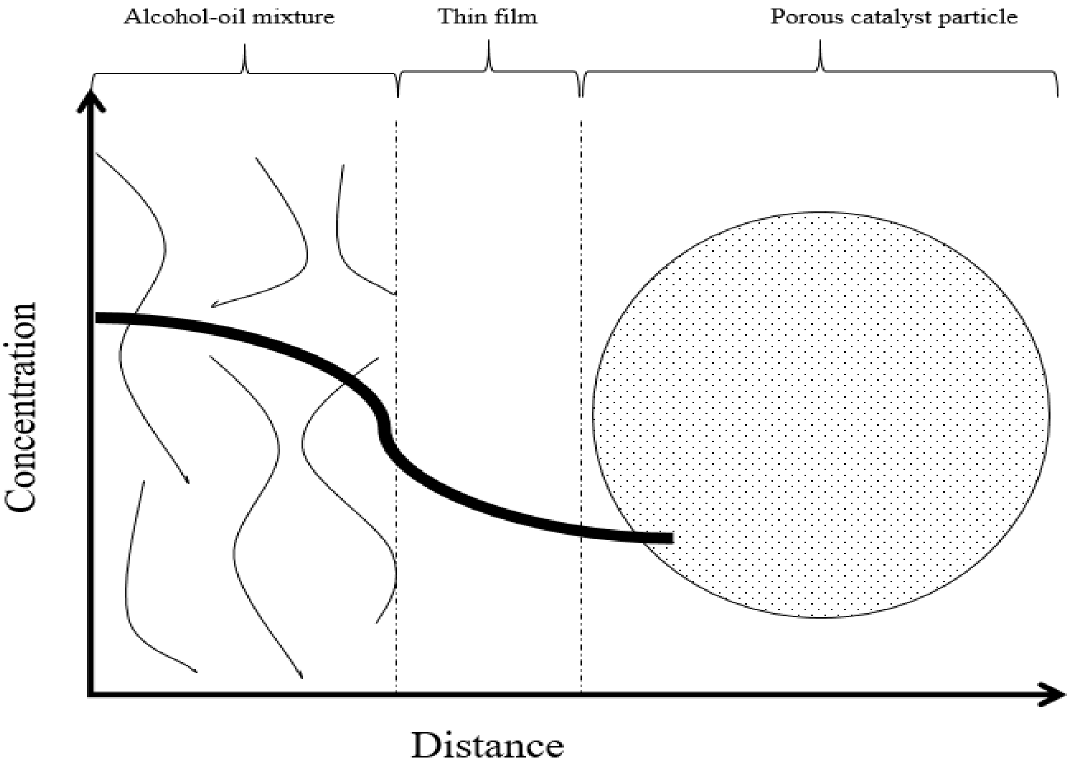

Figure 2: Illustration of concentration profile of the reactants in the presence of the solid catalyst particles.

The catalytic reaction takes place when the reactants come into contact with the catalyst active site which is located within the internal surface of the porous catalyst pellet. The process of heterogeneous catalysis can be explained in seven classic steps; the first two steps describe the diffusion of the reactants from the bulk phase of the fluid to the external surface of the catalyst pellet; external mass transfer, then from the external surface through the pores to the internal surface where the reaction would take place; internal mass transfer (Portha et al. 2012; Veny et al. 2014 ; Chen et al. 2001). The third step describes the adsorption of the reactants on to the active site of the catalyst, the reaction takes place in the fourth step and the desorption of the products from the active sites occur during the fifth step. The last two steps involve the diffusion of the products from the internal surface of the catalyst, and the diffusion through the pores (Portha et al. 2012; Veny et al. 2014; Chen et al. 2001; Chulalaksananukul et al. 1992).

The little research available on the study of mass transfer effects on heterogeneously catalyzed transesterification has demonstrated the possibility of minimizing the effect of external mass transfer limitation. This can be done introducing vigorous mixing to the transesterification reaction thereby reducing the thickness of the thin film; as a result, the reaction rates are improved (Kumar et al. 2010; Rashid et al. 2009; Bambase et al. 2007). Among other factors, internal mass transfer occurring inside the pores of catalyst pellet depends on the catalyst particle size (Yori et al. 2007).

2.8. Kinetic studies for transesterification reaction

Over the last decades, researchers have studied kinetics of biodiesel production process using homogeneously catalyzed transesterification reaction. Extensive literature exists for kinetic studies of transesterification reaction with the use of homogeneous transesterification reaction, where the impact of temperature and reaction time was demonstrated (Jain & Sharma 2010; Darnoko & Cheryan 2000; Noureddini & Zhu 1997). In recent years, research developments have gradually been made on the investigation of the kinetics on the heterogeneously catalyzed transesterification for biodiesel production. Most researchers have demonstrated that the experimental data for heterogeneously catalyzed transesterification reactions suitably fit into a pseudo first order (PFO) kinetic model (Jacob et al. 2008; Liu et al. 2008; Di Serio et al. 2008; Vujicic et al. 2010; Zhang et al. 2010; Jaya & Ethirajulu 2011; Birla et al. 2012; Fatah et al. 2016; Olutoye & Hameed 2016; Nasreen et al. 2016; Vafakish & Barari 2017). These researchers successfully determined the values of reaction rates, activation energies and pre-exponential factors which are essential for reactor design. Particularly informing the reactor design process in terms of the predictive extent of the transesterification reaction, and the efficiency of solid catalysts usable during conversion of a range of oil sources. However, there are no published reports on kinetics of transesterification reaction catalyzed using H-SOD.

CHAPTER 3: PROPERTIES OF WCO AND ANIMAL FAT

A number of factors including the quality of the feedstock oil during production process influences the quality of the biodiesel. Presented in this chapter, is the results and methodology used to determine some of the properties of animal fat or waste cooing oil used in this study. These are acid value, saponification value and iodine value.

3.1. Acid value (AV)

Compared to other oils used for transesterification reaction, animal fat and waste cooking oil potentially contain high percentage of FFA i.e. way more than the ideal 1%. As a result, animal fat or waste cooking oil would not be ideal feedstock for transesterification reaction over a homogeneous alkaline catalyst. To confirm the need for a heterogeneous catalyst, FFA content in the BTO and WCO was determined to ensure that it exists in a considerable amount. It was also required to prove the tolerance of H-SOD to the high content of FFA in biodiesel production. Determination of the FFA content was carried out and the acid value of the beef tallow oil/ waste cooking oil/ biodiesel produced was calculated using Equation 1:

$$Acid\ value = \frac{KVC}{m} \tag{1}$$

Where K is the neutralization number for oil/fat with a value of 56.1, it is the mass of KOH in milligrams required to neutralize 1 g of chemical substance. C is the concentration of the titrate solution (g/ml). The volume of KOH required to neutralize the fat/oil sample is denoted as V (ml). The mass of fat/oil sample used is denoted as m (g).

3.2. Saponification value (SV)

The process of saponification involves the breaking down neutral fat molecules into glycerol and fatty acid by treating it with an alkali substance. This value defines the number of milligrams of potassium hydroxide required to neutralize 1 gram of fat, containing fatty acids thereby giving insights on the degree of fatty acids contained in the fat/oil, whether the proportion is high or low. To carry out the experiment, 2 grams of the fat/oil sample was weighed in a flask, where a 25 ml alcoholic Potassium hydroxide solution was added (1.0 N) and then stirred. A condenser was attached to the flask and the mixture was gently boiled using a water bath, thereby allowing saponification to proceed at a reaction time of about 45 minutes. The mixture was then cooled down, and 1ml of phenolphthalein indicator was added to the resulting mixture. Titration on the mixture was then carried out using hydrochloric acid (0.5N) until the end point, where the pink color disappeared; the blank titration was carried out in a similar manner and at the same time as the fat/oil sample test. Saponification value was then calculated using Equation 2 as follows:

$$Saponification\ value = \frac{56.1\ \times N \times (V_b - V_s)}{W_s} \tag{2}$$

Where N specifies the normality of hydrochloric acid, V_b is the volume of hydrochloric acid used in the blank (ml), V_s is the volume of hydrochloric acid used in the fat/oil sample (ml) and W_s is the weight of the fat/oil sample (g) (Odoom & Eduse, 2015).

3.3. Iodine value (IV)

The iodine number defines the grams of iodine consumed by 100 g of fat/oil. It is used to estimate the degree of unsaturation in fats and oils. It indicates the number of double bonds present in the length of the carbon chain. Generally, iodine value is lower in animal fats than vegetable oil. To estimate the iodine value, an experiment was conducted using Wij’s methodology (Odoom & Eduse, 2015). 1 gram of fat/oil sample was weighed and transferred to a 500 ml volumetric flask, where 15 ml of carbon tetrachloride was added and the mixture was stirred to allow the sample to dissolve, 25 ml of Wijs solution was the pipetted into the flask, and the mixture was further stirred to ensure that it is well mixed. The resulting mixture was left in a dark place for about 30 min, where the temperature was kept at room temperature. The solution of potassium iodide was then added (10 %) at a volume of 20 ml, as well as 150 ml of distilled water. Titration was then conducted on the resulting mixture using a solution of 0.1N thiosphate until the yellow color disappeared, indicating end point. The blank titration was carried out in a similar manner and at the same time as the fat/oil sample test. Iodine value was then calculated using Equation 3 as follows:

$$Iodine\ Value = \frac{12.69 \times (V_b - V_s) \times N}{W_s} \tag{3}$$

Where N specifies the normality of thiosulphate solution, V_b is the volume of thiosulphate used in the blank (ml), V_s is the volume of thiosulphate used in the fat/oil sample (ml) and W_s is the weight of the fat/oil sample (g).

3.4.Results and discussion

Table 1 and Table 2 show the physical properties of WCO and BTO used in this study, particularly saponification value, iodine value and the acid value. According to previous studies, the base-catalyzed transesterification requires that oil samples should have FFA content less than 1% to avoid the occurrence of hydrolysis and saponification reactions (Atadashi et al. 2012; Banković-Ilić et al. 2014; Farooq et al. 2016). In this study, the FFA contents of WCO and BTO were determined at 3.28% and 4.53%, respectively (correspondingly acid values of 6.53 mg KOH/g and 9.01 mg KOH/g). Compared to literature, the values obtained from the FFA content of the oils used in this study were relatively high. This can be attributed to the age and storage of these oils; these oils were stored in the laboratories for a long time, over 2 years. As demonstrated in the study conducted by Obahiagbon (2012), the longer storage time of the oils correspond to increased level of FFA content. The high amount of FFA found in BTO and WCO justified the need to use a solid catalyst during transesterification reaction. Unlike homogeneous catalysts, heterogeneous catalysts are less sensitive to FFA; as a result, the likelihood of soap formation, a side reaction that reduces the biodiesel yield is minimized.

Although the FFA content was relatively high, the production of biodiesel was successful owing to the use of solid H-SOD as a catalyst for transesterification. Since the structure of H-SOD is made up of Si-O-Si, it tends to exhibits the behavior similar to that of sodium metasilicate, whereby hydrolysis reaction with sodium silicate and water resulted in the formation of NaOH and Si-O-H (Guo & Fang 2012), thereby suppressing the formation of soap because of the decreased water content (less than 4%) Guo et al. (2012). The tolerance of H-SOD to water could be attributed partly to its porous structure. Furthermore, the unique structure of the catalyst could enhance sequential hydration to occur in three steps when there are high amounts of water present. In addition, the Si-O-Si bridges that form the cages of the

H-SOD could hydrolyze and cause H_4SiO_2 monomers to be released and thus produce -OH which prevents soap formation.

Other properties of the raw material such as saponification value and iodine value fell within the range of values reported in literature (Raqeeb & Bhargavi 2015; Chuah et al. 2017; Mata et al. 2014; Ma & Hanna 1999) as shown in Table 1 and Table 2. Furthermore, the Fatty Acid profile obtained from the GC-MS results confirmed the quality of feedstock used in this study, in terms of the content of fatty acid in the oil samples. Compared to vegetable oils which are generally rich in unsaturated fatty acids, animal fat oils are rich in saturated fatty acids (Talwar 2016). Acid profile for the tallow used in this experiment is shown in Table 4; it shows that the BTO is rich in saturated palmitic acid. This is in agreement with results reported in literature where it was demonstrated that about 50% of the total fatty acids in BTOs are saturated. The studies specifically demonstrated the high contents of palmitic and stearic acids hence BTOs are high in viscosity and melting points (Adewale et al. 2014; 2015; da Cunha et al. 2009). This explains why they are solid at room temperature and therefore the need for heating prior the transesterification reaction. As anticipated, the acid profile for the WCO shown in Table 3 confirms results in literature where high content of unsaturated acids is reported by some researchers (Talwar 2016; Hassani et al. 2016).

Table 1: Physico-chemical characteristics of WCO.

Properties	**Units**	**Present study**	**Literature** (Raqeeb & Bhargavi 2015) (Chuah et al. 2017)
Saponification value	mg KOH/g	188.3	188.0 - 207.0 203.4 - 206.2
Iodine value	gI2/100 g	60.33	83.0 - 141.5 57.2 - 58.2
Acid Value	mg KOH/g	6.53	1.32 - 3.60 2.01 - 2.07

Table 2: Physico-chemical characteristics of BTO.

Properties	**Units**	**Present study**	**Literature** (Raqeeb & Bhargavi 2015) (Chuah et al. 2017)
Saponification value	mg KOH/g	188.3	188.0 - 207.0 203.4 - 206.2
Iodine value	gI_2/100 g	60.33	83.0 - 141.5 57.2 - 58.2
Acid Value	mg KOH/g	6.53	1.32 - 3.60 2.01 - 2.07

Table 3: Fatty Acid Composition of WCO.

System name	**Common name**	**Lipid number**	**Weight %**
Tridecanoic acid	Tridecylic acid	C13:0	0.39
Undecanoic acid	Undecylic acid	C11:0	5.41
Linoleic acid	Linoleic acid	C18:2	56.95
Oleic acid	Oleic acid	C18:1	20.15
Octadecanoic acid	Stearic acid	C18:0	0.39
Other	Other	-	16.71

Table 4: Fatty Acid Composition of BTO.

System name	**Common name**	**Lipid number**	**Weight %**
Decanoic acid	Capric acid	C10:0	0.92
Undecanoic acid	Undecylic acid	C11:0	0.01
Tridecanoic acid	Tridecylic acid	C13:0	9.42
Hexadecanoic acid	Palmitic acid	C16:0	83.88
Oleic acid	Oleic acid	C18:1	0.17
Docosenoic acid	Urucic acid	C22:1	1.89
Other	Other		3.71

CHAPTER 4: CATALYST PREPRATION AND CHARACTERIZATION

4.1. Introduction

This chapter focuses on the synthesis and characterization of the H-SOD particles. H-SOD is naturally a crystalline aluminosilicate, which is a type of a zeolite material belonging to a clathrasils group (Teimouri et al. 2015; Narimani & Kharamesh 2014). Due to high thermal stability, high mechanical strength and increased surface active sites, zeolites find their use in chemical industry as catalysts, molecular sieves or membranes, adsorbents as well as ionic exchangers (Nabavi et al. 2014; Xu et al. 2004; Fernando & Singh 2007; Li & Xie, 2006; Helwani et al. 2009). Researchers have emphasized the advantages of using highly basic materials to catalyze the transesterification reaction such as faster reaction speeds and less corrosiveness (Freedman et al. 1984; Watkins, et al. 2004). As a result , H-SOD was proposed and used in this study as solid catalyst for transesterification reaction due to its high alkalinity and low costs (Teimouri et al. 2015). The hydroxy sodalite particles were prepared by hydrothermal synthesis method, similar to the one described by Daramola et al. (2016) in their study on the synthesis and characterization of nanocomposite hydroxy sodalite as a membrane.

4.2. Materials

Anhydrous sodium metal silicate (Na_2SiO_3), sodium hydroxide (NaOH), anhydrous sodium aluminate ($NaAlO_2$) were purchased from Sigma-Aldrich, South Africa. Deionized water was prepared in-house, at the school of chemical and metallurgical engineering laboratories, University of the Witwatersrand.

4.3. Methods

4.3.1. Catalyst preparation

The synthesis solution was prepared from a mixture of the anhydrous sodium metal silicate (Na_2SiO_3), sodium hydroxide (NaOH), anhydrous sodium aluminate ($NaAlO_2$) and in-house de-ionized water. The materials were mixed in a polytetrafluoroethylene (PTFE) bottle and stirred for an hour on a hot plate magnetic stirrer at room temperature. The vigorously stirred precursor solution resulted in a molar composition ratio: $5SiO_2$:Al_2O_3:50 Na_2O: $1005H_2O$, 45 ml of the solution was then transferred into a portable Teflon-lined stainless steel autoclave which was subjected to heat in an oven at 140˚C for 3.5 h. At the end of the hydrothermal synthesis, the hot autoclave was cooled down by running tap water and the prepared hydroxy sodalite crystals were filtered from the resulting product mixture and washed thoroughly with deionized water until the pH of the washed water was neutral. The washed crystals were then collected on the filter paper and transferred to a crucible from where they were left to dry overnight at 100˚C in an oven. Prior to transesterification reaction, the dried hydroxy sodalite particles were calcined at 200 ˚C for 2 h to remove moisture and possible volatile substances thereby increasing the catalyst activity.

4.3.2. Catalyst characterization

To investigate the surface chemistry, Fourier transform infrared spectroscopy (FTIR) was used to check for the chemical functional groups of the catalyst, with a wave number range from 400 to 4000 cm^{-1}. In order to carry out the scanning electron microscope (SEM) analysis, the hydroxy sodalite catalyst was coated with ultrathin gold/palladium alloy due to its nonconductive nature. The determination of surface topology and morphology of the catalyst was determined by SEM, performed on a Carl Zeiss, which was operated at an accelerated voltage of 5.00 kV. Pore size, pore volume and surface area measurements were obtained on a Micrometrics Tri-Star 3000 surface area and porosity analyzer at 77K using nitrogen gas~~, by Brunauer, Emmett and Teller (BET) method~~. Thermal gravimetric analysis (TGA) was carried out to understand thermal stability of the hydroxy sodalite particles. To measure the crystallinity of the catalyst, X-ray powder diffraction(XRD) analysis was carried out using the Rigaku's Ultima IV X-ray diffractometer operating with CuKα radiation ((λ = 1.5406 Å), and equipped with a graphite monochromator in the diffracted beam. Approximation of the H-SOD crystalline size was done using the Scherrer Equation as follows:

$$D = \frac{K\lambda}{\beta cos\theta} \tag{4}$$

Where D is the average particle size (Å), K is the dimensionless shape factor also known as Scherrer constant, λ is the X-ray wavelength (Å), β is the FWHM i.e. Line broadening at half the maximum intensity (radians), θ is the Bragg angle (degrees).

4.3.3. Results and discussion

Figure 3 shows the SEM images for the synthesized H-SOD particles. The Energy Dispersive X-ray (EDX) of the H-SOD crystals showed that Si/Al= 1-1.5, which indicates an identification of the H-SOD (Makgaba & Daramola 2015). Although the SEM image shows the successful synthesis of the H-SOD crystals, a mixture of H-SOD particles with cubic shape and nano rod-like shape were also observed. The morphology observed during this study is consistent with literature where hydroxy sodalite particles were synthesized at different shapes; during the investigation conducted on the emulsion derived synthesis of urchin- shaped H-SOD particles, Kundu et al. (2010) observed particles composed of various nanorods. Furthermore, in another study, cube shaped, thread-ball shape and flowerlike shapes were observed during an investigation on the aqueous – based hydrothermal synthesis in the presence of Cetyltrimethylammonium bromide (Naskar et al. 2011).

The FTIR spectrum in Figure 4 shows the asymmetric stretching vibration of T-O-T (T-Si, Al) at ~1000 cm^{-1}. In addition, the peaks around 740 cm^{-1} and 660 cm^{-1} can be assigned to the symmetric stretching vibration of T-O-T. The presence of water molecules in the framework of the synthesized H-SOD is vividly shown with the strong broad band centered at ~3600 cm^{-1} (Breck, 1974) This information confirms the synthesis of pure H-SOD particles and is in agreement with literature (Buhl et al. 2011). In addition to the FTIR results, XRD results in Figure 5 confirmed the formation of H-SOD particles. The H-SOD crystallite sizes were found to be 276 Å as per Scherrer equation based on the resulting XRD diffractogram. Furthermore, the synthesized pattern agrees with the simulated XRD pattern which is documented in the database of zeolite structures by IZA (International Zeolite Association 2017)

TGA results for the synthesized H-SOD particles shown in Figure 6 are in agreement with literature (Li et al. 2007; Yao et al. 2006), where mass loss of about 12.3% is observed with the increase in temperature. Loss of mass could be due to the loss of structural water during heating up to just above 200 ˚C. The additional drastic mass loss of the H-SOD up to above 400 ˚C may be attributed to the possible decomposition of organic functional groups occurring at higher temperatures (Li et al. 2007; Yao et al. 2006). The BET Surface area, pore volume and the pore size derived from the nitrogen adsorption data for the synthesized H-SOD particles are 0.1643 m²/g, 0.0013 cm³/g and 30.9192 nm, respectively as shown in Table 5. Similar results were observed by Daramola et al. (2016) in their study on a statistical approach of investigating the influence of process variables on the transesterification reaction of WCO over sodium silicate catalyst. During this study, the BET surface area, pore volume and the pore size were reported at 0.39 m²/g, 6.24 × 10^{-3} cm³/g and 59.18 nm, respectively. Considering the very low surface area of the catalyst, it cab be concluded that the cage of the sodalite is occluded with materials such as water molecules as described elsewhere(Daramola et al. 2016).

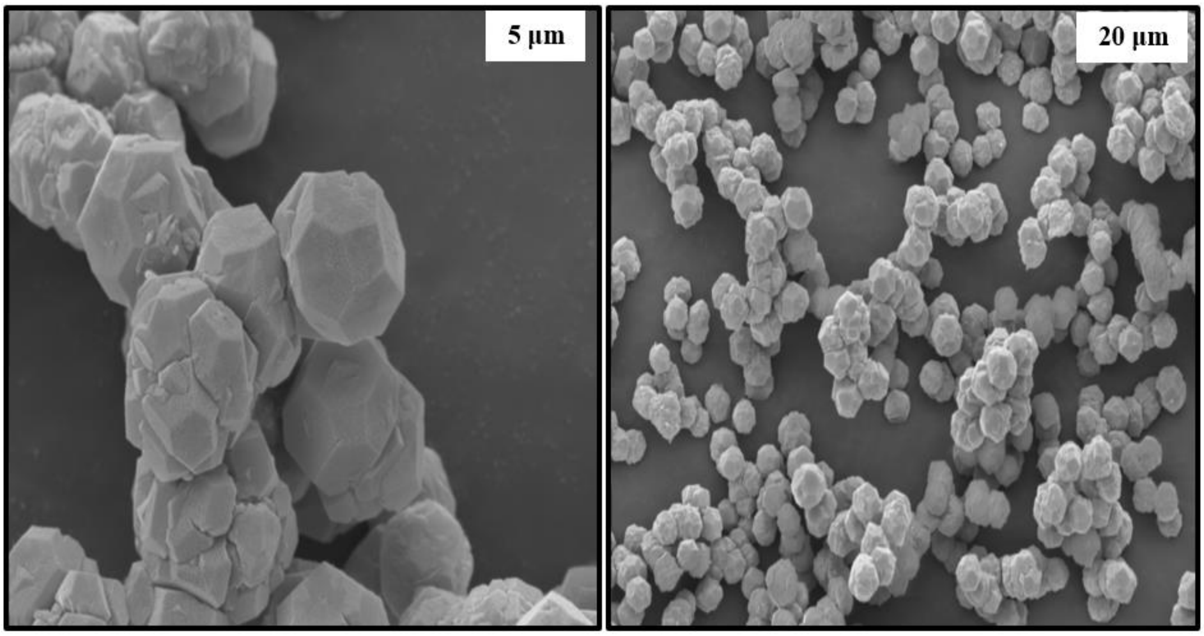

Figure 3: SEM images for the H-SOD catalyst particles.

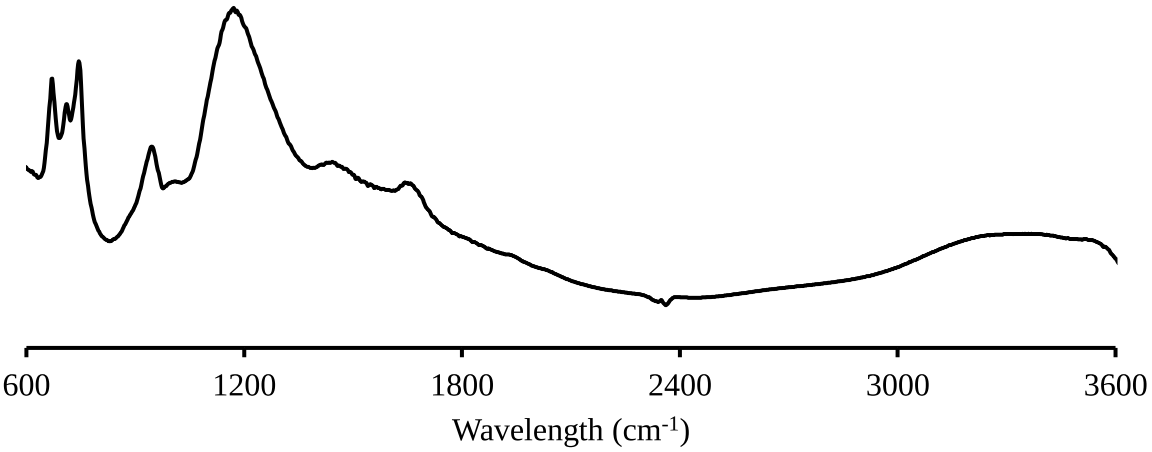

Figure 4: FTIR Spectrum for the H-SOD catalyst particles.

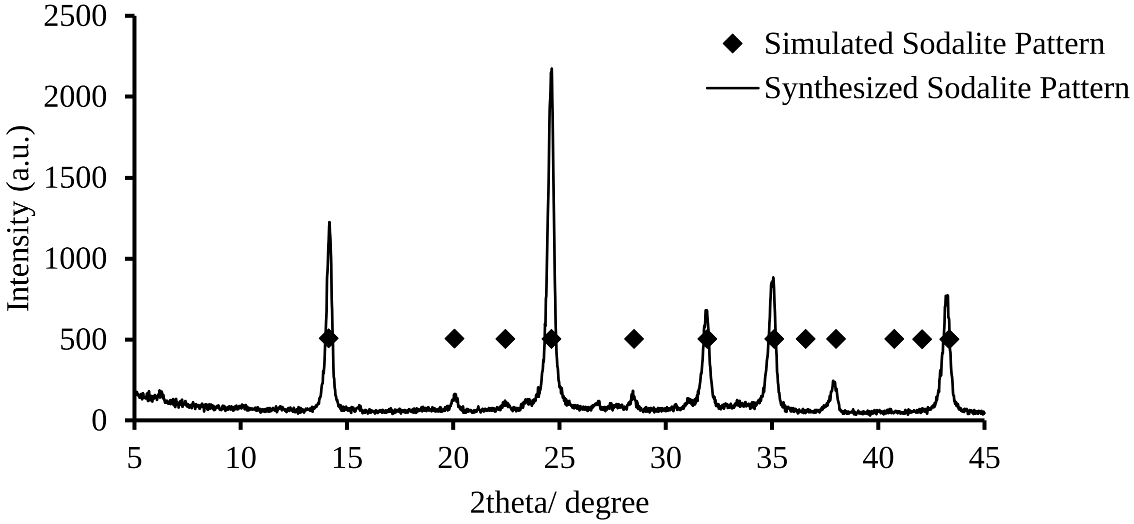

Figure 5: XRD results for the synthesized H-SOD particles compared to the IZA simulated sodalite pattern.

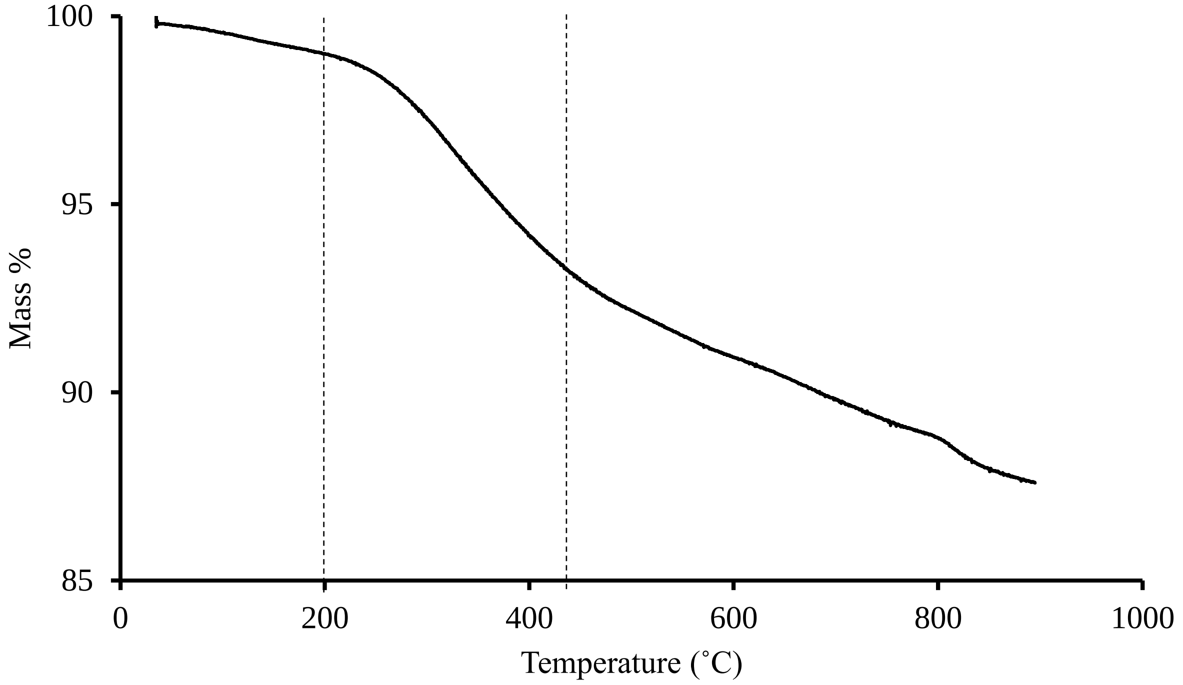

Figure 6: TGA results for the synthesized H-SOD particles synthesized

Table 5: BET Surface area, pore volume and pore size derived from the nitrogen adsorption data for the synthesized H-SOD particles

Parameter	**Value**
BET Surface Area (m^2/g)	0.1643
Pore Volume (cm^3/g)	0.0013
Pore Size (nm)	30.9192

CHAPTER 5: TRANSESTERIFICATION REACTION OF WCO OVER A SOLID H-SOD CATALYST

5.1. Introduction

In this chapter, a preliminary investigation was carried out to investigate the feasibility of using the hydroxy sodalite particles to catalyze transesterification reaction. The investigation was conducted on the batch methanolysis process for the conversion of waste cooking oil (WCO) to biodiesel over the heterogeneous H-SOD catalyst. Numerous studies demonstrated the use of typical edible plant oils, such as soybean, rapeseed oil and palm oil for the production of biodiesel (Guo & Fang 2012; Canakci & Sanli 2008; Jacob et al. 2008). These raw materials are not entirely suitable, more especially in developing countries, due to the limited supply and high cost associated with their application, as well as competition with the food chain. Therefore, low cost, non-edible oils such as Jatropha oil, animal fat and waste cooking oil have been suggested and tested as alternatives (Guo et al. 2012; Aransiola et al. 2012; 2013; Daramola et al. 2016).

However, the main disadvantage of these non-edible types of feedstock is the high content of free fatty acid (FFA) within the oils, which poses problems in the production process. Consequently, Biodiesel from high FFA content feedstock is conventionally produced by a two-stage process: esterification, followed by transesterification (Abbaszaadeh et al. 2012; Aransiola et al. 2013). The esterification step serves to reduce the amount of FFAs present in the oil in order to allow for the transesterification reaction to commence. The implication of this additional process unit is inevitably the additional costs associated with the biodiesel production. In recent times, the use of heterogeneous catalysts has been proven to be very effective in converting high FFA feedstock directly to biodiesel, thereby by-passing the esterification stage (Guo & Fang 2012).

The most commonly used heterogeneous catalysts for the production of biodiesel are ion-exchange resins, inorganic-oxide solid acids and supported noble-metal oxides. However, a dramatic decrease in the catalytic activity of these catalysts has been observed due to their absorption of water during biodiesel production. Besides the sharp reduction in the catalytic activity, the catalysts can form a slurry with the products by absorbing water and carbon dioxide, thereby increases the viscosity of the product mixture, making product separation very difficult (Li et al. 2014). In this chapter, H-SOD, a type of zeolite material is introduced as a catalytic material for transesterification reaction. Among other solid catalysts, H-SOD is much attractive owing to its ability to thrive during intense reaction conditions, without dramatic loss in catalytic activity. Furthermore, H-SOD is relatively inexpensive and is easy to synthesize and implement Teimouri et al. (2015). The results from the preliminary investigation on the use of H-SOD particles to catalyze the transesterification of WCO into FAME when a batch reactor is use are presented in this chapter.

5.2. Materials

Waste cooking oil used for the preliminary investigation was obtained from a local restaurant, in Braamfontein, Johannesburg, South Africa. Gas Chromatography analytical standard chemicals; FAME (MIX, C4-C24, 100MG NEAT) and glycerol (99 %) used in this study were purchased from Sigma-Aldrich (Pty), South Africa.

5.3. Transesterification reaction using WCO as feedstock

H-SOD particles were firstly prepared using hydrothermal synthesis method as described in Chapter 4, and used as a catalyst for the transesterification process. The experimental set up for the transesterification reaction is shown in Figure 7. The WCO was boiled at 100 ˚C to remove moisture, and was filtered to remove solid particles. The reaction was carried out in a 250 ml three necked round bottomed flask, batch reactor setup; equipped with a reflux condenser to prevent loss of methanol. The flask charged with relevant amount of WCO, methanol and H-SOD particles was immersed in a temperature controlled water bath placed on a hot plate magnetic stirrer. The reaction conditions were: reaction time 6 h; reaction temperature 60 ˚C; methanol-to-WCO ratio 7.5:1; catalyst weight percentage 3 wt. %; stirrer intensity 400 rpm. After the completion of the reaction, the catalyst particles were recovered from the mixture by filtration through nylon filter paper (0.45 µm pore dimension). A separating funnel was used to separate the products; the resulting glycerol was drained from the bottom of the funnel while biodiesel was collected from the top. Analysis of the samples was performed using a pre-calibrated Gas Chromatograph equipped with a LECO GCxGC Thermal Modulator (GC-MS, model: Agilent 7890N) described in section 5.4 below. .

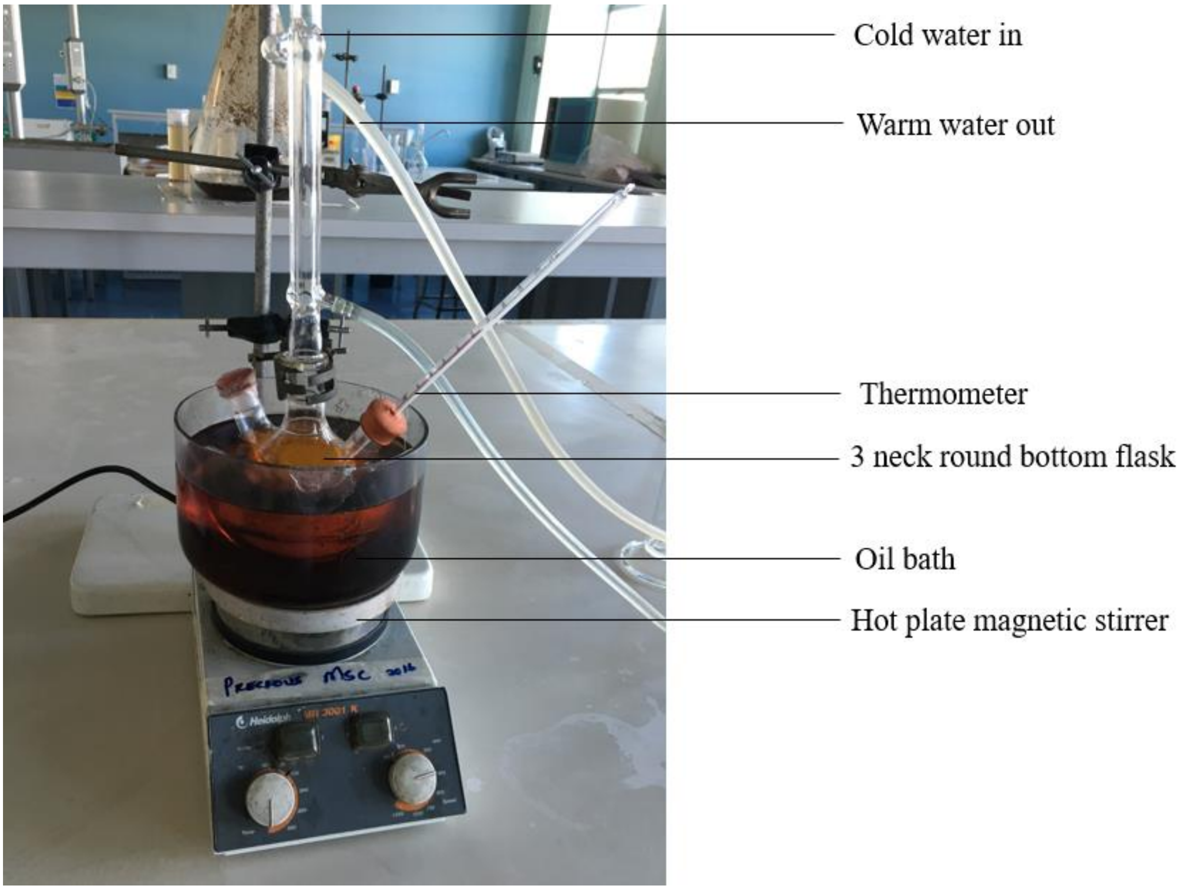

Figure 7: Transesterification experimental set up.

5.4. GC-MS method

Analysis of biodiesel and oil samples (animal fat and waste cooking oil) was performed on a Gas Chromatography (Agilent 7890B) coupled with a mass spectrometer (LECO GC x GC-TOF Low resolution mass spectrophotometer) due to its accuracy in identifying and quantifying minor components.

Sample preparation: For quantitative analysis, a 10-ppm stock solution was prepared, by diluting the neat biodiesel standard in a 10-mL volumetric flask. This stock was stored in a fridge at 4 °C pre-to analysis. Then 8 calibration points (0.001, 0.005, 0.01, 0.025, 0.05, 0.1, 0.5, 1 ppm) / standards were prepared into 2 mL GC vails by taking an appropriate volume from the stock and diluting with dichloromethane (DCM, HPLC grade). For qualitative analysis, samples were prepared such that their concentration was within the limit of quantification.

Injection Method: Samples to be analysed were placed in a 98 sample tray and the syringe was pre-washed 3 times with 8 uL of Chloroform (HPLC grade). A 1 µL oil sample or standard biodiesel was injected into the injection port which had a blue-sky liner (split single taper gooseneck w/Wool 4mm x 6.5 x 78.5) ; Gerstel Multi-Purpose Auto sampler.

GC Methods: Column type (Rxi-5 Sil MS), length 29.002 m of (30m), with internal diameter 250µm, and film thickness of 0.25 µm with a maximum temperature of 360 °C was used. Carrier gas was Helium (99.999%); front inlet type was Split/splitless with a split mode activated (split ratio 20:1). The Flow rate was 1.5 ml/min at constant flow while front inlet temperature was 280 °C throughout the run. The initial oven temperature of 50 °C for maintained for 0.2 min and ramped at 15 °C/min, to 200 °C, then ramped at 8 °C/min to 300 °C and held at this temperature for 2 min. Transfer line temperature was 250 °C.

MS Methods: Acquisition delay of 4.0 min, mass range of between 40 to 600 m/z, with acquisition rate of 10 spectra/second, acquisition voltage at 1552 eV and electron energy (ionization energy) of -70 eV was used. The ion source temperature was 250 °C.

Data Processing Methods: For qualitative analysis: The base line offset of 1 (just above the noise) was used, with a peak width of 4 secs and signal to noise (S/N) ratio of 10. The library search mode was normal and forward. The number of library hit was 10, while the minimum molecular weight allowed was 40 m/z and maximum molecular weight was 600 m/z. Mass threshold was 2% and minimum similarity before name was assigned was 50%. The library used was Replib and mainlb from NIST. For quantitative analysis, a data processing method using the 8-point calibration curve was used where the area of each standard has been equated to the concentration.

5.5. Results and discussion

The results for catalyst synthesis are shown as explained in Chapter 4, demonstrating the successful formation of H-SOD materials via hydrothermal synthesis. Biodiesel mixture obtained comprised major components of fatty acid methyl esters of long chain carbon chains (C6-C24). The sample obtained after the transesterification reaction is depicted in Figure A1 in the Appendix A. As an important qualitative property of biodiesel, the ester content of the produced biodiesel was evaluated chromatographically using GC-MS according to EN 14103 standards. According to this standard, majority of the carbon chains that constitute biodiesel are from C14 to C24 and does not contain C7. Qualitatively, the results of the GC-MS analysis of the reaction products are shown in Figures 8 - 9 and Tables 6 - 7. It can be deduced that FAME components in the mixtures for both the standard and produced biodiesel could be identified and compared. FAME peaks are only identified between 13 minutes and 19 minutes' retention times for the produced biodiesel when compared to peaks in the standard. This can be attributed to the fact that the FAME components in the biodiesel largely depend on the type of feedstock used (Mata et al. 2014). However, major components making up biodiesel mixture are common in the two mixtures; confirming the feasibility of using the synthesized H-SOD as a catalyst for the transesterification reaction of WCO to biodiesel.

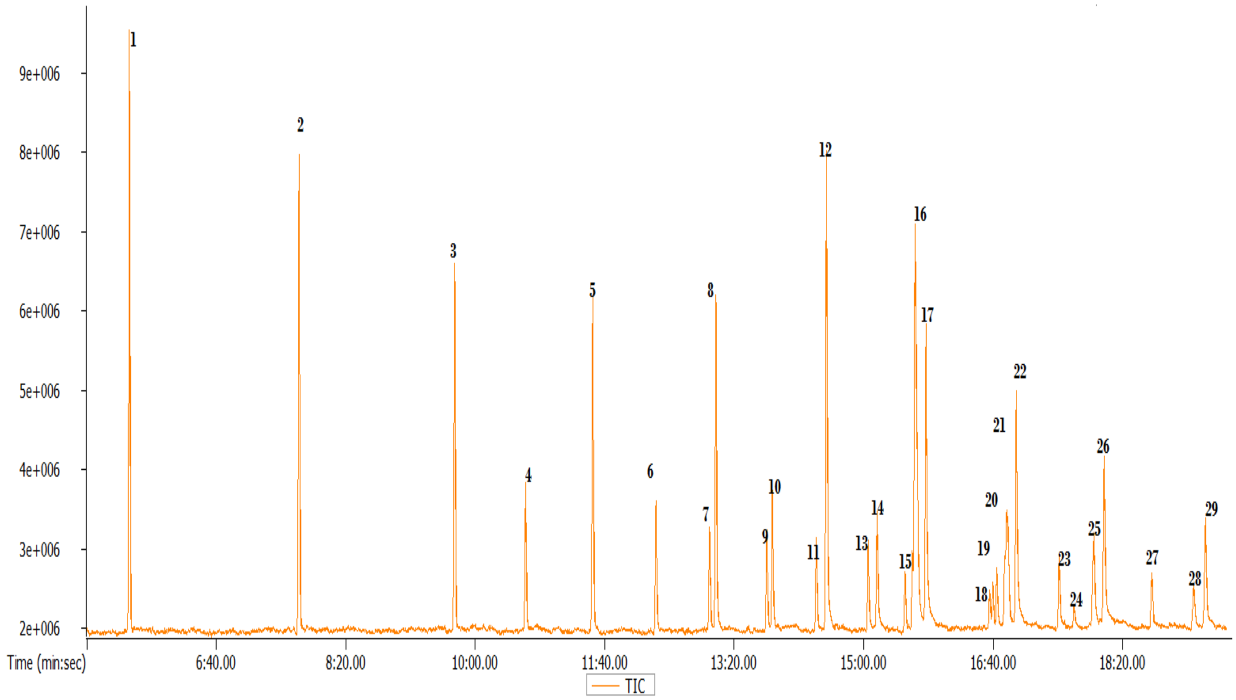

Figure 8: Chromatogram showing standard biodiesel components to validate WCO biodiesel (names provided in Table 6).

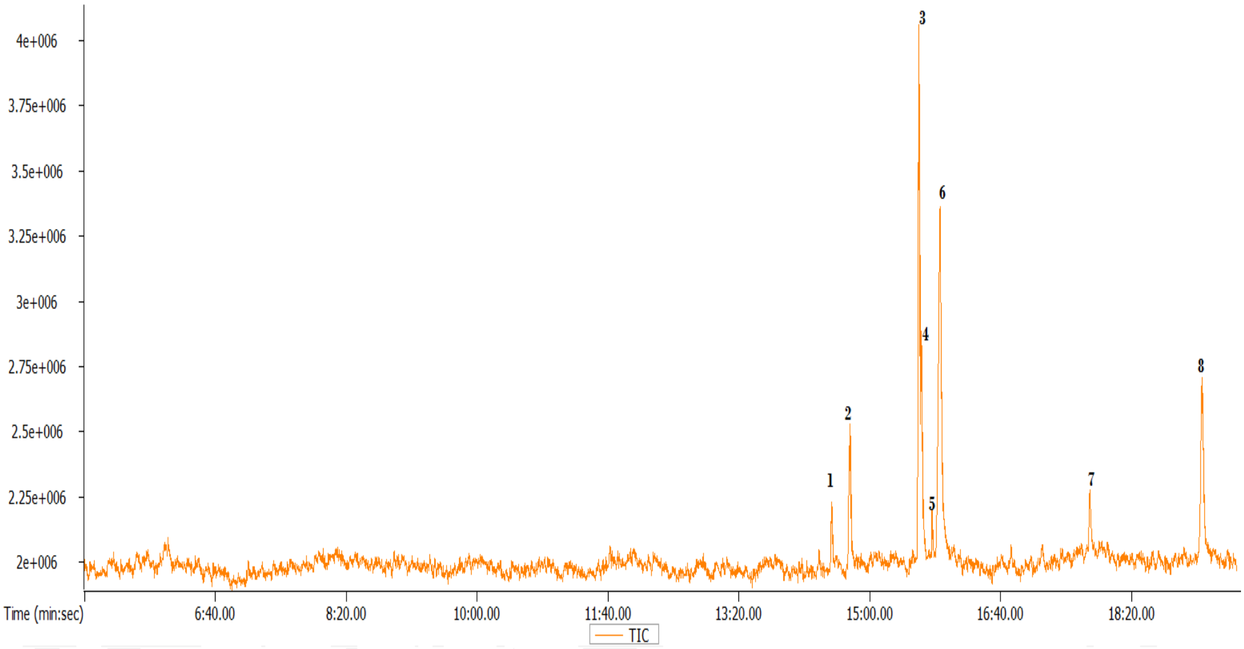

Figure 9: Chromatogram showing WCO biodiesel components (names provided in Table 7).

Table 6: GC-MS analysis results for the biodiesel standard to validate WCO biodiesel

Peak no.	**Name**		**RT (min:sec)**	**Peak no.**	**Name**		**RT (min:sec)**
1	Hexanoic acid, methyl ester	C6:0	05:33	16	Linoleic acid, methyl ester	C18:2	15:37
2	Octanoic acid, methyl ester	C8:0	07:44	17	Oleic acid, methyl ester	C18:1	15:39
3	Decanoic acid, methyl ester	C10:0	09:44	18	Linolenic acid, methyl ester	C18:2	15:40
4	Tridecanoic acid, methyl ester	C13:0	10:39	19	Octadecanoic acid, methyl ester	C18:0	15:48
5	Dodecanoic acid, methyl ester	C12:0	11:30	20	Arachidonic acid	C20:4n6	16:37
6	Tridecanoic acid, methyl ester	C13:0	12:19	21	5,11,14,17-Eicosapentaenoic acid, methyl ester(all-Z)	-	16:39
7	Tetradecanoic acid, methyl ester	C14:0	13:01	22	Linolenic acid, methyl ester	C18:2	16:43
8	Methyl tetradecanoic acid	C14:0	13:06	23	11,14-Eicosadienoic acid, methyl ester,(Z,Z,Z)	-	16:48
9	Oleic acid, methyl ester	C18:0	13:45	24	Oleic acid, methyl ester	C18:0	16:50
10	Tridecanoic acid, methyl ester	C13:0	13:49	25	Linolenic acid, methyl ester	C18:2	16:51
11	Hexadecanoic acid, methyl ester(Z)	C16:0	14:23	26	Eicosanoic acid, methyl ester	C20:0	16:57
12	Hexadecanoic acid, methyl ester	C16:1	14:31	27	Hexadecanoic acid, methyl ester	C16:1	17:31
13	Cyclopropaneoctanoic acid, methyl ester	C17:1	15:03	28	Oleic acid, methyl ester	C18:0	19:15
14	Tridecanoic acid, methyl ester	C13:0	15:11	29	Hexadecanoic acid, 15-methyl-, methyl ester	-	19:24
15	ç-Linolenic acid, methyl ester	C18:2	15:32				

Table 7: GC-MS analysis results for the synthesized WCO biodiesel.

Peak no.	**Name**		**RT(min:sec)**
1	Tridecanoic acid, methyl ester	C13:0	14:31
2	Undecanoic acid, methyl ester	C11:0	14:45
3	Linoleic acid, methyl ester	C18:2	15:37
4	Oleic acid, methyl ester	C18:1	15:39
5	Octadecanoic acid, methyl ester	C14:0	15:48
6	9,12 Octadecanoic acid	C18:2	15:54
7	10-Undecyn-1-ol	-	17:48
8	9,12 Octadecadienoyl chloride	-	19:14

5.6. Summary

The results of the preliminary investigation revealed the possibility of converting WCO to biodiesel over calcined H-SOD catalyst. Although information about the conversion and the biodiesel yield with this catalyst is not provided in this chapter. This piece of information served as a basis for studies in the subsequent chapters.

CHAPTER 6: TRANSESTERIFICATION OF ANIMAL FAT OIL TO BIODIESEL OVER SOLID SODALITE CATALYST

6.1. Introduction

Recent researchers have suggested and tested the use of non-edible oils such as Jatropha oil, animal fat and waste cooking oil as alternative feedstock for biodiesel production (Guo et al. 2012; Aransiola et al. 2012; 2013; Daramola et al. 2016). However, the main disadvantage of these non-edible types of feedstock is the high content of free fatty acids (FFA) within the oils, which poses problems in the production process. Conventionally used base homogeneous catalysts are highly sensitive to FFA and water in the oil feedstock and thus have the tendency to react with the FFA to form soap which further complicates the glycerol-fame separation process. Consequently, biodiesel from high FFA content feedstock is conventionally produced by a two-stage process: esterification, followed by transesterification (Yaakob et al. 2013). The esterification step serves to reduce the amount of FFAs present in the oil in order to allow for the transesterification reaction to commence (Sharma et al. 2010). The implication of this additional process unit is inevitably the additional costs associated with the biodiesel production. In this chapter, an investigation on the feasibility of using the hydroxy sodalite particles to catalyze transesterification reaction for the conversion of cheap waste animal fat-beef tallow- was conducted and the results are explicitly presented.

6.2. Transesterification reaction using BTO as feedstock.

The detailed description of the catalyst synthesis is given in Chapter 4 of the study, and the transesterification reaction of BTO to biodiesel was carried out similar to the method described in Chapter 5. The tallow oil was extracted during the pre-treatment process where the fat was melted at temperatures just above 100 ˚C. This process allowed the removal of moisture; about 70% and possible volatile substances, water can potentially hydrolyze the triglyceride to form free fatty acids, hence it is important that the oil feedstock used is low in moisture content. The oil was then filtered, to separate the liquid oil from solids such as gums and other suspended particles. The conversion of BTO and biodiesel yield were calculated using the following equations:

$$Conversion(\%) = \frac{M_{FAME}/W_{FAME}}{3M_{BTO}/W_{BTO}} \times 100 \tag{5}$$

$$Biodiesel\,Yield = \frac{M_{FAME}}{M_{BTO}} \times 100 \tag{6}$$

Where:

M_{FAME} = Mass of FAME produced

M_{BTO} = Mass of BTO feed

W_{FAME} = Average molecular weight of FAME components

W_{BTO} = Average molecular weight of BTO

6.3. Results and discussion

Chromatographs for both the standard FAME (Figure 10) and experimentally produced FAME mixtures (Figure 11) were obtained, where the peaks for the two mixtures were identified and compared. FAME components observed between 8 and 11 minutes' retention times for the produced biodiesel are also observed in the Standard biodiesel round about the same retention times. Since FAME components of the product is a function of the type of feedstock used, the produced biodiesel does not contain all the FAME components identified in the standard FAME mixture. However, major components making up biodiesel mixture are common in the two mixtures; confirming the feasibility of using the synthesized H-SOD as a catalyst for the transesterification reaction of animal fat oil to biodiesel.

The reaction performance was relatively moderate, with conversions of oil to methyl ester of 68.8% and biodiesel yield of only 39.6%. Liu et al. (2007) obtained higher reaction conversions of greater than 90% during the study of the transesterification of poultry fat with methanol using Mg–Al hydrotalcite derived catalysts. However, the reaction parameters used in this study were relatively high, for an instance, a reaction conducted for 15 h at 120 °C and 100 psi, 30:1 molar ratio of methanol to poultry fat and stirring speed of 1417 rpm, 93% conversion and 83% biodiesel yield were obtained. Although Liu et al. (2011) obtained the beef tallow biodiesel with 96.3% conversion rate in a shorter reaction times, the reaction was homogeneously catalyzed using Sodium Hydroxide solution, the process would require an additional product separation step which would potentially increase production costs. Fröhlich et al. (2010) demonstrated the disadvantage of using homogeneous catalyst especially with low grade feedstock (High FFA content), a percentage conversion as low as 55% was achieved and the value further decreased to about 14% as the feedstock with even greater content of FFA was used.

As demonstrated in Table 10, the results obtained in this chapter are similar to the results reported by some researchers (da Cunha et al. 2009) where the majority of the ester contents ranged between C14: 0 and C20:2. This complies with the specification by EN 14103 standards where the majority of carbon chains contained in the biodiesel range from C14:0 to C24:1 and does not contain C17:0, further confirming successful synthesis of BTO biodiesel using H-SOD catalyst.

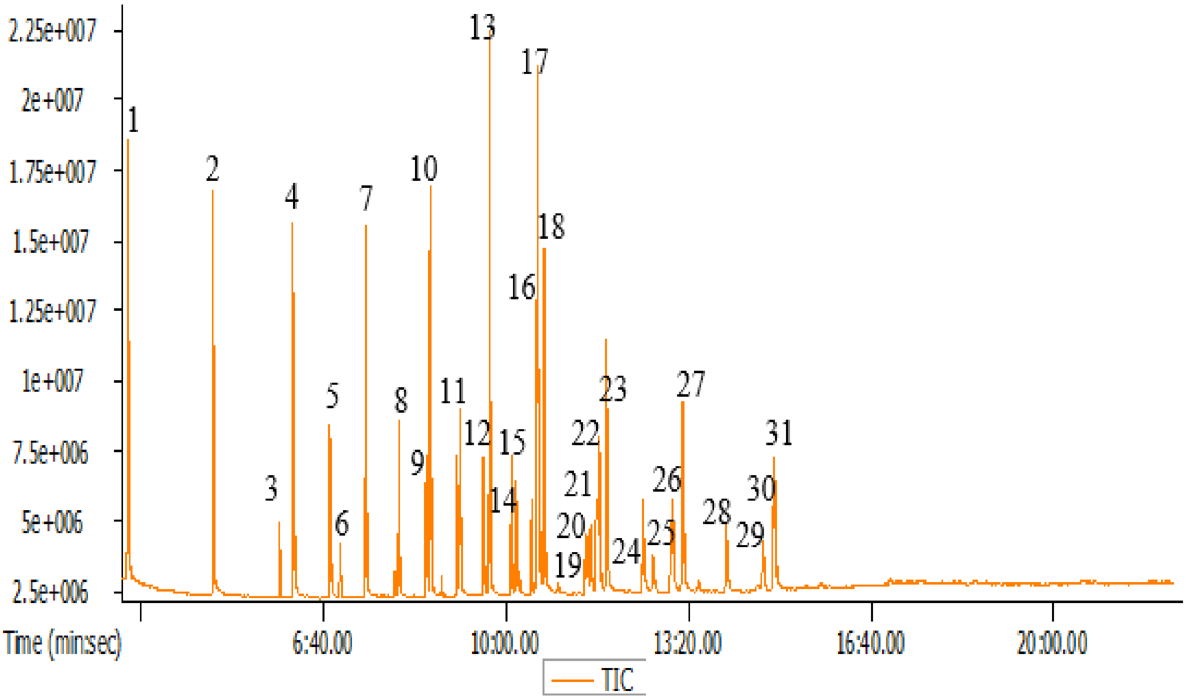

Figure 10: Chromatogram of the standard biodiesel used to validate BTO biodiesel (Names provided in Table 8)

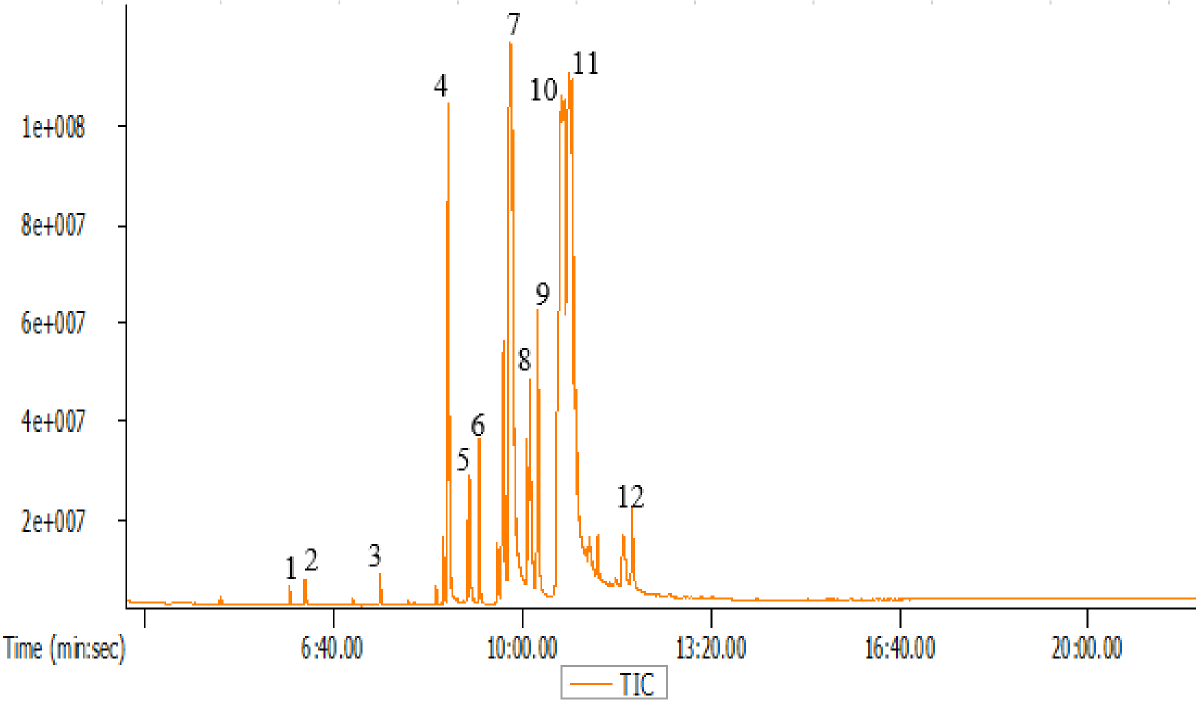

Figure 11: Chromatogram of the biodiesel sample obtained from the transesterification of BTO over H-SOD catalyst. (Names provided in Table 9)

Table 8: Standard FAME mixture composition to validate BTO biodiesel.

Peak No.	**Identified Compound**	**R.T. (min:sec)**	**Formula**	**Peak No.**	**Identified Compound**	**R.T. (min:sec)**	**Formula**
1	Hexanoic acid, methyl ester	03:06.1	$C_7H_{14}O_2$	17	Dodecanoic acid, methyl ester	10:41.9	$C_{13}H_{26}O_2$
2	Hexanoic acid, methyl ester	03:52.6	$C_7H_{14}O_2$	18	5,8,11,14-Eicosatetraenoic acid, methyl ester, (all-Z)-	11:26.8	$C_{21}H_{34}O_2$
3	Octanoic acid, methyl ester	04:39.2	$C_9H_{18}O_2$	19	5,8,11,14,17-Eicosapentaenoic acid, methyl ester, (all-Z)-	11:29.3	$C_{21}H_{32}O_2$
4	Undecanoic acid, methyl ester	06:07.0	$C_{12}H_{24}O_2$	20	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	11:32.9	$C_{19}H_{32}O_2$
5	Undecanoic acid, methyl ester	06:47.6	$C_{12}H_{24}O_2$	21	11,14-Eicosadienoic acid, methyl ester	11:39.6	$C_{21}H_{38}O_2$
6	Undecanoic acid, methyl ester	07:26.1	$C_{12}H_{24}O_2$	22	9-Octadecenoic acid (Z)-, methyl ester	11:41.2	$C_{19}H_{36}O_2$
7	Dodecanoic acid, methyl ester	08:02.6	$C_{13}H_{26}O_2$	23	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	11:42.3	$C_{19}H_{32}O_2$
8	9-Octadecenoic acid (Z)-, methyl ester	08:33.4	$C_{19}H_{36}O_2$	24	Pentadecanoic acid, 14-methyl-, methyl ester	11:50.1	$C_{17}H_{34}O_2$
9	Dodecanoic acid, methyl ester	08:37.2	$C_{13}H_{26}O_2$	25	Hexadecanoic acid, 15-methyl-, methyl ester	12:29.7	$C_{18}H_{36}O_2$
10	9-Octadecenoic acid (Z)-, methyl ester	09:06.7	$C_{19}H_{36}O_2$	26	11,14-Eicosadienoic acid, methyl ester	13:01.1	$C_{21}H_{38}O_2$
11	Undecanoic acid, methyl ester	09:10.2	$C_{12}H_{24}O_2$	27	Cyclopropanepentanoic acid, 2-undecyl-, methyl ester	13:02.8	$C_{20}H_{38}O_2$
12	9-Octadecenoic acid (Z)-, methyl ester	09:35.6	$C_{19}H_{36}O_2$	28	Heneicosanoic acid, methyl ester	13:13.6	$C_{22}H_{44}O_2$
13	Dodecanoic acid, methyl ester	09:41.7	$C_{13}H_{26}O_2$	29	Heneicosanoic acid, methyl ester	14:01.7	$C_{22}H_{44}O_2$
14	9-Octadecenoic acid (Z)-, methyl ester	10:06.0	$C_{19}H_{36}O_2$	30	Cyclopropanepentanoic acid, 2-undecyl-, methyl ester	14:41.4	$C_{20}H_{38}O_2$
15	Dodecanoic acid, methyl ester	10:11.7	$C_{13}H_{26}O_2$	31	Heneicosanoic acid, methyl ester	14:53.9	$C_{22}H_{44}O_2$
16	ç-Linolenic acid, methyl ester	10:27.9	$C_{19}H_{32}O_2$				

Table 9: BTO Biodiesel mixture composition.

Peak No.	**Identified Compound**	**R.T.(min:sec)**	**Formula**
1	Butyric acid, methyl ester	03:07.9	$C_7H_{14}O_2$
2	Capric acid, methyl ester	06:06.6	$C_{12}H_{24}O_2$
3	Myristoleic acid (Z)-, methyl ester	08:33.7	$C_{19}H_{36}O_2$
4	Myristic acid, methyl ester	08:36.8	$C_{13}H_{26}O_2$
5	Pentadecanoic acid, methyl ester	09:08.7	$C_{19}H_{36}O_2$
6	Pentadecanoic acid, methyl ester	09:08.7	$C_{19}H_{36}O_2$
7	Palmitic acid, methyl ester	09:40.8	$C_{13}H_{26}O_2$
8	Stearic acid, methyl ester	10:43.4	$C_{13}H_{26}O_2$
9	11,14,17-Eicosatrienoic acid, methyl ester	11:32.5	$C_{19}H_{32}O_2$
10	11,14-Eicosadienoic acid, methyl ester	11:38.7	$C_{21}H_{38}O_2$
11	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	11:41.7	$C_{19}H_{36}O_2$
12	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	11:41.7	$C_{19}H_{36}O_2$

Table 10: BTO biodiesel ester component in comparison with literature.

This study		**da Cunha et al. (2009)**	
Butyric	C4:0	Miristic	C14:0
Capric	C10:0	Pentadecanoic	C15:0
Myristic	C14:0	Palmitic	C16:0
Pentadecanoic	C15:0	Palmitoleic	C16:1
Palmitic	C16:0	Heptadecanoic	C17:0
Stearic	C18:0	Stearic	C18:0
Myristoleic (Z)-	C18:2	Elaidic	C18:1 (trans)
9,12,15-Octadecatrienoic (ZZZ)-	C18:2	Oleic	C18:1(cis)
11,14,17-Eicosatrienoic	C20:2	Linoleic	C18:2
		Arachidic	C20:0

6.4. Summary

In this chapter, the conversion of animal fat oil (beef tallow oil) into biodiesel over a solid H-SOD catalyst was carried out and the results have demonstrated the possibility of biodiesel production using this catalyst. The observed biodiesel yield of 39.6% and a conversion of 68.4% are relatively low, however, the information contained in this study serves as a foundation for further research which is reported in subsequent chapters.

CHAPTER 7: EFFECT OF REACTION PARAMETERS ON THE TRANSESTERIFICATION OF ANIMAL FAT OIL TO BIODIESEL OVER A SOLID HYDROXY SODALITE (SOD) CATALYST

7. 1. Introduction

In this chapter, an investigation of the influence of some of reaction parameters on the performance of the transesterification reaction of BTO over solid H-SOD catalyst. The aim of this chapter was to investigate a potentially economic and environmentally attractive process for biodiesel production by analyzing the optimal conditions, which would yield best results for the method at hand. Production of biodiesel via the transesterification of beef tallow with methanol over a solid hydroxy sodalite (H-SOD) catalyst was investigated, particularly the effect of process variables on the conversion and yield of biodiesel. The current investigation was laboratory based where beef tallow was tested for the content of FFA among other properties, to confirm the need for a heterogeneous catalyst.

7. 2. Method

7.2.1. Catalyst Synthesis

The H-SOD particles were prepared by the hydrothermal synthesis method as described in Chapter 3 of the dissertation, but for the reduction of the particle size of the catalyst, a small amount of ethanol was added onto the synthesis solution as an organic solvent after an hour of stirring. The mixing was allowed to continue for a further 1 h. The resulting mixture was transferred into a Teflon lined autoclave which was subjected to heat at 140 °C for 3.5 h. At the end of the hydrothermal reaction, the autoclave was cooled down by running tap water. The resulting crystals were washed using deionized water by a filtration system until the pH of the water reached a value of 7. The washed hydroxy sodalite crystals were then dried overnight, and then calcined at 200 °C prior the transesterification reaction.

7.2.2. The transesterification reaction

The transesterification reaction was carried out similar to the one performed in the preliminary investigation described in Chapter 5. The reaction was conducted at variety of reaction conditions with methanol-to-animal fat oil ratio 7.5:1 and catalyst weight percentage 3 wt. %; Mixing intensity (700 – 1250 rpm), catalyst particle size (200 – 300 Å), reaction time (6 – 24 h) and reaction temperature (40 – 60 °C). Each process variable was varied at a time while others were kept constant at reaction time 24 h; reaction temperature 60 ˚C; mixing intensity of 1000rpm. At the completion of each reaction, the catalyst particles were recovered from the mixture by filtration through nylon filter paper (0.45 µm pore dimension). Separating funnel was used to separate the products and glycerol, where the glycerol was drained from the bottom of the funnel while biodiesel was collected from the top. Analysis of the samples was performed using a pre-calibrated Gas Chromatograph equipped with a LECO GC x GC Thermal Modulator (GC-MS, model: Agilent 7890N) as described in the previous chapters.

7. 3. Results and discussion

7.3.1. Catalyst characterization

Various attempts were made to synthesize hydroxy sodalite particles with different particle size distributions. This was achieved by adding controlled amounts of ethanol to the synthesis solution prior to the hydrothermal synthesis. The use of ethanol as an organic solvent to control size is common in hydrothermal synthesis of zeolites (Huang et al. 2011; Li et al. 2007). The BET surface area, pore size and average pore volume measurements shown in Table 11 are important characteristics closely associated with the catalytic activity. Researchers have demonstrated that the extent of the catalyst reactivity depends on the external surface area properties (Liu et al. 2008). The surface characteristics of the H-SOD were found to be dependent to some extent on the washing of the synthesis solution with ethanol. The results show that the surface characteristics of the H-SOD particles proportionally changes with addition of ethanol during the synthesis. Both the BET surface area and the pore volume increase accordingly, while the pore size decreased with the ethanol addition. H-SOD sample exhibited a reduction in size thereby improving conversion and biodiesel compared to the ethanol free H-SOD. Ethanol reduces the rate of the sodalite crystallization process, thereby allowing formation of smaller H-SOD crystals The particle size estimation using Scherrer equation show that with sufficient addition of ethanol, the particle sizes reduced from 276 Å to 199 Å. The XRD results in Figure 12 shows that the XRD patterns for the three samples correlate with the simulated sodalite XRD pattern documented in the database of zeolite structures by the International Zeolite Association (IZA), confirming the successful formation of H-SOD particles. The extra peaks which are very minimal indicates the possible formation of other zeolite impurities, some researchers have demonstrated that the addition of ethanol as an organic solvent potentially affects the phase purity of the H-SOD crystals (Li et al. 2007; Yao et al. 2006). These results are in agreement with the work reported by Pankaj et al. (2014) where an investigation on the Effect of ethanol as an additive on the morphology and crystallinity of LTA (Linde Type A) zeolite was successfully studied. TGA results for the synthesized hydroxy sodalite particles shown in Figure 13 are in agreement with literature (Li et al. 2007; Yao et al. 2006) where mass loss was observed for all the three samples of hydroxy sodalite particles synthesized at different amounts of ethanol contents. Due to the loss of structural water during heating up to 1000oC, the mass loss of H-SOD 0E (Figure 13a), H-SOD 10E (Figure 13b), and H-SOD 20E (Figure 13c) were 12.27%, 14.18% and 16.46% respectively. Compared to the pure H-SOD 0E, the additional mass loss of H-SOD 10E (2.53 %) and H-SOD 20E (4.19%) is attributed to the possible decomposition of organic functional groups occurring at higher temperatures (Li et al. 2007; Yao et al. 2006).

Table 11: BET Surface area, pore volumes and pore sizes derived from the nitrogen adsorption data for the synthesized H-SOD particles.

Sample id.	**Ethanol Added (ml)**	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Pore Size(nm)**
a	0	0.164	0.0013	30.92
b	10	17.623	0.0724	16.43
c	20	23.356	0.1626	27.84

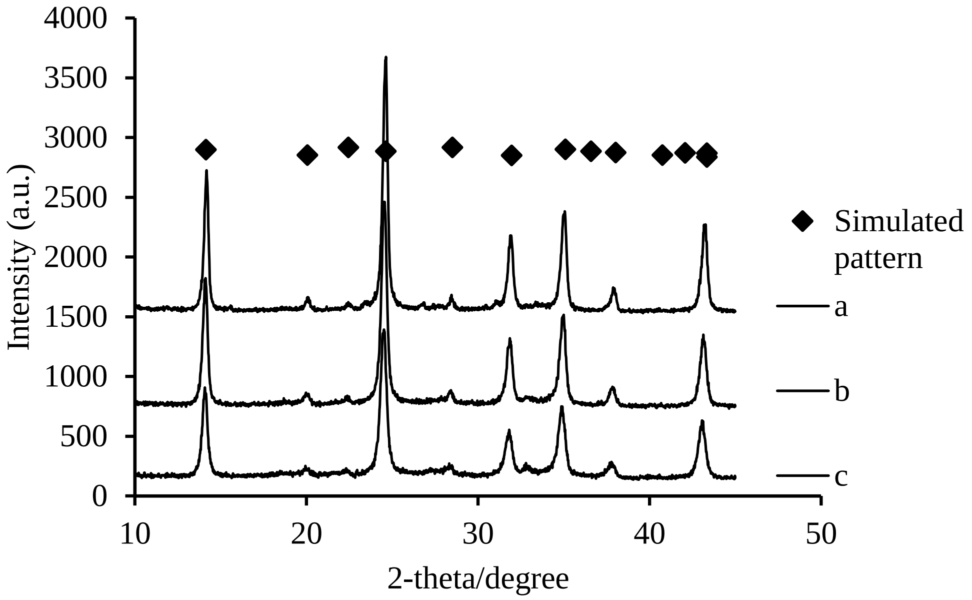

Figure 12: XRD patterns of (a) H-SOD Particles synthesized with no addition of ethanol as an organic solvent, (b) H-SOD particles synthesized with 10ml addition of ethanol as an organic solvent , (c) H-SOD particles synthesized with 20ml addition of ethanol as an organic solvent and the simulated sodalite pattern according to the International Zeolite Association(IZA).

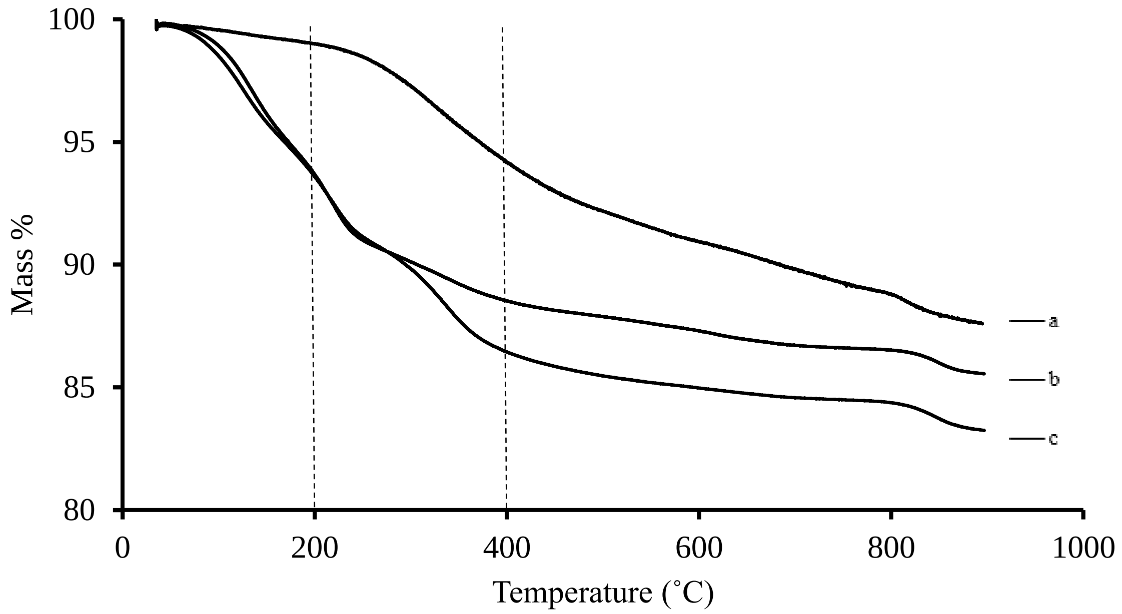

Figure 13: TGA Curves of (a) H-SOD Particles synthesized with no addition of ethanol as an organic solvent (b) H-SOD particles synthesized with 10ml addition of ethanol as an organic solvent and (c) H-SOD particles synthesized with 20ml addition of ethanol as an organic solvent.

7.3.2. Effect of reaction parameters on transesterification

7.3.2.1.The effect of mixing intensity on the transesterification reaction

Without stirring, the transesterification reaction occurs slowly at the interphase of the two layers of oil and alcohol due to the external mass transfer limitation, thereby making the process impractical (Kumar et al. 2010; Rashid et al. 2009). As shown in Figure 14, mixing plays a role in the heterogeneously catalyzed transesterification reaction. Lower conversion rate and biodiesel yield were obtained at the slowest mixing rate of 700rpm where the values obtained were 43% and 42%, respectively. The results show that the reaction performs better at the speed of 1000 rpm, where a conversion of 66% was achieved. Other researchers have achieved better results at a mixing intensity of 600 rpm (Rashid et al. 2009; Noureddini & Zhu 1997). However, other than the type of feedstock used, the results were obtained from homogeneously catalyzed transesterifications which have proven to be less prone to the effect of mixing intensity as compared to the heterogeneously catalyzed transesterification. The impact of agitation intensity is only observed during the initial stage of the transesterification reaction where mass transfer limitation is dominant over time (Bambase et al. 2007) . By increasing the stirring speed, the reaction rate is accelerated because of the reduction in mass transfer limitation. However, it was observed that too high mixing speeds are not favorable. In this study, the conversion reduced to 62%, attributed to the reversible nature of the transesterification reaction which tends to decrease the biodiesel yield over time.

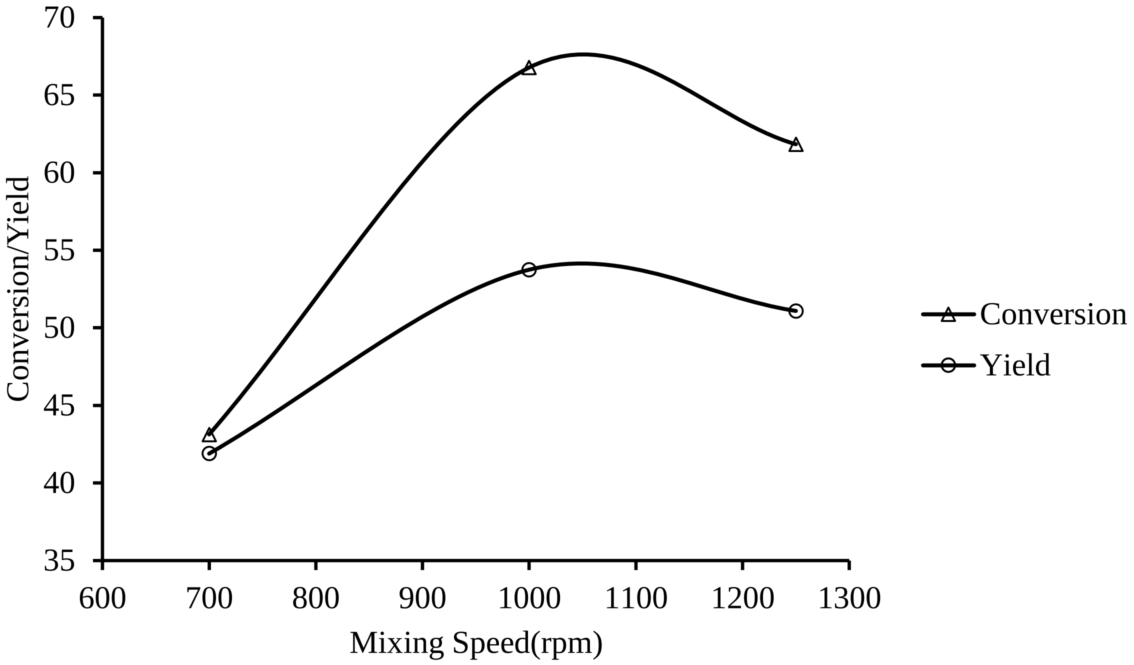

Figure 14: The effect of mixing intensity on the yield of biodiesel.

7.3.2.2.The effect of catalyst particle size on the transesterification reaction

The rate of transesterification reaction is affected by the efficiency of the internal diffusion, which to a certain extent is controlled by the diameter of the crystalline particles. A number of researchers have demonstrated the dependence of transesterification reaction on the particle size of the catalyst used. Generally, the reaction conversion increases with an increase in catalyst concentration as the catalysts sites are supposedly improved. However, this tends to reduce the specific surface area of the catalyst. Therefore, during a study of catalyst efficiency, it is essential to consider methods for improving the catalyst surface areas, one of the measures to achieve this is by reducing the catalyst particle size (Yulianti et al. 2014). In this chapter, various attempts were made to synthesize H-SOD particles with different size distributions using ethanol organic solvent; the particle size was slightly reduced by 77 Å. As shown in Figure 15, without the ethanol additive during the hydrothermal synthesis, the resulting H-SOD (276 Å) catalyzed the transesterification to a TG conversion of 66.8%. The addition of 10 ml and 20 ml ethanol resulted in a reduction of H-SOD crystalline sizes and the transesterification reaction performance was slightly improved to a conversion of 68.4% as expected. The results in Figure 15 demonstrated that conversion and biodiesel yield increased to 68.4 % and 57.0%, respectively, owing to a reduction in H-SOD particle size. This is due to the slight reduction in mass transfer limitation, thereby contributing to an increase in the rate of reaction. Mass transfer or diffusion occurs between the different phases; hence heterogeneously catalyzed reactions are more prone to mass transfer limitation than homogeneous catalytic reactions (Klaewkla et al. 2011). The catalytic reaction occurs when the reactants come into contact with the active site of the catalyst along the internal surface of the porous catalyst pellet. The observation made in this study on the possibility of improving reaction conversions by reducing catalyst crystalline size is consistent with what other researchers have found where nanoparticles of sizes between 22 nm -25 nm (i.e. 220 Å -250 Å) were studied (Yulianti et al. 2014; Ngamcharussrivichai et al. 2008; Kanade et al. 2006).

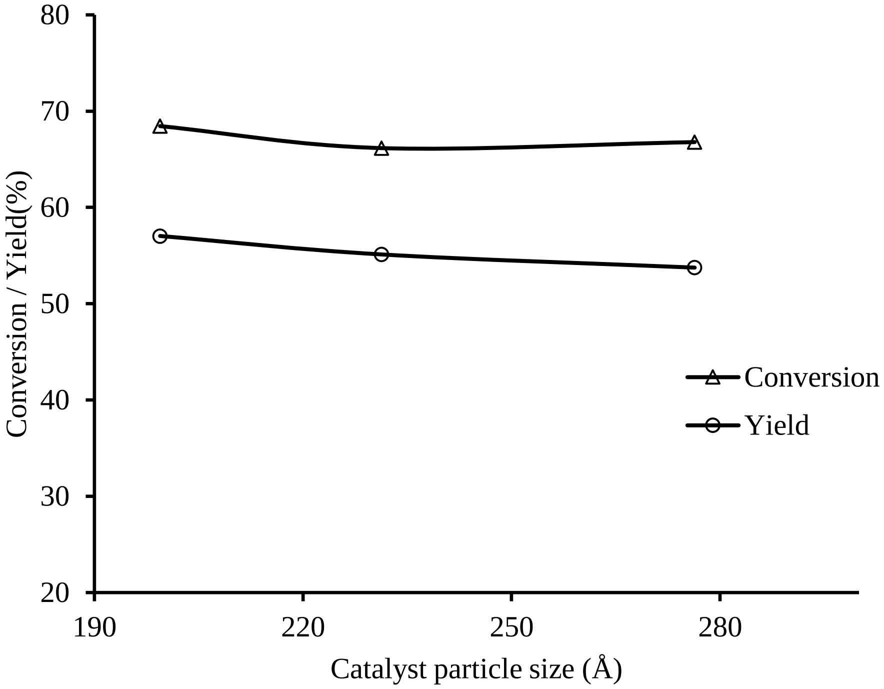

Figure 15: The effect of catalyst particle size on the conversion/ yield of biodiesel

7.3.2.3.The effect of reaction time on the transesterification reaction

As demonstrated Freedman et al. (1984), as well as Vyas et al. (2009) among other researchers, there exists a positive relationship between fatty acid esters conversion rate and reaction time, the reaction is slow in the initial stages due to the effect of phase mixing and proceeds much faster after some time. The period at which transesterification reaction is allowed to proceed influences the behavior of the reaction as shown in Figure 16. Both conversion and yield increased with increasing reaction times as the contact time between the three-phase reactants is extended, thereby allowing prolonged contact time. The transesterification reaction is reversible in nature; the observed decrease in yield over time is due to the possible loss of fatty acids as the reaction continues at extended reaction times (Daramola et al. 2016; Eevera et al. 2009; Mathiyazhagan & Ganapathi 2011). Nonetheless, due to maximum conversion rate of 78.3% after 24 h, it could be established that the suitable reaction time for beef tallow oil transesterification over hydroxy sodalite under the conditions in the study is 24 h. This is in agreement with the study conducted by Bhatti et al.(2008) where a study was conducted on the conversion of chicken and mutton tallow using a homogeneous sulfuric acid catalyst.

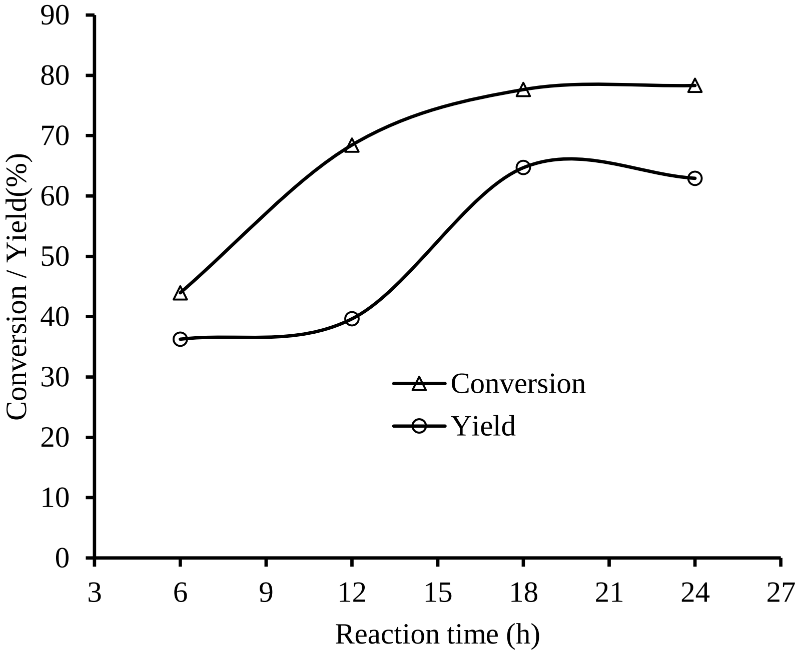

Figure 16: The effect of reaction time on the conversion/ yield of biodiesel.

7.3.2.4.The effect of reaction temperature on the transesterification reaction

The effect of reaction temperature on biodiesel yield is illustrated in Figure 17. It can be seen the reaction temperature essentially influence the performance of the transesterification reaction. Both the yield of biodiesel and conversion rate increases with an increase in reaction temperature, and maximum performance was obtained at a temperature of 60°C, where the values of conversion and yield are 78.3% and 62.9% respectively. Higher temperature conditions favor the transesterification reaction due to its endothermic behavior (Daramola et al. 2016; Farooq et al. 2016), attributed by the reactant molecule collisions which are accelerated at higher temperatures, thereby facilitating miscibility among the three phased reaction (solid catalyst-oil-alcohol) as well as the mass transfer (Farooq et al. 2016). Other researchers have achieved conversion rates above 90% (Liu et al; 2011; da Cunha et al. 2009), however, the transesterification reaction was homogeneously catalyzed using potassium hydroxide and sodium hydroxide solutions respectively. Homogeneously catalyzed transesterification reactions tend to require an additional process stages such as esterification reaction to reduce FFA content, as well as a step for product separation, thereby affecting the economic efficiency of the biodiesel production process.

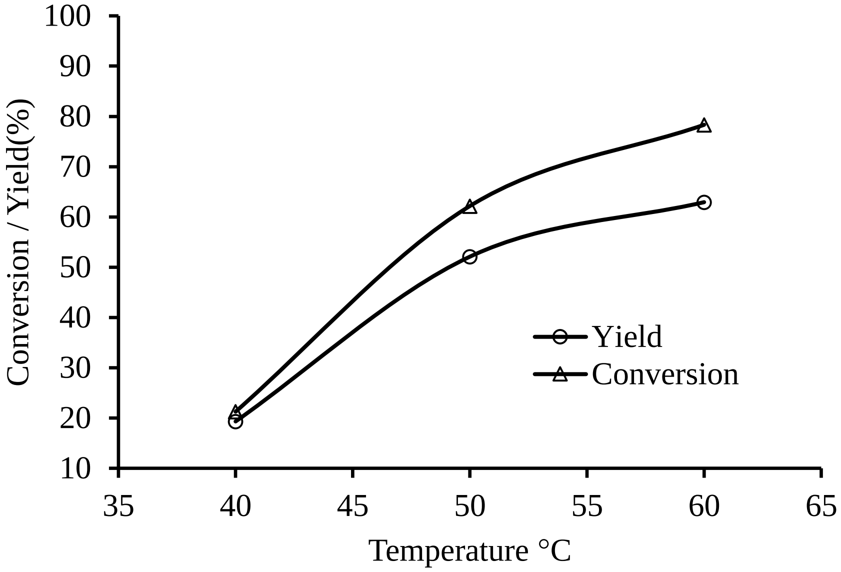

Figure 17: The effect of reaction temperature on the conversion/ yield of biodiesel.

7. 4. Summary

This chapter has successfully demonstrated the influence of reaction parameters on the rate of methanolysis of beef tallow oil over a solid hydroxy sodalite catalyst. Most of the reaction parameters found as optimum for the transesterification of BTO in the presence of H-SOD were consistent with literature. Table 12 shows a summary of comparison of the results obtained in this study with results obtained in open literature. There is a room for improvement in the reaction process considering other factors such as the effect of catalyst concentration and methanol to oil ratio.

Table 12: Comparison of process variables applied during biodiesel production in literature.

Oil Feed	Type of Catalyst	T/°C	RPM	% Conversion	Alcohol: Oil Ratio	t (h)	Reference
BTO	H-SOD	60	1000	78	7.5:1	24	This study
BTO	$Cs_2O/\gamma\text{-}Al_2O_3$	66	-	95	10.5:1	2	Zhao et al. 2013
BTO	KOH	65	400	96	6:1	3	da Cunha et al. 2009
BTO	KOH	65	150	87	12:1	2	Hoque et al. 2011
Cotton seed oil	Cation Exchange Resin	65	600	80	6:1	3	Jaya & Ethirajulu 2011
Soybean oil	Sodium methoxide	60	600	95	6:1	2.67	Jacob et al. 2008
Jatropha oil	MgZnAlO (Dual site heterogeneous oxide)	182	300	97	11:1	-	Olutoye & Hameed 2016
WCO	Silica Sulfuric Acid	120		98	20:1	8	Shah et al. 2014
Sunflower oil	NaOH		600	98	20:1	2	Bambase et al. 2007
Palm oil	Tungstated zirconia catalyst	40	300	25	5:1	0.83	Zubir & Chin, 2010
WCO	Snail shell	60		99	6.03:1	8	Birla et al. 2012
Sunflower Oil	CaO	100	200	91	6:1	5.5	Vujicic et al. 2010
Thespesia populnea seed oil	$NaOCH_3$	65	650	98	7:1	1.5	Rashid et al. 2015
Palm oil	KOH (in a solvent free system)	100	-	96	9:1	8	Zhang et al. 2010
Sunflower oil	Mg-Al hydrotalcites commercial	60	-	50	12:01	24	Navajas et al. 2010

RPM: Revolution per minute

CHAPTER 8: KINETICS STUDY OF SOLID HYDROXY SODALITE CATALYST FOR THE BEEF TALLOW TRANSESTERIFICATION IN A BATCH BIODIESEL PRODUCTION PROCESS

8. 1. Introduction

Following the study of the effect of reaction parameters on the transesterification reaction in this study, a further investigation was conducted to quantify the effects of reaction temperature and time by correlation of the data obtained from the experiments. Presented in this chapter is a detailed study conducted on the kinetics of H-SOD during the transesterification of beef tallow oil to biodiesel in a batch reactor process. This chapter particularly focused on the determination of the amount of energy required to for the reaction to occur; Activation Energy (E_A) and the rate at which transesterification reaction proceeds. Reaction kinetic studies for the process at hand are essential for predictive analysis of the behavior of solid H-SOD catalyst during reactor design, in terms of the scale up process for practical biodiesel process applications. Furthermore, the work conducted in study provides parameters that can be used to estimate the extent of a reaction at any time during the transesterification reaction under certain process variables (Shah et al. 2014). A number of researchers have reported on the kinetics of transesterification reaction.

8. 2. Determination of kinetic parameters

Transesterification reaction involves the catalytic reaction of triglyceride with an alcohol molecule to form an ester; glycerol also makes up a part of the reaction product during this process. Vegetable oils and animal fats are commonly used as a source of triglyceride in the transesterification process. During biodiesel production, a reversible reaction of three moles of alcohol; methanol (MeOH) with one mole of triglyceride (TG) occurs where one mole of glycerol (GL) and three moles of Fatty Acid Methyl Ester(FAME) are produced as shown by the overall reaction Equation 8. The mechanism in which transesterification proceeds involves stepwise reactions where TG is initially converted to diglyceride (DG), followed by a monoglyceride (MG) and finally the glycerol (GL) as shown in Equation 9 (a-c) where *k* represents the reaction rate constant. The stoichiometry of the transesterification reaction requires that alcohol is in excess to provide a shift in the reaction equilibrium to the product side, thereby facilitating a forward reaction according to *Le Chatelier's principle* (Baroutian et al. 2010; Soetaredjo et al. 2011). Over the years, many researchers have demonstrated that for transesterification reactions, kinetics for forward reaction is much more dominant than the kinetics of the reverse reactions (Leevijit et al. 2004). Consequently, the kinetics for a forward transesterification reaction is presented in this chapter. The method used for determination of reaction kinetics was adapted from the work reported by Olutoye & Hameed (2016).

Overall transesterification reaction:

$$TG + 3\,MeOH \leftrightarrow 3\,FAME + GL \qquad (7\,)$$

Stepwise reactions:

$$TG + MeOH \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} DG + FAME \qquad (8\,a)$$

$$DG + MeOH \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} MG + FAME \qquad (8\,b)$$

$$MG + MeOH \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} GL + FAME \qquad (8\,c)$$

Where k_1, k_2, k_3 are the reaction rate constants for the forward reaction, and k_{-1}, k_{-2}, k_{-3} are the reaction rate constants for the reverse reaction.

Although the transesterification reaction rate is affected by multiple stepwise reactions, for the purpose of this study, a first order transesterification reaction was assumed thereby using the overall transesterification Equation 8 as a basis to determine the reaction kinetics. Furthermore, it was assumed that there is no formation of products (i.e. FAME and Glycerol) at the beginning of transesterification - $C_{FAME} = 0$ and $C_{GL} = 0$. The reaction rate can therefore be written as:

$$-r_{TG} = k_m a C_{TG} C_{MeOH} = \; k C_{TG} C_{MeOH} \tag{9}$$

Where k_m is the mass transfer coefficient, and a is the surface area of the catalyst, and k is the product of a and k_m which is the reaction rate constant.

The change in concentration of MeOH can be assumed to be constant if it is present in excess during the transesterification reaction. The effect of MeOH concentration on the reaction order is therefore minimal (Birla et al. 2012; Olutoye & Hameed, 2016). TG tends to run out fast during the reaction, it becomes the limiting reactant, and therefore the rate determining species. In the absence of mass transfer resistance, both internal and external, the reaction rate can therefore be expressed as the rate at which concentration of triglycerides changes across the theoretical film layer between the solid H-SOD catalyst surface and the bulk reactants as follows:

$$-\frac{dC_{TG}}{dt} = k\left[C_{TG,b} - C_{TG,s}\right] \tag{10}$$

Where $C_{TG,b}$ and $C_{TG,s}$ are the triglyceride concentrations in the bulk phase and on the catalyst surface respectively.

During the mechanism of the transesterification reaction over the catalyst, when the rate of transport of reactants from the bulk phase is slower than the rate of the surface reaction on the solid H-SOD catalyst, the rate of transport of the reactants becomes the overall rate determining step (RDS) and as a result $C_{TG,\,s} = 0$. The intrinsic kinetics of the transesterification reaction of beef tallow oil to biodiesel was consequently derived as follows:

$$-\frac{dC_{TG}}{dt} = kC_{TG,b} \tag{11}$$

Integrating the Equation 11 gives:

$$\ln\left[\frac{C_{TG,O}}{C_{TG}}\right] = kt \qquad (11\,a)$$

Or

$$-\ln(1 - X_{TG})kt \qquad (11\,b)$$

Where $C_{TG,0}$ is the initial concentration of triglycerides and X_{TG} is the conversion of triglycerides.

The reaction rate constant is independent of the concentrations of species involved in the reaction; it depends on temperature and the presence of the catalyst. In liquid systems, k can also be a function of other parameters such as ionic strength and choice of solvent; however, the effect of these parameters is small compared to that of temperature. Reaction rate constants obtained at different temperatures were used to determine the activation energy and the pre exponential factor using linearization of Arrhenius equation as follows:

$$k = Ae^{\left(\frac{-E_A}{RT}\right)} \qquad (13\,a)$$

$$\ln k = \frac{1}{T}\left(\frac{-E_A}{R}\right) + \ln A \qquad (13\,b)$$

Where E_a is activation energy (J/mol), R is the gas constant with a value of 8.31 $JK^{-1}mol^{-1}$ and A is the pre exponential factor or frequency factor. The plot of (-ln $k_)$ versus the inverse of reaction temperature (1/T) was plotted, with a slope E_a/R from where E_a was calculated and A was given by the constant of the resulting linear equation.

8. 3. Results and discussion

Batch transesterification experiments were carried out to investigate the kinetics of the catalytic reaction at various reaction temperatures. Other reaction parameters such as mixing intensity and H-SOD particle size were kept constant. Figure 18 illustrates the rate of consumption of beef tallow oil as the transesterification reaction proceeds, the concentration of triglyceride decreases with an increase with reaction time. This is because triglyceride molecules are gradually converted in to products, mainly fatty acid methyl esters. Figure 19 shows the graphical form of the PFO kinetic model used in the study to estimate the overall reaction rate constants at various temperatures. The estimated values of reaction constants, activation energy and pre-exponential factor are given in Table 13. The Arrhenius plot from which activation energy and pre-exponential plots were determined is shown in Figure 20. The value of pre-exponential factor gives details about frequency of reactant molecule collisions and their orientation, it was estimated at 5.52 x10^8 min^{-1} which is in the same range as values obtained by other researchers varying between 1.26 x10^9 min^{-1} and 2.98 x10^{10} min^{-1} (Birla et al. 2012; Zhang et al. 2010; Zubir & Chin 2010). The obtained value of activation energy, 74.23 kJ /mol is roughly in agreement with values reported by other researchers; Zhang et al. (2010) achieved activation energies around 79.20 kJ/mol during a successful Pseudo First Order kinetic model which was proposed for the transesterification of palm oil using dimethyl carbonate into biodiesel over a heterogeneous KOH catalysis.

Similar levels of activation energies were observed in the work done by Birla et al. (2012) during a heterogeneously catalyzed transesterification of waste frying oil using a snail shell derived catalyst. Jaya & Ethirajulu (2011) obtained even better results in their PFO kinetic study to demonstrate the efficiency of using cation exchange resins as catalyst for lowering activation energies to about 22 kJ/mol (Jaya & Ethirajulu 2011). Although up to 80% FAME content was achieved at around 65 °C reaction temperatures, the downside of their study is identified in the use of edible cotton seed oil, as it does not favor the economic aspect of the process. The use of edible oils results in potential competition between food market and fuel industries thereby triggering hikes in both fuel and food prices. During a study on the conversion of refined sunflower oil to biodiesel over a solid calcium oxide (CaO) catalyst, Vujicic et al. (2010) achieved a PFO reaction where separate kinetic and diffusion regime were considered. The reaction proceeded at relatively high activation energies for the kinetic regime, 161 kJ/mol to achieve a product of 91% biodiesel content in less than 5.5 h.

Moreover, other reaction conditions were slightly intense, the reaction temperatures investigated were between 60 °C and 120 °C, pressures under which the reaction was carried out were kept between 1 bar and 15 bar. Additionally, temperature required for the catalyst activation was 900°C. Similar results were recently reported by Olutoye & Hameed (2016) during a kinetic study of a methanolysis of Jatropha oil over a dual-site heterogeneous oxide catalyst where PFO kinetic reaction methodology was applied. Generally, heterogeneously transesterification reactions proceed much slower than homogeneously catalyzed reactions; this is because of the three phase reaction system which exposes the process to factors such as mass transfer limitation (Jaya & Ethirajulu 2011).

During early development of studies in biodiesel production process, relatively high values of reaction rate constants around 0.215 min-1 – 0.242 min-1 for the homogeneously catalyzed transesterification reaction for feedstock with either fairly low FFA content after a pre-esterification step have been reported (Noureddini & Zhu 1997; Freedman et al. 1984). Reaction rates reported in the present study are however relatively low as shown in Table 13. The reaction constant for the reactions with maximum conversion was obtained at 0.0011 min-1 when reaction temperature was kept at 60 °C. Similar reaction rate constants in the range 0.0026 min^{-1} - 0.0083 min^{-1} were observed by Vujicic et al.(2010), although the transesterification in this study was conducted over shorter reaction times, the sunflower oil used as feedstock has negative impact on the biodiesel production costs as explained earlier.

Table 13: Reaction kinetics for transesterification of beef tallow oil over solid H-SOD catalyst.

E_a (kJ/mol)	74.23
A ($Lmol^{-1}$ min^{-1})	5.52 $x10^8$
Temperature (°C)	**k (min^{-1})**
40	0.0002
50	0.0007
60	0.0011

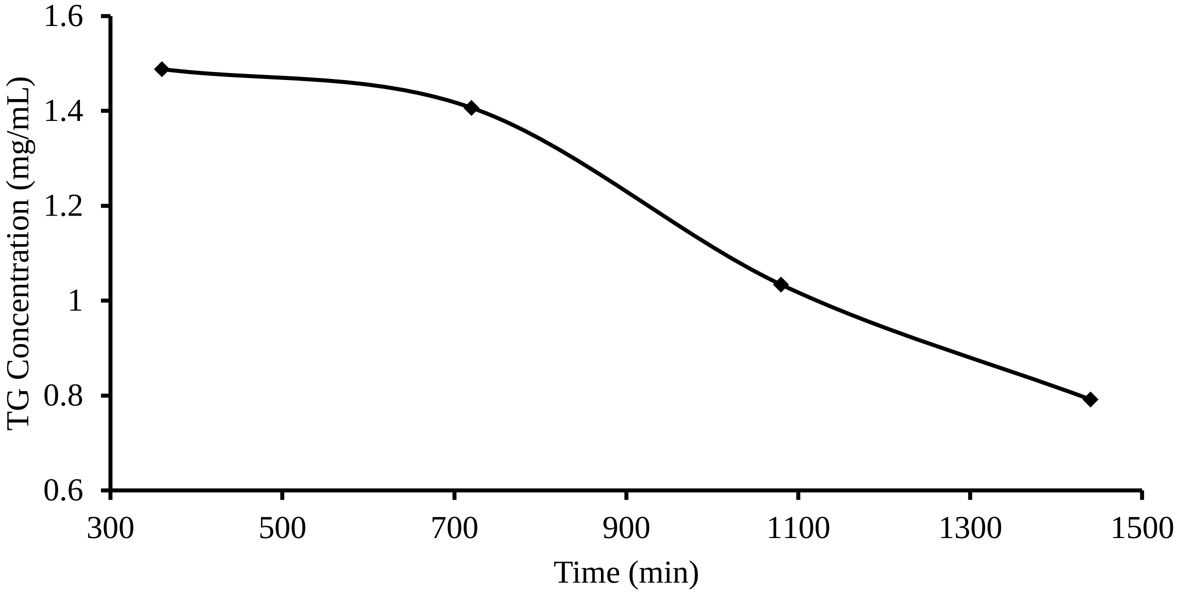

Figure 18: Concentration profile of Triglyceride molecules over a period of time.

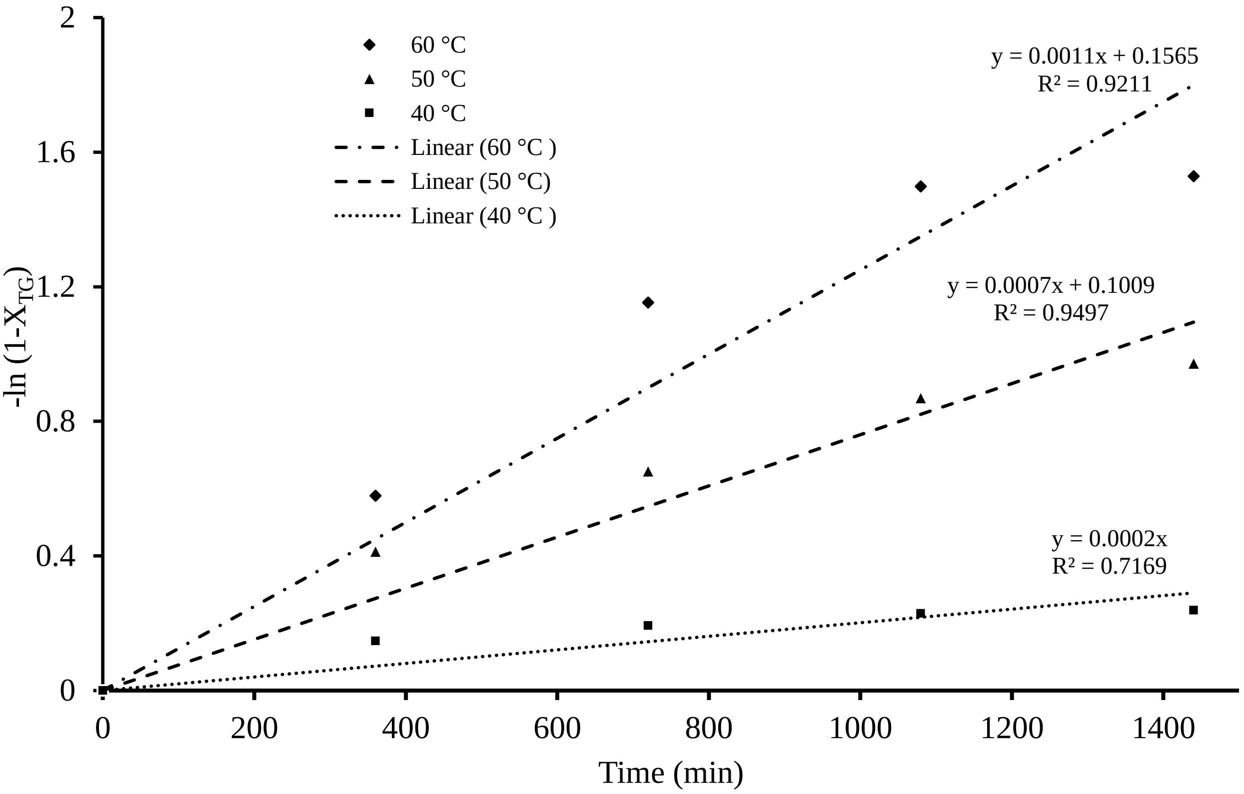

Figure 19: Plots of ln (1- X_{TG}) versus reaction time for PFO kinetic model at different temperatures (40°C - 60°C), for the transesterification of beef tallow oil into biodiesel over a solid H-SOD catalyst.

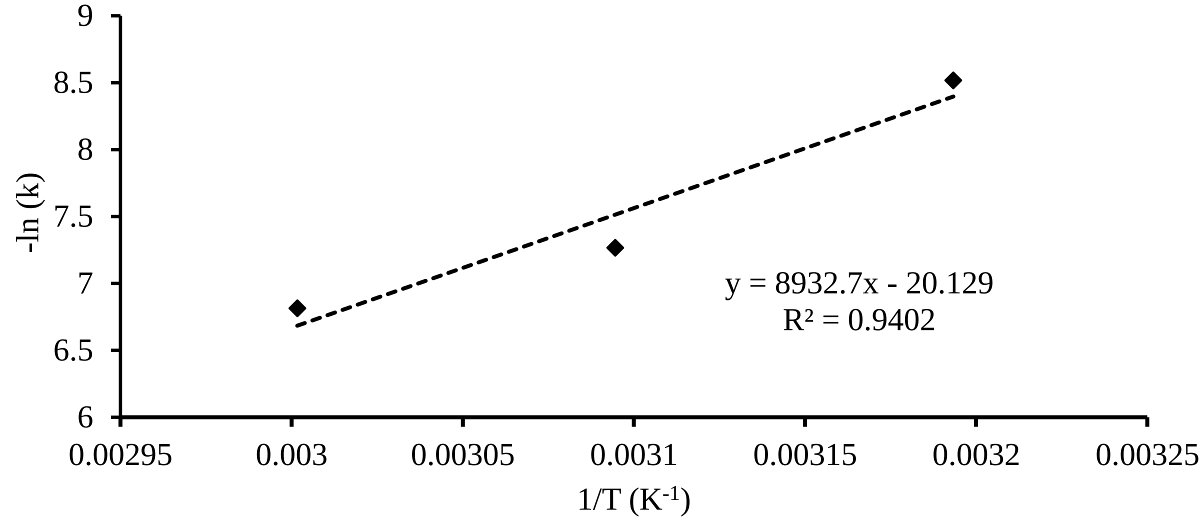

Figure 20: Arrhenius plot of ln(k) versus the inverse of temperature (1/T) used to estimate E_a and pre- exponential factor A.

8. 4. Summary

Kinetic results reported in this chapter demonstrated the efficiency of using H-SOD catalyst for transesterification of BTO to biodiesel. The kinetic model used for this study is simplified by the assumptions detailed during the model development steps. The values of activation energy, reaction constants and frequency factor obtained at 0.0011 min^{-1}, 5.52 $x10^{8}$ min^{-1} and 79.20 kJ/mol respectively, fell within the range of the results reported in literature as shown in Table 14. Solid H-SOD is therefore proposed as an ideal catalyst for efficient batch transesterification of high FFA content BTO. In a case where little or no assumptions are specified, robust kinetic parameter estimation models such as nonlinear least-squares fitting techniques will be required for a more accurate estimation of kinetic parameters (Marasović et al. 2017).

Table 14: Results compared with literature on the kinetic study

Oil Feed	Type of Catalyst	T/°C	RPM	% Conversion	Kinetic Model	Alcohol: Oil Ratio	t (h)	k (min^{-1})	Ea (KJ/mol)	A ($Lmol^{-1}$ min^{-1})	Reference
BTO	H-SOD	60	1000	78	PFO	7.5:1	24	0.0011	74.23	5.52×10^{8}	This study
Cotton seed oil	Cation Exchange Resin	65	600	80	PFO	6:1	3		22.00	-	(Jaya & Ethirajulu 2011)
Soybean oil	Sodium methoxide	60	600	95	Second Order	6:1	2.7	0.0149	-	-	(Jacob et al. 2008)
Jatropa oil	MgZnAlO(Dual site heterogeneous oxide)	182	300	97	PFO	11:1		2.600	161.00	9.9×10^{3}	(Olutoye & Hameed 2016)
WCO	Silica Sulfuric Acid	120		98	PFO	20:1	8	0.0085	52.00	1.5×10^{10}	(Shah et al. 2014)
Palm oil	Tungstated zirconia catalyst	40	300	25	Second Order	5:1	0.8		51.90	1.5×10^{10}	(Zubir & Chin 2010)
WCO	Snail shell	60		99	PFO	6.03:1	8		79.00	2.98×10^{10}	(Birla et al. 2012)
Sunflower Oil	CaO	100	200	91	PFO	6:1	5.5	0.061	161.00	-	(Vujicic et al. 2010)
Palm oil	KOH (in a solvent free system)	100		96.	PFO	9:1	8		79.1	1.26×10^{9}	(Zhang et al. 2010)

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

9. 1. Conclusions

In this dissertation, H-SOD, a type of zeolite material is proposed as a catalytic material for transesterification reaction of WCO or BTO to biodiesel. The H-SOD catalyst particles were synthesized in-house using the classic hydrothermal synthesis method. The results from the SEM images have confirmed the successful synthesis of H-SOD catalyst, which composed of a mixture of particles with different shapes, including nanorod-like shapes and cubic shapes; these results are in agreement with literature where researchers observed similar shapes. XRD results further confirmed the formation of H-SOD particles by demonstrating that the pattern for the synthesized particles correlates with the patterns for the simulated sodalite as proposed by the International Zeolite Association. An attempt to reduce catalyst particles size was successfully carried out by adding small amounts of ethanol as an organic additive to the hydrothermal synthesis solution.

Along with the XRD results, the use of Scherrer equation demonstrated a reduction in particle size with the addition of small amounts of ethanol. A slight reduction in crystallite sizes from an average of 276 Å to 199 Å was achieved. Although some researchers have reported on the effect of ethanol additive on the phase purity, there were no extra peaks observed on the XRD patterns which would possibly indicate traces of zeolite impurities. It can therefore be suggested that the effect of ethanol on the purity of the synthesized H-SOD particles is insignificant; besides, the information provided by the FTIR spectrum confirmed the synthesis of pure H-SOD particles which is consistent with literature. In retrospect, specific objectives of the study included a preliminary study on the feasibility of using the solid H-SOD particles to catalyze transesterification process in a batch reactor. Subsequently, an attempt to use this material as a catalyst for the transesterification of BTO was successfully made. Furthermore, a more effective way of producing biodiesel was sought for, by investigation the influence of process variables such as reaction temperature, reaction time, mixing intensity and catalyst particle size on the transesterification reaction of BTO to FAME.

The results obtained during the preliminary studies have demonstrated the feasibility of using the H-SOD particles to catalyze the transesterification WCO to biodiesel, where components of FAME were identified using a pre-calibrated GC-MS as described in Chapter 5. The reaction was conducted at 60 ^{o}C for 12 h at a methanol-to- oil ratio of 7.5:1 using 3 wt. % hydroxy sodalite catalyst with a particle size of just below 300 Å. The stirring intensity was kept at 1000 rpm to ensure uniform mixing throughout the reaction. Under the same conditions, the investigation of the use of beef tallow which contained even higher FFA content than waste cooking oil was conducted and the results have shown that FAME was produced, at a yield of 39.6% and a conversion of 68.4%. The results from the investigation on the influence of some of reaction parameters on the performance of the transesterification reaction of BTO, have shown that maximum performance of H-SOD catalyst for a transesterification reaction which resulted in the highest conversion of BTO, 78.3% and 62.9% obtained at optimum conditions: a stirrer speed of 1000 rpm, with the smallest catalyst particle size of 200 Å at maximum temperature of 60 °C and the longest reaction time of 24 h.

A kinetic study was conducted to evaluate the efficiency of the H-SOD to catalyze the transesterification process under the determined optimal conditions. During the kinetic study of the H-SOD catalyst within the given conditions, the values of activation energy, reaction constants and frequency factor obtained at 0.0011 min-1, 5.52 x108 min-1 and 79.20 kJ/mol respectively, fell within the range of the results reported in literature and even better. Solid H-SOD is therefore proposed as an ideal catalyst for a batch transesterification of high FFA content BTO. Among other catalysts, H-SOD material is an inexpensive material with the ability to withstand vigorous conditions without significant loss of activity Teimouri et al. (2015).

9. 2. Recommendations

- This study has demonstrated the possibility of using H-SOD catalyst for the transesterification of BTO to biodiesel; and it has shown the extent at which the type of feedstock can have an impact on the biodiesel quality; further studies may focus on the use of other feedstock with lower FFA content.

- Comparative study between the produced biodiesel and standard biodiesel was not detailed in the work presented in this dissertation, future work may conduct an in-depth comparative analysis on the physico-chemical properties between the standard biodiesel
- This study presents a biodiesel production method with a potential economic advantage, however, a detailed process cost evaluation was not carried out, future work may look into the quantitative costs of production for the scale up commercial production process
- To improve the quality of the results, experiments may be repeated a number of times at different scales of operation, this will help provide insights regarding scale up issues such as changes in reaction performance due to mass transfer variation across the phases of the reactants.
- This study provides kinetic studies on a very basic level; further studies may look into sophisticated chemical equations and process modelling on a higher realistic level, perhaps considering details for each stepwise transesterification reactions with minimal assumptions used for simplifying the model solution.
- This study has successfully demonstrated the effect of some reaction parameters on performance of the transesterification reaction, not all parameters are covered, such as the influence of alcohol to oil ratio and catalyst concentration. Future work may also look into these parameters.

REFERENCES

Abbah, E. C., Nwandikom, G. I. & Nwakuba, N. R., 2016. Effect of Reaction Temperature on the Yield of. *American Journal of Energy Science*, 3(3), pp. 16-20.
Abbaszaadeh, A., Ghobadian, B., Omidkhah, M. R., & Najafi, G. (2012). Current biodiesel production technologies: A comparative review. *Energy Conversion and Management*, *63,* 138-148.

Adewale, P., Dumont, M., & Ngadi, M. (2014). Rheological, thermal, and physicochemical characterization of animal fat wastes for use in biodiesel production. *Energy Technology*, *2*(7), 634-642.

Adewale, P., Dumont, M., & Ngadi, M. (2015). Recent trends of biodiesel production from animal fat wastes and associated production techniques. *Renewable and Sustainable Energy Reviews*, *45*, 574-588.

Agarwal, A. K. (2007). Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science*, *33*(3), 233-271.

Alptekin, E. K., Canakci, M., & Sanli, H. (2014). Biodiesel production from vegetable oil and waste animal fats in a pilot plant. *Waste Management*, *34*(11), 2146-2154.

Anastopoulos, G., Zannikou, Y., Stournas, S., & Kalligeros, S. (2009). Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. *Energies*, *2*(2), 362-376.

Aransiola, E.F., Daramola,M.O., Ojumu,T.V., Aremu,M.O., Layokun,S.K., & Solomon, B.O. (2012). Nigerian jatropha curcas oil seeds: prospect for biodiesel production in Nigeria. *International Journal of Renewable Energy Research*. 2(2), 317-325.

Aransiola, E. F., Daramola, M. O., Ojumu, T. V., Solomon, B. O., & Layokun, S. K. (2013). Homogeneously catalyzed Transesterification of Nigerian jatropha curcas oil into biodiesel: A kinetic study. *Modern Research in Catalysis*, *2*(3), 83-89.

Aransiola, E., Ojumu, T., Oyekola, O., Madzimbamuto, T., & Ikhu-Omoregbe, D. (2014). A review of current technology for biodiesel production: State of the art. *Biomass and Bioenergy*, *61*, 276-297.

Atadashi, I., Aroua, M., Abdul Aziz, A., & Sulaiman, N. (2012). Production of biodiesel using high free fatty acid feedstocks. *Renewable and Sustainable Energy Reviews*, *16*(5), 3275-3285.

Ayompe, L., Duffy, A., McCormack, S., & Conlon, M. (2011). Measured performance of a 1.72kW rooftop grid connected photovoltaic system in Ireland. *Energy Conversion and Management*, *52*(2), 816-825.

Bambase, M. E., Nakamura, N., Tanaka, J., & Matsumura, M. (2007). Kinetics of hydroxide-catalyzed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters. *Journal of Chemical Technology & Biotechnology*, *82*(3), 273-280.

Banković-Ilić, I. B., Stojković, I. J., Stamenković, O. S., Veljkovic, V. B., & Hung, Y. (2014). Waste animal fats as feedstocks for biodiesel production. Renewable and Sustainable Energy Reviews, 32, 238-254.

Baroutian, S., Aroua, M. K., Raman, A. A., & Sulaiman, N. M. (2010). Methanol recovery during transesterification of palm oil in a TiO2/Al2O3 membrane reactor: Experimental study and neural network modeling. *Separation and Purification Technology, 76*(1), 58-63.

Beer, T., Grant, T., Brown, R., Edwards, J., Peter, N., Watson, H., & Williams, D. (2000). *Life-cycle emissions analysis of alternative fuels for heavy vehicles.* The Commonwealth Scientific and Industrial Research Organisation (CSIRO).

Belgharza, M., Azzouzi, E. h., Kitane, M., El Bouzaidi, H., Idrissi, Y., & El Belghiti, M. A. (2014). Study of manufacturing biodiesel from waste animal fats (chicken). *Journal of Chemical and Pharmaceutical Research*, *6*(12), 844-849.

Berchmans, H. J., Morishita, K., & Takarada, T. (2013). Kinetic study of hydroxide-catalyzed methanolysis of jatropha curcas–waste food oil mixture for biodiesel production. *Fuel*, *104*, 46-52.

Bhaduri, S., & Mukesh, D. (2001). *Homogeneous Catalysis: Mechanisms and Industrial Applications*. New York: John Wiley & Sons.

Bhatti, H., Hanif, M., Qasim, M., & Rehman, A. (2008). Biodiesel production from waste tallow. *Fuel*, *87*(13-14), 2961-2966.

Birla, A., Singh, B., Upadhyay, S., & Sharma, Y. (2012). Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. *Bioresource Technology, 106,* 95-100.

Bora, P., Konwar, L. J., Phukan, M. M., Deka, D., & Konwar, B. K. (2015). Microemulsion based hybrid biofuels from Thevetia peruviana seed oil: Structural and dynamic investigations. *Fuel*, *157*, 208-218.

Bozbas, K. (2008). Biodiesel as an alternative motor fuel: Production and policies in the European Union. *Renewable and Sustainable Energy Reviews*, *12*(2), 542-552.

Breck, D. W. (1974). *Zeolite molecular sieves. Structure, chemistry, and use*. New York, NY: Wiley-Interscience.

Brennan, L., & Owende, P. (2010). Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. *Renewable and Sustainable Energy Reviews*, *14*(2), 557-577.

Buhl, J., Schuster, K., & Robben, L. (2011). Nanocrystalline sodalite grown from superalkaline NaCl bearing gels at low temperature (333K) and the influence of TEA on crystallization process. *Microporous and Mesoporous Materials*, *142*(2-3), 666-671.

Canakci, M., & Sanli, H. (2008). Biodiesel production from various feedstocks and their effects on the fuel properties. *Journal of Industrial Microbiology & Biotechnology*, *35*(5), 431-441.

Chai, J., Liang, T., Zhou, X., Ye, Y., Xing, L., & Lai, K. (2016). Natural gas consumption of emerging economies in the industrialization process. *Sustainability*, *8*(11), 1089.

Chen, D., Li, F., & Ray, A. K. (2001). External and internal mass transfer effect on photocatalytic degradation. *Catalysis Today*, *66*(2-4), 475-485.

Chuah, L. F., Klemeš, J. J., Yusup, S., Bokhari, A., & Akbar, M. M. (2016). Influence of fatty acids in waste cooking oil for cleaner biodiesel. *Clean Technologies and Environmental Policy*, *19*(3), 859-868.

Chulalaksananukul, W., Condoret, J., & Combes, D. (1992). Kinetics of geranyl acetate synthesis by lipase-catalysed transesterification in n-hexane. *Enzyme and Microbial Technology*, *14*(4), 293-298.

Da Cunha, M. E., Krause, L. C., Moraes, M. S., Faccini, C. S., Jacques, R. A., Almeida, S. R., & Caramão, E. B. (2009). Beef tallow biodiesel produced in a pilot scale. *Fuel Processing Technology*, *90*(4), 570-575.

Daramola, M., Dinat, A., & Hasrod, S. (2015). Synthesis and characterization of nanocomposite hydroxy- sodalite/ceramic membrane via pore-plugging hydrothermal synthesis technique. *Journal of Membrane and Separation Technology*, *4*(1), 1-7.

Daramola, M., Mtshali, K., Senokoane, L., & Fayemiwo, O. (2016). Influence of operating variables on the transesterification of waste cooking oil to biodiesel over sodium silicate catalyst: A statistical approach. *Journal of Taibah University for Science*, *10*(5), 675-684.

Darnoko, D., & Cheryan, M. (2000). Kinetics of palm oil transesterification in a batch reactor. *Journal of the American Oil Chemists' Society*, *77*(12), 1263-1267.

Molaei Dehkordi, A., & Ghasemi, M. (2012). Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts. *Fuel Processing Technology*, *97*, 45-51.

Demirbas, A. (2007). Importance of biodiesel as transportation fuel. *Energy Policy*, *35*(9), 4661-4670.

Demirbas, A. (2008). *Biodiesel: A realistic fuel alternative for diesel engines*. London: Springer.

Demirbas, A. (2008). *Biofuels: Securing the Planet's Future Energy Needs*. Turkey: Springer.

Deshmane, V. G., & Adewuyi, Y. G. (2013). Synthesis and kinetics of biodiesel formation via calcium methoxide base catalyzed transesterification reaction in the absence and presence of ultrasound. *Fuel*, *107*, 474-482.

Dias, J. M., Alvim-Ferraz, M. C., Almeida, M. F., Méndez Díaz, J. D., Polo, M. S., & Utrilla, J. R. (2012). Selection of heterogeneous catalysts for biodiesel production from animal fat. *Fuel*, *94*, 418-425.

Dias, J. M., Alvim-Ferraz, M. C., Almeida, M. F., Méndez Díaz, J. D., Sánchez Polo, M., & Rivera Utrilla, J. (2013). Biodiesel production using calcium manganese oxide as catalyst and different raw materials. *Energy Conversion and Management, 65*, 647-653.

Di Serio, M., Tesser, R., Pengmei, L., & Santacesaria, E. (2008). Heterogeneous Catalysts for Biodiesel Production. *Energy & Fuels*, *22*(1), 207-217.

Ebenaza, G. T., & Vinoth, E. (2015). Biodiesel production from waste cooking oil. International Journal of Students' Research in Technology & Management. *Energy Conversion and Management*, *3*(8), 448-450.

Eevera, T., Rajendran, K., & Saradha, S. (2009). Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. *Renewable Energy*, *34*(3), 762-765.

Ellabban, O., Abu-Rub, H., & Blaabjerg, F. (2014). Renewable energy resources: Current status, future prospects and their enabling technology. *Renewable and Sustainable Energy Reviews*, *39*, 748-764.

Eloka-Eboka, A. C., Igbum, O. G,. & Inambao, F. L. (2014). Optimization and effects of process variables on the production and properties of methyl ester biodiesel. *Journal of Energy in Southern Africa*, *25*(2), 39-47.

Farooq, M., Ramli, A., & Naeem, A. (2016). Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. *Renewable Energy*, *76*, 362-368.

Fatah, M. A., Mansour, M. S. & Fouad, Y. O.(2016). Biodiesel production optimization from waste cooking oil using nano heterogeneous catalyst. *International Journal of Chemical and Biochemical Sciences*, 9, 33-43.

Singh, A., & Fernando, S. (2007). Reaction kinetics of soybean oil transesterification using heterogeneous metal oxide catalysts. *Chemical Engineering & Technology*, *30*(12), 1716-1720.

Foley, A. M., Leahy, P. G., Marvuglia, A., & McKeogh, E. J. (2012). Current methods and advances in forecasting of wind power generation. *Renewable Energy*, *37*(1), 1-8.

Freedman, B., Pryde, E. H., & Mounts, T. L. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists Society, 61*(10), 1638-1643.

Fröhlich, A., Rice, B., & Vicente, G. (2010). The Conversion of low grade tallow into biodiesel-grade methyl ester. *Journal of the American Oil Chemists' Society*, *87*(7), 825-833.
Galvez, R. P. & Berge, J.-P.(2013). *Utilization of Fish Waste.* London, Great Britain: CRC Press.

Gashaw, A. & Teshita, A. (2014). Production of biodiesel from waste cooking oil and factors affecting its formation: A review. *International Journal of Renewable and Sustainable Energy,* 3(5), 92-98.

Goodstein, E. S.(2008). *Economics and the Environment.* New York: Wiley.

Guo, F., & Fang, Z. (2012). Biodiesel production with solid catalysts. In M. Stoytcheva & G. Montero (Eds.), *Biodiesel – feedstocks and processing technologies*. Rijeka: InTech.

Guo, F., Wei, N., Xiu, Z., & Fang, Z. (2012). Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Fuel, 93*, 468-472.

Gupta, R. B., & Demirbas, A. (2010). Gasoline, Diesel, and Ethanol Biofuels from Grasses and Plants.

Gupta, V. K. & Tuohy, M. G. (2013). *Biofuel technologies: recent developments.* Berlin Heidelberg: Springer.

Hassani, H., Najafpour, G. D. & Mohammadi, M.(2016). Transesterification of waste cooking oil to biodiesel using γ-alumina coated on zeolite pellets. *Journal of Materials and Environmental Science,* 7(4), 1193-1203.

He, B. B., Singh, A. P. & Thompson, J. C., 2005. Experimental optimization of a continuous-flow reactive distillation reactor for biodiesel production. *American Society of Agricultural Engineers*, 48(6), pp. 2237-2243.

Heberle, F., & Brüggemann, D. (2010). Exergy based fluid selection for a geothermal Organic Rankine Cycle for combined heat and power generation. *Applied Thermal Engineering, 30*(11-12), 1326-1332.

Helwani, Z., Othman, M., Aziz, N., Kim, J., & Fernando, W. (2009). Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. *Applied Catalysis A: General, 363*(1-2), 1-10.

Hemmat, Y., Ghobadian, B., Loghavi, M., Kamgar, S., & Fayyazi, I. (2013). Biodiesel Fuel Production from residual animal fat as an inedible and inexpensive feedstock. *International Research Journal of Applied and Basic Sciences*, *5*(1), 84-91.

Hill, J., Nelson, E., Tilman, D., Polasky, S., & Tiffany, D. (2006). Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proceedings of the National Academy of Sciences, 103*(30), 11206-11210.

Hinchee, M., Rottmann, W., Mullinax, L., Zhang, C., Chang, S., Cunningham, M., & Nehra, N. (2010). Short-rotation woody crops for bioenergy and biofuels applications. In: *Biofuels.* New York: Springer 139-156.

Hindryawati, N., Maniam, G. P., Karim, M. R., & Chong, K. F. (2014). Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst. *Engineering Science and Technology, an International Journal*, *17*(2), 95-103.

Huang, Y., Yao, J., Zhang, X., Kong, C., Chen, H., Liu, D.,& Wang, H. (2011). Role of ethanol in sodalite crystallization in an ethanol–Na2O–Al2O3–SiO2–H2O system. *CrystEngComm*, *13*(14), 4714.
Hubacek, K., Guan, D., & Barua, A. (2007). Changing lifestyles and consumption patterns in developing countries: A scenario analysis for China and India. *Futures*, *39*(9), 1084-1096.

International Zeolite Association. (2017, August 15). Database of zeolite structures. Retrieved from http://www.iza-structure.org/databases/

Islam, A., Taufiq-Yap, Y. H., Chu, C., Chan, E., & Ravindra, P. (2013). Studies on design of heterogeneous catalysts for biodiesel production. *Process Safety and Environmental Protection*, *91*(1-2), 131-144.

Islam, M. R., & Speight, J. G. (2016). Peak Energy: myth or reality? : John Wiley & Sons, Inc

Ito, T., Sakurai, Y., Kakuta, Y., Sugano, M., & Hirano, K. (2012). Biodiesel production from waste animal fats using pyrolysis method. *Fuel Processing Technology*, *94*(1), 47-52.

Jacob, I., Clausen, E. & Carrier, D. J. (2008). *Kinetics determination of soybean oil transesterification in the design of a continuous biodiesel production process.* (Honours thesis). Retrieved from http://scholarworks.uark.edu/baeguht/34.

Jagadale, S. S., & Jugulkar, L. M. (2012). Review of various reaction parameters and other factors affecting on production of chicken fat based biodiesel. *International Journal of Modern Engineering Research*, *2*(2), 407-411.

Jain, S., & Sharma, M. (2010). Kinetics of acid base catalyzed transesterification of jatropha curcas oil. *Bioresource Technology*, *101*(20), 7701-7706

Jaya, N. & Ethirajulu, K. (2011). Kinetic studies of heterogeneously catalyzed transesterification of cottonseed oil to biodiesel. Journal of Environmental Research And Development, 5(3A), pp. 689-695.

Kamaruddin, A. H., Serri, N. A., Sim, J. H., Halim, F. A., & Rahaman, R. A. (2013). A Bio-Route production of biodiesel. In *Advances in biofuels*. New York: Springer.

Kanade, K., Kale, B., Aiyer, R., & Das, B. (2006). Effect of solvents on the synthesis of nano-size zinc oxide and its properties. *Materials Research Bulletin*, *41*(3), 590-600.

Karmakar, A., Karmakar, S., & Mukherjee, S. (2010). Properties of various plants and animals feedstocks for biodiesel production. *Bioresource Technology*, *101*(19), 7201-7210.

Kibbey, T. C., Chen, L., Do, L. D., & Sabatini, D. A. (2014). Predicting the temperature-dependent viscosity of vegetable oil/diesel reverse microemulsion fuels. *Fuel*, *116*, 432-437.

Kim, H., Kang, B., Kim, M., Park, Y. M., Kim, D., Lee, J., & Lee, K. (2004). Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today*, *93-95*, 315-320.

Klaewkla, R., Arend, M. & Hoelderich, W.(2011). A review of Mass Transfer controlling the reaction rate in heterogeneous catalytic systems. *Mass Transfer - Advanced Aspects*.

Klaewkla, R., Arend, M., & Hoelderich, W. (2011). A review of mass transfer controlling the reaction rate in heterogeneous catalytic systems. In *Mass Transfer- Advanced Aspects* (pp. 668-686). Rijeka: InTech.

Knothe, G. (2001). Analytical methods used in the production and fuel quality assessment of biodiesel. *American* Society *of* Agricultural *Engineers*, 44(2), 193–200

Kumar, G., Kumar, D., Singh, S., Kothari, S., Bhatt, S., & Singh, C. P. (2010). Continuous low cost transesterification process for the production of coconut biodiesel. *Energies*, *3*(1), 43-56.

Kundu, D., Dey, B., Naskar, M., & Chatterjee, M. (2010). Emulsion-derived urchin-shaped hydroxy sodalite particles. *Materials Letters*, *64*(14), 1630-1633.

Leevijit,T., Wisutmethangoon, W., Prateepehaikul, G., Tongurai, C.,& Allen,M. (2004) A second order kinetics of palm oil transesterification in a batch reactor, in Proceedings of the Joint International Conference on Sustainable Energy and Environment, 277–281.

Li, D., Yao, J., Wang, H., Hao, N., Zhao, D., Ratinac, K. R., & Ringer, S. P. (2007). Organic-functionalized sodalite nanocrystals and their dispersion in solvents. *Microporous and Mesoporous Materials*, *106*(1-3), 262-267

Li, H., & Xie, W. (2006). Transesterification of soybean oil to biodiesel with Zn/I2 catalyst. *Catalysis Letters*, *107*(1-2), 25-30

Li, M., Zheng, Y., Chen, Y., & Zhu, X. (2014). Biodiesel production from waste cooking oil using a heterogeneous catalyst from pyrolyzed rice husk. *Bioresource Technology*, *154*, 345-348

Liu, J., (2013). *Biodiesel synthesis via transesterification reaction in supercritical methanol: a) A kinetic study, b) Biodiesel synthesis using microalgae oil,* New York : Biomedical and Chemical Engineering – Theses. Paper 3.

Liu, S., Wang, Y., Oh, J., & Herring, J. L. (2011). Fast biodiesel production from beef tallow with radio frequency heating. *Renewable Energy*, *36*(3), 1003-1007.

Liu, X., Piao, X., Wang, Y., & Zhu, S. (2008). Calcium ethoxide as a solid base catalyst for the Transesterification of Soybean Oil to Biodiesel. *Energy & Fuels*, *22*(2), 1313-1317.

Liu, X., Piao, X., Wang, Y., Zhu, S., & He, H. (2008). Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. *Fuel*, *87*(7), 1076-1082.

Liu, Y., Lotero, E., Goodwin, J. G., & Mo, X. (2007). Transesterification of poultry fat with methanol using Mg–Al hydrotalcite derived catalysts. *Applied Catalysis A: General*, *331*, 138-148.

Li, Z., Lin, P., Wu, J. C., Huang, Y., Lin, K., & Wu, K. C. (2013). A stirring packed-bed reactor to enhance the esterification–transesterification in biodiesel production by lowering mass-transfer resistance. *Chemical Engineering Journal, 234*, 9-15.

Luque, R. & Melero, J. A. (2012). *Advances in Biodiesel production.* 1st ed. Cambridge: Woodhead Publishing.

Ma, F., & Hanna, M. A. (1999). Biodiesel production: a review1Journal Series #12109, Agricultural Research Division, Institute of Agriculture and Natural Resources, University of Nebraska–Lincoln.1. *Bioresource Technology, 70*(1), 1-15.

Makama, B. Y. (2012). Effect of Temperature on the transesterification of Cod Liver oil. *Research Journal of Chemical Sciences,* 2(7), 82-84

Makgaba, C. P., & Daramola, M. O. (2015). Transesterification of Waste Cooking Oil to Biodiesel over Calcined Hydroxy Sodalite (HS) Catalyst: A preliminary investigation. *Proceedings of the 2015 International Conference on Sustainable Energy and Environmental Engineering*.

Mann, U.(2009). *Principles of Chemical Reactor Analysis and design:New Tools for Industrial Chemical Reactor.* New Jersey: John Wiley & Sons.
Marasović, M., Marasović, T., & Miloš, M. (2017). Robust Nonlinear Regression in Enzyme Kinetic Parameters Estimation. *Journal of Chemistry, 2017,* 1-12.

Marchetti, J., Miguel, V., & Errazu, A. (2007). Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews, 11*(6), 1300-1311.

Mata, T. M., Martins, A. A., & Caetano, N. S. (2010). Microalgae for biodiesel production and other applications: A review. *Renewable and Sustainable Energy Reviews, 14*(1), 217-232.

Mata, T. M., Mendes, A. M., Caetano, N. S. & Martins, A. A. (2014). Properties and sustainability of biodiesel from animal fats and fish oil. Chemical Engineering Transactions, 38, 175-180.

Mathiyazhagan, M. & Ganapathi, A. (2011). Factors affecting biodiesel production. *Research in Plant Technology,* 1(2), 0-5.

Melo-Espinosa, E. A., Piloto-Rodríguez, R., Goyos-Pérez, L., Sierens, R., & Verhelst, S. (2015). Emulsification of animal fats and vegetable oils for their use as a diesel engine fuel: An overview. *Renewable and Sustainable Energy Reviews, 47*, 623-633.

Menon, V., & Rao, M. (2012). Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science, 38*(4), 522-550.

Milano, J., Ong, H. C., Masjuki, H., Chong, W., Lam, M. K., Loh, P. K., & Vellayan, V. (2016). Microalgae biofuels as an alternative to fossil fuel for power generation. *Renewable and Sustainable Energy Reviews, 58*, 180-197.

Moser, B. R. (2009). Biodiesel Production, Properties, and Feedstocks. *Biofuels*, 285-347

Mutreja, V., Singh, S., & Ali, A. (2011). Biodiesel from mutton fat using KOH impregnated MgO as heterogeneous catalysts. *Renewable Energy*, *36*(8), 2253-2258.

Nabavi, M. S., Mohammadi, T., & Kazemimoghadam, M. (2014). Hydrothermal synthesis of hydroxy sodalite zeolite membrane: Separation of H2/CH4. *Ceramics International*, *40*(4), 5889-5896.

Naik, S., Goud, V. V., Rout, P. K., & Dalai, A. K. (2010). Production of first and second-generation biofuels: A comprehensive review. *Renewable and Sustainable Energy Reviews*, *14*(2), 578-597.

Narimani, F. & Kharamesh, M. (2014). Synthesis of nano-porous molecular sieve from some natural materials. *International Journal of Nano Dimension*, 5(1), 69-75.

Naskar, M. K., Kundu, D., & Chatterjee, M. (2011). An Aqueous-Based Synthesis of Flower-Like Hydroxy Sodalite Particles in the Presence of Cetyltrimethylammonium bromide. *Journal of the American Ceramic Society*, *94*(6), 1643-1646.
Nasreen, S., Liu, H., Lukic, I., Qurashi, L., & Skala, D. (2016). Heterogeneous kinetics of vegetable oil transesterification at high temperature. *Chemical Industry and Chemical Engineering Quarterly*, *22*(4), 419-429.

Navajas, A., Campo, I., Arzamendi, G., Hernández, W., Bobadilla, L., Centeno, M. & Gandía, L. (2010). Synthesis of biodiesel from the methanolysis of sunflower oil using PURAL® Mg–Al hydrotalcites as catalyst precursors. *Applied Catalysis B: Environmental*, *100*(1-2), 299-309.

Naveen, G. & Krishnakumar, G. (2012). Biochemical analysis and Sed oil Characterizations of Garcinia indica, G. xanthochymus and G. gummi-guta for nutritional qualities. *Indian Journal of Science*, 1(1), 71-73.

Nejat, P., Jomehzadeh, F., Taheri, M. M., Gohari, M., & Abd. Majid, M. Z. (2015). A global review of energy consumption, CO2 emissions and policy in the residential sector (with an overview of the top ten CO2 emitting countries). *Renewable and Sustainable Energy Reviews*, *43*, 843-862.

Ngamcharussrivichai, C., Totarat, P., & Bunyakiat, K. (2008). Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. *Applied Catalysis A: General*, *341*(1-2), 77-85.

Noureddini, H., & Zhu, D. (1997). Kinetics of transesterification of soybean oil. *Journal of the American Oil Chemists' Society*, *74*(11), 1457-1463.

Obahiagbon, F. (2012). A Review: Aspects of the African oil palm (Elaeis guineesis jacq.) and the implications of its bioactives in human health. *American Journal of Biochemistry and Molecular Biology*, *2*(3), 106-119

Odin, E. M., Onoja, P. K. & O chala, A. U. (2013). Effect of process variables on the biodiesel production via transesterification of Quassia Undulata seed oil, using homogeneous catalyst. *International Journal of Scientific and Technology Research*, 2(9), 267-276.

Odoom, W. & Eduse, V. O. (2015). Evaluation of Saponification value, Iodine value and Insoluble impurities in coconut oils from jomoro district in the western region of Ghana. *Asian Journal of Agriculture and Food Sciences,* 3(5), 494-499.

Olutoye, M., & Hameed, B. (2016). Kinetics and deactivation of a dual-site heterogeneous oxide catalyst during the transesterification of crude jatropha oil with methanol. *Journal of Taibah University for Science*, *10*(5), 685-699.

Padula, D. A., Santos, S. d., Santos, B. O. & Borenstein, D. (2014). *Liquid Biofuels: Emergence, Development and Prospects.* London: Springer Verlag.

Sharma, P., Yeo, J., Yu, J., Han, M. H., & Cho, C. H. (2014). Effect of ethanol as an additive on the morphology and crystallinity of LTA zeolite. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(2), 689-704.

Panwar, N., Kaushik, S., & Kothari, S. (2011). Role of renewable energy sources in environmental protection: A review. *Renewable and Sustainable Energy Reviews*, *15*(3), 1513-1524.

Parawira, W. (2010). Biodiesel production from Jatrophacurcas:A reviwe. *Scientific Research and Essays,* 5(14), 1796-1808.

Parikka, M. (2004). Global biomass fuel resources. *Biomass and Bioenergy*, *27*(6), 613-620.

Pathak, S. (2015). Acid catalyzed transesterification. *Journal of Chemical and Pharmaceutical Research,* 7(3), 1780-1786.

Pinto, A. C., Guarieiro, L. L., Rezende, M. J., Ribeiro, N. M., Torres, E. A., Lopes, W. A. & Andrade, J. B. (2005). Biodiesel: an overview. *Journal of the Brazilian Chemical Society*, *16*(6b), 1313-1330.

Portha, J., Allain, F., Coupard, V., Dandeu, A., Girot, E., Schaer, E., & Falk, L. (2012). Simulation and kinetic study of transesterification of triolein to biodiesel using modular reactors. Chemical Engineering Journal, 207-208, 285-298.

Rachmanto, T., Allanson, D., Matthews, C. & Jenkinson, I., (2014). Monitoring of Biodiesel Transesterification Process Using Impedance Measurement. International Journal of Materials, Mechanics and Manufacturing, 2(4), 265-271.

Ramadhas, A. S., Jayaraj, S. & Muraleedharan, C. (2005). Biodiesel production from high FFA rubber seed oil. *Fuel*, *84*(4), 335-340.

Raqeeb, M. A. & Bhargavi, R.,(2015). Biodiesel production from waste cooking oil. *Journal of Chemical and Pharmaceutical Research,* 7(12), 670-681.

Rashid, U., Anwar, F., & Knothe, G. (2009). Evaluation of biodiesel obtained from cottonseed oil. *Fuel Processing Technology*, *90*(9), 1157-1163.

Rashid, U., Anwar, F., Yunus, R., & Al-Muhtaseb, A. H. (2014). Transesterification for Biodiesel Production UsingThespesia PopulneaSeed Oil: An Optimization Study. *International Journal of Green Energy*, *12*(5), 479-484.

Razzaque, J. (2013). *Environmental Governane in Europe and Asia: A Comparative Study of Institutional and Legislative Framework.* New York: Routledge.

Salameh, Z. (2014). *Renewable Energy System Design*. San Diego: Elsevier Inc.

Schenk, P. M., Thomas-Hall, S. R., Stephens, E., Marx, U. C., Mussgnug, J. H., Posten, C., …

Hankamer, B. (2008). Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production. *BioEnergy Research*, *1*(1), 20-43.

Schuchardt, U., Sercheli, R., & Vargas, R. M. (1998). Transesterification of vegetable oils: a review. *Journal of the Brazilian Chemical Society*, *9*(3), 199-210.
Shah, K. A., Parikh, J. K., & Maheria, K. C. (2013). Optimization Studies and Chemical Kinetics of Silica Sulfuric Acid-Catalyzed Biodiesel Synthesis from Waste Cooking Oil. *BioEnergy Research*, *7*(1), 206-216.

Sharma, Y. C., Singh, B., & Korstad, J. (2010). Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel. *Biofuels, Bioproducts and Biorefining*, *5*(1), 69-92.

Mabrouk, P. A. (2008). Green Chemistry and Catalysis By Roger A. Sheldon, Isabel W. C. E. Arends, and Ulf Hanefeld (Delft University of Technology, The Netherlands). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim.

Soetaredjo, F. E., Ayucitra, A., Ismadji, S., & Maukar, A. L. (2011). KOH/bentonite catalysts for transesterification of palm oil to biodiesel. *Applied Clay Science, 53*(2), 341-346.

Speight, J. G. (2011). An Introduction to Petroleum Technology, Economics, and Politics. New Jersey: Scrivener Publishing.

Stamenković, O. S., Veljković, V. B., Todorović, Z. B., Lazić, M. L., Banković-Ilić, I. B., & Skala, D. U. (2010). Modeling the kinetics of calcium hydroxide catalyzed methanolysis of sunflower oil. *Bioresource Technology, 101*(12), 4423-4430.

Stöcker, M. (2008). Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. *Angewandte Chemie International Edition*, *47*(48), 9200-9211.

Tabak, J. (2009). *Biofuels.* New York: Infobase Publishing.

Talwar, G. P. (2016). *Textbook of Biochemistry, Biotechnology, Allied and Molecular Medicine.* 4th ed. Delhi: PHI Learning Private Limited.

Teimouri, F., Khezri, S. H. & Azizian, J. (2015). Hydroxy sodalite zeolite as a recyclable catalyst for the green synthesis of tetrahydrobenzo [b] pyrans via one-pot three-component condensation reaction. *Iranian Journal of Catalysis*, 5(3), pp. 253-259.
Tri-State Biodiesel. (2015). *Biodiesel Facts*. Retrieved from http://tristatebiodiesel.com/biodiesel-facts

U.S. Department of Energy. (2013). Fossil Energy:A brief history of coal use. Retrieved from http://www.fe.doe.gov/education/energylessons/coal/coal_history.html

U.S. Energy Information Administration.(2016). *International Energy Outlook 2016*. Retrieved from website: https://www.eia.gov/outlooks/ieo/pdf/0484(2016).pdf

Vafakish, B., & Barari, M. (2017). Biodiesel Production by Transesterification of Tallow Fat Using Heterogeneous Catalysis. *Kemija u industriji*, *66*(1-2).

Veny, H., Aroua, M. K., & Sulaiman, N. M. (2014). Kinetic study of lipase catalyzed transesterification of jatropha oil in circulated batch packed bed reactor. *Chemical Engineering Journal*, *237*, 123-130.

Viele, E. L., Chukwuma, F. O., & Uyigue, L. (2013). Esterification of high free fatty acid crude palm kernel oil as feedstock for base-catalysed transeterification reaction. *International Journal of Application or Innovation in Engineering & Management*, 2(12),361-365.

Vujicic, D., Comic, D., Zarubica, A., Micic, R., & Boskovic, G. (2010). Kinetics of biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst. *Fuel*, *89*(8), 2054-2061.

Vyas, A. P., Subrahmanyam, N., & Patel, P. A. (2009). Production of biodiesel through transesterification of Jatropha oil using KNO3/Al2O3 solid catalyst. *Fuel*, *88*(4), 625-628.

Wang, X., Liu, X., Zhao, C., Ding, Y., & Xu, P. (2011). Biodiesel production in packed-bed reactors using lipase–nanoparticle biocomposite. *Bioresource Technology*, *102*(10), 6352-6355.

Watkins, R. S., Lee, A. F., & Wilson, K. (2004). Li–CaO catalysed tri-glyceride transesterification for biodiesel applications. *Green Chem*, *6*(7), 335-340.

World Energy Outlook 2008. (2008). Retrieved from International Energy Agency website: http://www.worldenergyoutlook.org/media/weowebsite/2008-1994/weo2008.pdf

Wrigley, E. A. (2013). Energy and the English Industrial Revolution. *Philosophical transactions of the royal society A.*

Xu, X., Bao, Y., Song, C., Yang, W., Liu, J., & Lin, L. (2004). Microwave-assisted hydrothermal synthesis of hydroxy-sodalite zeolite membrane. *Microporous and Mesoporous Materials*, *75*(3), 173-181.

Yaakob, Z., Mohammad, M., Alherbawi, M., Alam, Z., & Sopian, K. (2013). Overview of the production of biodiesel from Waste cooking oil. *Renewable and Sustainable Energy Reviews*, *18*, 184-193.

Yang, H., Lu, L., & Zhou, W. (2007). A novel optimization sizing model for hybrid solar-wind power generation system. *Solar Energy*, *81*(1), 76-84.

Yao, J., Wang, H., Ratinac, K. R., & Ringer, S. P. (2006). Formation of colloidal hydroxy-sodalite nanocrystals by the direct transformation of silicalite nanocrystals. *Chemistry of Materials*, *18*(6), 1394-1396.

Yao, J., Zhang, L., & Wang, H. (2008). Synthesis of nanocrystalline sodalite with organic additives. *Materials Letters*, *62*(24), 4028-4030.

Yori, J. C., D'Ippolito, S. A., Pieck, C. L., & Vera, C. R. (2007). Deglycerolization of biodiesel streams by adsorption over silica beds. *Energy & Fuels*, *21*(1), 347-353.

Yoshida, A., Hama, S., Tamadani, N., Fukuda, H., & Kondo, A. (2012). Improved performance of a packed-bed reactor for biodiesel production through whole-cell biocatalysis employing a high-lipase-expression system. *Biochemical Engineering Journal*, *63*, 76-80.

Yulianti, C. H., Ediati, R., Hartanto, D., Purbaningtias, T. E., Chisaki, Y., Jalil, A. A., &Prasetyoko, D. (2014). Synthesis of CaOZnO Nanoparticles Catalyst and Its Application in Transesterification of Refined Palm Oil. *Bulletin of Chemical Reaction Engineering & Catalysis*, *9*(2), 100-110.

Zhang, L., Sheng, B., Xin, Z., Liu, Q., & Sun, S. (2010). Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst. *Bioresource Technology*, *101*(21), 8144-8150.

Zhang, Y. (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology*, *89*(1), 1-16.

Zhou, W., Lou, C., Li, Z., Lu, L., & Yang, H. (2010). Current status of research on optimum sizing of stand-alone hybrid solar–wind power generation systems. *Applied Energy*, *87*(2), 380-389.

Zubir, M., & Chin, S. (2010). Kinetics of modified Zirconia-catalyzed heterogeneous esterification Reaction for biodiesel Production. *Journal of Applied Sciences*, *10*(21), 2584-2589.

APPENDIX A: Experimental

Below is a picture of the transesterification products. The top layer is the biodiesel produced from BTO and the bottom part comprises a mixture of unreacted fat and glycerol.

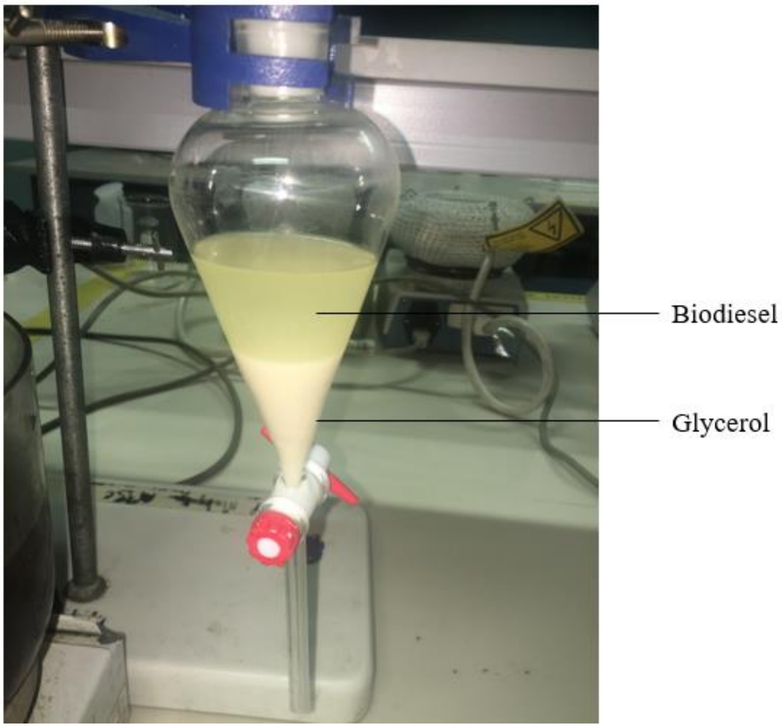

Figure 21: The separation funnel containing the layers of biodiesel and glycerol products from the transesterification reaction.

Figure A1: The separation funnel containing the layers of biodiesel and glycerol products from the transesterification reaction.

APPENDIX: Copy of publications

Waste to Energy: Effect of reaction parameters on the transesterification of animal fat oil to biodiesel over a solid hydroxy sodalite (SOD) catalyst

Abstract: In this study, production of biodiesel via the transesterification of beef tallow oil with methanol over a solid hydroxy sodalite (SOD) catalyst was investigated, particularly the effect of process variables on the yield of biodiesel. The current investigation was laboratory based where beef tallow oil was tested for the content of Free Fatty Acid (FFA) to confirm the need for a heterogeneous catalyst. SOD crystals were synthesized via a hydrothermal synthesis method for use as basic solid catalyst to convert beef tallow oil into biodiesel. Transesterification reaction was conducted at methanol-to-animal fat oil ratio of 7.5:1 using 3 wt. % SOD catalyst with variations in the mixing intensity (700 – 1250 rpm), catalyst particle size (200 – 300 Å), reaction time (6 – 24 h) and reaction temperature (40 – 60 °C). Each process variable was varied at a time while others were kept constant. The FFA content was sufficiently high, determined to be 4.53 % justifying the need for solid catalysed transesterification reaction. The physicochemical characterization of the SOD catalyst was conducted using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), N_2 physisorption at 77 K (for textural property) and thermogravimetric analysis (for thermal stability). Results of characterization reveal that SOD crystals were synthesized. The reaction products analysed with a pre-calibrated Gas Chromatography-Mass spectrometer (GC-MS) confirmed the influence of reaction process parameters on the yield of biodiesel leading to a highest FAME (fatty acid methyl ester) yield of 78.3% at an agitation speed of 1000 rpm with a catalyst particle size of 200Å. The reaction temperature and reaction time to achieve the highest biodiesel yield were 60^oC and 24 h, respectively.

Keywords: Biodiesel; Animal fat, Hydroxy sodalite, Waste beneficiation, Solid catalyst

Reference to this paper should be made as follows: Author. (xxxx) ‘Title’, *Int. J. xxxxxxxxxxx xxxxxxxxxxx*,

Biographical notes: *This paper is a revised and expanded version of a paper entitled [Waste to Energy: Effect of reaction parameters on the transesterification of animal fat oil to biodiesel over a solid hydroxy sodalite (SOD) catalyst] presented at [the 2nd International Conference of Engineering for a Sustainable World ICESW 2017 July 3-7, 2017, Ota, Nigeria].*

1 Introduction

Fossil fuels (oil, coal, natural gas) are the major source of energy accounting for about 86% global energy consumption (Nicole, 1994) that drives the worldwide technological advancement. Consequent to heavy consumption of fossil fuels, the world is faced with detrimental challenges such as future energy security and environmental concerns (Gupta & Tuohy, 2013; Milano et al., 2016). Combustion of fossil fuels results in emission of greenhouse gases such as CO_2 and SO_2 thereby contributing to global warming and acid rain crises. These concerns drive the need for exploration of alternative energy source to reduce dependency on fossil fuels. One possible solution is the extended exploitation of biodiesel as an alternative fuel. Biodiesel has a higher flash point than petrol diesel and lower volatile compounds. It is easy to use and is a clean burning and safer for handling compared to petrol diesel. Chemically known as Fatty Acid Methyl Ester (FAME), biodiesel is a biodegradable, non-toxic and environmentally benign diesel fuel and its study as an alternative fuel to reduce dependency on fossil fuels has become an attractive area of research(Makgaba & Daramola, 2015; Ramadhas, Jayaraj, & Muraleedharan, 2005) (Zhang, Dube, McLean, & Kates, 2003). It is a viable alternative fuel as it meets the strict fuel quality and engine performance and satisfied the environmental impact assessment requirements by the 1990 Clean Air Act Amendments in terms of the reduction of environmental pollution(Guo, Wei, Xiu, & Fang, 2012). Furthermore, biodiesel can be mixed at any proportion with diesel; hence it can be applied in diesel engines without much additional modification. Biodiesel is commonly produced from vegetable oils or animal fat using transesterification reaction. The reaction involves the use of short chain alcohol, usually methanol, as well as a catalytic material. The cost of biodiesel remains high compared to petroleum diesel, due to huge operating and capital costs required for its production process.

Competitive source of feedstocks such as edible oils and fats that bring about high cost of production have spawn interest of researchers into alternative feedstock for an economically viable route to biodiesel production. These include non-edible Jatropha oil, animal fat and waste cooking oil (Aransiola et al., 2012; Aransiola, Daramola, Ojumu, Solomon, & Layokun, 2013; M. O. Daramola, Nkazi, & Mtshali, 2015; Islam, Taufiq-Yap, Chu, Chan, & Ravindra, 2013). Non-edible oils usually contain high content of Free Fatty acids which tends to be unfavourable for transesterification reaction, more especially when homogeneous base catalysts are used. Saponification reaction occurs in conjunction with the transesterification reaction thereby reducing the yield of biodiesel. Furthermore, an additional process unit for product separation is required to recover the resulting biodiesel from the mixture with the catalyst(Canakci & Sanli, 2008; Marchetti, Miguel, & Errazu, 2007). The use of heterogeneous catalysts tends to override the saponification reaction, reduces the need for an esterification reaction used as oil pre-treatment step to reduce content of the free fatty acids(Jagadale & Jugulkar, 2012) and potentially eliminates the need for high investments in the additional product separation step.

The process of transesterification reaction is influenced by process variables such as reaction temperature, reaction time and catalytic properties amongst others (Alptekin, Canakci, & Sanli, 2014; Atadashi, Aroua, Aziz, & Sulaiman, 2012;

Kim et al., 2004). This work explored the influence of some reaction parameters on the performance of the transesterification reaction of waste beef tallow over solid hydroxy sodalite catalyst. The aim of this study was to obtain a more economic and environmentally attractive process for biodiesel production using cheap non-edible animal fat (beef tallow).

2 Experimental

2.1. Catalyst synthesis

The hydroxy sodalite particles were prepared by hydrothermal synthesis method, similar to the one described in our previous study(Jagadale & Jugulkar, 2012). The synthesis solution was prepared from a mixture of anhydrous sodium metasilicate (Na_2SiO_3), sodium hydroxide (NaOH), anhydrous sodium aluminate ($NaAlO_2$) and in-house de-ionized water. The mixture was stirred in a 45ml polypropylene bottle for an hour. An addition of small amount of ethanol as an organic solvent was done an hour later, and the mixing was allowed to continue for a further 1 h, for the purpose of reducing the morphology and particle size distribution of the synthesized crystals. The resulting mixture was transferred into a Teflon lined autoclave which was subjected to heat at 140 °C for 3.5 h. At the end of the hydrothermal reaction, the autoclave was cooled down by running tap water. The resulting crystals were washed using deionized water by a filtration system until the pH of the water reached a value of 7. The washed hydroxy sodalite crystals were then dried overnight, and then calcined at 200 °C prior to the transesterification reaction.

2.2. Catalyst synthesis

For the surface chemistry of the hydroxy sodalite particles, Fourier transform infrared spectroscopy (FTIR) was used to characterize the chemical functional groups of the catalyst, with a wave number range from 400 to 4000 cm^{-1}. In order to carry out the scanning electron microscope (SEM) analysis, the hydroxy sodalite catalyst was initially coated with ultrathin gold/palladium alloy due to its non-conductive nature. The determination of surface topology and morphology of the catalyst was determined by SEM, performed on a Carl Zeiss, operating at an accelerated voltage of 5.00 kV. Pore size, pore volume and surface area measurements were obtained on a Micrometrics Tri-Star 3000 surface area and porosity analyzer via Nitrogen physisorption at 77 K. Thermogravimetric analysis (TGA) was carried out to help understand the thermal stability of the hydroxy sodalite particles. To measure the crystallinity of the catalyst, X-ray diffraction (XRD) analysis was carried out using the Rigaku's Ultima IV X-ray diffractometer operating with CuKα radiation ($\lambda = 1.5406$ Å), and equipped with a graphite monochromator in the diffracted beam. Scherrer equation (Equation 1) was used for the calculation of the size of the SOD crystals.

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

Where D is the average particle size (Å), K is the dimensionless shape factor also known as Scherrer constant, λ is the X-ray wavelength (Å), β is the FWHM i.e. Line broadening at half the maximum intensity (radians), θ is the Bragg angle (degrees).

2.3. Transesterification reaction

The transesterification reaction was carried out similar to the one performed in our previous study (Adewale, Dumont, & Ngadi, 2015; Marchetti et al., 2007) in batch reactor set-up, using a 250 ml round bottom flask equipped with a reflux condenser to prevent loss of methanol due to evaporation. The flask charged with relevant amount of animal fat oil, methanol and hydroxy sodalite particles was immersed in a thermostat-controlled oil bath. The reaction was conducted at varied reaction conditions with methanol-to-animal fat oil ratio 7.5:1 and catalyst weight percentage 3 wt. %; Mixing intensity (700 – 1250 rpm), catalyst particle size (200 – 300 Å), reaction time (6 – 24 h) and reaction temperature (40 – 60 °C). Each process variable was varied at a time while others were kept constant at reaction time 24h; reaction temperature 60 ˚C; mixing intensity of 1000rpm. At the completion of each reaction, the catalyst particles were recovered from the mixture by filtration through nylon filter paper (0.45 µm pore dimension). Separating funnel was used to separate the products and glycerol, where the glycerol was drained from the bottom of the funnel while biodiesel was collected from the top. Analysis of the samples was performed using a pre-calibrated Gas Chromatograph equipped with a LECO GC x GC Thermal Modulator (GC-MS, model: Agilent 7890N).

3 Results and discussion

3.1. Characterization of beef tallow oil

Compared to vegetable oils which are generally rich in unsaturated fatty acids, animal fats are rich in saturated fatty acids (Huang et al., 2011). Acid profile for the tallow used in this experiment is shown in Table 1; it shows that the BTO is rich in saturated palmitic acid. This is in agreement with results reported in literature where it was demonstrated that about 50% of the total fatty acids in BTOs are saturated. The studies specifically demonstrated the high contents of palmitic and stearic acids hence BTOs are high in viscosity and melting points(Banković-Ilić, Stojković, Stamenković, Veljkovic, & Hung, 2014; Kim et al., 2004) (Talswar, 2016). This explains why they are solid at room temperature and therefore the need for heating prior the transesterification reaction. Furthermore, as expected, the sample constitutes little or no fatty acids of 10 carbon atoms or less (Huang et al., 2011).

Other properties of the beef tallow such as saponification value, iodine value and the acid value were evaluated and are shown in Table 2. Many researchers in literature have demonstrated that base-catalysed transesterification requires that oil samples should have FFA content less than 1%, to minimize the occurrence of hydrolysis and saponification reactions (Adewale et al., 2015; Li et al., 2007; Yulianti et al., 2014). In this study, the FFA contents beef tallow oil was determined at 4.53% (correspondingly acid value of 9.01 mg KOH/g). Compared to literature, the value obtained from the FFA content of the oil used in this study was relatively high. This may be attributed to the age and storage of the fat as it stored in the laboratories for a long time. As demonstrated in the study conducted(Yulianti et al., 2014), the longer storage times of the oils correspond to increased level of FFA content. The high amount of FFA found in the beef tallow oil justified the need to use a basic solid catalyst during transesterification reaction. Unlike homogeneous catalysts, heterogeneous catalysts are less sensitive to FFA; as a result, the likelihood of soap formation side reaction which reduces the biodiesel yield is minimized.

3.2 Catalyst characterization

Various attempts were made to synthesize hydroxy sodalite particles with different morphologies and size distributions. This was achieved by adding controlled amounts of ethanol to the synthesis solution prior hydrothermal synthesis. The use of ethanol as an organic solvent is common in hydrothermal synthesis of zeolites(Liu, Piao, Wang, Zhu, & He, 2008; O'Keeffe, Peskov, Ramsden, & Yaghi, 2008). The BET surface area, pore size and average pore volume measurements shown in Table 3 are important characteristics closely associated with the catalytic activity. The extent of the catalyst reactivity depends on the external surface area properties(Yao, Zhang, & Wang, 2008). The results show that the surface characteristics of the SOD particles proportionally changes with addition of ethanol to the synthesis solution. Both the BET surface area and the pore volume increased accordingly, however, there is a discrepancy observed in sample b, where addition of 10 ml ethanol was made to the hydrothermal synthesis solution. The pore volume was expected to be higher than the one observed in sample c, the observed decrease may be attributed to possible contamination prior the BET analysis, nonetheless, this SOD sample exhibited a reduction in size thereby improving conversion and biodiesel compared to the ethanol free SOD. Ethanol reduces the rate of the sodalite crystallization process, thereby allowing formation of SOD crystals in smaller sizes. The Scherrer estimation of the SOD particle size show that with sufficient addition of ethanol, the particle sizes reduced from 276 Å to 199 Å. The XRD results in Figure 1 show that the XRD patterns for the synthesized SOD samples correlate with the simulated sodalite XRD pattern obtained from the database of zeolite structures by the International Zeolite Association(IZA)(Sharma, Yeo, Yu, Han, & Cho, 2014), confirming the successful formation of SOD particles. The extra peaks which are very minimal indicates the possible formation of other zeolite impurities, some researchers have demonstrated that the addition of ethanol as an organic solvent potentially affects the phase purity of the SOD crystals (Liu et al., 2008; Yao, Wang, Ratinac, & Ringer, 2006). These results are in agreement with the work done by (Kumar et al., 2010) where an investigation on the effect of ethanol as an additive on the morphology and crystallinity of LTA (Linde Type A) zeolite was successfully studied.

Table 1 Fatty Acid Composition of BTO.

System name	Common name	Lipid number	Weight %
Decanoic acid	Capric acid	C10:0	0.92
Undecanoic acid	Undecylic acid	C11:0	0.01
Tridecanoic acid	Tridecylic acid	C13:0	9.42
Hexadecanoic acid	Palmitic acid	C16:0	83.88
Oleic acid	Oleic acid	C18:1	0.17
Docosenoic acid	Behenic acid	C22:1	1.89
Other	Other		3.71

Table 2 Physico-chemical characteristics of BTO

Properties	Units	Present study	Literature [38,49]
Saponification value	mg KOH/g	196.3	- 193 – 202

Title

Iodine value	$gI_2/100$ g	48.2	45.3 35 - 48
Acid value	mg KOH/g	9.01	2.13 -

Table 3 Textural property of the SOD catalyst from N_2 physisorption at 77 K

Sample id.	Ethanol Added (ml)	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size(nm)
a	0	0.1643	0.0013	30.9192
b	10	17.6237	0.0724	16.4336
c	20	23.3560	0.1626	27.8443

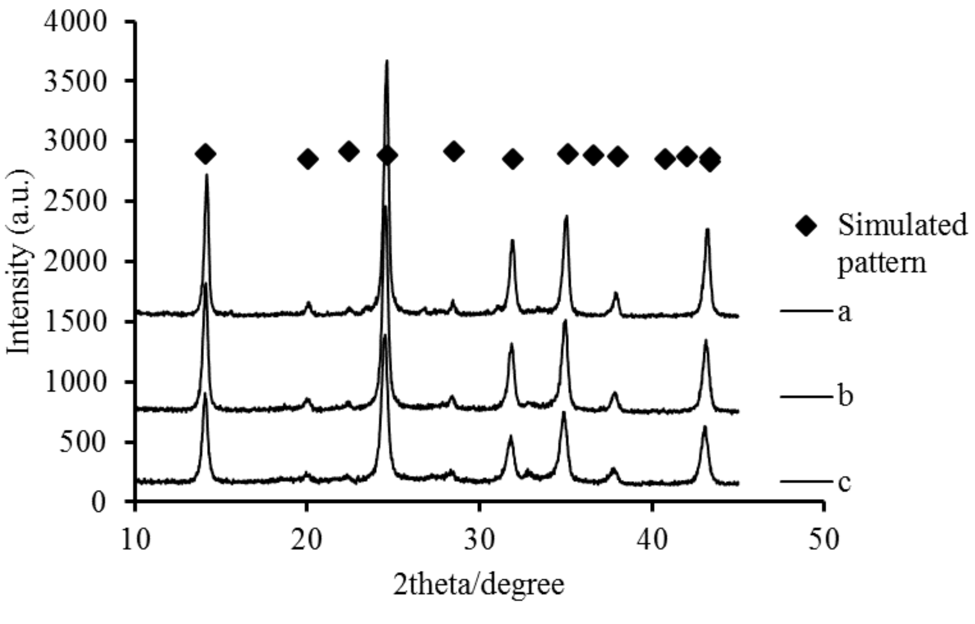

Fig. 1 XRD patterns of (a) SOD particles synthesized with no addition of ethanol as an organic solvent, (b) SOD particles synthesized with addition of 10 ml ethanol as an organic solvent, (c) SOD particles synthesized with addition of 20

ml ethanol as an organic solvent; and the simulated sodalite pattern according to the International Zeolite Association database (IZA).

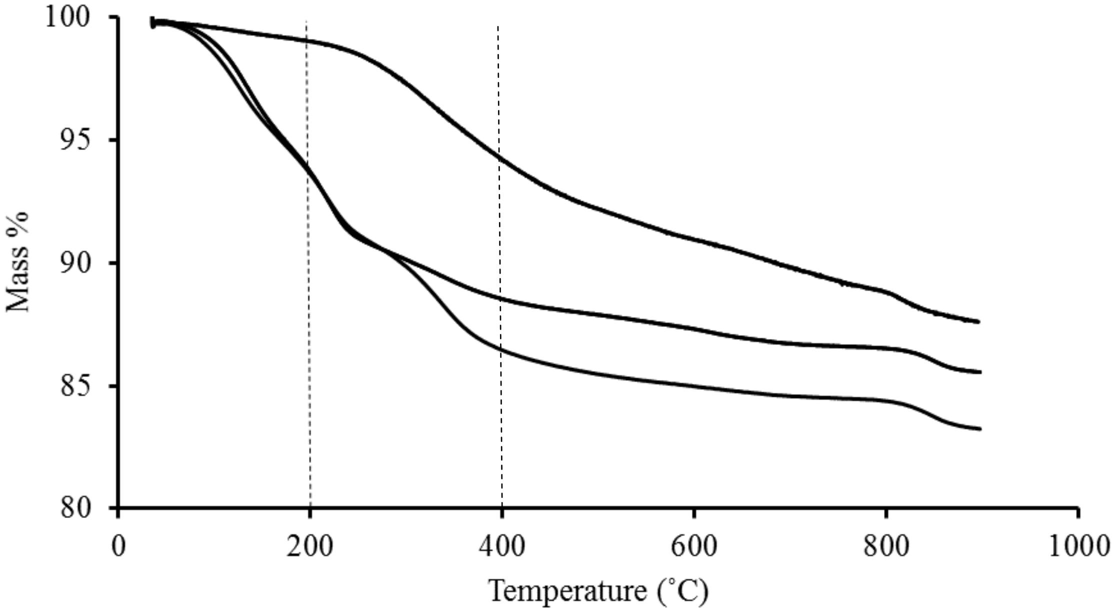

Fig. 2 TGA curves of (a) SOD Particles synthesized with no addition of ethanol as an organic solvent, (b) SOD particles synthesized with addition of 10 ml ethanol as an organic solvent; and (c) SOD particles synthesized with addition of 20 ml ethanol as an organic solvent.

3.3. Effect of mixing intensity

Without stirring, the transesterification reaction occurs slowly at the interphase of the two layers of oil and alcohol due to the external mass transfer limitation, thereby making the process impractical (Bambase, Nakamura, Tanaka, & Matsumura, 2007; Noureddini & Zhu, 1997). As shown in Figure 3, mixing plays a role in the heterogeneously catalyzed transesterification reaction. Lower conversion rate and biodiesel yield were obtained at the slowest mixing rate of 700 rpm where the values obtained were 43% and 42% respectively. The results show that the reaction performs better at the speed of 1000 rpm, where a conversion of 66% was achieved. Other researchers have achieved better results at a mixing intensity of 600 rpm (Bambase et al., 2007; Freedman, Pryde, & Mounts, 1984) however, other than the type of feedstock used; the results were obtained from homogeneously catalyzed transesterifications which have proven to be less prone to the effect of mixing intensity as compared to the heterogeneously catalyzed transesterification. The impact of agitation intensity is only observed during the initial stage of the transesterification reaction where mass transfer is dominant over time(Vyas, Subrahmanyam, & Patel, 2009). By increasing the stirring speed, the reaction rate is accelerated because of mass transfer enhancement, however, it is observed that too high speeds are not favorable, in this study, the conversion reduced to 62%; this can be attributed to the reversibility nature of the transesterification reaction which tends to decrease the biodiesel yield over time.

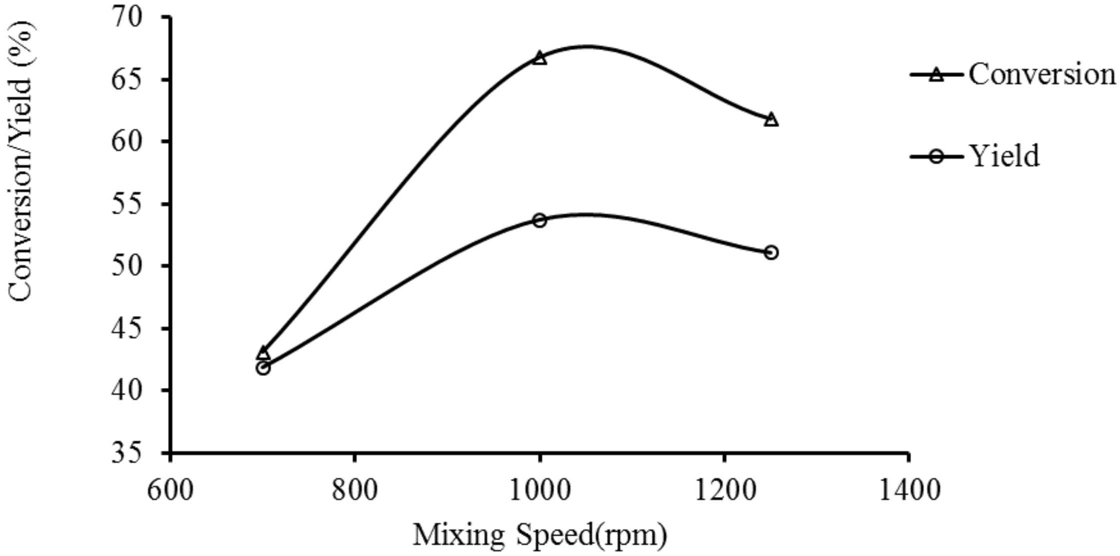

Fig. 3 The effect of mixing intensity on the yield of biodiesel

3.4. Effect of catalyst particle size

The rate of transesterification reaction is affected by the efficiency of the internal diffusion which to a certain extent is controlled by the diameter of the crystalline particles. A number of researchers have demonstrated the dependence of transesterification reaction on the particle size of the catalyst used. Generally, the reaction conversion increases with an increase in catalyst concentration as the catalysts sites are supposedly improved. However, this tends to reduce the specific surface area of the catalyst. Therefore, during a study of catalyst efficiency, it is essential to consider methods for improving the catalyst surface areas; one of the measures to achieve this is by reducing the catalyst particle size(Ngamcharussrivichai, Totarat, & Bunyakiat, 2008). In this chapter, various attempts were made to synthesize SOD particles with different morphologies and size distributions. This was achieved by adding controlled amounts of ethanol to the synthesis solution prior hydrothermal synthesis, where the size slightly reduced by 77 Å. As shown in Figure 4, without the ethanol additive during the hydrothermal synthesis, the resulting SOD (276 Å) catalyzed the transesterification to a TG conversion of 66.8%. The addition of 10ml and 20ml ethanol saw a reduction in SOD crystalline sizes and the transesterification reaction performance was slightly improved to a conversion of 68.4% as expected.

The results in Figure 4 demonstrated that conversion and biodiesel yield increased to 68.4 % and 57.0% respectively, owing to a reduction in SOD particle size. This is due to the slight acceleration of the diffusion rate thereby contributing to an increase in the rate of reaction. Mass transfer or diffusion occurs between the different phases; hence heterogeneously catalysed reactions are more prone to mass transfer limitation than homogeneous catalytic reactions (Klaewkla, Arend, & Hoelderich, 2011). The catalytic reaction occurs when the reactants come into contact with the active site of the catalyst along the internal surface of the porous catalyst pellet. The observation made in this study on the possibility of improving reaction conversions by reducing catalyst crystalline size is consistent with what other researchers have found where nanoparticles of sizes between 22 nm - 25 nm (i.e. 220 Å -250 Å) were studied (Klaewkla et al., 2011; Mata, Mendes, Caetano, & Martins, 2014; Ngamcharussrivichai et al., 2008).

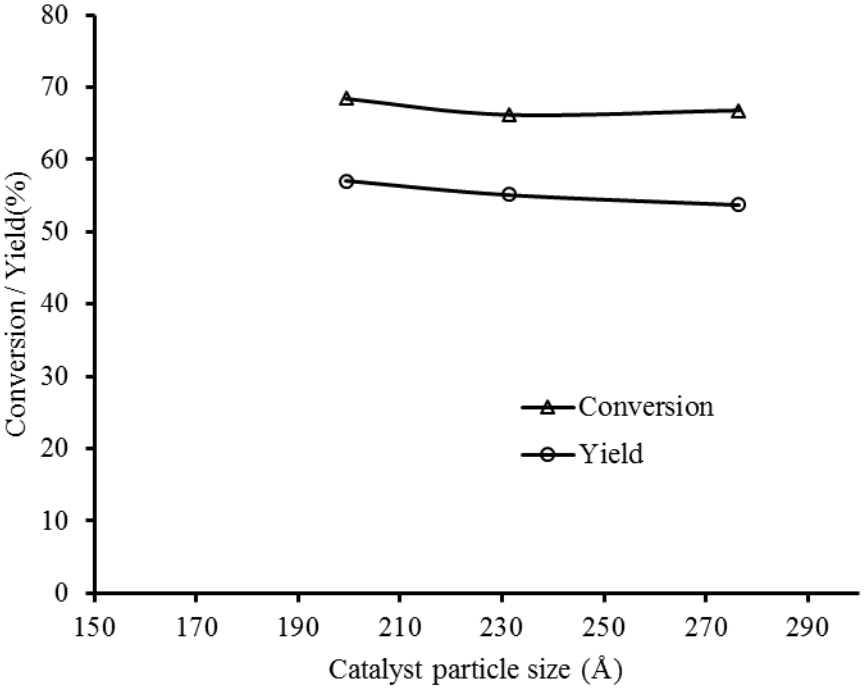

Fig. 4 The effect of catalyst particle size on the conversion/ yield of biodiesel

3.5. Effect of reaction time

As demonstrated by (Freedman et al., 1984), decades ago as well as (Vyas et al., 2009) among other researchers, there exists a positive relationship between fatty acid esters conversion rate and reaction time, the reaction is slow in the initial stages due to the effect of phase mixing that and proceeds much faster after some time(Ma, Clements, & Hanna, 1999). The effect of reaction time on the production of biodiesel is depicted in Figure 5. Both conversion and yield tend to increase with increasing reaction times as the contact time between the three-phase reactants is extended, thereby allowing prolonged mass transfer. The transesterification reaction is reversible in nature, the observed decrease in yield over time is due to the possible loss of fatty acids as the reaction continues at extended reaction times(M. Daramola, Mtshali, Senokoane, & Fayemiwo, 2016; Eevera, Rajendran, & Saradha, 2009; Mathiyazhagan & Ganapathi, 2011) Nonetheless, due to maximum conversion rate of 78% percent after 24h, it was established that the suitable reaction time for beef tallow transesterification over hydroxy sodalite under the conditions in the study is 24 h. This is in agreement with the study conducted by (Liu et al., 2011) where a study was conducted on the conversion of chicken and mutton tallow using a homogeneous sulfuric acid catalyst.

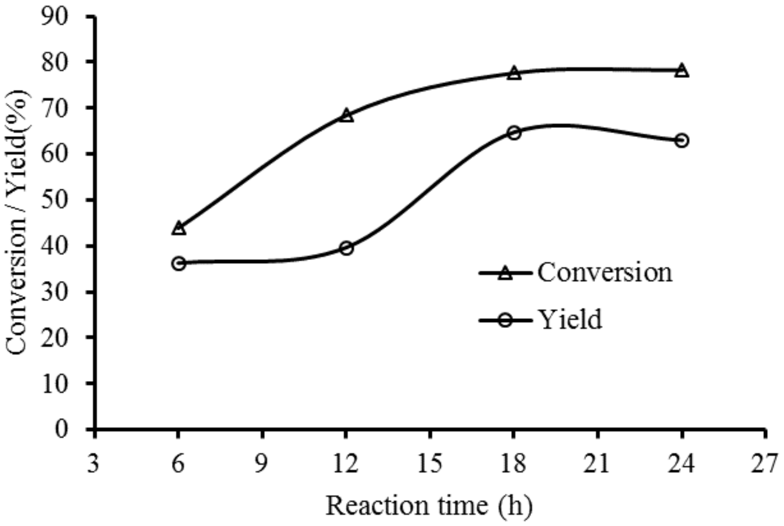

Fig. 5 The effect of reaction time on the conversion/ yield of biodiesel

3.6. Effect of reaction temperature

The effect of reaction temperature on biodiesel yield is illustrated in Figure 6. It can be seen the reaction temperature essentially influence the performance of the transesterification reaction. Both the yield of biodiesel and conversion rate increases with an increase in reaction temperature, and maximum performance was obtained at a temperature of 60°C, where the values of conversion and yield are 78% and 63% respectively. Higher temperature conditions tend to favour the transesterification reaction due to its endothermic behaviour (M. Daramola et al., 2016; Farooq, Ramli, & Naeem, 2015) this is because the reactant molecule collisions are accelerated at higher temperatures, thereby facilitating miscibility among the three-phased reaction (solid catalyst-oil-alcohol) as well as the mass transfer (Farooq et al., 2015). Other researchers have achieved conversion rates above 90% (da Cunha et al., 2009; Yulianti et al., 2014); however, the transesterification reaction was homogeneously catalysed using potassium hydroxide and sodium hydroxide solutions respectively. Homogeneously catalysed transesterification reactions tend to require an additional process stages such as esterification reaction to reduce FFA content, as well as a step for product separation, thereby affecting the economic viability of the biodiesel production process.

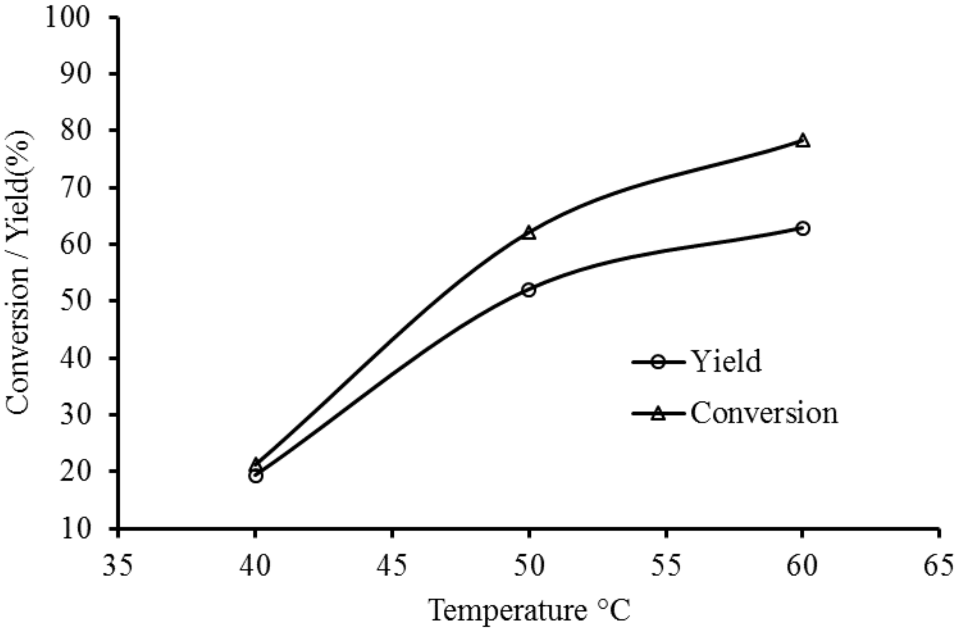

Fig. 6 The effect of reaction temperature on the conversion/ yield of biodieselVarious attempts were made to synthesize hydroxy sodalite particles with different morphologies and size distributions. This was achieved by adding controlled amounts of ethanol to the synthesis solution prior hydrothermal synthesis.

4 Conclusions

The effect of reaction parameters on the rate of transesterification of beef tallow oil over a solid hydroxy sodalite catalyst was successfully studied. Various attempts to alter particle size distributions of the sodalite catalyst were made, and the reduction in particle size from 276 Å to 199 Å was achieved. The smaller particle size proved to enhance the transesterification reaction performance at a conversion of 68.4%, from 61.8% which was obtained from the initial reaction conditions. The behaviour of the transesterification reaction was further affected by the alterations of temperature, where the highest temperature of 60 °C resulted in a much higher percentage conversion of 78.3% at the longest reaction time of 24 h.

5 References

Adewale, P., Dumont, M.-J., & Ngadi, M. (2015). Recent trends of biodiesel production from animal fat wastes and associated production techniques. *Renewable and Sustainable Energy Reviews, 45*, 574-588.

Alptekin, E., Canakci, M., & Sanli, H. (2014). Biodiesel production from vegetable oil and waste animal fats in a pilot plant. *Waste management, 34*(11), 2146-2154.

Aransiola, E. F., Daramola, M. O., Ojumu, T. V., Aremu, M. O., kolawole Layokun, S., & Solomon, B. O. (2012). Nigerian Jatropha curcas oil seeds: prospect for biodiesel production in Nigeria. *International Journal of Renewable Energy Research, 2*(2), 317-325.

Aransiola, E. F., Daramola, M. O., Ojumu, T. V., Solomon, B. O., & Layokun, S. K. (2013). Homogeneously catalyzed transesterification of Nigerian Jatropha curcas oil into biodiesel: a kinetic study.

Atadashi, I., Aroua, M., Aziz, A. A., & Sulaiman, N. (2012). Production of biodiesel using high free fatty acid feedstocks. *Renewable and Sustainable Energy Reviews, 16*(5), 3275-3285.

Bambase, M. E., Nakamura, N., Tanaka, J., & Matsumura, M. (2007). Kinetics of hydroxide-catalyzed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters. *Journal of Chemical Technology and Biotechnology, 82*(3), 273-280.

Banković-Ilić, I. B., Stojković, I. J., Stamenković, O. S., Veljkovic, V. B., & Hung, Y.-T. (2014). Waste animal fats as feedstocks for biodiesel production. *Renewable and Sustainable Energy Reviews, 32*, 238-254.

Canakci, M., & Sanli, H. (2008). Biodiesel production from various feedstocks and their effects on the fuel properties. *Journal of industrial microbiology & biotechnology, 35*(5), 431-441.

da Cunha, M. E., Krause, L. C., Moraes, M. S. A., Faccini, C. S., Jacques, R. A., Almeida, S. R., . . . Caramão, E. B. (2009). Beef tallow biodiesel produced in a pilot scale. *Fuel Processing Technology, 90*(4), 570-575.

Daramola, M., Mtshali, K., Senokoane, L., & Fayemiwo, O. (2016). Influence of operating variables on the transesterification of waste cooking oil to biodiesel over sodium silicate catalyst: A statistical approach. *Journal of Taibah University for Science, 10*(5), 675-684.

Daramola, M. O., Nkazi, D., & Mtshali, K. (2015). Synthesis and evaluation of catalytic activity of calcined sodium silicate for transesterification of waste cooking oil to biodiesel. *International Journal of Renewable Energy Research (IJRER), 5*(2), 517-523.

Eevera, T., Rajendran, K., & Saradha, S. (2009). Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. *Renewable Energy, 34*(3), 762-765.

Farooq, M., Ramli, A., & Naeem, A. (2015). Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. *Renewable Energy, 76,* 362-368.

Freedman, B., Pryde, E., & Mounts, T. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists' Society, 61*(10), 1638-1643.

Guo, F., Wei, N.-N., Xiu, Z.-L., & Fang, Z. (2012). Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Fuel, 93*, 468-472.

Gupta, V. K., & Tuohy, M. G. (2013). Biofuel technologies. *Recent Developments. Editorial Springer*.

Huang, Y., Yao, J., Zhang, X., Kong, C. C., Chen, H., Liu, D., . . . Wang, H. (2011). Role of ethanol in sodalite crystallization in an ethanol–Na 2 O–Al 2 O 3–SiO 2–H 2 O system. *CrystEngComm, 13*(14), 4714-4722.

Islam, A., Taufiq-Yap, Y. H., Chu, C.-M., Chan, E.-S., & Ravindra, P. (2013). Studies on design of heterogeneous catalysts for biodiesel production. *Process Safety and Environmental Protection, 91*(1), 131-144.

Jagadale, S., & Jugulkar, L. (2012). Review of various reaction parameters and other factors affecting on production of chicken fat based biodiesel. *International Journal of Modern Engineering Research, 2*(2), 407-411.

Kim, H.-J., Kang, B.-S., Kim, M.-J., Park, Y. M., Kim, D.-K., Lee, J.-S., & Lee, K.-Y. (2004). Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis today, 93*, 315-320.

Klaewkla, R., Arend, M., & Hoelderich, W. F. (2011). A review of mass transfer controlling the reaction rate in heterogeneous catalytic systems *Mass Transfer-Advanced Aspects*: InTech.

Li, D., Yao, J., Wang, H., Hao, N., Zhao, D., Ratinac, K. R., & Ringer, S. P. (2007). Organic-functionalized sodalite nanocrystals and their dispersion in solvents. *Microporous and Mesoporous Materials, 106*(1), 262-267.

Liu, X., Piao, X., Wang, Y., Zhu, S., & He, H. (2008). Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. *Fuel, 87*(7), 1076-1082.

Ma, F., Clements, L. D., & Hanna, M. A. (1999). The effect of mixing on transesterification of beef tallow. *Bioresource technology, 69*(3), 289-293.

Makgaba, C. P., & Daramola, M. O. (2015). *Transesterification of Waste Cooking Oil to Biodiesel over Calcined Hydroxy Sodalite (HS) Catalyst: A preliminary investigation.* Paper presented at the 2015 International Conference on Sustainable Energy and Environmental Engineering.

Marchetti, J., Miguel, V., & Errazu, A. (2007). Possible methods for biodiesel production. *Renewable and Sustainable Energy Reviews, 11*(6), 1300-1311.

Mata, T. M., Mendes, A. M., Caetano, N. S., & Martins, A. A. (2014). Properties and sustainability of biodiesel from animal fats and fish oil. *Chemical Engineering Transactions, 38*, 175-180.

Mathiyazhagan, M., & Ganapathi, A. (2011). Factors affecting biodiesel production. *Research in plant Biology, 1*(2).

Milano, J., Ong, H. C., Masjuki, H., Chong, W., Lam, M. K., Loh, P. K., & Vellayan, V. (2016). Microalgae biofuels as an alternative to fossil fuel for power generation. *Renewable and Sustainable Energy Reviews, 58*, 180-197.

Ngamcharussrivichai, C., Totarat, P., & Bunyakiat, K. (2008). Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. *Applied Catalysis A: General, 341*(1), 77-85.

Nicole, J.-F. (1994). International Energy Agency. World Energy Outlook. *Politique étrangère, 59*(2), 564-565.

Noureddini, H., & Zhu, D. (1997). Kinetics of transesterification of soybean oil. *Journal of the American Oil Chemists' Society, 74*(11), 1457-1463.

O’Keeffe, M., Peskov, M. A., Ramsden, S. J., & Yaghi, O. M. (2008). The reticular chemistry structure resource (RCSR) database of, and symbols for, crystal nets. *Accounts of Chemical Research, 41*(12), 1782-1789.

Ramadhas, A. S., Jayaraj, S., & Muraleedharan, C. (2005). Biodiesel production from high FFA rubber seed oil. *Fuel, 84*(4), 335-340.

Sharma, P., Yeo, J.-g., Yu, J.-h., Han, M. H., & Cho, C. H. (2014). Effect of ethanol as an additive on the morphology and crystallinity of LTA zeolite. *Journal of the Taiwan Institute of Chemical Engineers, 45*(2), 689-704.

Vyas, A. P., Subrahmanyam, N., & Patel, P. A. (2009). Production of biodiesel through transesterification of Jatropha oil using KNO 3/Al 2 O 3 solid catalyst. *Fuel*, *88*(4), 625-628.

Yao, J., Wang, H., Ratinac, K. R., & Ringer, S. P. (2006). Formation of colloidal hydroxy-sodalite nanocrystals by the direct transformation of silicalite nanocrystals. *Chemistry of materials*, *18*(6), 1394-1396.

Yao, J., Zhang, L., & Wang, H. (2008). Synthesis of nanocrystalline sodalite with organic additives. *Materials Letters*, *62*(24), 4028-4030.

Yulianti, C. H., Ediati, R., Hartanto, D., Purbaningtias, T. E., Chisaki, Y., Jalil, A. A., . . . Prasetyoko, D. (2014). Synthesis of CaOZnO nanoparticles catalyst and its application in transesterification of Refined Palm Oil. *Bulletin of Chemical Reaction Engineering & Catalysis*, *9*(2), 100.

Zhang, Y., Dube, M., McLean, D., & Kates, M. (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource technology*, *89*(1), 1-16.

Waste to Energy: Conversion of animal fat to biodiesel over a solid Hydroxy Sodalite (HS) catalyst

Chabisha, P. Makgaba, Patrick T. Sekoai, Michael O. Daramola*

Sustainable Energy & Environment Research Unit, School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa

* Corresponding Author. E-mail: Michael.Daramola@wits.ac.za, Tel: +27117177536

Abstract

The high reliance on fossil fuels necessitates a need for clean energy resources. Biodiesel is gaining increasing attention among researchers owing to its environmental merits and its ability to use waste products. This study evaluated the feasibility of using Hydroxy Sodalite (HS) catalyst for the transesterification of animal fat (beef tallow) for biodiesel production. This follows a successful preliminary investigation that was conducted to produce biodiesel from waste cooking oil using the solid HS catalyst. The current study was carried out to synthesize the HS crystals using the hydrothermal synthesis approach. The crystals were applied in the transesterification reaction. The process was conducted at 60 °C for 12 h at a methanol-to-animal fat ratio of 7.5:1 using 3 wt. % HS catalyst with a particle size less than 300 Å. The synthesized fatty acid methyl ester (FAME) was evaluated using a calibrated GC-MS and the results showed a yield of 39.6% and a conversion of 68.4%.

Keywords
Biodiesel
Animal Fat
Hydroxy Sodalite
Waste Beneficiation
Solid Catalyst

1. INTRODUCTION

Over the past decades, energy consumption has significantly increased due to high population growth, advancement in technology and urbanization. According to the International Energy Agency, energy demands are expected to increase by about 48% between 2012 and 2040 (International Energy Agency, 2016). Fossil fuels are the major source of energy, contributing about 86% of the global energy consumption (International Energy Agency, 2008). However, their utilization has resulted into increased emission of greenhouse gas which causes global warming that resulted in climate change. Consequently, scientists and engineers around the globe are exploring alternative ways of producing energy, such as biofuel production, that is environmentally benign (Brennan and Owende, 2008; Foleya et al., 2012; Schenk et al., 2008; Yang et al., 2007; Zhou et al., 2010).

Biodiesel produced from transesterification of vegetable oils and methanol using either a homogeneous or a heterogeneous catalyst. The use of edible oils and homogeneous base catalysts contributes to high costs of production, making biodiesel more expensive than the fossil fuel diesel. In addition, utilization of edible feedstocks is discouraged because of its negative impact on food security. As a result of the aforementioned reasons, scientists and engineers are exploring non-edible feedstocks such as animal fat, Jatropha oil, and waste cooking oil for the production of biodiesel (Aransiola et al., 2013; Aransiola et al., 2012; Daramola et al., 2015; Guo et al., 2012). However, most of these substrates contain free fatty acids (FFAs) which affect the transesterification process. The employment of conventional homogeneous catalysts, such as potassium hydroxide, sodium hydroxide and sodium methoxide, introduces additional operating costs for separation and recovery of the catalyst and the product. To circumvent this problem, production of biodiesel from feedstock with high FFAs is conducted as a two-stage process where the high FFA feedstock is first esterified to reduce the FFA content and then followed by the transesterification of the pre-treated oil to biodiesel (Yaakob et al., 2013; Sharma et al., 2011). However, the two-stage process requires additional reactor unit translating thereby into additional capital cost. Against this background, this study explores the feasibility of using hydroxy sodalite (HS) as a solid catalyst for biodiesel production using animal fat oil as the feedstock.

2. MATERIALS AND METHODS

2.1 Material

Beef tallow (animal fat) was obtained from a local abattoir at Springs, in the East of Johannesburg, South Africa. The analytical grade methanol (99%), isopropanol (99%), ethanol (95%), phenolphalein, potassium hydroxide (KOH), catalyst materials; anhydrous sodium metal silicate (Na_2SiO_3), sodium hydroxide (NaOH), anhydrous sodium aluminate ($NaAlO_2$), FAME (MIX, C4-C24, 100MG NEAT), glycerol (99 %) and other analytical chemicals were purchased from Sigma Aldrich (Pty), South Africa. All chemicals were used as received without further purification.

2.2 Catalyst preparation

The hydroxy sodalite (HS) particles were prepared via hydrothermal synthesis as documented elsewhere (Daramola et al., 2015). The precursor solution for the synthesis was prepared using a mixture of Na_2SiO_3, NaOH, $NaAlO_2$ and distilled water in appropriate amount. The resulting mixture poured in a 45 ml Teflon-lined autoclave and subjected to hydrothermal synthesis at 140 °C for 3.5 h. At the end of the reaction, the autoclave was cooled down by running tap water and the hydroxy sodalite (HS) crystals were obtained through filtration and rinsed with deionized water until the pH of the wash water was neutral. The washed HS crystals were subsequently dried overnight. The dried HS crystals were calcined at 200 °C before using them in the transesterification reaction.

2.3 Catalyst characterization

Fourier transform infrared spectroscopy (FTIR) was used to examine the surface nature (chemical) of the HS catalyst. The morphology of the catalyst was checked with scanning electron microscopy (SEM) (Carl Zeiss, Germany). The textural properties (surface area, pore size and pore volume) of the catalyst were obtained on a Micrometrics Tri-Star 3000 surface area and porosity analyzer at with nitrogen physisorption experiment as 77 K. Thermal stability of the catalyst was assessed on a thermal gravimetric analyzer (TGA). Crystallinity and phase of the catalyst was obtained via a X-ray powder diffraction (XRD) using the Rigaku's Ultima IV X-ray diffractometer operating with CuKα radiation ($\lambda = 1.5406$ Å). The average size of the crystals was obtained using the XRD data and the Scherrer Equation (1):

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (1)$$

Where D represents the average particle size (Å), K symbolizes the dimensionless shape factor (Scherrer constant), λ is the X-ray wavelength (Å), β is the Full Width at Half Maximum, θ is the Bragg angle (^{o}C).

2.4 Free Fatty Acids (FFAs) content of the Animal Fat

Compared to other oils used for transesterification reaction, animal fat oil usually contains high content of Free Fatty Acids (FFAs), i.e. way more than 1% of FFAs. As a result, animal fat oil would not be an ideal feedstock for transesterification reaction over a homogeneous alkaline catalyst due to the parallel reaction such as saponification that competes with transesterification at FFAs content >1%. To confirm the need for a heterogeneous catalyst, FFAs content of the animal fat oil was determined to ensure that it exists in a considerable amount. It was also required to prove the tolerance of the HS catalyst to a high content of free fatty acid during biodiesel production. Determination of the FFA content was carried out as described elsewhere (Daramola et al., 2015) and the acid value of the beef tallow oil was calculated using Equation (2):

$$Acid\ value = \frac{KVC}{m} \qquad (2)$$

where K represents the acid value constant for cooking oil (56.1). This value shows the mass of KOH (g) that is needed to neutralize 1 g of chemical substance. The concentration of titrate solution is denoted by C (g/ml). V (ml) represents the volume of titrate that is used to neutralize the sample. Whereas, the mass of sample used is represented by m (g).

2.5 Transesterification

The transesterification reaction was carried out as reported elsewhere (Daramola et al., 2015; Daramola et al., 2016; Hemmat et al., 2013; Alptekin et al., 2014) . The HS catalyst was first calcined at 200˚C for 2 h to remove moisture and volatile matter that may block the pores of the catalyst surface. The transesterification reaction was conducted in a batch reactor (250 ml round bottom flask) setup equipped with a reflux condenser to prevent loss of methanol. The reactor, charged with proportionate amount of animal fat oil, methanol and HS catalyst was, immersed in a thermostat controlled oil bath to ensure the reaction was carried out at an isothermal condition. The reaction conditions were as follows: time 12 h; temperature 60 ˚C; methanol-to-animal fat oil ratio 7.5:1; catalyst weight percentage 3 wt. %; stirrer intensity 1000 rpm. After the completion of the reaction, the catalyst particles were recovered from the mixture by filtration using a 0.45 μm membrane filter. The liquid product mixture was separated into glycerol and biodiesel using a separating funnel and the glycerol was drained from the bottom of the funnel while biodiesel was collected from the top. Analysis of the biodiesel samples was performed using a pre-calibrated Gas Chromatograph equipped with a LECO GC x GC Thermal Modulator (GC-MS, model: Agilent 7890N).

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

Figure 1 depicts the thermal behaviour of the HS catalyst. The trend observed in Figure 1 is in agreement with observation reported in previous studies regarding the thermal stability of hydroxyl sodalite where mass loss of about 12.3% is observed with the increase in temperature (Li et al., 2007; Yao et al., 2006; Daramola et al., 2017). The loss of mass could be due to the loss of water during heating up to just above 200 ˚C. The additional drastic mass loss of the HS at a temperature above 400°C could be attributed to the possible decomposition of the material at higher temperatures (Li et al., 2007; Yao et al., 2006). The BET Surface area, pore volume and the pore size as obtained from N_2 physisorption experiments were 0.1643 m^2/g, 0.0013 cm^3/g and 30.9192 nm, respectively. In addition, the FTIR results obtained in this study are in agreement with the results documented in the previous study, thereby confirming the reproducibility of the synthesis (Makgaba and Daramola, 2015). The XRD patterns depicted in Figure 2 confirm the formation of HS particles. The average size of the HS crystallite was found to be 276 Å using the XRD data and the Scherrer equation. Furthermore, the XRD pattern for the synthesized HS in the study agrees with the simulated XRD pattern documented in the database of zeolite structures by the International Zeolite Association (International Zeolite Association, 2016).

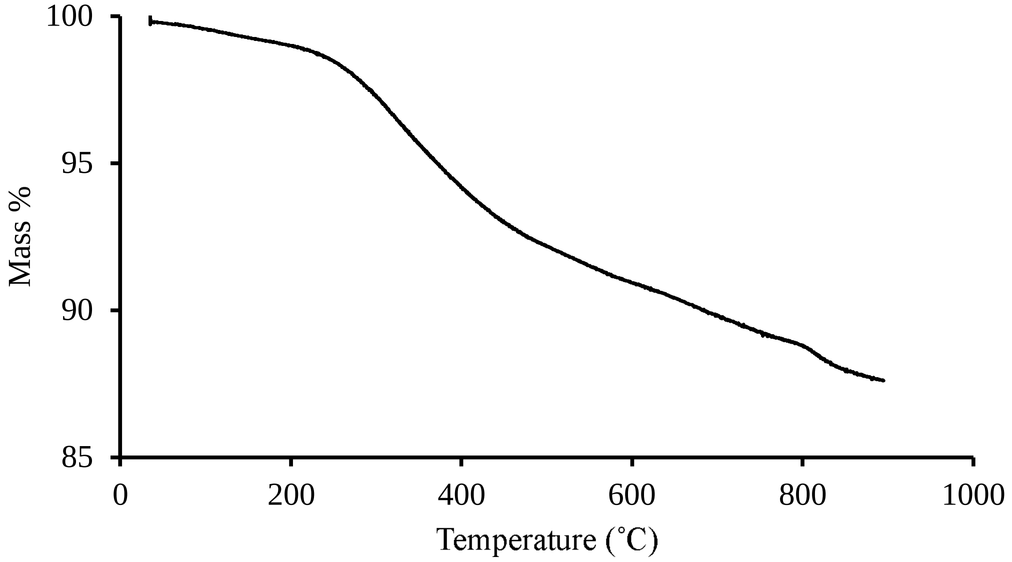

Figure 1 TGA results of the synthesized HS catalyst

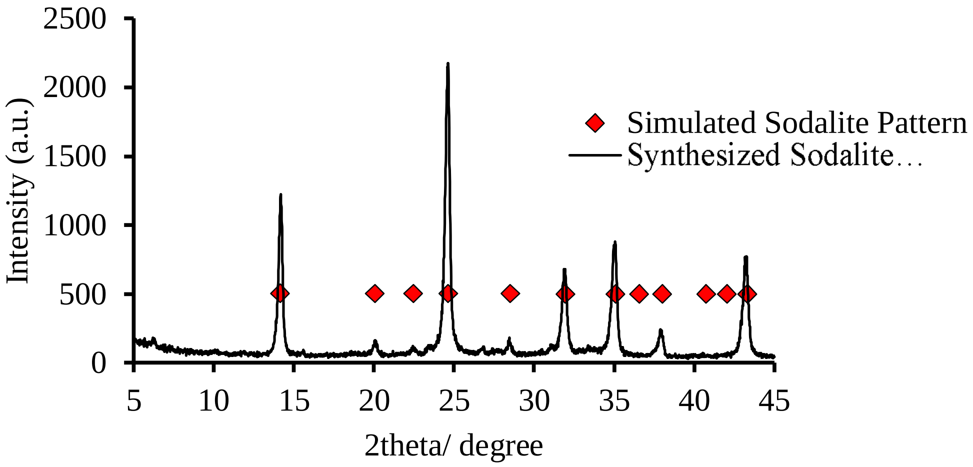

Figure 2 XRD pattern of the synthesized HS catalyst.

3.2 Raw material

Unlike vegetable oils which are generally rich in unsaturated fatty acids, animal fats are rich in saturated fatty acids (Talswar et al., 2016). In most beef tallows, about 50% of the total fatty acids are saturated, with higher contents of palmitic and stearic acids hence they are high in viscosity and melting points (Adewale et al., 2014; Adewale et al., 2015). This explains why they are solid at room temperature and therefore the need for heating prior the transesterification reaction. Acid profile for the tallow used in this experiment is shown in Table 1, Hexadecanoic acid (Palmitic acid) is abundant in this sample, furthermore, as expected, there exist little or no fatty acids of 10 carbon atoms or less (Talswar et al., 2016). Other properties of oil such as % FFAs, saponification value and density were found to be, 4.53%, 188 mg KOH/g and 0.870 g/ml, respectively. The high amount of FFAs found in the Beef tallow oil justified the need to use a heterogeneous catalyst during transesterification reaction. Unlike homogeneous catalysts, heterogeneous catalysts are less sensitive to FFAs; as a result, the likelihood of soap formation side reaction which affects the biodiesel yield is overridden.

Table 1 Composition of the Fatty Acid animal fat oil

Fatty Acid		Weight %
Decanoic acid	C10:0	0.92
Undecanoic acid	C11:0	0.01
Tridecanoic acid	C13:0	9.42
Hexadecanoic acid	C16:0	83.88
Oleic acid	C18:1	0.17
Docosenoic acid	C22:1	1.89
Other	-	3.71

3.2 Biodiesel production

Figure 3 and Figure 4 depict the chromatograms the standard FAME (obtained from Sigma Aldrich (Pty) South Africa) and the as-produced FAME mixtures from the transesterification reaction, respectively. The same FAME components were obtained at the retention times between 8 and 11 min for the as-produced biodiesel and the standard biodiesel, indicating the successful transesterication of the animal fat oil to FAME using the synthesized HS catalyst. Since the composition of biodiesel depends on the type of feedstock, the as-produced biodiesel does not show all types of FAME contained in the standard biodiesel. It is should be noticed that the standard biodiesel sample is expected to contain all the expected components of biodiesel for analysis and bench-marking. However, main components usually found in biodiesel mixture are common in the two mixtures.

The animal fat oil conversion and the biodiesel yield of 68.8% and 39.6%, respectively, were obtained in this study. Previous report from Liu et al. (2007) where the transesterification of poultry fat oil with methanol using Mg-Al hydrotalcite catalyst was carried out shows oil conversion of about 90% and a biodiesel yield of 83%. The operating conditions employed by Liu et al. in their study were reaction time of 15 h, reaction temperature of 120 °C; reaction pressure of 100 psi, methanol/oil ratio of 30:1 and a stirring speed of 1417 rpm. In another study by Liu et al. (2011) during which beef tallow oil was transesterified into using homogeneous sodium hydroxide catalyst, a conversion of 96.3% was reported at a shorter reaction time. However, the process where homogeneous catalyst is used would require an additional product separation step which would potentially increase the production costs. The lower conversion and yield obtained in this study could be attributed to the lower operating conditions employed in this as compared to the report of Liu et al. In addition, the different type of the feedstock used in this study could be another contributing factor. The need for developing heterogeneous catalyst for biodiesel production especially with low grade feedstock (High in FFAs content) was showcased by Fröhlich et al. (2010). The authors demonstrated that using homogeneous catalyst for the transesterification of low grade feedstock could yield a conversion as low as 55% and the conversion could even reduce as the feedstock with even greater content of FFA is used.

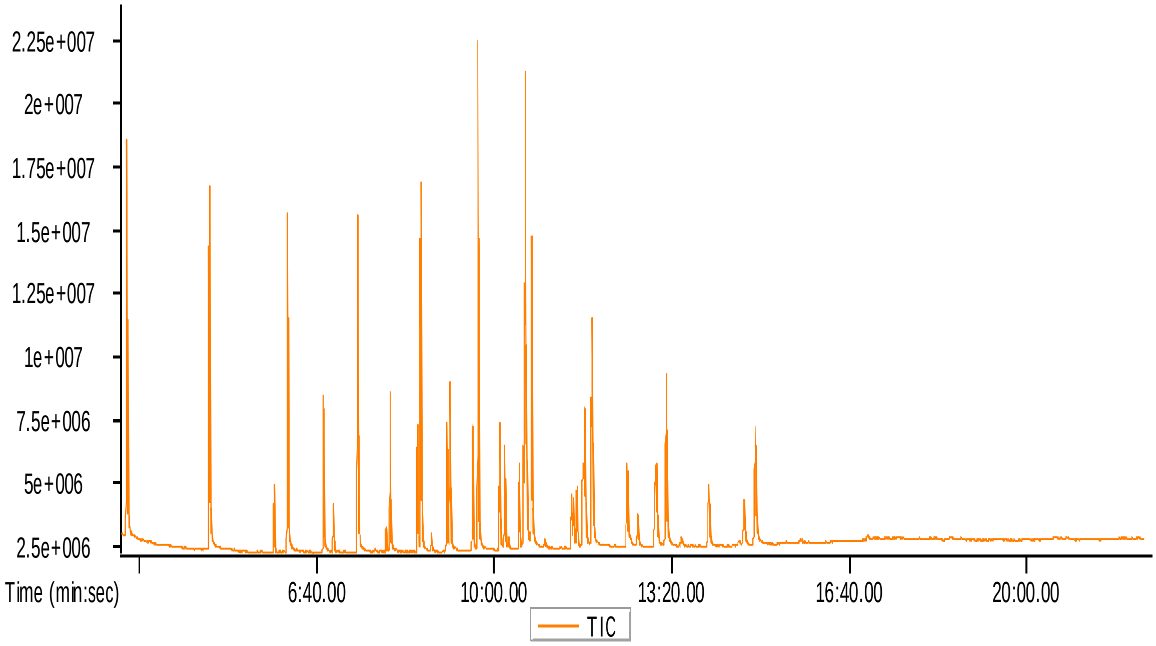

Figure 3 Chromatograph for standard biodiesel

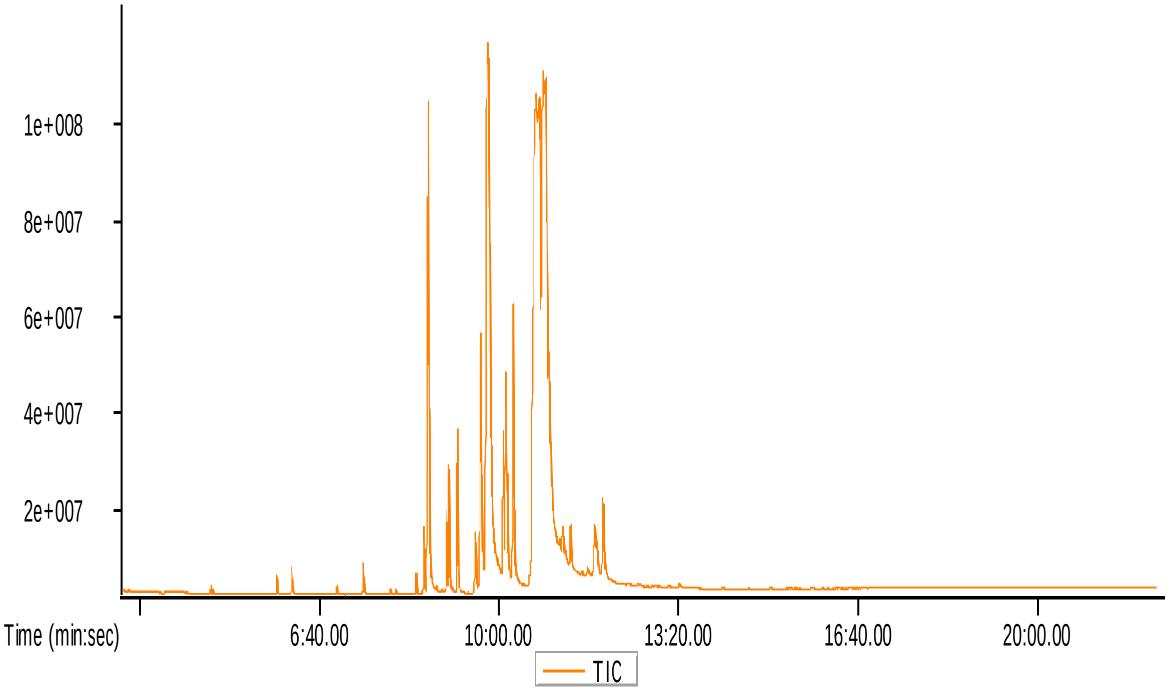

Figure 4 Chromatograph for the synthesized biodiesel

Peak No.	Identified Compound	R.T. (min:sec)	Formula	Peak No.	Identified Compound	R.T. (min:sec)	Formula
1	Hexanoic acid, methyl ester	03:06.1	C7H14O2	17	Dodecanoic acid, methyl ester	10:41.9	C13H26O2
2	Hexanoic acid, methyl ester	03:52.6	C7H14O2	18	5,8,11,14-Eicosatetraenoic acid, methyl ester, (all-Z)-	11:26.8	C21H34O2
3	Octanoic acid, methyl ester	04:39.2	C9H18O2	19	5,8,11,14,17-Eicosapentaenoic acid, methyl ester, (all-Z)-	11:29.3	C21H32O2
4	Undecanoic acid, methyl ester	06:07.0	C12H24O2	20	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	11:32.9	C19H32O2
5	Undecanoic acid, methyl ester	06:47.6	C12H24O2	21	11,14-Eicosadienoic acid, methyl ester	11:39.6	C21H38O2
6	Undecanoic acid, methyl ester	07:26.1	C12H24O2	22	9-Octadecenoic acid (Z)-, methyl ester	11:41.2	C19H36O2
7	Dodecanoic acid, methyl ester	08:02.6	C13H26O2	23	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	11:42.3	C19H32O2
8	9-Octadecenoic acid (Z)-, methyl ester	08:33.4	C19H36O2	24	Pentadecanoic acid, 14-methyl-, methyl ester	11:50.1	C17H34O2
9	Dodecanoic acid, methyl ester	08:37.2	C13H26O2	25	Hexadecanoic acid, 15-methyl-, methyl ester	12:29.7	C18H36O2
10	9-Octadecenoic acid (Z)-, methyl ester	09:06.7	C19H36O2	26	11,14-Eicosadienoic acid, methyl ester	13:01.1	C21H38O2
11	Undecanoic acid, methyl ester	09:10.2	C12H24O2	27	Cyclopropanepentanoic acid, 2-undecyl-, methyl ester	13:02.8	C20H38O2
12	9-Octadecenoic acid (Z)-, methyl ester	09:35.6	C19H36O2	28	Heneicosanoic acid, methyl ester	13:13.6	C22H44O2
13	Dodecanoic acid, methyl ester	09:41.7	C13H26O2	29	Heneicosanoic acid, methyl ester	14:01.7	C22H44O2
14	9-Octadecenoic acid (Z)-, methyl ester	10:06.0	C19H36O2	30	Cyclopropanepentanoic acid, 2-undecyl-, methyl ester	14:41.4	C20H38O2
15	Dodecanoic acid, methyl ester	10:11.7	C13H26O2	31	Heneicosanoic acid, methyl ester	14:53.9	C22H44O2
16	ç-Linolenic acid, methyl ester	10:27.9	C19H32O2				

Table 2 Composition of the Standard FAME mixture

Table 3 Composition of the as-produced FAME from Animal Fat oil

Peak No.	Identified Compound	R.T. (min:sec)	Formula
1	Butyric acid, methyl ester	03:07.9	C7H14O2
2	Capric acid, methyl ester	06:06.6	C12H24O2
3	Myristoleic acid (Z)-, methyl ester	08:33.7	C19H36O2
4	Myristic acid, methyl ester	08:36.8	C13H26O2
5	Pentadecanoic acid, methyl ester	09:08.7	C19H36O2
6	Pentadecanoic acid, methyl ester	09:08.7	C19H36O2
7	Palmitic acid, methyl ester	09:40.8	C13H26O2
8	Stearic acid, methyl ester	10:43.4	C13H26O2
9	11,14,17-Eicosatrienoic acid, methyl ester	11:32.5	C19H32O2
10	11,14-Eicosadienoic acid, methyl ester	11:38.7	C21H38O2
11	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	11:41.7	C19H36O2
12	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	11:41.7	C19H36O2

4. CONCLUSION

In this study, conversion of beef tallow oil into biodiesel over a solid HS catalyst was carried out and reported. The results have demonstrated the possibility of using solid HS catalyst to transesterify animal fat oil into biodiesel. Although the obtained biodiesel yield of 39.6% and a conversion of 68.4% are relatively low, but the information documented in this article serves as a platform for further research development in this field. At the moment the investigation of the effect of process variables on biodiesel yield during the transesterification of animal fat to biodiesel over this catalyst sodalite catalyst is underway to pave the way for optimization study.

5. ACKNOWLEDGMENT

The authors are grateful to the National Research Foundation (NRF), South Africa for the bursary provided PCM for the MSc degree programme at the University of Witwatersrand.

6. REFERENCES

Adewale, P., Dumont, M.J., and Ngadi, M., 2014. Rheological, thermal and physicochemical characterization of animal fat wastes destined for biodiesel production. *Energy Technology*, 2, 634–642.

Adewale, P., Dumont, M.J., and Ngadi, M., 2015. Recent trends of biodiesel production from animal fat wastes. *Renewable and Sustainable Energy Reviews*, 45, 574–588.

Alptekin, E., Canakci, M., and Sanli, H., 2014. Biodiesel production from vegetable oil and waste animal fats in a pilot plant. *Waste Management*, 34(11), 2146-2154.

Aransiola, E.F., Daramola, M.O., Ojumu, V.T., Layokun, S.K., and Solomon, B.O., 2012. Nigerian Jatropha curcas oil seeds: prospect for biodiesel production in Nigeria. *International Journal of Renewable Energy Research*, 2, 317-325.

Aransiola, E.F., Daramola, M.O., Ojumu, V.T., Layokun, S.K., Solomon, B.O., 2013. Homogeneously catalyzed transesterification of Nigerian Jatropha curcas oils to Biodiesel: a kinetic study. *Modern Research in Catalysis*, 2, 83-89.

Brennan, L. and Owende, P., 2010. Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. *Renewable and Sustainable Energy Reviews*, 14(2), 557–577.

Cunha, M.D., Krause, L., Moraes, M.S., Faccini, C.S., Jacques, R., Almeida, S.R., et al., 2009. Beef tallow biodiesel produced in a pilot scale. *Fuel Processing Technology*, 90(4), 570–575.

Daramola, M.O., Dinat, A., and Hasrood, S. , 2015, Synthesis and characterization of nanocomposite ceramic/hydroxy sodalite membrane via pore-plugging technique, *Journal of Membrane and Separation Technology*, 4(1): 1-7.

Daramola, M.O., Nkazi, D., and Mtshali, K., 2015. Synthesis and evaluation of catalytic activity of calcined sodium silicate for transesterification of waste cooking oil to biodiesel. *International Journal of Renewable Energy Research*, 5(2), 517-523.

Daramola, M.O., Mitshali, K., Senokoane, L., and Fayemiwo, O.M., 2016. Understanding the influence of operating variables on the transesterification of waste cooking oil to biodiesel over Sodium silicate catalyst: A statistical approach, *Journal of Taibah University for Science*, 10(5), 675–684.

Daramola, M.O., Oloye, O., and Yaya, A. , 2017. Nanocomposite sodalite/ceramic membrane for pre-combustion CO_2 capture: Synthesis and morphological characterization, *Int. J. Coal Sci. & Technol.*, 4(1), 60-69.

Foleya, A.M., Leahy, P.G., Marvuglia, A., and McKeogh, E.J., 2012. Current methods and advances in forecasting of wind power generation. *Renewable Energy*, 37(1), 1-8.

Fröhlich, A., Rice, B., and Vicente, G., 2010. The Conversion of Low Grade Tallow into Biodiesel-Grade Methyl Ester. *Journal of the American Oil Chemists' Society*, 87(7), 825-833.

Guo, F., Wei, N., Xui, Z., and Fang, Z., 2012. Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Fuel*, 93, 468-472.

Hemmat, Y., Ghobadian, B., Loghavi, M., Kamgar, S., and Fayyazi, E., 2013. Biodiesel Fuel Production from Residual Animal Fat as an Inedible and Inexpensive Feedstock. *International Research Journal of Applied and Basic Sciences*, 5(11), 84-91.

International Zeolite Association, 2016. Available at: http://www.iza-structure.org

International Energy Agency, World Energy Outlook, 2016. Available at: http://www.worldenergyoutlook.org/publications/weo-2016/

International Energy Agency, World Energy Outlook, 2008. http://www.worldenergyoutlook.org/publications/weo-2016/

Li, D., Yao, J., Wang, H., Hao, N., Zhao, D., Ratinac, K.R., and Ringer, S.P., 2007. Organic-functionalized sodalite nanocrystals and their dispersion in solvents. *Microporous and Mesoporous Materials*, 106(1-3), 262-267.

Liu, S., Wang, Y., Oh, J.H., and Herring, J.L., 2011. Fast biodiesel production from beef tallow with radio frequency heating. *Renewable Energy*, 36, 1003-1007.

Liu, Y., Lotero, E., Goodwin, J.G., and Mo, X., 2007. Transesterification of poultry fat with methanol using Mg–Al hydrotalcite derived catalysts. *Applied Catalysis A-General*, 331, 138–148.

Makgaba, C.P., and Daramola, M.O., 2015. Transesterification of Waste Cooking Oil to Biodiesel over Calcined Hydroxy Sodalite (HS) Catalyst: A preliminary investigation. *International Conference on Sustainable Energy and Environmental Engineering*, 53-56.

Schenk, P.M., Thomas-Hall, S.R., Stephens, E., Marx, U.C., Mussgnug, J.H., Posten, C., and Hankamer, B., 2008. Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production. *BioEnergy Resource*, 1(1), 20-43.

Sharma, Y., Singh, B., and Korstad, J., 2011. Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel. *Biofuels*, 5(1), 69-92.

Talswar, G.P., Hasnain, S.E., and Sarin, S.K., 2016. Textbook of Biochemistry, Biotechnology, Allied and Molecular Medicine, 4th Ed. Delhi: PHI Learning Private Limited.

Yaakob, Z., Mohammad, M., Alherbawi, M., Alam, Z., and Sopian, K., 2013. Overview of the production of biodiesel from waste cooking oil. *Renewable and Sustainable Energy Reviews*, 18, 184-193.

Yang, H., Lu, L., and Zhou, W., 2007. A novel optimization sizing model for hybrid solar-wind power generation system. *Solar Energy*, 81(1), 76–84.

Yao, J., Wang, H., Ratinac, K.R., and Ringer, S.P., 2006. Formation of Colloidal Hydroxy-Sodalite Nanocrystals by the direct Transformation of Silicate Nanocrystals. *Chemistry of Materials*, 18(6), 1394-1396.

Zhou, W., Lou, C., Li, Z., Lu, L., and Yang, H., 2010. Current status of research on optimum sizing of stand-alone hybrid solar–wind power generation systems. *Applied Energy*, 87(2), 380-389.

International Conference on Sustainable Energy and Environmental Engineering (SEEE 2015)

Transesterification of Waste Cooking Oil to Biodiesel over Calcined Hydroxy Sodalite (HS) Catalyst: A preliminary investigation

Chabisha P. Makgaba and Michael O. Daramola*
School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Wits 2050, Johannesburg, South Africa
* Corresponding author

Abstract— **In this article, preliminary investigation on the use of hydroxy sodalite (HS) as a solid catalyst for the transesterification of waste cooking oil (WCO) to biodiesel is presented. Hydroxy sodalite was synthesized in our laboratory via the conventional hydrothermal synthesis technique and the crystals were used as basic solid catalyst to convert waste cooking oil to biodiesel. Physicochemical properties of the as-synthesized HS catalyst were obtained using Fourier Transform Infrared Spectroscopy (FT-IR) for surface chemistry and Scanning Electron Microscopy (SEM) for the morphology. The reaction was conducted at 60°C for 6 h at a methanol-to-WCO ratio of 7.5:1 using 3 wt.% HS catalyst. The stirring was at 400 rpm to ensure uniform concentration and heat distribution during the reaction. The product obtained after the reaction was analyzed using a pre-calibrated Chromatography- Mass Spectrometer (GC-MS). The SEM images of the solid catalyst and the FTIR spectra show that HS particles were synthesized. The result of the analysis of the product revealed that biodiesel was produced. As far as could be ascertained, this is the first open report on the use of HS as solid catalyst for biodiesel production. The results of the investigation opened up further on-going research efforts in this area in our laboratory and subsequent results will be communicated in the future.**

Keywords-hydroxy sodalite; catalyst; waste cooking oil; biodiesel component

I. INTRODUCTION

The Combustion of fossil fuels has an immense detrimental effect on the environment. The release of pollutant gases such as NOx, SOx, and CO is inevitable during this process. In addition, the price instability of fossil fuels poses a serious threat to countries with limited resources. Taking into account the limited amount of energy resources, their increasing prices and environmental issues associated with the use of conventional fuels for energy, other means of producing energy sustainably have become the forefront of research. Amongst the studies for other means of providing sustainable energy is biodiesel, which is a branch of biofuels and has become an essential alternative for liquid fuels.

Previous studies have demonstrated the use of typical edible plant oils, such as soybean, rapeseed oil and palm oil for the production of biodiesel [1]. These raw materials are not entirely suitable, more especially in developing countries, due to the limited supply and high cost associated with their application, as well as competition with the food chain [3]. Therefore, low cost, non-edible oils such as Jatropha oil, animal fat and waste cooking oil have been suggested and tested as alternatives [4-7]. However, the main disadvantage of these non-edible types of feedstock is the high content of free fatty acid (FFA) within the oils, which poses problems in the production process. Consequently, Biodiesel from high FFA content feedstock is conventionally produced by a two-stage process: esterification, followed by transesterification [8]. The esterification step serves to reduce the amount of FFAs present in the oil in order to allow for the transesterification reaction to commence [9]. The implication of this additional process unit is inevitably the additional costs associated with the biodiesel production.

In recent times, the use of heterogeneous catalysts has been proven to be very effective in converting high FFA feedstock directly to biodiesel, thereby by-passing the esterification stage [4,7,10-11]. The most commonly used heterogeneous catalysts for the production of biodiesel are ion-exchange resins, inorganic-oxide solid acids and supported noble-metal oxides. However, a dramatic decrease in the catalytic activity of these catalysts has been observed due to their absorption of water during biodiesel production [10].Besides the sharp reduction in the catalytic activity, the catalysts can form a slurry with the products by absorbing water and carbon dioxide, thereby increases the viscosity of the product mixture, making product separation very difficult [12]. In recent times, a few research efforts have been expended on the development of heterogeneous catalysts for biodiesel production [4,7,12-13]. For biodiesel production from WCO, recent concerted research efforts have investigated the use of solid-base catalysts obtained from pyrolyzed rice husk [10] and silica sulfuric acid [14]. As far as could be ascertained, there is no report in the open literature on the conversion of WCO to biodiesel over calcined solid hydroxy sodalite (HS) catalyst. As a contribution to the concerted research efforts in this area, this paper presents results of a preliminary investigation on the conversion of WCO to biodiesel over heterogeneous HS catalyst.

II. MATERIAL AND METHOD

A. Materials

Waste cooking oil was obtained from a local restaurant in Braamfontein, Johannesburg, South Africa. The analytical grade methanol (99%), isopropanol (99%), ethanol(95%), catalyst materials; anhydrous sodium metal silicate (Na_2SiO_3), sodium hydroxide (NaOH), anhydrous sodium aluminate ($NaAlO_2$) and all GC analytical standard chemicals; FAME (MIX, C4-C24, 100MG NEAT) and Glycerol(99 %) were used in this study. All chemicals were purchased from Sigma-Aldrich, South Africa.

B. Free Fatty Acid (FFA) Content and Characterization of Catalyst

Free fatty acid content in WCO was determined to ensure that a considerable amount of free fatty acids exist in the WCO. This was done to confirm the need for a heterogeneous catalyst. It was also required to prove the tolerance of HS to a high content of free fatty acid in biodiesel production. Determination of the FFA content was carried out as described elsewhere [7] and the acid value of the WCO was calculated using Equation (1):

$$Acid\ value = \frac{KVC}{m} \qquad (1)$$

Where K is the acid value constant (a neutralization number) for cooking oil amounting to 56.1 (this is the mass of KOH in milligrams that is required to neutralize 1 g of chemical substance). The concentration of titrate solution is denoted as C in units of (g/ml). The volume of titrate required to neutralize the sample is denoted as V in units of (mL). Lastly, the mass of sample used is denoted as m in units of (g).

C. Catalyst Preparation and Characterization

Hydroxy sodalite particles were prepared from a mixture of the anhydrous Sodium meta silicate (Na_2SiO_3), sodium hydroxide (NaOH), anhydrous sodium aluminate ($NaAlO_2$) and de-ionized by hydrothermal synthesis method via hydrothermal synthesis described elsewhere [15]. The FT-IR was used to characterize the chemical functional groups of the catalyst, with a wave number range from 400 to 4000 cm^{-1}. In order to carry out an SEM analysis, the hydroxy sodalite catalyst was initially coated with ultrathin gold/palladium alloy due to its nonconductive nature. The determination of surface topology and morphology of the catalyst was determined by SEM, performed on a Carl Zeiss, operating at an accelerated voltage of 5.00 kV.

D. Biodiesel Production

The procedure and some of the reaction parameters used for the transesterification reaction were adapted from the work done by Guo, Peng, Dai, & Xio (2010). Hydroxy sodalite particles were first calcined at 200°C for 2 hours to increase the catalyst activity; by removing moisture and volatile matter that may block the pores of the catalyst surface. The transesterification reaction was carried out in a 250 ml three necked round bottomed flask, batch reactor setup; equipped with a reflux condenser to prevent loss of methanol. The flask charged with relevant amount of waste cooking oil, methanol and HS particles was immersed in a thermostat controlled water bath placed on a hot plate magnetic stirrer. The reaction conditions were: reaction time 6 h; reaction temperature 60 ˚C; methanol-to-WCO ratio 7.5:1; catalyst weight percentage 3 wt. %; stirrer intensity 400 rpm. After the completion of the reaction, the catalyst particles were recovered from the mixture by filtration through nylon filter paper (0.45 µm pore dimension). Separating funnel was used to separate the products and glycerol was drained from the bottom of the funnel while biodiesel was collected from the top. Analysis of the samples was performed using a pre-calibrated Gas Chromatograph equipped with a LECO GCxGC Thermal Modulator (GC-MS, model: Agilent 7890N).

III. RESULTS AND DISCUSSION

The SEM image and the FTIR spectrum of the HS particles are presented in Figure I (a) Figure I (b), respectively. The EDX analysis of the HS crystals showed that Si/Al= 1-1.5, indicating HS framework. The SEM image (Figure 1(a)) shows that HS crystals were successfully synthesized. However, a mixture of HS particles with cubic shape and nanorod-like shape were also observed. The observed morphology is consistent with previous studies where other shapes of hydroxy sodalite such as nanorods, flower-like, urchin, thread-ball and cubic/octahedral shape have been reported [16-17]. The FTIR spectrum in Figure I (b) shows the asymmetric stretching vibration of T-O-T (T-Si, Al) at ~1000 cm^{-1}. In addition, the peaks around 740 cm^{-1} and 660 cm^{-1} can be assigned to the symmetric stretching vibration of T-O-T. The presence of water molecules in the framework of the synthesized HS is vividly shown with the strong broad band centered at ~3600 cm^{-1} [18]. This information confirms the synthesis of pure HS particles and is in agreement with literature [19].

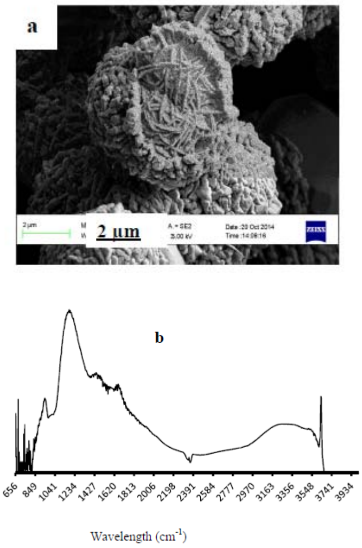

FIGURE I. PHYSICO-CHEMICAL CHARACTERIZATION OF THE HS CATALYST. SEM IMAGES (A); FTIR SPPECTRUM (B).

The free fatty acid content in the WCO sample was determined to be 3.28%. According to previous studies, the base-catalyzed trans-esterification requires that oil samples should have FFA content less than 1% to avoid the occurrence of hydrolysis and saponification reactions [20]. The production of biodiesel was successful even though the FFA content exceeded the recommended 1% because of the use of hydroxy sodalite as a catalyst for trans-esterification. Since the structure of HS is made up of Si-O-Si, it could be speculated that it exhibits the same behavior as sodium metasilicate whereby hydrolysis reaction with sodium silicate and water resulted in the formation of NaOH and Si-O-H [4], thereby suppressing the formation of soap because of the decreased water content (less than 4%) [12].The tolerance of HS to water could be attributed partly to its porous structure. Furthermore, the unique structure of the catalyst could enhance sequential hydration to occur in three steps when there are high amounts of water present. In addition, the Si-O-Si bridges that form the cages of the HS could hydrolyze and cause H_4SiO_2 monomers to be released and thus produce -OH which prevents soap formation [12].

Since biodiesel mixture comprises major components of fatty acid methyl esters of long chain carbon chains (C6:0-C24:1) was used as the standard. Qualitatively, the results of the GC-MS analysis of the reaction products are shown in Figure II (top & bottom) and Table I (for the biodiesel standard) and Table II (for the produced biodiesel). From the peaks depicted by Figure 2, FAME components in the mixtures for both the standard and produced biodiesel could be identified and compared. FAME peaks are only identified between 13 minutes and 19 minutes retention times for the produced biodiesel when compared to peaks in the standard. This can be attributed to the fact that the FAME components in the biodiesel largely depend on the type of feedstock used. However, major components making up biodiesel mixture are common in the two mixtures; confirming the feasibility of using the synthesized HS as a catalyst for the transesterification reaction of WCO to biodiesel.

IV. CONCLUSION

The results of the preliminary investigation reveal the possibility of converting WCO to biodiesel over calcined HS catalyst. Although information about the conversion and the biodiesel yield with this catalyst is not provided in this article. However, the information contained in this piece serves as impetus for further research efforts on the use of HS as solid catalyst for biodiesel production. At the moment, research efforts are geared towards an in-depth understanding of the mechanism and kinetics of the HS catalyzed transesterification process for biodiesel production in our laboratory. Results of our findings will be communicated in the future.

ACKNOWLEDGMENT

The authors are grateful to the National Research Foundation (NRF), South Africa for the bursary provided PCM for the MSc degree programme at the University of the Witwatersrand.

REFERENCES

[1] F.Guo and Z. Fang, “Biodiesel Production with Solid Catalysts, Biodiesel - Feedstocks and Processing Technologies,”In M. Stoytcheva and G. Montero , Eds. Rijeka: InTech, 2011, p. 339.

[2] O.J. Alamu, M.A.Waheed and S.O. Jekayinfa, “Effect of ethanol–palm kernel oil ratio on alkali-catalyzed biodiesel yield”, Fuel, vol. 87, 2008, pp. 1529–1533.

[3] J. Gerpen, G. Knothe and J. Krahl, “ Biodiesel production - biodiesel handbook,” Champaign: AOCS PRESS, 2005.

[4] F.Guo, N. Wei,Z. Xui and Z. Fang, “Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate,” Fuel, vol. 93, pp. 468-472.

[5] E.F. Aransiola, M.O. Daramola, V.T. Ojumu, S.K. Layokun, B.O. Solomon, “Homogeneously catalyzed transesterification of Nigerian Jatropha curcas oils to Biodiesel: a kinetic study,” MRC, vol. 2, 2013, pp. 83-89.

[6] E.F. Aransiola, M.O. Daramola, V.T. Ojumu, S.K. Layokun, B.O. Solomon ,“ Nigerian Jatropha curcas oil seeds: prospect for biodiesel production in Nigeria,” IJRER, vol.2 ,2012, pp. 317-325.

[7] M.O. Daramola, D. Nkazi, K. Mtshali, “Synthesis and evaluation of catalytic activity of calcined sodium silicate for transesterification of waste cooking oil to biodiesel,” IJRER, vol.5, 2015, pp.517-523.

[8] Z. Yaakob, M. Mohammad, M. Alherbawi, Z. Alam, and K.Sopian, “Overview of the production of biodiesel from waste cooking oil,” Renew. Sustainable Energy Rev., vol. 18, 2013, pp.184-193.

[9] Y. Sharma, B. Singh and J. Korstad, “(2011). Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel. Biofuels,vol. 5, 2011, pp. 69-92.

[10] M. Li, Y. Zheng, Y. Chen and X. Zhu, “Biodiesel production from waste cooking oil using heterogeneous catalyst from pyrolyzed rice husk,” Bioresour. Technol. ,vol. 154, 2014, pp. 345-348.

[11] A.Gnanaprakasam,V.Sivakumar, A. Surendhar, M. Thirumarimurugan and T. Kannadasan, “Recent strategy of biodiesel production from waste cooking oil and process influencing parameters,” Energy, 2013, pp. 1-8.

[12] F.Guo , Z. Peng, J. Dai and Z. Xui, “Calcined sodium silicate as solid base catalyst for biodiesel production,” Fuel Processing Technology, ,2010, vol. 91, pp. 322-328.

[13] A. Talebian-Kiakalaieh, N.A.S. Amin, A. Zarei and H. Jaliliannosrati, “Biodiesel production from high free fatty acid waste cooking oil by solid acid catalyst,” In: proceedings of the 6th International Conference on Process Systems Engineering, 2013, pp. 572-576.

[14] K.A. Shah, J.K. Parikh and K.C. Maheria, “Optimization studies and chemical kinetics of silica sulfuric acid-catalysed biodiesel synthesis from waste cooking oi,” Bioenergy Resources, vol. 7, 2014, pp. 206-216.

[15] M.O. Daramola, A. Dinatand S. Hasrood, “Synthesis and characterization of nanocomposite ceramic/hydroxy sodalite membrane via pore-plugging technique,” J. Memb. Separ. Tech, vol. 4 pp. 1-7.

[16] B. Bayati, A.A Babaluo and R. Karimi, (2008) J. Eur. Ceram. Soc, vol. 28, 2008,pp. 2653-2657.

[17] M.K Naskar,D Kundu and M. Chatterjee, “Effect of process parameters on surfactant-based synthesis of hydroxy sodalite particles, ” Mater. Lett., vol.65 ,2011, pp.436-438.

[18] D.W. Breck ,”Zeolite molecular sieves: structure, chemistry and use,” USA, New York: Wiley, 1974.

[19] J.C. Buhl, K. Schuster and L. Robben,“Nanocrystalline sodalite grown from superalkaline NaCl bearing gels at low temperature(333K) and the influence of TEA on crystalization process“, Micropor. Mesopor. Mater., vol. 142, 2011, pp. 666-671.

[20] M. Mathiyazhagan and A. Ganapathi, “ Factors affecting biodiesel production,” Research in Plant Biology, vol.1 , 2011, pp. 01-05.

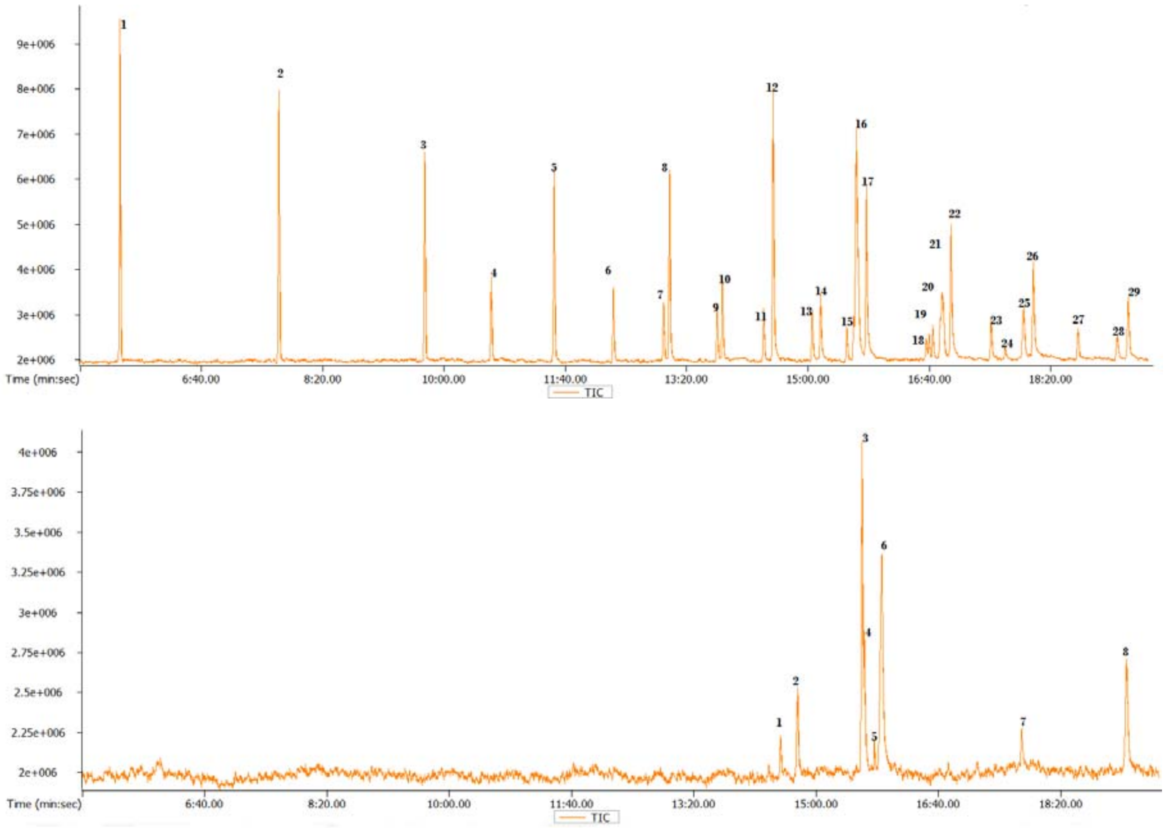

FIGURE II. CHROMATOGRAMS OF THE BIODIESEL SAMPLES. OBTAINED FROM THE STANDARD BIODIESEL (TOP); OBTAINED FROM THE TRANSESTERIFICATION OF WCO OVER HS CATALYST (BOTTOM).

TABLE I. GC-MS ANALYSIS OF THE BIODIESEL STANDARD

Peak no.	Name		RT (min:sec)	Peak no.	Name		RT (min:sec)
1	Hexanoic acid, methyl ester	C6:0	05:33	16	Linoleic acid, methyl ester	C18:2	15:37
2	Octanoic acid, methyl ester	C8:0	07:44	17	Oleic acid, methyl ester	C18:1	15:39
3	Decanoic acid, methyl ester	C10:0	09:44	18	Linolenic acid, methyl ester	C18:2	15:40
4	Tridecanoic acid, methyl ester	C13:0	10:39	19	Octadecanoic acid, methyl ester	C18:0	15:48
5	Dodecanoic acid, methyl ester	C12:0	11:30	20	Arachidonic acid	C20:4n6	16:37
6	Tridecanoic acid, methyl ester	C13:0	12:19	21	5,11,14,17-Eicosapentaenoic acid, methyl ester(all-Z)	-	16:39
7	Tetradecanoic acid, methyl ester	C14:0	13:01	22	Linolenic acid, methyl ester	C18:2	16:43
8	Methyl tetradecanoic acid	C14:0	13:06	23	11,14-Eicosadienoic acid, methyl ester,(Z,Z,Z)	-	16:48
9	Oleic acid, methyl ester	C18:0	13:45	24	Oleic acid, methyl ester	C18:0	16:50
10	Tridecanoic acid, methyl ester	C13:0	13:49	25	Linolenic acid, methyl ester	C18:2	16:51
11	Hexadecanoic acid, methyl ester(Z)	C16:0	14:23	26	Eicosanoic acid, methyl ester	C20:0	16:57
12	Hexadecanoic acid, methyl ester	C16:1	14:31	27	Hexadecanoic acid, methyl ester	C16:1	17:31
13	Cyclopropaneoctanoic acid, methyl ester	C17:1	15:03	28	Oleic acid, methyl ester	C18:0	19:15
14	Tridecanoic acid, methyl ester	C13:0	15:11	29	Hexadecanoic acid, 15-methyl-, methyl ester	-	19:24
15	ç-Linolenic acid, methyl ester	C18:2	15:32				

TABLE II. GC-MS ANALYSIS OF THE PRODUCED BIODIESEL

Peak no.	**Name**		**RT(min:sec)**
1	Tridecanoic acid, methyl ester	C13:0	14:31
2	Undecanoic acid, methyl ester	C11:0	14:45
3	Linoleic acid, methyl ester	C18:2	15:37
4	Oleic acid, methyl ester	C18:1	15:39
5	Octadecanoic acid, methyl ester	C14:0	15:48
6	9,12 Octadecanoic acid	C18:2	15:54
7	10-Undecyn-1-ol	-	17:48
8	9,12 Octadecadienoyl chloride	-	19:14