

**MODELLING OF IN-SITU REAL-TIME MONITORING OF
CATALYSED BIODIESEL PRODUCTION FROM SUNFLOWER OIL
USING FOURIER TRANSFORM INFRARED**



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DECLARATION

I, Pascal Kilunji MWENGE, declare that the work contained in this thesis is the representation of my original work except stated otherwise. It has not been submitted for any academic examination toward any degree qualification in any university or institution. References used in this work were stated and acknowledged.

Pascal Kilunji Mwenge

October 2020

A handwritten signature in black ink, appearing to read 'Pascal Kilunji Mwenge', with stylized loops and flourishes.

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DEDICATION

I want to dedicate this work to my parents Mr Amos Muteta Mulunga and Mrs Felicite Kabulo Muteta whose lives have been an inspiration and taught me sacrifice for others and to reach your goals. To my late elder sister Luise Mwenge Kikunda and late grandfather Zabulon Mulunga Muteta who are resting in peace.

ABSTRACT

The industrialisation of the twenty-first century and the worldwide population growth led to the high demand for energy. Fossil fuels are the leading contributor to the global energy, and subsequently, there is a high demand of fuels. The decrease of global fossil fuels and the environmental air pollution caused by these fuels are concerning. Therefore, eco-friendly and renewable fuel such as biodiesel is one the leading alternative. Chromatography and Spectroscopy are the most used analytical methods and proven reliable but are time-consuming, requires qualified personal, extensive samples preparation, costly and do not provide in-situ real-time monitoring. Fourier Transform Infrared (FTIR) has mainly been used for qualitative analysis of biodiesel, but not much work has been reported in real-time monitoring. This study focused on the modelling of in-situ real-time monitoring of the biodiesel production from sunflower oil using FTIR (Fourier Transform Infrared).

The first part of the study investigated the effect of catalyst ratio and methanol to oil ratio on biodiesel production by using central composite design (CCD). Biodiesel was produced by transesterification using Sodium Hydroxide as a homogeneous catalyst. A laboratory-scale reactor consisting of; flat bottom flask mounted with a reflux condenser, a hot plate as heating element equipped with temperature, timer and stirring rate regulator was used. Key parameters including, time, temperature and mixing rate, were kept constant at 60 minutes, 60 oC and 600 RPM, respectively. From the results obtained, it was observed that the biodiesel yield depends on catalyst ratio and methanol to oil ratio. The highest yield of 50.65 % was obtained at a catalyst ratio of 0.5 wt% and methanol to oil mole ratio 10.5. The analysis of variances of biodiesel yield showed the R² value of 0.8387. A quadratic mathematical model was developed to predict the biodiesel yield in the specified parameters range. The same set-up was used to produce waste margarine biodiesel using a homogeneous catalyst, potassium hydroxide (KOH). The effects of four reaction parameters were studied, these were: methanol to oil ratio (3:1 to 15:1), catalyst ratio (0.3 to 1.5 wt. %), temperature (30 to 70 oC), time (20 to 80 minutes). The highest yield of 91.13 % was obtained at 60°C reaction temperature, 9:1 methanol to oil molar ratio, 0.9 wt. % catalyst ratio and 60 minutes. The important biodiesel fuel properties were found to be within specifications of the American Standard Test Method specifications (ASTM). It was concluded that waste margarine can be used to produce biodiesel as a low-cost feedstock.

The core of the study was performed using EasyMax Mettler Toledo reactor equipped with a DiComp (Diamond) probe. The quantitative monitoring of the biodiesel production was performed by building a quantitative model with multivariate calibration using iC Quant module from iC IR 7.0 software. Fourteen samples of known concentrations were used for the modelling which were taken in duplicate for model calibration and cross-validation, data were pre-processed using mean centring and variance scale, spectrum math square root and solvent subtraction. These pre-processing methods improved the performance indexes from 7.98 to 0.0096, 11.2 to 3.41, 6.32 to 2.72, 0.9416 to 0.9999, RMSEC, RMSECV, RMSEP and R^2_{Cum} , respectively. The R^2 values of 1 (training), 0.9918 (test), 0.9946 (cross-validation) indicated the fitness of the model built. The model was tested against the univariate model; small discrepancies were observed at low concentration due to unmodelled intermediates but were quite close at concentrations above 18%. The software eliminated the complexity of the Partial Least Square (PLS) chemometrics. It was concluded that the model obtained could be used to monitor transesterification of sunflower oil at industrial and lab scale.

The model thus obtained, a batch reactor setup, EasyMax Mettler Toledo reactor was used, the experiments were designed and monitored using iControl software. The results were recorded and quantified using iC IR software based on the biodiesel calibrated monitoring model built. The optimisation of the biodiesel was performed using three key parameters (methanol to oil ratio, catalyst ratio and temperature) while keeping time at 60 minutes and mixing rate at 150RPM. The highest yield of 97.85 % was obtained at 60 °C, 0.85 wt % catalyst ratio and 10.5 methanol to oil mole ratio. The analysis of variances of biodiesel production showed the values of 0.9847, 0.9674 and 0.8749, for R-squared, adjusted R-squared and predicted R-squared, respectively. A quadratic mathematical model was developed to predict the biodiesel conversion in the specified parameters ranges. Using the Arrhenius equation, activation energy (E_a) and frequency factor were found to be 41.279 kJ.mole⁻¹ and 1.08 x10⁻⁴ M⁻¹. s⁻¹, respectively. The proposed kinetics model was a pseudo-first-order reaction. It was concluded that the model obtained can be used for industrial and laboratory-scale biodiesel production monitoring.

Keywords

Biodiesel, Calibration, Catalyst, Chemometrics, Fourier Transform Infrared (FTIR), Kinetics, Multivariate analysis, Optimisation, Real-time monitoring, Transesterification.

LIST OF PUBLICATIONS AND CONFERENCE PROCEEDINGS

Mwenge, P. , Pilusa, J. , Seodigeng, T. (2018), 'Optimization of Biodiesel Production from Sunflower Oil Using Central Composite Design', World Academy of Science, Engineering and Technology, Open Science Index 137, *International Journal of Biotechnology and Bioengineering*, 12(5), 139 - 145

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LIST OF ABBREVIATION

| | |
|---------------------|--|
| ^1H NMR | Proton Nuclear Magnetic Resonance |
| ACE | Associate Chemical Enterprises |
| AN | Acid Number |
| ANN | Artificial Neural Network |
| ANOVA | Analysis Of Variance |
| ASTMD | American Standards and Measurements |
| ATR-FTIR | Attenuated Total Reflection Fourier Transform Infrared |
| CaCO_3 | Calcium Carbonate |
| Ca(OH)_2 | Calcium Hydroxide |
| $\text{Ca(NO}_3)_2$ | Calcium Nitrate |
| CaO | Calcium Oxide |
| CCD | Central Composite Design |
| CLS | Classical Least Square |
| CN | Cetane Number |
| CFPP | Cold-Filter Plugging Point |
| CGC | Capillary Gas Chromatography |
| CP | Cloud Point |
| CO_2 | Carbon Dioxide |
| CV | Calorific Value |
| DG | Diglyceride |
| EFA | Evolving Factor Analysis |
| EFCM | Enformatic FTIR Collection Manager |
| EU | European Union |
| DOE | Design of Experiments |
| FAEE | Fatty Acid Ethyl Esters |
| FAME | Fatty Acid Methyl Ester |
| FFA | Free Fatty Acid |
| FID | Flame Ionisation Detection |
| FP | Flash Point |

| | |
|------------------------------------|---|
| FPUI | Flat plate ultrasonic irradiation |
| FTIR | Fourier Transform Infrared Spectroscopy |
| GC | Gas Chromatography |
| GC MS | Gas Chromatography Mass Spectroscopy |
| GHG | Green House gases |
| GL | Glycerol |
| HCA | Hierarchical Cluster Analysis |
| HFRR | High Frequency Reciprocating Rig |
| HPLC | High Performance Liquid Chromatography |
| iPCA | Interval Principal Component Analysis |
| iPLS | Interval Partial Least Squares |
| IV | Iodine value |
| KOCH ₃ | Potassium methoxide |
| KOH | Potassium Hydroxide |
| MG | Monoglycerides |
| MS | Mechanical Stirring |
| MW | Molecular weight |
| NaOH | Sodium Hydroxide |
| NaOCH ₃ | Sodium Methoxide |
| NaOCH ₂ CH ₃ | Sodium Ethoxide |
| NFSA | Non-Saturated Fatty Acids |
| MIR | Mid-Infrared |
| MSC | Multiplicative Signal Correction |
| NIR | Near-Infrared |
| NMR | Nuclear Magnetic Resonance |
| NO ₂ | Nitrogen dioxide |
| NO _x | Nitrous oxide |
| OFAT | One Factor at a Time |
| PCA | Principal Component Analysis |
| PCR | Principal Component Regression |
| PLS | Partial Least Square |

| | |
|-----------------|---|
| PP | Pour Point |
| PUI | Probe Ultrasonic Irradiation |
| RMSEC | Root Mean Square Error of Calibration |
| RMSECV | Root Mean Square Error of Cross Validation |
| RMSEP | Root Mean Square Error of Prediction |
| RMSPD | Root Mean Square Prediction Difference |
| RPM | Revolutions Per Minute |
| RSM | Response Surface Methodology (RSM) |
| SFA | Saturated Fatty Acids |
| SFO | Sunflower Oil |
| SIMCA | Soft Independent Modeling of Class Analogy |
| siPLS | Synergy Partial Least Squares |
| SNV | Standard Normal Variance |
| SO _x | Sulphur Oxide |
| SrO | Strontium Oxide |
| SEC | Size Exclusion Chromatography |
| SV | Saponification Value |
| TG | Triglycerides |
| TGA | Thermogravimetric Analysis |
| TiO | Titanium Oxide |
| TLC | Thin Layer Chromatography |
| TR | Transesterification Reaction |
| UASI | Ultra-Sonation Assisted Spray Ionization |
| UCO | Used Cooking Oil |
| UIMS | Ultrasonic Irradiation with Mechanical Stirring |
| UN | United Nations |
| USEPA | United States Environmental Protection Agency |
| USA | United States of America |
| W _t | Weigh |
| ZnO | Zinc Oxide |
| ZrO | Zirconium Oxide |

CHAPTER ONE

1. INTRODUCTION

1.1 Background

The current worldwide industrialisation has led to the high demand for energy, leading to increased consumption of fuels. The energy consumption doubled from 1973 to 2013, for which 81.4 % is from fossil fuels. This rise in consumption is expected to increase by a third during the period leading from 2017 to 2035 (Ilmi et al., 2017). Fossil fuels (coal, oil and gas) are the mainly used fuels and are obtained from old carbonaceous mineral deposits, which are not renewable sources. This leads to the diminishing of these fuel resources for which petroleum oil is expected to decrease by 60 % in 2080 (Mohd Noor, Noor and Mamat, 2018). Other sources of energy are solar, geothermal energy, biomass, hydropower. Solar is the fastest growing renewable energy sector, and biomass is classified as the only green carbon-based fuel (Ilmi et al., 2017).

There is an important role that vegetable oils can play in the search to alternative fuels (Meher, Vidya Sagar and Naik, 2006). A century ago the inventor of the diesel engine Rudolph Diesel used vegetable oils as substitute fuel by firstly testing peanut oil in his compression ignition engine. By then he declared that the significance of using vegetable oils as engine fuel could not be considered at that time, but in later time vegetable oils could be considered as petroleum oils and the coal tar products have been considered (Meher, Vidya Sagar and Naik, 2006).

As the first energy source used by Rudolph Diesel in directed injection engine, vegetable oils posed some challenges when compared to petroleum oil-derived fuels. These challenges are:

- coking and trumpet formation on the injectors to the extent that fuel atomisation does not occur as a result of plugged orifices,
- carbon deposits and oil ring sticking,
- thickening and lubrication problems,
- high viscosity due to the high molecular mass of triglyceride.

To address these challenges, the engine using vegetable oils needed to be modified as in the case in Germany and Malaysia by Elsbett, in the USA and Germany by Diesel Morten und Geraetebau GmbH (DMS) demonstrated a better performance (Srivastava and Prasad, 2000).

Vegetable oils often contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. It is due to these components that these oils pose challenges of direct use as fuel. The oil needs chemical modification such as transesterification, pyrolysis and emulsification to overcome these challenges. Transesterification is used for the production of clean and environmentally friendly fuel from vegetable oils. Biodiesel is mono-alkyl esters of long-chain fatty acids derived from renewable feedstocks such animal fats and vegetable oil, for use in compression ignition engine. Biodiesel, an alternative of conventional diesel fuel is mainly constituted of alkyl esters produced from vegetable oils triglycerides by transesterification with short chains alcohols. The product has similarities that match that of conventional diesel fuel in its main characteristics (Meher, Vidya Sagar and Naik, 2006). Biodiesel is considered as an environmentally friendly fuel as it fulfils requirements such as less SO_x, NO_x and CO₂ emissions, biodegradability, high cetane number, high combustion efficiency (Marchetti, Miguel and Errazu, 2007; Lukovi, Kneževi and Bezbradica, 2011; Sani, Daud and Abdul, 2013). Different world blends of biodiesel blend with petroleum diesel are shown in Table 1-1.

Table. 1-1: World's major biodiesel produced in 2016 (Mohd Noor, Noor and Mamat, 2018)

| Rank | Country | Biodiesel Volume (Million cubic meters) |
|-------------|----------------|--|
| 1 | USA | 5.5 |
| 2 | Brazil | 3.8 |
| 3 | Germany | 3.0 |
| 4 | Indonesia | 3.0 |
| 5 | Argentina | 3.0 |
| 6 | France | 1.5 |
| 7 | Thailand | 1.4 |
| 8 | Spain | 1.1 |
| 9 | Belgium | 0.5 |
| 10 | Colombia | 0.5 |

Catalysts used in biodiesel production are categorised into two classes, chemical and enzymatic catalysts. Chemical catalysts, in turn, are classified into two categories, namely alkalis and acids which are categorised as heterogeneous and homogeneous. Alkalis homogeneous catalysts are the most used in the transesterification of lipids for commercial purposes (Lam et al., 2010; Al-zuhair et al., 2007; Talha & Sulaiman 2016; Khurshid, 2014; Meher et al., 2006). Enzymatic catalysts such as lipases in liquid or immobilised have attracted researchers attention due to the advantages such as insensitivity to FFA and water, no soap formation, purity of the products, the low energy required, recycling of enzymes, more environments friendly, separation of enzymes with products and avoids

production of undesired products (Du et al., 2004; Dizge et al., 2009; Cesarini et al., 2015; Amoah et al., 2016; Pourzolfaghar et al., 2016; Yusoff et al., 2016; Santin et al., 2017; Villardi et al., 2017).

The most used method of analysing fatty acid alkyl esters has been Gas Chromatography, which has many requirements such as time-consuming for analysis, extensive samples preparation, destructive sample method (Rabelo et al., 2015), Fourier Transform Infrared (FTIR) is being preferred as it is fast and has fewer requirements and is an effective analytical method (Rabelo et al., 2015; Gao et al., 2017). Fourier Transform Infrared (FTIR) is a spectroscopy analytical technique which has attracted researchers for its accuracy, its cost efficiency, its performance, and eliminating the need for sample preparation. Infrared spectroscopy operates by sending infrared radiation on a sample where part of the sample is absorbed, and the remaining is transmitted, which produces spectrum expressing the sample's molecular absorption and transmission, therefore the sample's molecular fingerprint. This implies that; there is only one infrared spectrum for a specific molecular structure. It is for this reason that spectroscopy is very effective for numerous analytical methods. A sample's fingerprint is represented by an infrared spectrum with absorption peaks corresponding to vibrations' frequencies of different atomic bonds constituting the sample. The infrared is a qualitative method as the fingerprint can lead to material composition determination and the size of the peaks in the spectrum is directly proportional to the quantity of diverse material (Introduction to Fourier Transform Infrared Spectrometry, 2001).

Infrared spectroscopy has been in use for analysis for the past 70 years; infrared spectrums are classified as fingerprints of materials or samples; these fingerprints are constituted of absorption peaks that correspond to the frequencies of vibrations of atomic bonds constituting the material. Fourier Transform Infrared spectroscopy operates by sending infrared radiation on a sample where part of the sample is absorbed, and the remaining is transmitted, which produces spectrum expressing the sample's molecular absorption and transmission, therefore the sample's molecular fingerprint. The abovementioned implies that; there is only one infrared spectrum for a specific molecular structure (Singh et al., 2011).

Transesterification monitoring of vegetable oils using FTIR has been reported as an analytical method with accuracy and less time-consuming. Univariate analysis has been used but becomes challenging due to spectral overlapping as the one occurring in transesterification, therefore the measured spectrum and properties of interests might lead to non-linear correlation (Zagonel, Peralta-

Zamora and Ramos, 2004). To overcome this situation, there will be a need of applying multi-linear analysis such as Partial Least Square (PLS) which will exploit the entire band of the spectra, the use of multivariate analysis has been reported be reliable (Zagonel, Peralta-Zamora and Ramos, 2004; Yuan et al., 2014; Cunha et al., 2017; Mahamuni et al., 2017). FTIR coupled with multivariate analysis for complex reaction attracted researchers since the late 90s (Zagonel, Peralta-Zamora and Ramos, 2004) PLS is a mathematical method based on Beer's law principle for quantification (Yuan et al., 2014).

Chemometrics such as Partial least square regression (PLS) and principal component analysis (PCA) have been developed and added the effectiveness of FTIR method (Mueller *et al.*, 2013; Rabelo *et al.*, 2015; Gao *et al.*, 2017). Partial least square regression (PLS) combining with attenuated total reflection Fourier can be used in designing models to determine fatty acid alkyl ester and was found to be suitable in the fatty acid alkyl ester determination (Rabelo *et al.*, 2015).

This work focuses on the modelling of *in-situ* real-time monitoring of catalysed biodiesel production from sunflower oil using FTIR (Fourier Transform Infrared). However, there was a study performed on the optimisation of the biodiesel production from sunflower oil using Sunflower oil, methanol to oil ratio and catalyst ratio were the two factors optimised, in this study the challenged of analysis was observed. There was also a study in which biodiesel produced from waste margarine (most South African margarine are mainly produced from the emulsification of sunflower oil and water). The main focus of the study was to used FTIR for an *in-situ* real-time transesterification monitoring in which sodium hydroxide was used as catalyst, the main focus of the study was performed using an EasyMax Mettler Toledo reactor, a model was built, calibrated using cross-validation, pre-processing data tools were used, PLS was performed using iC Quant module from iC IR 7.0 Software and the model obtained was used to optimise biodiesel production, methanol to oil ratio, catalyst ratio and reaction temperature were used as variables for optimisation.

1.2 Problem Statement

The 21st century industrialisation has brought high demand of energy resulting in high demand of fossil fuel and causing the depletion of fossil fuels and environmental pollution. Thus, leading to the increase in carbon dioxide emission, also the emissions of nitrogen oxide and Sulphur oxide, one of the major contributors of smog and can pose serious respiratory issues. These have become major

worldwide problems. Therefore, there is a need for developing new forms of renewable fuel that produces less carbon dioxide i.e. biodiesel. Biodiesel is a fuel produced from renewable feedstocks and has been classified as a closed carbon cycle fuel.

Biodiesel has been produced for the past three decades, and there has been a high increase in global biodiesel production. Chromatography has been the most used methods of qualitative and quantitative analysis of biodiesel and is reputed for their accuracy. Nevertheless, they have drawbacks such as time-consumption as they require extensive sample preparation, require highly qualified personnel, they are sample destruction methods, and their usage for in-situ transesterifications (fast reversible reactions) has not been feasible. Spectroscopy has also been used for qualitative and quantitative analysis of biodiesel. Though spectroscopy can be used for in-situ monitoring, they all offer some limitation for the fact that they can only be performed when the reaction had occurred, or by an off-taking sample from the reaction mixture. It is necessary to monitor real-time transesterification. FTIR spectroscopy can be used as an accurate, fast and reliable method for quantitative and qualitative of in situ transesterification monitoring and offer the possibility of in-situ real-time monitoring of the process and was found non-destructive, user-friendly and rapid analytical technique. Using Mettler Toledo Easymax reactor equip with a DiComp probe, the in-situ real-time monitoring of biodiesel production is made possible.

1.3 Research Objectives

The main objective of this study was to model *in-situ* real-time monitoring of batch biodiesel production system from sunflower oil using a homogenous catalyst.

The specific objectives were:

- a) To optimise biodiesel production from sunflower oil, analysed using traditional method Gas Chromatography.
- b) To produce biodiesel from margarine waste using a homogenous catalyst.
- c) To develop a model for *in-situ* real-time monitoring of the biodiesel production using FTIR produced in a Mettler Toledo Easymax 102 reactor.
- d) To characterise the biodiesel production in real-time using FTIR probe in Mettler Toledo reactor with respect to the concentration of reactants and product as a function of time.

- e) To evaluate the effect of process variables (temperature, catalyst ratio, methanol to oil ratio) on the yield of biodiesel produced in a Mettler Toledo Easymax 102 reactor using the model developed.
- f) To determine a quadratic mathematic model to correlate the process variables to yield of biodiesel using Central Composite Design (CCD) from Response Surface Methodology (RSM).
- g) To determine the kinetics of the biodiesel from sunflower oil produced in a Mettler Toledo Easymax reactor.

1.4 Research Questions

- a) What are the optimum points of biodiesel produced from sunflower oil, analysed using traditional method Gas Chromatography?
- b) Can margarine waste be used as a feedstock for the biodiesel produced using homogenous catalyst?
- c) How was the model developed for the *in-situ* real-time monitoring of the biodiesel production using FTIR produced in a Mettler Toledo Easymax reactor?
- d) Is the model obtained suitable for the *in-situ* real-time monitoring of the biodiesel production?
- e) Is FTIR suitable to be used to characterise the biodiesel production in real-time using FTIR probe in Mettler Toledo reactor with respect to the concentration of reactants and product as a function of time?
- f) Among the process which one has the highest and lowest effect on the yield of biodiesel using the model developed produced in a Mettler Toledo Easymax reactor?
- g) What are the optimum conditions of the process (temperature, catalyst ratio, methanol to oil ratio) and correlation of the process variables to yield of biodiesel using Central Composite Design (CCD) from Response Surface Methodology (RSM)?
- h) What is the order of the kinetics of the biodiesel produced from sunflower oil?

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CHAPTER TWO

2. LITERATURE REVIEW

2.1 Feedstock used in biodiesel production

Vegetable oils and animal fats are the primary feedstocks used in biodiesel production. Their physical appearance distinguishes them. Oils are liquid at standard conditions of temperature and pressure, while fats are solid at standard temperature and pressure. There is a wide variety of Triglycerides (oils) used in the production of biodiesel. The most commonly used are lauric, myristic, palmitic, stearic, oleic, linoleic, and linolenic acids (Uriarte, 2010).

There are two types of oils in nature. The first type is called fixed oils, which do not vaporise when exposed to air, among these are corn and sunflower oils. The second type is named essential oils, among them, are citronella and cinnamon oils. Essential oils evaporate when exposed to air. The production process of fixed oils is mostly by crushing using pressure, boiling, or chemical extraction using solvents. Essential oils production process involves distillation, from flowers such as ilang-ilang oil and Sampaguita oil. Some fixed oils keep their liquid state at very high temperatures; such oils present interest to be used as fuel to replace diesel. On the other hand, essential oils are mostly used in cosmetics and pharmaceutical industries (Uriarte, 2010).

There are more than 350 oil-producing plants around worldwide that have been classified as prospective sources of oil for the production of biodiesel. Out of the 350 crops of oil sources, only sunflower, soybean, palm, jatropha, rapeseed, cottonseed, safflower, and peanut oils are commercially feasible, and these are classified as edible and non-edible oils ((Leung, Wu and Leung, 2010); Al-zuhair, Wei and Song, 2007). The feedstocks used for biodiesel production are naturally bio-renewable and environmentally friendly with such potential to be produced in significant quantity. The most widely used are edible oils account for 95%, this is primarily due to the availability in many countries, and the properties of biodiesel produced from these oils meet the requirement as an alternative to diesel (Leung, Wu and Leung, 2010).



Fig. 2-1: Sources of oils (Uriarte, 2010)

Table 2-1: Physicochemical properties of biodiesel from different oil source and the yields (Leung, Wu and Leung, 2010)

| Oil | Viscosity(cst, at 40 °C) | Density (g,cm³) | Acid Value(mg KOH/g) | Cetane Number | Heating Value (MJ/kg) | Yield % |
|------------------------------|-------------------------------------|---------------------------------------|-------------------------------------|--------------------------|--------------------------------------|----------------|
| Soybean | 4.08 | 0.885 | 0.15 | 52 | 40 | >96 |
| Rapeseed | 4.3-5.83 | 0.88-0.888 | 0.25-0.45 | 49-50 | 45 | 95-96 |
| Sunflower | 4.9 | 0.88 | 0.24 | 49 | 45.3 | 97.1 |
| Palm | 4.42 | 0.86-0.9 | 0.08 | 62 | 34 | 89.23 |
| Peanut | 4.42 | 0.883 | - | 54 | 40.1 | 89 |
| Corn | 3.39 | 0.88-0.89 | - | 58-59 | 45 | 85-96 |
| Camelina | 3.12-7.0 | 0.882-0.888 | 0.08-0.52 | - | - | 97.9 |
| Canola | 4.07 | 0.88-0.9 | - | 56 | 45 | 80-95 |
| Cotton | 3.53 | 0.875 | 0.16 | 54 | 45 | 96.9 |
| Pumpkin | 4.41 | 0.8837 | 0.48 | - | 38 | 97.5 |
| Jatropha | 4.78 | 0.8836 | 0.496 | 61-63 | 40-42 | 98 |
| Curcas | | | | | | |
| Pongamina pinnata | 4.8 | 0.883 | 0.62 | 60-61 | 42 | 97-98 |
| Sea mango | 3.99 | - | - | - | - | 83.8 |
| Palanga | - | 0.869 | - | - | 41 | 85 |
| Tallow | - | 0.856 | 0.65 | 59 | - | 98.28 |
| Nile tilapia | - | - | 1.4 | 51 | - | 98.2 |
| Pultry | - | 0.867 | 0.25 | 61 | - | 99.72 |
| Used Cooking oil | 4 | 0.86-0.9 | 0.15 | 52-59 | 40-45 | 94.6 |

Table 2-2: Major/possible biodiesel feedstocks in each country (Avinash, Subramaniam and Murugesan, 2014)

| Country | Biodiesel feedstock |
|-------------------|---|
| Argentina | Soybean, Sunflower, Crambe abyssinica and Jatropha macrocarpa |
| Australia | Physic nut (Jatropha curcas) |
| Bangladesh | Rubber seed |
| Brazil | Soybean and Palm |
| Canada | Canola, Sunflower and Soybean |
| Chile | Rapeseed |
| China | Rapeseed and Microalgae |
| Cuba | Jatropha curcas and Moringa |
| Ghana | Palm |
| Greece | Sunflower |
| India | Jatropha curcas |
| Indonesia | Palm oil |
| Iran | Palm, Jatropha, Castor, Algae and Fish oil |
| Ireland | Animal tallow and Used cooking oil |

| | |
|---------------------|--|
| Italy | Rapeseed, Soybean and Sunflower |
| Kenya | Castor |
| Mali | Jatropha curcas |
| Malaysia | Palm, Jatropha Curcas and Calophyllum inophyllum |
| Mexico | Palm and Tallow |
| Mozambique | Jatropha curcas |
| New Zealand | Waste oil and tallow |
| Norway | Animal Fats |
| Pakistan | Jatropha curcas |
| Peru | Palm and Jatropha |
| Philippines | Coconut oil |
| South Africa | Sunflower, Canola and Soybean |
| Spain | Linseed and sunflower |
| Sweden | Rapeseed |
| Tanzania | Jatropha |
| Thailand | Palm and Jatropha |
| Turkey | Sunflower and Rapeseed |
| UK | Rapeseed and waste oil |
| USA | Soybean |
| Zimbabwe | Jatropha curcas |

2.1.1 Edible oil

Edible oils are oils which are mainly used for human consumption. These depend on the availability in different countries. Edible oils such as palm oil, coconut, soybean oil, sunflower oil, rapeseed oil, peanut oil, canola, oil olive oil and corn oil are produced in different countries across the world (Demirbas, 2009; Demirbas *et al.*, 2016). The use of edible oils in the production of fuels is a controversial topic as it can put food security at risk.

2.1.2 Non-edible oil

As the use of edible oil for fuel production causes food-for-fuel-conflict, to overcome this challenge and lower the biodiesel production cost, non-edible oils are used as feedstocks for biodiesel production. Different types of non-edible oils are produced from Pongamia pinnata (Karanja or honge), Jatropha curcas, castor bean seed (*Ricinus communis*), Hevea brasiliensis (rubber seed tree), neem (*Azadirachta indica*), *Azadirachta indica* (neem), *Madhuca indica* and *Madhuca longifolia* (mahua), tobacco seed (*Nicotiana tabacum*), rice bran (Demirbas *et al.*, 2016). Non-edible oils plants can be grown in land that is not used or not suitable for edible food plants, and do not need intensive care, thereby decreasing the cost of production (Atabani *et al.*, 2013; Demirbas *et al.*, 2016). The high free fatty acids (FFA) of most non-edible oils lead to numerous chemical steps for the biodiesel

production this affect the cost of production and may yield low biodiesel (Leung, Wu and Leung, 2010).

Non-edible oils have advantages that attract biodiesel producers. These include their adaptability to be cultivated in wastelands or in non-agricultural areas where there are low soil fertility and low watering demand, ability to be cultivated in both low and high rainfall zones; ability to restore degraded land, and non-competitive behaviour with agricultural resources available and food. Moreover, they require less land per harvest quantity (Atabani et al., 2013).

2.1.3 Used cooking oil as feedstock

Used Cooking or Frying Oil (UFO) is not suitable for human consumption. Also, it causes environmental concerns as it needs to be disposed off safely. Research has found used cooking oil to be a potential raw material for biodiesel production with the benefit of reducing the cost of feedstock (Meher, Vidya Sagar and Naik, 2006). The challenge faced by producing biodiesel using used cooking oil is that the physical and chemical property depends on the content of the original oil. It usually contains impurities from previous processes such as free fatty acids, water and solid particles which will need to be removed by pretreatment (Meher, Vidya Sagar and Naik, 2006).

2.1.4 Microalgae

The use of microalgae in biodiesel production has attracted researchers as it is reported to have high oil content. The rapid growth and low production cost give added advantages associated with the use of algae oil as a biodiesel feedstock (El-Shimi *et al.*, 2013; González *et al.*, 2015). El-Shimi *et al.* (2013) reported that the microalgae have the potential of self-reproduction every two (2) weeks. The oil yield from microalgae can exceed that of the best oilseed tenfold. They also reduce CO₂ from the environment as every kilogram of algal biomass requires about 1.8kg of CO₂. Moreover, they can be grown in wastewater, for each cubic meter of wastewater can produce 800g of dry algae. The other advantage of microalgae as a biodiesel feedstock is that they do not compete with the food market as it is a non-edible substance. Conventional methods have been tested to convert microalgae oil into biodiesel; however, the use of alkali catalyst has shown poor results due to the high FFA content in algae oil. In this case, the acid catalyst or enzyme catalysed processes will be preferred (El-Shimi *et al.*, 2013).

2.1.5 Alcohol

The process of producing biodiesel uses alcohol as acyl acceptors to convert the triglyceride to esters. In such a process, alcohol is always in excess to favour the production of biodiesel. Different types of alcohols are used in biodiesel production; methanol and ethanol are the most preferred. Other alcohols such as propanol, butanol, isopropanol, tert-butanol, branched alcohols and octanol, are not preferred due to their high cost. Methanol is preferred to ethanol since it is less costly and more reactive. Also, the fatty acid methyl esters (FAME) produced from methanol are more volatile as compared to fatty acid ethyl esters (FAEE) produced using ethanol. However, ethanol is less toxic compared to methanol and it can also be from renewable sources via fermentation processes as compared to methanol, which is usually produced from fossil sources. The fuel properties of the FAME and FAEE have not shown much difference except for that FAEE fuels have slightly high viscosities, and low cloud and pour points when compared to FAME (Yusuf, Kamarudin and Yaakub, 2011).

2.1.6 Characteristics of oils

Lipids, which are oils and fats, are hydrophobic materials, they do not dissolve in water and are derived from vegetable plants or animals. At normal condition of temperature and pressure, they are differentiated by their physical states. Chemically lipids are fatty glycerol esters, well-known as triglycerides (Romano and Sorichetti, 2011). Fig. 2-2 shows a general chemical structure of lipids.

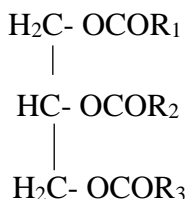


Fig. 2-2: General chemical structure of lipids

Where: R_1 , R_2 and R_3 are hydrocarbon chains of fatty acids, which is mainly from C_{12} to C_{18} . This depends as well on the type of oil and may vary in the presence of double-covalent bonds in each chain.

According to Romano and Sorichetti (2011), the lipids or oils may be from fatty acids which are saturated know as saturated fatty acids (SFA) or non-saturated know as non-saturated fatty acids (NSFA). The saturated fatty acids contain only single covalent bonds in their molecules while the

non-saturated fatty acids containing one or more double covalent bonds in their molecules. The names and chemical formulas of the most fatty acid oils are presented in Table 2-3. The symbolization x:y shows the number of carbon atoms in the oil molecule (x) and the number of unsaturations (y), i.e. double-covalent bonds (y) — for example, y = 0 for all the SFAs. The contents in weight percent of some SFA and NSFA oils are shown in Table 2-4.

Table 2-3: Chemical formulas of the main fatty acids in vegetable oils (Romano and Sorichetti, 2011)

| Fatty acid | Chemical Formula |
|--------------------------|---|
| Lauric (12:0) | $\text{CH}_3 (\text{CH}_2)_{10} \text{COOH}$ |
| Palmitic (16:0) | $\text{CH}_3 (\text{CH}_2)_{14} \text{COOH}$ |
| Stearic (18:0) | $\text{CH}_3 (\text{CH}_2)_{16} \text{COOH}$ |
| Oleic (18:1) | $\text{CH}_3 (\text{CH}_2)_7 \text{CH} = \text{CH} (\text{CH}_2)_7 \text{COOH}$ |
| Linoleic (18:2) | $\text{CH}_3 (\text{CH}_2)_4 \text{CH} = \text{CH} \text{CH}_2 \text{CH} = \text{CH} (\text{CH}_2)_7 \text{COOH}$ |
| Linolenic (18:3) | $\text{CH}_3 (\text{CH}_2)_4 \text{CH} = \text{CH} \text{CH}_2 \text{CH} = \text{CH} (\text{CH}_2)_7 \text{COOH}$ |
| Erucic (22:1) | $\text{CH}_3 (\text{CH}_2)_4 \text{CH} = \text{CH} \text{CH}_2 \text{CH} = \text{CH} (\text{CH}_2)_7 \text{COOH}$ |
| Ricinoleic (18:1) | $\text{CH}_3 (\text{CH}_2)_4 \text{CH} = \text{CH} \text{CH}_2 \text{CH} = \text{CH} (\text{CH}_2)_7 \text{COOH}$ |

The most common fatty acids in oils are lauric, palmitic, stearic, linoleic and linolenic, though other oils may also be found present. It has to be noted that plant oils vary in the composition of fatty acids. To name some, castor oil contains mainly ricinoleic acid, while oleic acid is the main component of soybean oil and linolenic acid in linseed oil. It has to be noted that Table 2-4 does not give the composition of saturated and non-saturated of the fatty acids. For example, the saturated fatty acids in the coconut oil are averaging 90% in which about 45% is lauric acid, while palm oil averaging 49% of saturated fatty acids in which 80% is palmitic acid and soybean oils contains about 60% of non-saturated fatty acids in which 50% is oleic acid. (Romano and Sorichetti, 2011).

Plants oils may have small quantities of monoglycerides and diglycerides; the general formula is shown in Fig. 2-3 and Fig. 2-4. Furthermore, free fatty acids (FFA) may also be presents this may account of less than 1%, excluding palm oil, which can contain up to 15% of FFA. The properties of biodiesel are influenced by the composition of the oil. For example, the cloud point, pour point, iodine value, cetane number is dependent on the numbers of unsaturated bonds and the length of the fatty acid chains. A high iodine value and low solidification point are given by the high content of double-covalent bonds (Romano and Sorichetti, 2011).

Table 2-4: Approximate composition of (SFA) and (NSFA) of some oils and fats (Romano and Sorichetti, 2011)

| Oil/fat | SFA (Weight %) | NSFA (Weight %) |
|---------------|----------------|-----------------|
| Coconut | 90 | 10 |
| Corn | 13 | 87 |
| Cottonseed | 26 | 74 |
| Olive | 14 | 86 |
| Palm | 49 | 51 |
| Peanut | 17 | 83 |
| Rapeseed | 6 | 94 |
| Soybean | 14 | 86 |
| Sunflower | 11 | 89 |
| Safflower | 9 | 91 |
| Castor | 2 | 98 |
| Yellow grease | 33 | 67 |
| Lard | 41 | 59 |
| Beef tallow | 48 | 52 |

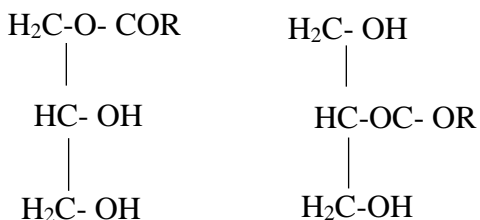


Fig. 2-3: Chemical structure of monoglyceride

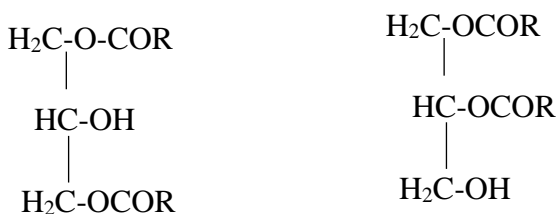


Fig. 2-4: Chemical structure of diglyceride

2.2 Catalysts Used for Biodiesel Production

Catalysts used in biodiesel production can be characterised in three categories; acids, alkalis, and enzymes. Acids and alkalis are classified in two are homogenous and heterogeneous. Alkalis and acids catalysts are the most used in biodiesel production. Recently enzymatic catalysts have attracted the attention of researchers as they have the advantage to prevent soap formation and hence making the separation process simpler (Talha and Sulaiman, 2016). Though enzymatic catalysts have attracted the attention of researchers, their cost implication does not make it cost-effective, and the high reaction time is an added disadvantage. Therefore enzymatic catalysts have been mainly used for experiments purposes, and very few implementations on commercially wise have been reported (Cesarini *et al.*, 2015; Amoah *et al.*, 2016; Pourzolfaghar *et al.*, 2016; Yusoff *et al.*, 2016; Villardi *et al.*, 2017).

2.2.1 Homogeneous base catalysts

Homogeneous alkali catalyst or base catalysts are the most used catalysts in biodiesel production mainly due to the high reaction rate has compared to homogenous acid catalyst (Meher, Vidya Sagar and Naik, 2006; Al-zuhair, Wei and Song, 2007; Lam, Lee and Mohamed, 2010; Talha and Sulaiman, 2016). The mostly use alkali catalysts are: sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium hydroxide forms sodium methoxide (NaOCH_3) and sodium ethoxide ($\text{NaOCH}_2\text{CH}_3$), and potassium hydroxide forms potassium methoxide (KOCH_3). Potassium methoxide (KOCH_3) and Sodium methoxide (NaOCH_3), are more effective catalysts compare to sodium hydroxide (NaOH) and potassium hydroxide (KOH). Those above mainly due to the methoxide having the facility to separate into CH_3O^- and Na^+ and CH_3O and K^+ increasing the biodiesel yield (Talha and Sulaiman, 2016). According to Silitonga *et al.* (2014), the biodiesel production yield can go up to 98.53% with *Calophyllum inophyllum* oil, 1wt. % KOH and 9:1 methanol to oil ratio as feed.

2.2.2 Homogeneous acid catalysts

Some oils contain high FFA that make it challenging to use alkali catalyst, as they lead to soap formation, which affects the separation of esters, glycerol and wash waters. To overcome the separation challenge, homogeneous acid catalysts are suggested. The mainly used acid catalysts in the biodiesel production are sulfuric acid, sulfonic acid, hydrochloric acid, organic sulfonic acid,

and ferric sulphate. Hydrochloric acid and sulfuric acid are preferred and are the most used acid catalysts in biodiesel production. The main disadvantage of acid catalysts is the low reaction rate. Therefore, the main influencing reaction factor is alcohol to oil molar ratio (Atadashi *et al.*, 2013).

2.2.3 Heterogeneous alkali catalysts

Numerous researches have been focused on the use of heterogeneous catalysts to face the challenges of homogeneous catalyst used in biodiesel production. Most of the heterogeneous catalysts used in biodiesel production are either alkali oxide or alkali earth metal oxide which are reinforced by large surface area. Heterogeneous alkali catalysts are reputed to be more active as compared to heterogeneous acid catalyst. Furthermore, solid alkali catalysts, such as calcium oxide (CaO) have many advantages such as higher activity, long catalyst lifetimes, and can be used in moderate reaction condition. However, CaO as a catalyst can also slow down the reaction rate of biodiesel production. CaO can react with glycerol to leach out calcium diglyceride during transesterification reach, consequently requiring much more purification steps such as ion exchange (Lam, Lee and Mohamed, 2010; Avhad and Marchetti, 2015).

2.2.4 Heterogeneous acid catalysts

Though the homogenous acid catalysts are considered to be effective in the biodiesel production, however, they lead to contamination issues which require good separation and product purification processes. The use of homogeneous acid catalysts can lead to high production costs. To solve the challenge emanating from the use of acid catalysts, there is a need to shift to heterogeneous acid catalysts which have the potential as an alternative to homogeneous acid catalysts. Some of the advantages of heterogeneous acid catalyst are insensitive to FFA content, used for both esterification and transesterification, thereby eliminating the washing step of biodiesel, more straightforward separation process of catalyst from the product, regenerating and reusing the catalyst is possible and also reduce the corrosion problems. Furthermore, solid acid catalysts are favoured over liquid acid catalysts because they contain numerous sites with different strength of Bronsted or Lewis acidity. Bronsted acid catalysts have the advantage of being used for both esterification and transesterification with the use of low-cost feedstock having a high concentration of free fatty acids (Lam, Lee and Mohamed, 2010).

2.2.5 Enzymatic catalysts

Enzymatic catalysts lipases liquid or immobilised have attracted researchers' attention due to the advantages such as insensitivity to FFA and water, no soap formation, purity of the products, the low energy required, recycling of enzymes, more environments friendly, separation of enzymes with products and avoids the production of undesired products. Some disadvantages are sensitivity to excess methanol, low rate and cost of catalysts (Dizge *et al.*, 2009; Cesarini *et al.*, 2015; Amoah *et al.*, 2016; Pourzolfaghar *et al.*, 2016; Santin *et al.*, 2017; Villardi *et al.*, 2017). Some factors affecting this process is economic viability, yield, oil to alcohol ratio (substrates), acyl acceptors and bioreactor design. Lipases are carboxylesterases characterised as animal, plant and microbial- based on their origins, the more stables are the ones from microbiological source and used in biodiesel catalysis. Though lipases are classified as fatty acid-specific; 1, 3-specific; and non- specific, for high yield the non-specifics should be used as they can convert all forms of triglycerides. The immobilisation of the pure lipase increases the production cost; this furthermore increases the mass transfer resistance this caused by the fact that the enzyme is solid and other substrates are liquids. Though enzymatic catalysis avoids the formation of undesired products, this is the cause of the low reaction rate and affect the yield (Alvarez *et al.*, 2016; Price *et al.*, 2017). Alvarez *et al.* (2016) reported that the production of biodiesel using lipases could yield up to 96%.

2.2.6 Waste-derived heterogeneous catalysts

Biodiesel production has been challenged by the high production cost due to the cost of feedstocks, therefore, to reduce this cost of manufacturing, the use of heterogeneous catalyst is a promising option which will make the biodiesel being competitive with petro-diesel fuels. Researchers have been working towards developing an environmentally friendly and low-cost heterogeneous catalyst for biodiesel production. For the sustainability of biodiesel production, the interest has been shifted to the use of waste heterogeneous. Due to their higher activity at low temperature and atmospheric pressure, alkaline earth metal oxides such as MgO, CaO, and SrO have been used. The raw materials to produce CaO are: $\text{Ca}(\text{NO}_3)_2$, CaCO_3 , or $\text{Ca}(\text{OH})_2$. CaO has been synthesised for catalysis using different methods than the conventional. Natural sources of Calcium from waste such as mollusk shell, eggshell and bone have been reported to be used in transesterification. The use of waste to synthesise Calcium Oxide for catalysis has as the advantage of reducing the biodiesel production

cost and also reducing the waste management costs. A purity of 98.4% achieved in a 5 hours reaction time was reported in the literature (Talha and Sulaiman, 2016).

2.3 Methods of Biodiesel Production

There are various methods used in biodiesel production, which are currently available and have been approved for the production biodiesel. There are mainly four methods used in biodiesel: direct use and blending of raw oils, micro-emulsions, thermal cracking, and transesterification. The most used method reported by researchers is the catalytic transesterification reaction of oils (Mahanta and Shrivastava, 2004; Leung, Wu and Leung, 2010; Yusuf, Kamarudin and Yaakub, 2011; Idusuyi *et al.*, 2012; Atadashi *et al.*, 2013).

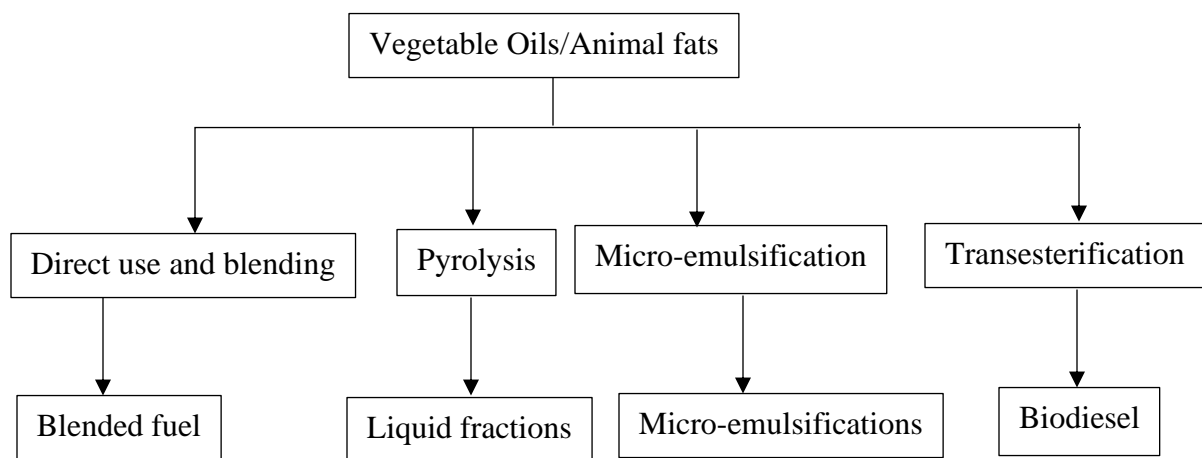


Fig. 2-5: Flow chart of methods used in biodiesel production (Atabani *et al.*, 2013)

2.3.1 Direct use and blending

It has been reported that 100% of vegetable oil has been used with some moderate modifications of the engine. The main challenges have been the high viscosity, acid composition, free fatty acid content, therefore need to be modified (Pramanik, 2003; Ramadhas, Jayaraj and Muraleedharan, 2004). Dilution oil blend is done by mixing with petroleum diesel in other ways called blending; oil has also been used directly as fuel in engines. Various researchers reported the successful experiment of bending vegetable oil with petroleum diesel. A blend consisted of 95% of filtered used oil and 5 % petroleum diesel; this experiment was performed in 1982. Earlier, in 1980 Caterpillar a Brazilian based company employed pre-combustion chamber engines in which the fuel was mix with 10% of

vegetable oil and 90% of petroleum diesel to maintain the full capacity of the engine without any modification (Yusuf, Kamarudin and Yaakub, 2011; Balakrishna, 2012).

2.3.2 Pyrolysis

Pyrolysis, also known as cracking, has been defined as the burning of organic matters in the absence of air producing gas, liquid, solid products. The cracking is done under the presence of catalysts, these break oils and fats into smaller components (Mahanta and Shrivastava, 2004; Yusuf, Kamarudin and Yaakub, 2011; Sani, Daud and Abdul, 2013). This method is used to produce olefins and paraffin having the same properties to petroleum diesel where such products derived the name “diesel-like-fuel” (Sani, Daud and Abdul Aziz, 2013). It has been reported that optimum temperature for high yield, should be between 400°C to 450°C. The temperature, catalysts and heat rate are the major parameters affecting the yield. The advantages of pyrolytic products are: they are clean liquids as they do not need washing, drying or filtering, they contain less sulfur and ash. However, the products of pyrolysis have made characterisation challenging as they contain substances such as water, sulfur, particulate matter, alkanes, alkenes and carboxylic acids. The pyrolysis requires high energy consumption and needs expensive distillation (Srivastava and Prasad, 2000; Sani, Daud and Abdul, 2013). The liquid fractions of pyrolysis of vegetable oils have properties approaching the ones of petroleum diesel fuels and have lower flash and pour point, viscosity, cetane number, sulfur, water and sediments, and copper corrosion values but ash, carbon residual and pour point are in unacceptable limits. The pyrolysis process is classified into three classes: conventional pyrolysis, fast pyrolysis and flash pyrolysis (Mahanta and Shrivastava, 2004).

2.3.3 Microemulsion

Microemulsion is a microstructure of dimensions ranging 1-150nm which is formed from two immiscible fluids and one or more ionic amphiphiles. This microstructure is a colloidal equilibrium dispersion of fluid. Microemulsion is often made of vegetable oils with an ester and a cosolvent or made with alcohols such as ethanol, butanol, hexanol and a surfactant, to this a cetane improver is added, this also or without the addition of diesel fuels. To overcome the challenge of high viscosity of vegetable oils microemulsion was found to be a reliable approach to decrease the viscosity. Using ethanol, butanol and hexanol, the produced fuel was reported to meet the specification of viscosity

required for diesel fuel. It was shown that short-term performances of ionic and non-ionic microemulsions of ethanol in soybean oil are comparable to the one of No.2 diesel fuel (Mahanta and Shrivastava, 2004; Ramadhas, Jayaraj and Muraleedharan, 2004; Demirbas, 2009; Parawira, 2010; Yusuf, Kamarudin and Yaakub, 2011; Balakrishna, 2012; Idusuyi *et al.*, 2012; Atabani, 2013).

2.3.4 Transesterification

Transesterification also known as alcoholysis is the most used method for biodiesel production mainly due to its simplicity and lower cost (Sharma and Singh, 2009; Balat and Balat, 2010; Sani, Daud and Abdul, 2013). Transesterification occurs by reacting oil or fat and alcohol generally methanol at a designed temperature in the presence of a catalyst. Therefore, there is a restructuration in the chemical structure of the oil or fat. The conversion adds as a benefit of reducing the high viscosity of the oils and fats. Transesterification occurs in three consecutive reversible reaction steps in which one molecule of alkyl ester is released at each step and glycerol being released at the end (Fangrui and Hanna, 1999; Lam, Lee and Mohamed, 2010; Knothe and Razon, 2017). The conversion yields three layers, which are: glycerol at the bottom, a middle layer of soapy substance, and biodiesel on top. Transesterification is a reversible reaction. Therefore there is a need to have alcohol in excess. Catalysts are required to improve the rate of transesterification. The type of catalyst dictates the reaction conditions, feedstock compositional limits and post-separation requirements (Balat and Balat, 2010; Shahid and Jamal, 2011; Sani, Daud and Abdul, 2013; Verma and M P Sharma, 2016).

The transesterification reaction is classified into two, which are catalytic transesterification and non-catalytic transesterification (Balat and Balat, 2010). The catalytic transesterification can either be: homogeneous (acid and alkaline) transesterification, where the catalyst is in the same phase as the reactants (liquid catalyst); heterogeneous (acid and alkaline) transesterification, where a solid catalyst is used or enzymatic transesterification, where enzymes are used as catalysts (Balat and Balat, 2010; Thanh *et al.*, 2012; Adewale, Dumont and Ngadi, 2015; Verma and Sharma, 2016; Hanis *et al.*, 2017), and assisted transesterification such as microwave-assisted transesterification (Adewale, Dumont and Ngadi, 2015) and ultrasound-assisted transesterification (Adewale, Dumont and Ngadi, 2015). The non-catalytic is supercritical alcohol transesterification (Ortiz-Martínez *et al.*, 2019). The catalysts used in the catalytic transesterification are discussed in section 2.3. A general transesterification reaction is shown in Fig. 2-7.

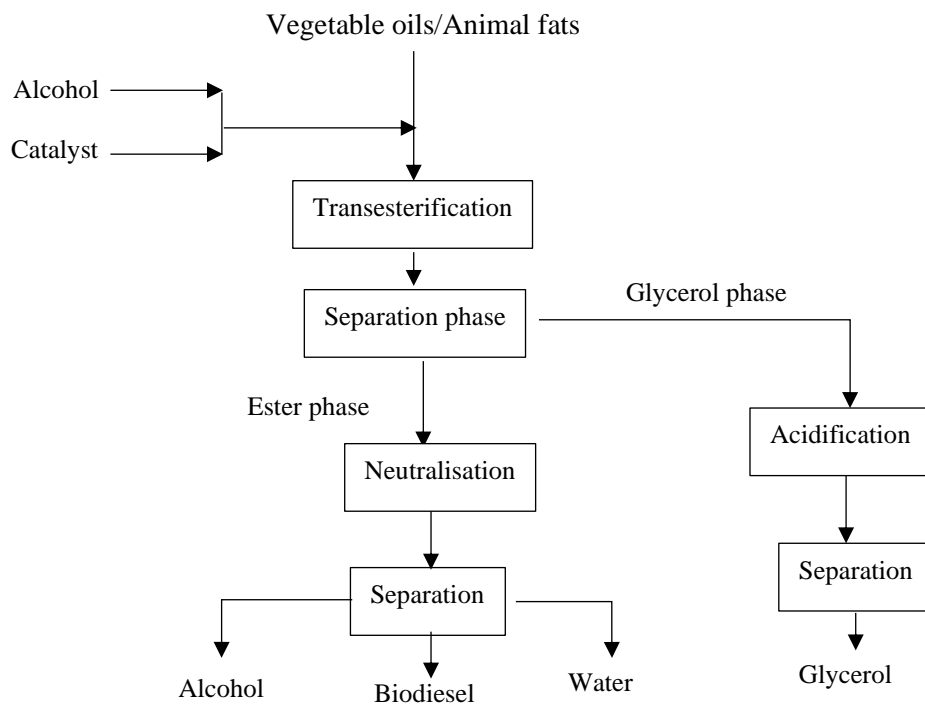


Fig. 2-6: Typical catalysed transesterification process

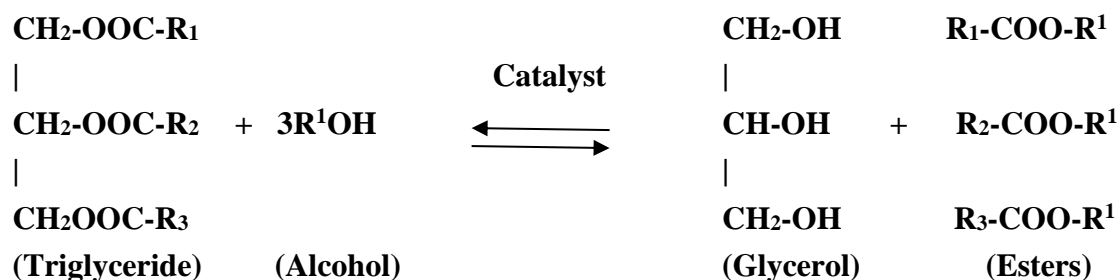


Fig. 2-7: Transesterification reaction

2.3.5 Supercritical alcohol transesterification

Supercritical transesterification is a single-phase homogeneous reaction which is different to conventional transesterification which involves the reaction of two heterogeneous liquid polar (alcohol) and non-polar (triglycerides). The reactants containing hydroxyl groups such as water and alcohol are subjected to parameters in excess of their critical points making them to act as superacids

(Kusdiana and Saka, 2004; Sani, Daud and Abdul, 2013). Under supercritical conditions, alcohol plays two roles firstly as an acid catalyst and secondly as a reactant (Kusdiana and Saka, 2004; Pinnarat and Savage, 2008). The mass transfer limit is solved by the absence of interphase. Therefore, the reaction time is shortened as the reaction is completed in a few minutes instead of several hours. The McGlyan Process was used to produce biodiesel under 4 seconds (McNeff *et al.*, 2008). Nevertheless, this process is not cost-effective, especially for industrial-scale production, as it requires expensive reacting equipment due to high temperature and pressure. Researchers are working towards reducing these high reacting conditions (Yin, Xiao and Song, 2008).

2.3.6 Microwave-assisted transesterification

The transfer of energy by microwave radiation is performed in the region of infrared radiation and radio-waves in the electromagnetic spectrum; their wavenumbers vary between 1 mm–1 m. Microwave irradiation has found application in different chemical reactions from organic synthesis to selective absorption of microwave energy by nonpolar and polar molecules these being inert to the microwave dielectric loss (Adewale, Dumont and Ngadi, 2015).

The microwave irradiation has attracted researchers attention as an energy stimulant. Mainly due to the speed of the reaction process, that can occur in a very short period of time, it uses a lower alcohol-oil ratio, and it decreases the number of by-products. It employs a continuously changing electrical and magnetic fields to activate the smallest degree of variance of the reacting molecules. These speedily rotating charged ions interrelate simply with minimal diffusion limitation (Azcan and Danisman, 2007). However, this process also has an industrial scale-up problem due to the high operating conditions and safety aspects. An even more discouraging challenge is in increasing the irradiation penetration depth beyond a few centimetres into the reacting molecules (Sani, Daud and Abdul, 2013).

2.3.7 Ultrasound-assisted transesterification

Chemical processes apply ultrasound to improve mass transfer and chemical reactions this with the advantage of shortening the reaction times and uses cheap chemicals. The application of ultrasound-assisted transesterification has been found to improve or have high reaction rates, hence decreasing reaction time. The used of sound energy at a frequency higher than human hearing is used in the ultrasound-assisted transesterification. The frequencies of the ultrasound range from 20 kHz and 10

MHz, this with associated acoustic wavelengths in liquids ringing 100–0.15 mm(Adewale, Dumont and Ngadi, 2015).

The reaction occurs by stretching and compressing molecules alternatively. The application of high negative pressure employed above critical molecular distance lead to cavitation bubbles. The emulsification and fast reaction rates with high yields are caused by some of the bubbles which suddenly expand to unstable sizes and falls violently as the phase boundary has been disrupted (Stavarache *et al.*, 2005; Adewale, Dumont and Ngadi, 2015; Ho, Patil *et al.*, 2018).

2.4 Major factors affecting Biodiesel yield.

The major factors affecting biodiesel yield are methanol to oil ratio, catalyst ratio, reaction temperature, reaction time, mixing rate, water content and FFA content. At subcritical alcohol states, the reaction rate is relatively low and increase proportionally with the increase in temperature (Demirbas *et al.*, 2016). In this work, a short discussion on five factors, namely alcohol to oil ratio, catalyst ratio, reaction time, reaction temperature and mixing rate, are reported.

2.4.1 Alcohol to oil molar ratio and type of alcohol

main factors affecting the biodiesel yield is the alcohol to oil molar ratio (Meher, Vidya Sagar and Naik, 2006; Leung, Wu and Leung, 2010; Verma and Sharma, 2016; Verma, Dwivedi and Sharma, 2017). Stoichiometrically triglyceride reacts with three moles of alcohol to yield three moles of fatty acid methyl ester and one molecule of glycerol. Transesterification reaction being a reversible reaction will favour the direction producing biodiesel when the methanol is added in excess (Barnwal and Sharma, 2005; Leung, Wu and Leung, 2010; Verma and Sharma, 2016). Leung, Wu and Leung (2010) stated that a further increase of alcohol to molar ratio would not increase the yield but increase the production cost since excess methanol increases recovery cost. According to Meher, Vidya Sagar and Naik (2006), higher alcohol to oil molar ratio than the optimum, interferences in the separation will be created as there will be an increase in solubility.

Moreover, having glycerol in the solution will favour the backward reaction. This implies that, with a low ratio and glycerol present, the yield will significantly be decreased. It is to be noted that, the molar ratio is proportional to the type of catalyst used and the most investigated ratio has been 6:1 where alkaline catalysis was employed (Barnwal and Sharma, 2005; Leung, Wu and Leung, 2010).

However, higher alcohol to oil molar ratio of about 40:1 in supercritical alcohol transesterification (Sharma and Singh, 2009). Freedman, Pryde and Mounts, (1984) produced alkaline catalysed biodiesel at a ratio of 6:1 yielding 98 %. The presence of free fatty acids at a considerable quantity such as in waste cooking oil, having high alcohol to oil ratio 15:1 is recommended, and acid catalysed transesterification will be employed (Ali, Hanna and Cuppett, 1995; Leung and Guo, 2006). With a high acid content, two step-transesterification can be preferred with a molar ratio of 6:1 for acid transesterification and 9:1 for alkaline transesterification (Sharma, Singh and Upadhyay, 2008).

The alcohols reported to be used in biodiesel production are methanol, ethanol, propanol, butanol, these were reported not to have much difference in the biodiesel yield. Methanol has been reported to be toxic, but the most preferred alcohol, mainly due to its low cost. Contrary to methanol, ethanol is not of preference due to its low reactivity as compared to methanol. The viscosity of ethyl esters is slightly higher as compared to one of the methyl esters, ethyl esters also have low cloud points and pour point (Dossin *et al.*, 2006). Methanol has been reported to be suitable in biodiesel production. Methanol has a lower boiling point of 64.7 °C, and the transesterification is performed around that temperature though methanol in its vapour phase has to be avoided due to high toxicity as it can cause blindness and can be found around the reaction site (Madras, Kolluru and Kumar, 2004). Alkaline catalysed transesterification causes the formation of stable emulsification, which is a challenge as they make difficult the separation process of glycerol and ethyl esters. In contrast, methanol emulsification during catalysed transesterification is not stable as they emulsions can simply and rapidly be broken down to produce glycerol and methyl ester (Zhou, Konar and Boocock, 2003). The formation of intermediate (mono and diglycerides) are the ones responsible for the formation of emulsions, and these intermediates have non-polar and polar hydrocarbon chains. The emulsions are formed at intermediate critical concentration level. There is a bigger non-polar group in ethanol as compared to methanol, this larger non-polar group in methanol is the factor affecting the stability of the emulsion in transesterification of oil with ethanol. Nevertheless, the mono and diglycerides are low, therefore making the emulsion to become unstable (Meher, Vidya Sagar and Naik, 2006).

2.4.2 Catalyst type and concentration

Generally, the catalyst used in the biodiesel production are: acid, alkaline and enzymatic, these catalysts can either be homogeneous or heterogeneous (Meher, Vidya Sagar and Naik, 2006). Ma

and Hanna, (1999) reported Sodium hydroxide, sodium methoxide, Potassium hydroxide, potassium methoxide to be the more effective catalysts used in the biodiesel production. However, the alkaline catalyst above mentioned are not suitable for oils and fats containing a high amount of free fatty acid and water as they will lead to saponification; therefore acid catalysts are preferred (Meher, Vidya Sagar and Naik, 2006). Among the most used acid catalyst are Sulfuric acid, hydrochloric acid, phosphoric acid and organic sulfonic acid (Meher, Vidya Sagar and Naik, 2006). According to Ahn *et al.*, (2006), the quality of biodiesel produced with alkaline catalysts depends on the quality of oil and the yield is affected by the amount of catalyst. Freedman, Butterfield and Pryde, (1986) reported almost the same yield at catalyst ratios of 1 wt. % and 0.5 wt. % of NaOH and NaOCH₃, respectively, at oil to alcohol ratio of 6:1 and 60 minutes.

Alkaline transesterification mainly uses potassium hydroxide or sodium hydroxide; the two catalysts are in the range of 0.4 to 2 wt. %. It has been reported that when using crude or refined oils 1 wt. % yielded high conversion or is the ratio of the optimum catalyst. This ratio also gave the best viscosity (Tomasevic and Siler-Marinkovic, 2003). Some alkaline earths have been employed in the catalysed transesterification. The use of alkoxides, alkaline-earth and oxides catalysed transesterification had low rate due to the three-phase system constituted of oil- methanol-catalyst, the reaction is inhibited by diffusion (Gryglewicz, 1999). Some heterogeneous oxide catalysts such as calcium hydroxide, magnesium oxide, calcium methoxide, calcium oxide, barium hydroxide were investigated and compared with the one of sodium hydroxide, though sodium hydroxide gave a high yield of about 85 % in 30min this yield was reached with an increase in time to 2.5 hours (Meher, Vidya Sagar and Naik, 2006).

Chemical catalysts being the most used and offer high yield however it is to be noted that they offer some disadvantages such as high energy consumption, difficulty in recovering glycerol, removal of acid or alkaline is needed, wastewater treatment required for alkaline catalysts and the presence of FFA and water interfere with the transesterification. Therefore, enzymatic catalyst can be preferred as they can be used in aqueous or non-aqueous systems overcoming the abovementioned challenges of chemical catalysts. However, the cost of the catalyst is reported to increase the production cost as the cost of lipase, the mainly used enzymatic catalyst is relatively high (Meher, Vidya Sagar and Naik, 2006). Ion-exchanger has been reported to be used in catalysed transesterification this with the success of convert up to 45.7 % FFA present in the oil (Özbay, Oktar and Tapan, 2008) this will make possible the soap stock to be used as a suitable feedstock as it has high FFA content.

2.4.3 Reaction time

Researchers reported that the fatty acid esters conversion rate depends on reaction time by increasing the yield as the time increase (Freedman, Pryde and Mounts, 1984; Meher, Vidya Sagar and Naik, 2006; Leung, Wu and Leung, 2010; Verma and Sharma, 2016; Verma, Dwivedi and Sharma, 2017). In the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil (Freedman, Pryde and Mounts, 1984; Meher, Vidya Sagar and Naik, 2006). Leung, Wu and Leung (2010) reported that usually, the yield reaches a maximum at a reaction time less than 90 minutes and then remains relatively constant with a further increase in the reaction time, the reaction time of 90 minutes is mainly when Sodium and Potassium hydroxide are used (Mwenge, Pilusa and Seodigeng, 2018). The time needed to reach a high yield becomes higher when heterogeneous solid catalysts are used (Modiba, Enweremadu and Rutto, 2015) and in enzymatic catalysis (Mumtaz *et al.*, 2014; Ilmi *et al.*, 2017; Villardi *et al.*, 2017). Also, the increase in time might cause the decrease of yield due to the reverse reaction, and causing loss of esters and leading to the formation of soaps (Leung, Wu and Leung, 2010).

2.4.4 Reaction temperature

The type of oil used for the transesterification reaction of triglyceride determine the range of temperature needed to be used. Temperature influences the reaction yield of biodiesel production. At high temperature, the viscosities of oils can increase the reaction rate and a shortened reaction time. The reaction temperature must be lower than the one of the boiling point of alcohol to avoid vaporisation of alcohol (Leung and Guo, 2006; Meher, Vidya Sagar and Naik, 2006; Leung, Wu and Leung, 2010; Verma, Sharma and Dwivedi, 2016).

Nevertheless, reports show that when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides (Leung, Wu and Leung, 2010; Verma, Sharma and Dwivedi, 2016). This is in disagreement with Sánchez *et al.*, (2015) who in their experiments with higher temperature observed better conversion with no much change with further increase. After using Methanol and ethanol, there was no significant change in the yield, but n-butanol and 2- propanol were affected by the increase in temperature. However, due to energy consumption being high at

high temperature, it will be advised to use the lowest temperature giving the highest yield. (Meher, Vidya Sagar and Naik, 2006; Leung, Wu and Leung, 2010).

2.4.5 Mixing rate

Mixing rate is one of the most critical factors affecting biodiesel production as oils and fats are immiscible with methanol and catalysts. When the two phases are mixed, the reaction, then starts (Barnwal and Sharma, 2005; Meher, Vidya Sagar and Naik, 2006; Sharma and Singh, 2009). Ma, Clements and Hanna, (1999) conducted experiments with mixing the reactant, and without mixing, their findings were that no reaction was observed when the mixture was not mixed. This implies that the mixing rate is one of the significant factors affecting biodiesel production yield. Meher, Dharmagadda and Naik, (2006) conducted experiments using three different mixing rate, very low yield was observed at 180RPM, while it was almost the same at 360RPM and 600RPM. Veljković *et al.*, (2006), obtain optimum yield at a mixing rate of 400RPM.

There are four reported methods used to stir components in the biodiesel production (Verma, Sharma and Dwivedi, 2016). Yin *et al.* (2012), give the four different methods used in biodiesel production.

- a) Mechanical stirring (MS).
- b) Flat plate ultrasonic irradiation (FPUI).
- c) Flat plate ultrasonic irradiation with mechanical stirring (UIMS).
- d) Probe ultrasonic irradiation (PUI).

It has been reported that using the same conditions, UIMS and PUI have less catalyst and alcohol consumption, they also have high reaction rate, and less energy consumption as compared to MS and FPUI for the same biodiesel production rate. Using the same catalyst and catalyst, the biodiesel production from high to low was PUI, UIMS, FPUI and MS (Verma, Sharma and Dwivedi, 2016).

2.5 Physicochemical Properties of biodiesel

Numerous researches have been done on the biodiesel production, and it is imperative to determine the biodiesel fuel properties to be used in replacement or in blending with petroleum diesel. With the advancement of biodiesel production, biodiesel quality has been developed worldwide to maintain the quality of the biodiesel produced to guarantee the standards of biodiesel storage and successful commercial purposes. Biodiesel being produced from various countries, as the biodiesel

quality is affected by the quality of feedstock, the implementation of standardisation of fuel to ensure engine performance (Balat and Balat, 2010; Lin et al., 2011).

Many Countries have come up with standards to regulate biodiesel producers. The first country was Austria, which firstly defined and approved the rapeseed biodiesel. Others countries have followed; these countries are Germany, France, Italy, the Czech Republic and the United States of America (Meher, Vidya Sagar and Naik, 2006). International biodiesel standard specifications that are nowadays available and globally referred to includes: the American Standards for Testing Materials (ASTM 6751-3) and the European Union (EN 14214) Standards for biodiesel fuel (Atadashi, Aroua and Aziz, 2010). Nevertheless, there are also other countries, which established their standards and have been made globally available; these countries are Austria (ON), Czech Republic (CSN) and Germany (DIN 51606) (Lin et al., 2011). The biodiesel standards are classified by their physiochemical properties. These properties are: density (kg/m³), viscosity (mm²/s), cetane number, caloric value (MJ/kg), acid value (mg KOH per g-oil), iodine number, cloud and pour points (oC), flash point (oC), carbon residue (wt. %), ash content (wt. %), water and sediment content (wt. %), Copper strip corrosion (3h at 50 oC), Cold filter plugging point (oC), glycerine (wt. %), Carbon (wt. %), Hydrogen (wt. %), Oxygen (wt. %), methanol content (wt. %), sulphur content (wt. %), Sulphated Ash (wt. %), phosphorus content (wt. %), monoglyceride (wt. %), diglyceride (wt. %), triglyceride (wt. %), distillation temperature (oC), Oxidation stability (hrs, 110 oC), lubricity (HFRR High Frequency Reciprocating Rig; μm) and oxidation stability (Demirbas, 2008; Atadashi, Aroua and Aziz, 2010; Jena et al., 2010; Lin et al., 2011; No, 2011). Table 6 summaries the physiochemical properties of diesel and biodiesel properties according to ASTM 6751 and EN 14214 specifications.

There are problems associated with the direct used of vegetable oils or blended in diesel engines; these problems are classified into long and short term. These problems make direct use or blending, not practical. These are: poor cold engine start-up, misfire, ignition delay, incomplete combustion, gum formation due to oxidation and polymerization during storage and combustion, the high viscosity, low volatility, acid composition, ring sticking, injector choking in engine free fatty acid and moisture content carbon deposition around the nozzle orifice and lubricating oil thickening (Agarwal, 2007; Bozbas, 2008; Yusuf, Kamarudin and Yaakub, 2011; Atabani, 2013).

Table 2-5:ASTM D975, ASTM 6751 and EN14214 specifications of diesel and biodiesel fuels (Liu, Xin and Yan, 2009; Atadashi, Aroua and Aziz, 2010; Balat and Balat, 2010; No, 2011; Ragit et al., 2011; Wang et al., 2011; Atabani, 2013).

| Property Specification | Unit | Diesel ASTM D975 | Biodiesel | |
|------------------------------|--------------------|------------------------|---------------|-----------|
| | | | ASTM D6751 | EN 14214 |
| Density at 15 °C | Kg/m ³ | 80-860 | 880 | 860-900 |
| Kinematic Viscosity at 40 °C | mm ² /s | 2.0 to 4.5 | 1.9-6.0 | 3.5-5.0 |
| Cetane Number | - | 46 | 47 min. | 51 min |
| Iodine Number | - | 38.3 | - | 120 max. |
| Calorific Value | MJ/kg | 42-46 | - | 35 |
| Acid Value (number) | mgKOH/g | 0.062 | 0.5 max. | 0.5 max. |
| Cloud Point | °C | -35 | -15 to -16 | - |
| Pour Point | °C | -20 | -3 to -12 | - |
| Flash Point | °C | 60 to 80 | 100 min. | 120 min |
| Cold filter plugging point | °C | -25 | 19 | 5 max |
| Copper strip corrosion | (3h at 50 °C) | 1 | 3 max | 1 min |
| Carbon Residue | wt. % | - | 0.50 max. | 0.30 max |
| Ash Content | wt. % | 0.01 | 0.02 | 0.02 |
| Water and sediment content | vol. % | 0.05 | 0.05 max | 0.05 max |
| Carbon | wt. % | 84-87 | 77 | - |
| Hydrogen | wt. % | 12-16 | 12 | - |
| Oxygen | wt. % | 0-0.31 | 11 | - |
| Methanol content | wt. % | - | 0.2 max. | - |
| Sulphur content | ppm | 500 max | 500 max. | 10 max. |
| Sulphated Ash | wt. % | 0.02 | 0.02 | |
| Phosphorus content | wt. % | 0.001 | 0.0004 | |
| Free glycerine | wt. % | - | 0.02 max | 0.02 max. |
| Total glycerine | wt. % | - | 0.24 max. | 0.25 |
| Monoglyceride | wt. % | - | 0.52 | 0.8 |
| Diglyceride | wt. % | - | - | 0.2 |
| Triglyceride | wt. % | - | - | 0.2 |
| Distillation temperature | °C | - | 360 max. | - |
| Oxidation stability | hrs, 110 °C | - | 3 min | 6min |
| Lubricity HFRR | µm | 685 | 314 | - |

2.6 Biodiesel yield Optimisation

The yield of the biodiesel production can be optimised by the use of statistical tools, applying the design of experiments. Design-Expert (Tshizanga, 2015) and Minitab (Hamze, Akia and Yazdani, 2015) software are among the tools that can be used for that end.

There are different statistical tools that can be used to optimise the biodiesel yield. Some of these tools are factorial design, fractional factorial, response surface methodology (RSM) and crossed and mixture design (Tshizanga, 2015). Response surface methodology will be discussed at length. It has been reported that the optimisation is a crucial step in production; the optimisation is accomplished by improving the operating parameters. The optimisation has been reported to be time-consuming and costly as it requires repeating of costly experiments. Additionally, it is to be noted that for the reason of concurrent effects of some operating parameters on the system, the design and application of modelling tools such as response surface methodology (RSM) is crucial for maximum production and as well as reducing the cost (Hamze, Akia and Yazdani, 2015; Mäkelä, 2017)

Response surface methodology (RSM) is defined as a package of mathematical and statistical techniques for an empirical model building. The objective of the response surface methodology is to optimise a response which is an output variable, this is done by carefully selecting the design of experiments, and this is influenced by the numerous input parameters which are considered as independent parameters. A series of tests are called experiments, and these tests are also called runs. The changes are made on the input with the purpose to determine the causes of the effect on the output response (Gunst, Myers and Montgomery, 2006; Hamze, Akia and Yazdani, 2015).

RSM uses three different mode of operation or techniques (Morshedi and Akbarian, 2014), which techniques are:

- i. statistical experimental design, this is mainly a two-level fractional or factorial design,
- ii. regression modelling techniques, and
- iii. Optimisation methods.

RSM finds its application in the various domain such as: in biological, clinical and industrial sciences, Food Science, Social Science, and Engineering and Physical Sciences. The primary objective of the RSM is to find the optimum response. In the case of more responses, it becomes

crucial to find the optimum compromise responses that optimise all responses in the system. The second objective is to determine the effect on the responses in a given direction by varying or adjusting the design parameters. In the probabilistic analysis, there is a need for developing a functional relationship between input parameters and output responses; this functional relationship can either be implicit or explicit. The functional relationship is often challenging to implement apart in simple cases but can also be complicated. There is a proposed concept of RSM in order to establish an approximate explicit functional relationship as shown in (2-1) (Morshedi and Akbarian, 2014).

$$Y = f(x_1, x_2, x_3 \dots \dots x_k) + e \quad (2-1)$$

Where x_1, x_2, x_3 are inputs, 'e' is the sources of uncertainty does not account in the function 'f', such as measuring errors on the output function and Y is the response.

Relationship denoted in (1) can be a simple linear or factorial model, or more complex quadratic or cubic model. Generally, a quadratic regression has been often used to approximate Y ; a quadratic equation is shown in (2) (Morshedi and Akbarian, 2014)

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_i^2 + \varepsilon \quad (2-2)$$

Where β_0 is the average value Y , β_i, β_{ij} and β_{ii} the first order, interaction and quadratic coefficients, respectively, x_i is the coded factors, and ε is the model residual. The response surface can be visualised graphically, and the visualisation can be three dimensional or on a contour plot (Morshedi and Akbarian, 2014).

2.6.1 Design of experiments

The design of experiments (DoE) is very crucial in optimising a specific process. DoE was initially established to fit the model of physical experiments; its application in numerical experiments was also reported. The aim is to select points that will help in the evaluation of the response. The criterion to optimise a system evolves around mathematical modelling. The mathematical models are mainly polynomials, which contain an unknown structure. The choice of a design of experiments has an essential effect on the precision of the approximation and the RSM constructing cost. When some variables are considered from the early stage of the building, the DoE to have little effect on the response screening is often performed, this to identify variables that significantly affect the response. Generic programming has been reported to be used for the screening process (Gunst, Myers and

Montgomery, 2006; Morshedi and Akbarian, 2014). Morshedi and Akbarian (2014), explained that DoE is defined by the combination of a set of runs, and the settings of independent parameters in the N dimension is defined as levels.

Design of experiments uses numerous methodologies, and the mainly used are Central Composite Design (CCD) and Box-Behnken (Gunst, Myers and Montgomery, 2006; Morshedi and Akbarian, 2014; Mäkelä, 2017). The other techniques or approaches are Fractional Factorial (Mäkelä, 2017), Full factorial design, D-optimal design, Latin hypercube design, Audze-Eglaiss' approach, Taguchi's contribution to experimental design and Van Keulen's approach (Gunst, Myers and Montgomery, 2006; Morshedi and Akbarian, 2014).

2.6.2 Central Composite Design

Central composite design (CCD) is the most used design of experiments and consists of points (from a 2^q design and 2^{q-k} fractional factorial design), central points, and axial. Axial points help in improving a model in which there is evidence of lack of fit in a first-order model. The axial points are added to the quadratic terms with more centre points to develop a CCD. CCD has as major parameters the number of centre points n_c at the origin and the distance a of the axial runs. The surface curvature information is contained in the centre runs. Efficient estimation of the quadratic terms can be obtained in a case where the curvature is significant by allowing additional axial points. The experimenter employs a second-order model to describe the model in the case where the first-order model showed a significant lack of fit. Since the response surface can represent maximum, minimum, ridge and saddle point, the location of the optimum value can be found on the stationary point. From this stationary point, an experimenter is used to give a conclusion on whether to stop continuing with surface study (Morshedi and Akbarian, 2014).

Fig. 2-8 bellow is an example of CCD, in comprises $2N$ factorial points, $2N$ axial points and one central point. CCD is an alternative to $3N$ designs to construct a second-order model; this helps in reducing the number of runs 15 as compared to a full factorial design which requires 27 runs (Gunst, Myers and Montgomery, 2006)

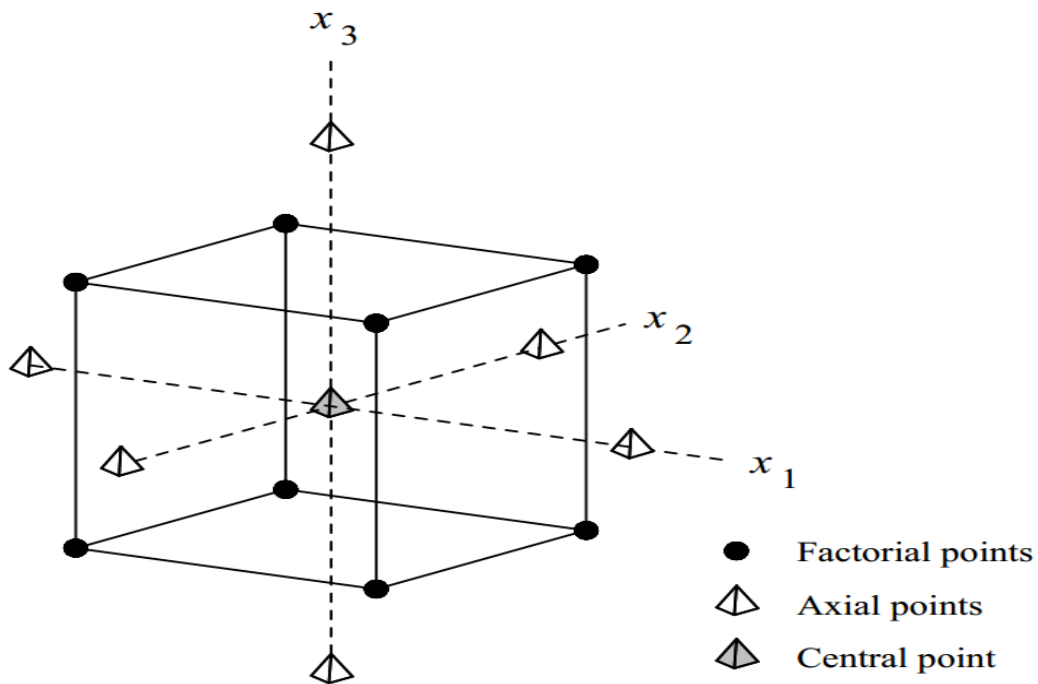


Fig. 2-8: Central composite Design for three design variables at two-level (Gunst, Myers and Montgomery, 2006)

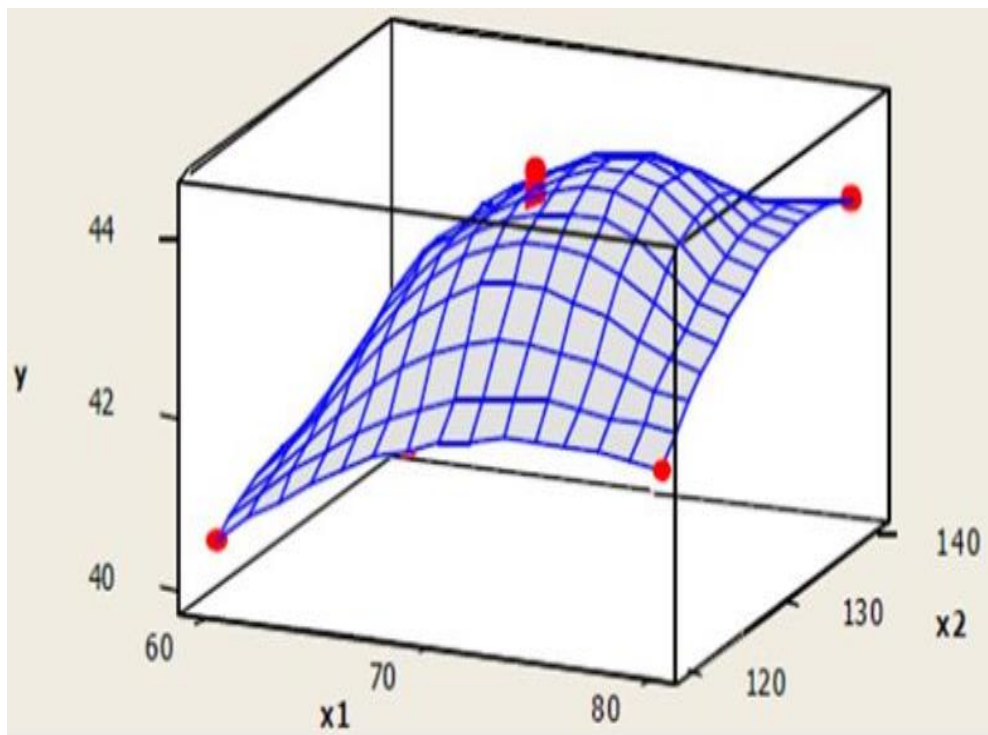


Fig. 2-9: Response surface 3-D plot (Morshedi and Akbarian, 2014)

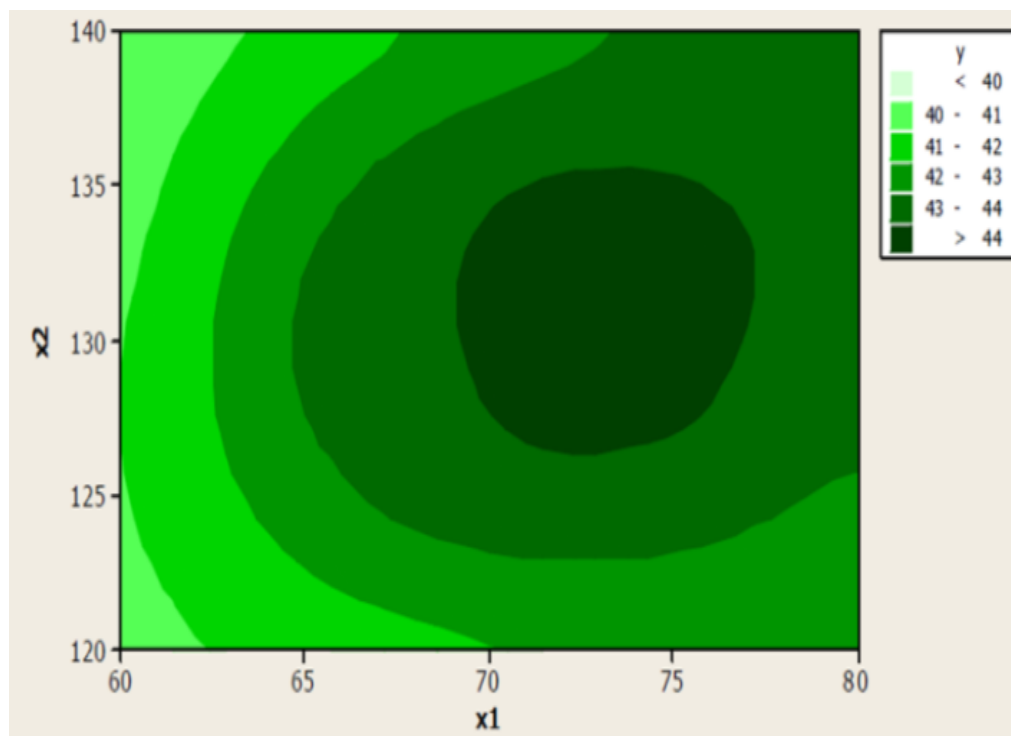


Fig. 2 10: Contour plot

2.6.3 Determination of Optimum Conditions

The primary objective of the RSM is to determine the optimum points of the input parameters that will yield a maximum or minimum response on the region of interest. In order to determine the optimum conditions or points of a system, there is a condition to be met, for a suitable fitting model, a good fitting gives a depiction of the response mean as the model will be used to determine the optimum value, an excellent fitted model define the optimisation techniques to be used in RSM. For first-degree models, the first remarkable ascent or descent is a parameter technique which is based on a sequential move to the optimum response. Later on, improvements were developed; this dealt with the stopping rule employed in this method. The first degree models are mainly utilised at the next step of experiments been done sequentially leading to a region that contains the location of optimum response (Morshedi and Akbarian, 2014).

2.6.4 Response Surface Methodology in the biodiesel production

RSM has been researched and established in many industrial applications, with the advantage of a broader framework that enables the design and analysis of experiments (Morshedi and Akbarian, 2014). One of these applications is the biodiesel production in which many researchers reported its

application in the production optimisation (Morshedi and Akbarian, 2014). Latchubugata *et al.* (2018), used RSM based on Box-Behnken Design to optimise the biodiesel production from palm oil using Calcium Oxide (CaO) as a heterogeneous catalyst, in their study, they optimised the effect of temperature, reaction time and methanol to oil molar ratio. Gupta, Agarwal and Dalai, (2016), optimised the biodiesel production from a mixture of edible and non-edible vegetable oils, their study used RSM based on CCD, they studied the four parameters as in the study done by Latchubugata *et al.* (2018), they also produced a quadratic model to predict the biodiesel yield, their optimum conditions were, temperature of 43.50 °C, methanol to oil molar ratio of 8.8:1, catalyst concentration of 1.9 g/100g oil, reaction time of 58.4 minutes to yield 97.02 % of biodiesel. Onukwuli *et al.* (2017), investigated the biodiesel of refined cotton oil using Potassium Hydroxide (KOH) as catalyst, the four major parameters were optimised using RSM used on CCD, optimum conditions were methanol to oil molar ratio, 6:1; 55 °C; 60 minutes; and catalyst concentration of 0.6% to yield 96 % of biodiesel. Hamze, Akia and Yazdani, (2015), Optimised the biodiesel production of waste cooking oil using the four primary parameters, they used RSM based on Box-Behnken, their optimum yield was 99.38 % of biodiesel. Mumtaz *et al.* (2014), reported the optimisation of biodiesel production from palm oil, in their study they used chemical and enzymatic catalysts, the optimisation was done using RSM based on CCD, their optimum yields were 47.6 %, 62.8 %, 92.7 %, 94.2, 95.4 % catalysed by Sodium Hydroxide (NaOH), A. n. Lipase, Potassium Hydroxide (KOH), NOVOZYME-435, Sodium Methoxide (NaOCH₃), respectively. (Modiba, Enweremadu and Rutto, 2015a), optimised the biodiesel production from waste vegetable oil using diatomite impregnated in Potassium Hydroxide (KOH), RSM was used based on CCD, the four major parameters were used, the optimum conditions were: methanol to oil mass ratio 30 wt. %, catalyst to oil mass ratio 5 wt. %, 4 hours, and 75 °C. A quadratic polynomial equation was acquired to correlating biodiesel yield to biodiesel production parameters.

2.7 Kinetics of biodiesel production

Numerous kinetics studies have been reported in the literature. The approaches in reported kinetics of biodiesel production differed from one author to another, the type of catalysts has been one of the elements that affected the kinetics. The complete reaction kinetics depends on the rate constant of every species converting from triglycerides to diglycerides, monoglycerides and alkyl esters (Yusuf, Kamarudin and Yaakub, 2011). The kinetics models are generally derived from the three consecutive

reversible reaction steps; it is to be noted that each reaction has a different rate of reaction (B. Likozar and Levec, 2014), the kinetics is mostly dependent on the reaction variables. However, most researchers reported the kinetics as being mainly influenced by the temperature. There is a challenge in developing a detailed, accurate kinetics model for biodiesel production since biodiesel is a mixture of several long chains hydrocarbon molecules (Tshizanga, 2015).

Latchubugata *et al.*, (2018), in their work on the transesterification reaction of biodiesel using a homogeneous catalyst, assumed pseudo-first-order kinetics. Likozar and Levec, (2014) studied the reaction kinetics of the biodiesel production of different feedstocks with methanol; they concluded that the obtained kinetics parameters of their study could only be used for the feedstocks studied this was due of the difference of fatty acid composition of different oils. They further stated that if different types of alcohol are used, the kinetics are often studied in a simple form. Gurunathan and Ravi (2015), reported the optimisation and kinetics of biodiesel production using a heterogeneous nanocatalyst, the first-order reaction kinetic model was found to be fitting experimental data with an R^2 of 0.9852, the activation energy was found to be 233.88kJ/mol. Muthukumaran *et al.* (2017), investigated the biodiesel optimisation and kinetics modelling produced from Madhuca indica oil; the suggested kinetics from the study followed pseudo-first-order kinetics, the activation energy and exponential factor were 22.306 kJ/mol and 60.51 min⁻¹ respectively. Feyzi and Shahbazi (2017), used novel Al-Sr nanocatalyst, they also assumed a pseudo-first-order model, it was reported that plotting $\ln k$ vs $1/T$ gave a straight line which confirmed that the first order was well fitted for the biodiesel production reaction. The activation energy E_a and exponential factor were 78.86 kJ/mol and 3.38×10^7 s⁻¹, respectively. Mathiarasi and Partha, (2016), investigated the kinetics of Daturametel Linn seed oil biodiesel as a nonconventional feedstock, the rate constant obtained by differential method gave a first-order kinetic mechanism, the activation energy E_a was found to be 25.8kJ/mol. Kostić *et al.*, (2016), studied the kinetics of biodiesel production of sunflower oil using a CaO-based palm kernel shell biochar catalyst, first order reaction rate law was utilised in their study, the activation energy was 108.8 kJ/mol. Baskar *et al.*, (2017), studied the kinetics using different temperature, the first order kinetics model was employed on Mahua oil catalysed by Mn doped ZnO this the activation energy was 181.91 kJ/mol. Zhang *et al.*, (2010), studied the biodiesel production from palm oil with dimethyl carbonate catalysed by potassium hydroxide (KOH), the proposed model was a pseudo-first-order, the activation energy and pre-exponential factor was 79.kJ/mol and 109 min⁻¹, respectively. Darnoko and Cheryan, (2000), reported the conversion of

triglycerides (TG), diglycerides (DG), and monoglycerides (MG) to follow a second-order kinetics until reaching the time of 30 minutes, the rate constants for TG, DG, and MG were 0.018–0.191 (wt%·min)⁻¹, with activation energy of 61.505, 59.413, 26.778 kJ/mol for the TG, DG, and MG, respectively, using a catalyst concentration of 1 wt. %. Priya *et al.*, (2017), studied the kinetics of jatropha oil with monoethanolamine, they estimated the rate constants and equilibrium constant using Arrhenius and van't Hoff equations, the developed kinetic model with second-order kinetics for forward and backward reactions was found to fit the reactions studied. Rezero *et al.* (2015), studied the kinetics modelling for the NaOH-catalysed biodiesel production from sunflower oil with ethanol and the activation energy was found to be 48.7 kJ/mol. Ma *et al.* (2017), studied the kinetics studies of biodiesel production from waste cooking oil using FeCl₃-modified resin as heterogeneous catalyst, they used a pseudo first order approach, they used the Arrhenius equation from there a $\ln k$ vs $1/T \times 10^3$ graph was plotted, from the slope and the intercept of the graph they got a value of activation energy (E_a) and pre-exponential factor A, 35.51 kJ/mol and 2.55×10^3 , respectively. The temperature has been reported to be the most influential factor affecting the rate of the reaction. They authors used a pseudo-first-order approach and some assumption were made in order to determine the kinetics of the reaction, some assumptions were considered, these assumptions are: (a) the reaction is considered to be forward as the reverse reaction is avoided by constant removal of glycerol, therefore the reaction was considered as a non-reversible reaction; (b) the reaction volume remained approximately constant during the reaction; (c) the methanol loss was neglected during glycerol removal this was mainly due to the difference in density between methanol and glycerol; (2-4) the reflux leaving the unit can guarantee the methanol remaining in the reaction process liquid phase, therefore the loss of methanol evaporated can be negligible (Ma *et al.*, 2017). Equations (2-3) to (2-10) are equations used to determine the kinetics and are adapted from (Feyzi and Shahbazi, 2017).

$$-r = \frac{-d[TG]}{dt} = k[TG][ROH]^3 \quad (2-3)$$

$$k' = k \cdot [ROH]^3 \quad (2-4)$$

$$-r = \frac{-d[TG]}{dt} = k' \cdot [TG] \quad (2-5)$$

$$\ln[TG]_0 - \ln[TG] = k't \quad (2-6)$$

$$X_{ME} = 1 - \frac{[TG]}{[TG]_0} \quad (2-7)$$

$$[TG] = [TG]_0[1 - X_{ME}] \quad (2-8)$$

$$\frac{d[X_{ME}]}{dt} = k' \cdot [1 - X_{ME}] \quad (2-9)$$

$$-\ln[1 - X_{ME}] = k't \quad (2-10)$$

$$k = A \times e^{\left(\frac{E_a}{RT}\right)} \quad (2-11)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2-12)$$

Where r is the rate of the reaction, k and k' constant, $[TG]$ the concentration of triglycerides, $[ROH]$ the concentration of alcohol, X_{ME} concentration of methyl Ester formed and t time, E_a activation energy, A pre-exponential factor, R universal gas constant and T temperature. From the above equations (2-3) to (2-10), the concentration of the methyl ester can be obtained first, and then the rate constants can be calculated as a slope from the plot of $-\ln(1 - X_{ME})$ vs time as per Fig. 2-11. Plotting a curve of the logarithm of the rate constants versus $1/T$ of the Arrhenius equation as per (2-11) and (2-12), from Fig. 2-12, the slope being $\frac{E_a}{R}$ the activation energy can be calculated, using (2-11) the pre-exponential factor also can be calculated (Feyzi and Shahbazi, 2017; Latchubugata *et al.*, 2018).

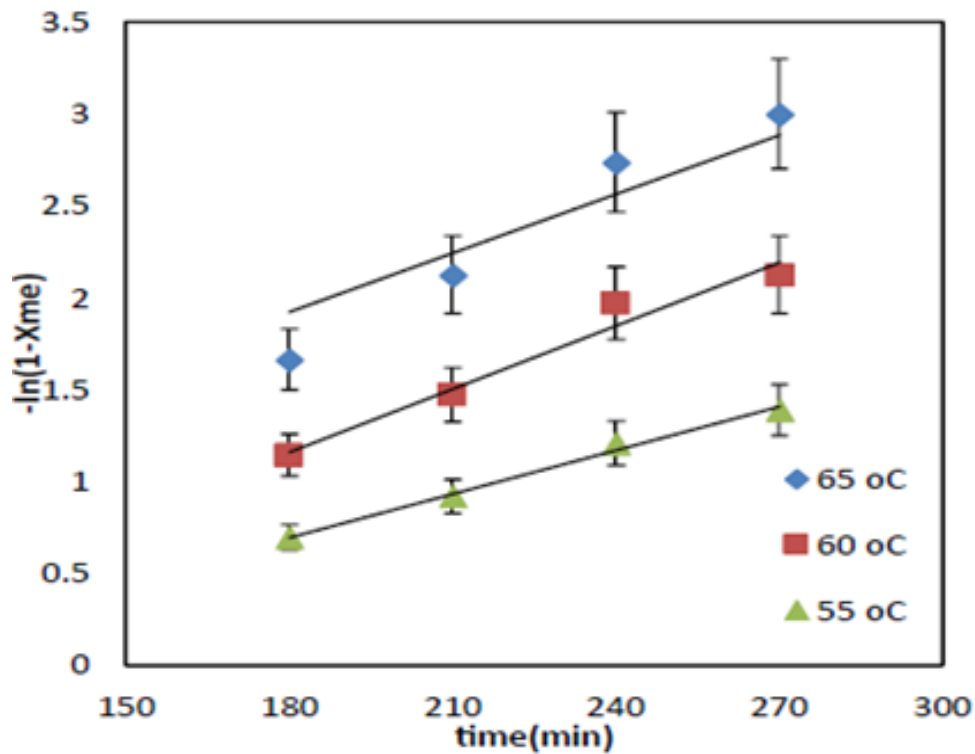


Fig. 2-10: Plot ($-\ln(1 - X_{ME})$) versus reaction time plot at three different temperatures (Latchubugata et al., 2018).

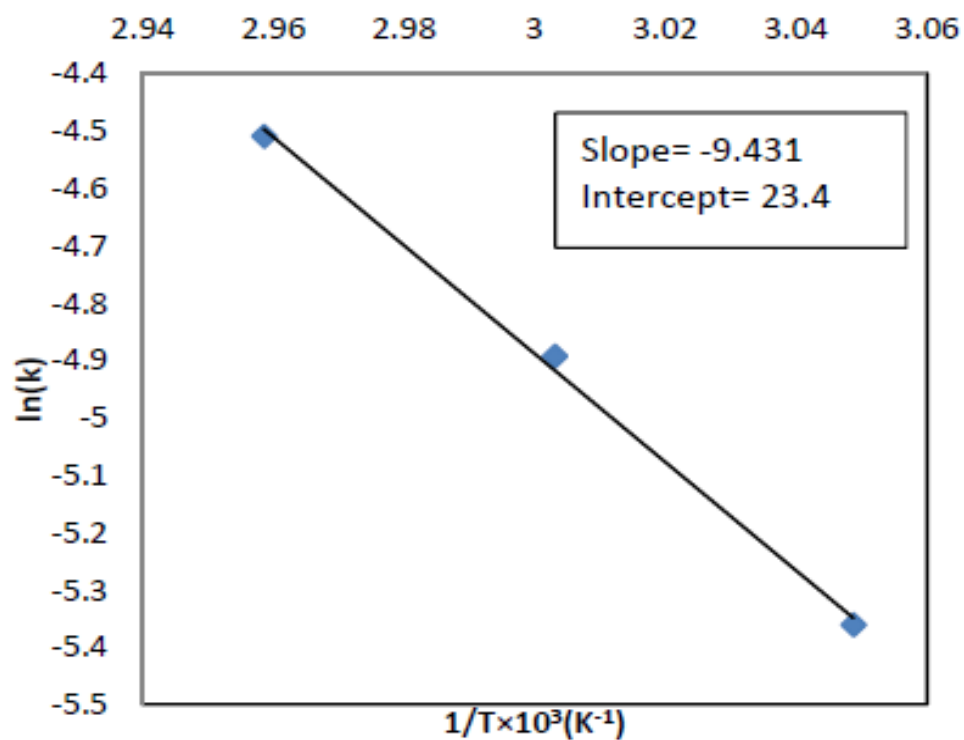


Fig. 2-11: Arrhenius plot of $\ln(k)$ versus $1/T \times 10^3 (K^{-1})$ (Latchubugata et al., 2018)

2.8 Biodiesel analysis Methods

Researchers reported various analytical techniques used in the biodiesel production, these techniques or methods, all have advantages and disadvantages, based on the advantages and disadvantages one can select the best suitable methods. Gas Chromatography (GC) has been widely used, this technique has the advantage of giving the composition of fatty alkyl esters including intermediates (diglycerides and monoglycerides), as well as the composition of glycerol and unreacted glyceride, the accuracy of this method has played a role in its usage (Monteiro *et al.*, 2008; Zhang, 2012; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017). Flame ionisation detection (FID), has been the most used detector; the accuracy was improved by the introduction of the mass spectrometer (Mahamuni *et al.*, 2017). It is to be noted that though the GC method has been reputed to be accurate, it has some disadvantages. The disadvantages are: required extensive samples preparation and therefore it is time consuming, there is a need for having internal standards, there is a need for using solvents, the method is known as a sample destructive method, and require highly qualified personnel (Zhang, 2012; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017).

Researchers have reported other analytical techniques used in the biodiesel production, these techniques are: Capillary Gas Chromatography (CGC) (Zagonel, Peralta-Zamora and Ramos, 2004; Yuan *et al.*, 2014), High Pressure Liquid Chromatography (HPLC) (Yuan *et al.*, 2014; Mahamuni *et al.*, 2017), Gel Permeation Chromatography (GPC) (Dubé *et al.*, 2004; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017), Fourier Transform Infrared (FTIR) Spectroscopy (Yuan *et al.*, 2014; Rabelo *et al.*, 2015; Cunha *et al.*, 2017; Mahamuni *et al.*, 2017; Mohamed Shameer and Ramesh, 2017; Mowla, Kennedy and Stockenhuber, 2018; Purandaradas *et al.*, 2018), Ramon Spectroscopy (Richard *et al.*, 2011; Yuan *et al.*, 2014), Size Exclusion Chromatography (Zagonel, Peralta-Zamora and Ramos, 2004; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017), Nuclear Magnetic Resonance (NMR) (De Lima *et al.*, 2014; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017), Ultra-sonication assisted spray ionization (UASI) spectroscopy, fluorescence spectroscopy (Chand *et al.*, 2008; Yuan *et al.*, 2014a; Rabelo *et al.*, 2015; Mahamuni *et al.*, 2017), UV spectroscopy (Richard *et al.*, 2011), Thin Layer Chromatography (TLC), thermogravimetric analysis (TGA) (Mahamuni *et al.*, 2017), Viscometry, (Yuan *et al.*, 2014; Mahamuni *et al.*, 2017).

2.8.1 Biodiesel analysis using Fourier Transform Infrared (FTIR)

FTIR analysis uses infrared qualitative analysis technique. In this technique, the energy of nonparticulate radiation spectrum is employed in infrared technique. This energy employed in qualitative analysis has wavelengths between the visible light and radio waves (Zhang, 2012). The region of operation of FTIR techniques is subdivided into three, and these are: Near-infrared (NIR) with wavenumber ($12500\text{--}400\text{ cm}^{-1}$), mid-infrared (MIR) ($4000\text{--}400\text{ cm}^{-1}$) and far-infrared (FIR) wavenumber ($400\text{ to }33\text{ cm}^{-1}$) (Zhang, 2012), mid-infrared spectroscopy has been the most used. According to Singh *et al.* (2011), Infrared spectroscopy has been employed in the qualitative analyses for the last seven decades. The infrared spectrums are classified as fingerprints of materials; this is explained by the fact that spectrums are constituted of peaks which are corresponding to the frequencies of vibrations of atomic bonds constituting the material. The operation of FTIR is done by sending infrared radiation on the sample, where there is the absorption of part the sample, the non-absorbed part of the sample is transmitted, this results in spectrum being produced expressing the sample molecular absorption and transmission, thus the sample's fingerprint. This implies that there is only one spectrum for a specific molecular structure (Singh *et al.*, 2011).

The quantification of biodiesel using FTIR is made possible by applying multivariate statistical tools, such as partial least square (PLS)(Rabelo *et al.*, 2015), Artificial neural network (ANN)(Oliveira *et al.*, 2006), interval partial least squares (iPLS) and synergy partial least squares (siPLS)(Ferrão *et al.*, 2011), principal component analysis (PCA), hierarchical cluster analysis (HCA), interval principal component analysis (iPCA) and soft independent modeling of class analogy (SIMCA)(Mueller *et al.*, 2013). The most used and reported multivariate statistical tool is PLS. PLS is a mathematical method based on Beer's law principle for quantification (Yuan *et al.*, 2014).

Oliveira *et al.* (2006), used partial least square (PLS) regression and artificial neural network (ANN) coupled with attenuated total reflection Fourier Transform Infrared (ATR-FTIR) and NIR spectroscopies to design calibration models for the methyl ester content determination of soybean, dende and used soybean oil biodiesel blends with fossil fuel. The results obtained were found to be suitable to be used with different feedstock of biodiesel. Ferrão *et al.* (2011), used PLS, interval partial least squares (iPLS) and synergy partial least squares (siPLS) regressions to determine biodiesel and petroleum diesel parameters quality. These parameters were biodiesel content, sulfur content, specific gravity and flashpoint, and these were achieved by selected the adequate region using iPLS and

siPLS. ATR-FTIR can be used together with multivariate statistical tools to categorise the vegetable oils used as feedstock in the biodiesel production. Mueller *et al.* (2013), used ATR-FTIR coupled with multivariate statistical tools to evaluate the biodiesel content produced from canola, corn, cotton, palm, soybean and sunflower. In their study they used hierarchical cluster analysis (HCA), principal component analysis (PCA), soft independent modelling of class analogy (SIMCA) and interval principal component analysis (iPCA) and there was an indication from their results that the model developed was fit to identify feedstock and determine the biodiesel content (Mueller *et al.*, 2013).

Though the use of multivariate statistical tools produce a reliable and robust model and the fact that they rely on Beer's law, the mathematics implication is of high complexity (Mahamuni *et al.*, 2017). Therefore, software is used, to ease the process and improve the model. The use of multivariate statistical tools in the quantification of biodiesel is improved by the use of pre-processing methods such as mean centring technique (Cunha *et al.*, 2017; Mahamuni *et al.*, 2017) and baseline correction (Cunha *et al.*, 2017). Mean centring has been the most used pre-processing technique. Executing mean centring over numerous factors brings about the removal of the mean sample vector from all sample vectors in the data collection. Afterwards, the relative contrasts of the spectrum intensity at different wavelengths are more straightforward to recognise (Cunha *et al.*, 2017). Performance index algorithms are used after pre-processing methods, and this has the purpose of accessing the performance and accuracy of the built models. The algorithms used are Root-Mean-Square-Error (RMSE), Root Mean Square Error of Calibration (RMSEC), Root Mean Square Error of Prediction (RMSEP) and Root Mean Square Error of Cross-Validation (RMSECV) (Mahamuni *et al.*, 2017).

Killner, Rohwedder and Pasquini (2011) used PLS regression model using NIR spectroscopy to develop a monitoring system of biodiesel production using soybean oil. A lab-made spectrophotometric flow cell was used to collect NIR spectra during transesterification. The reference method used to build the PLS calibration model in their work was Proton Nuclear Magnetic Resonance (^1H NMR) spectroscopy. The validation of the model was confirmed with a low value of RMSEP.

Rabelo *et al.* (2015) used PLS to build regression models for biodiesel quantification using mid-infrared spectrum and the narrow region ranging from $1800\text{--}600\text{ cm}^{-1}$, this region is the region giving differentiation in biodiesel concentration. Their results were based on RMSECV, RMSEP, the

number of latent variables, the Calibration Correlation Coefficient R_c , and the Validation Correlation Coefficient R_v using the Standard Normal Variance (SNV) and Multiplicative Signal Correction (MSC) pre-treatments were used to model the quantification of FAME in biodiesel. They further stated that the best model was selected based on RMSEC and RMSEP. The lower their value, the better the predictive capacity of the model.

Mueller *et al.* (2013), used infrared spectroscopy to identify the vegetable oils used as feedstock for the biodiesel production and applied multivariate analysis. In their work, the spectra obtained from the Fourier transformed infrared spectroscopy using universal attenuated total reflectance sensor (FTIR-UATR). PCA, iPCA, HCA and SIMCA were the multivariate analysis used. From their results, it was indicated that a methodology of identifying vegetable oils used as feedstock for the biodiesel production was feasible. The best spectral separation range was obtained from iPCA.

Mahamuni *et al.* (2017), developed an analytical technique using FTIR to determine the percentage of biodiesel in the reaction mixture. They further reported that small modification could be applied to the built model to determine the percentage of biodiesel in the mixture of biodiesel-petrodiesel blends. Soybean oil was used to produce biodiesel and build the model. The calibration method was developed employing a software viz. Enformatic FTIR Collection Manager (EFCM) to develop a model and predict the biodiesel and oil concentrations. The software uses a nonlinear classical least square (CLS), it was shown from the results that the model can be used to determine the biodiesel content to 98.11 % accurately in the blend biodiesel-oil and 99.99 % in a blend of biodiesel-petroleum diesel.

2.8.2 Real-Time Biodiesel Monitoring

The online monitoring of ethanolysis using mid-infrared spectroscopy was reported by Trevisan *et al.* (2008), the biodiesel yield was obtained using ^1H NMR spectroscopy. They used two different data treatment with the first using raw data and the second using evolving factor analysis (EFA). PLS was further utilised using different batches for calibration and validation to build models; the model was compared using root mean square error of prediction (RMSEP) and root mean square prediction difference (RMSPD), the obtained errors were below 3 %. Pre-processing method such as baseline correction, derivative, Savitzky–Golay smoothing, mean centring and autoscaling were used. The models thus built were used to predict other batches, this was compared to the results obtained from

NMR, analysis of batches were done using an ATR flow-cell equipped with continuous sampling of the reactor using a peristaltic pump (Trevisan *et al.*, 2008).

Richard *et al.* (2011), developed a fast-on-line analytical method monitoring the biodiesel production from sunflower oil, they focused on acid oleate reacting with ethanol, the monitoring was performed using Near-Infrared spectroscopy, and a multivariate method was used. They monitored the reaction through sequential scans of the reaction mixture in which a probe was inserted, and data were collected. The calibration of the NIR analytical method was performed using gas chromatography-flame ionisation detection as a reference. The method was validated by applying it on the kinetics study of ethoxide catalysed reaction.

De Souza and Cajaiba Da Silva (2013), used real-time attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) for quantification of soybean oil biodiesel. They used ^1H NMR as a reference method to verify the accuracy of data obtained from ATR-FTIR. They monitored the reaction by checking the methanol consumption of methanol reacting with the triglyceride; this was found to be reliable to quantify the glyceride conversion to biodiesel. The accuracy of the fast technique used in their research was confirmed by comparing with results obtained by off-line ^1H NMR analysis.

Richard *et al.* (2013), developed on-line monitoring of sunflower oil biodiesel produced in microreactors using NIR. The microreactors were circular PFA tube 1/1600 OD, 0.0200 ID. The direct monitoring was performed using sequential scans of the reaction media using a transfective optical probe. PLS regression was employed for the calibration and prediction of models and used GC-FID as a reference method. The focus on the prediction was based on ethyl oleate content. Baseline correction, a Savitzky–Golay smoothing, first derivative, mean-centring and variable scaling were used as pre-processing methods. The pre-processing method improved the RMSEC and RMSEP values to 4.08 % and 4.10 %, respectively. The correlation coefficient R^2 was 0.985.

De Lima *et al.* (2014), in their work, developed an analytical method to in-line monitor the biodiesel production of soybean oil using NIR spectroscopy. GC was used as a reference and for the determination of methyl ester (ME), monoglycerides (MG), diglycerides (DG) and triglycerides (TG) content. PLS and multivariate regression calibration models were developed using NIR spectra. In order to select the number of PLS parameters for multivariate regression, full cross-validation

was performed. The RMSEP was used to predict the accuracy of the model. The statistical significance of differences between RMSEP values was assessed using F-test at a confidence level of 95%.

Yuan *et al.* (2014) developed an on-line transesterification system using a mid-FTIR spectrometer, which was equipped with a temperature-controlled transmission flow cell. Spectra were collected at different regions to evaluate the changes during the transesterification of canola oil. PLS was used as a multivariate calibration model, and the results were compared with the one obtained from GC. They further reported that the model built was not adequate to give the concentration of intermediate, namely mono and diglycerides. However, the model built was adequate for monitoring the biodiesel production and could indicate the endpoint of the reaction.

2.9 References

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CHAPTER THREE

3. OPTIMISATION OF BIODIESEL PRODUCTION FROM SUNFLOWER OIL USING CENTRAL COMPOSITE DESIGN

3.1 Abstract

The current study investigated the effect of catalyst ratio and methanol to oil ratio on biodiesel production by using central composite design. Biodiesel was produced by transesterification using Sodium Hydroxide as a homogeneous catalyst, a laboratory scale reactor consisting of flat bottom flask mounts with a reflux condenser and a heating plate was used to produce biodiesel. Key parameters, including, time, temperature and mixing rate was kept constant at 60 minutes, 60°C and 600 RPM, respectively. From the results obtained, it was observed that the biodiesel yield depends on catalyst ratio and methanol to oil ratio. The highest yield of 50.65 % was obtained at catalyst ratio of 0.5 wt% and methanol to oil mole ratio 10.5. The analysis of variances of biodiesel yield showed the R Squared value of 0.8387. A quadratic mathematical model was developed to predict the biodiesel yield in the specified parameters ranges.

Keywords—ANOVA; Biodiesel; Catalyst; CCD; Transesterification.

3.2 Introduction

FUELS have become part of daily activities as they are used for heating, transportation and power plants; these fuels are generally produced from fossil sources. The increase in the worldwide population and the industrialisation of the 21st century have caused a high demand for fuels, and on the other hand, there is decreasing of global fossil fuels deposits and the increase of environmental air pollution caused by these fuels. Therefore, there is a need for developing new forms of environmentally friendly and renewable forms of fuels (Marchetti, Miguel and Errazu, 2007; Leung, Wu and Leung, 2010; Atabani *et al.*, 2013; Pourzolfaghar *et al.*, 2016; Yusoff *et al.*, 2016). According to research done in Turkey, the use of fuel has reached its highest level, which will lead to the lowest reserves in the next two decencies (Ediger, Akar and Uğurlu, 2006). Energy consumption (of which has doubled from 1973 to 2013, this is expected to increase by 34% from 2014 to 2035 for which the transportation sector is the primary CO₂ emitter accounting for 33.6%. Renewable energy comes from several sources such as geothermal energy, solar, biomass and

hydropower, for which solar is the most growing renewable energy. However, biomass is classified as the only green carbon (Ilmi *et al.*, 2017).

Biodiesel is defined as an alkyl ester which is derived from the Greek word bio (life) and diesel after Rudolf diesel and is produced from biological sources such as vegetable oils and animal fat which are triglyceride and with alcohol. Alcohols used for biodiesel production processes are methanol, ethanol, propanol and butanol, mainly used alcohols are methanol and ethanol (Demirbas, 2009a; Leung, Wu and Leung, 2010; Chouhan and Sarma, 2011). Using ethanol for biodiesel has the disadvantage of forming an azeotrope with the water molecules, which makes the recovery complicated. The performance of ethyl esters is less compared to the methyl esters due to the high molecular weight of ethanol (46.07 g/mole) compared to (32.04 g/mole) (Meng, Chen and Wang, 2008).

For biodiesel to be classified as renewable fuel, needs to fulfil certain requirements such as: low environmental impact, reduction of greenhouse gases effects due to less SO_x, NO_x and CO₂ gases emissions, biodegradability, high cetane number and high combustion efficiency (Marchetti, Miguel and Errazu, 2007; Lukovi, Knežević and Bezbradica, 2011; Sani, Daud and Abdul, 2013). According to estimations, each kilogram of biodiesel produced reduces the CO₂ emission by 3.2 kilograms as compared to petroleum diesel (Kim *et al.*, 2004; Patil and Deng, 2009).

There are two types of oils in nature, the first ones are called fixed oils and generally lipids and do not vaporise when exposed to air which sourced from plants or animal fats, and the second ones are essential oils vaporise when exposed to air generally produce from plants and flowers (Uriarte, 2010). Oils are classified as edible; which are mostly used for human consumption and non-edible oils which are not proper for human consumption (Demirbas, 2009a). Lipids can be differentiated into two categories as saturated known as saturated fatty acids (SFA) or non-saturated known as non-saturated fatty acids (NSFA). The saturated fatty acids are in such a way that only single covalent bonds are present in their structure while non-saturated fatty acids have double covalent bonds in their structures. Chemically lipids are fatty glycerol esters known as triglycerides which have small quantities of monoglycerides and diglycerides. Additionally, plant oil can as well contain free fatty acids (FFA) which are about 1% by mass except some oils such as palm oil containing up to 15% (Romano and Sorichetti, 2011).

Numerous researches have been done on biodiesel, and it has been found that properties of biodiesel may vary considerably this various depend on the chemical compositions and fatty acid composition, which give noticeable effect on engine performance and emissions. Therefore, it is very crucial to measure the properties of any oil before considering for usage in the biodiesel production. These properties are specified through the ASTM and EN standards. The properties to characterise the biodiesel is Cloud point (CP), Pour Point (PP), Flash Point (FP), Kinematic viscosity, Cetane Number (CN), Density, Acid number (AN), Calorific Value (CV), Sulphur content, Free and total glycerine (Atabani *et al.*, 2013).

Biodiesel is mostly produced by transesterification reaction, also known as alcoholysis. The transesterification reaction is the reaction of lipids and short chain alcohol such as methanol or ethanol at a specific temperature in the presence of a catalyst. The transesterification reaction occurs in three consecutive steps by releasing one mole of fatty acid methyl ester in each step, firstly converted to diglyceride, monoglyceride and releasing one molecule of triol mostly know as glycerol. The high viscosity of lipids is therefore reduced. Transesterification is a reversible reaction; hence, the alcohol has to be in excess to favour the forward reaction. The reaction conditions, feedstock compositional limits and post-separation requirements are determined by the nature of the catalyst (Zhang *et al.*, 2010; Sani, Daud and Abdul, 2013; Khritsayaporn, Thinnakorn and Tscheikuna, 2014; Amoah *et al.*, 2016). **Error! Reference source not found.** gives a general transesterification reaction equation.

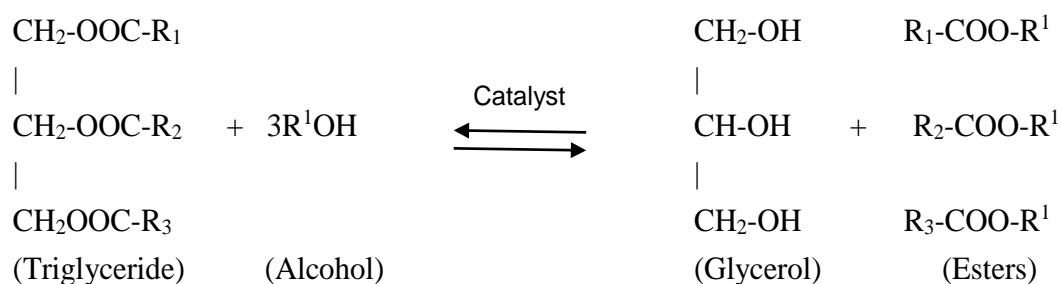


Fig. 3-1: Transesterification reaction

Generally, the catalysts used in biodiesel production are characterised in three categories which are known as alkalis, acids and enzymes. Alkalis (base) catalysts and acids catalysts are further categorized as: homogeneous base catalysts (such as: Potassium and Sodium hydroxide), homogeneous acid catalysts (such as: Sulfuric acid and Hydrochloric acid), heterogeneous base

catalysts (such as: Calcium Oxide) and heterogeneous acid catalysts (such as: Zirconium Oxide and Titanium Oxide). In comparison with enzyme catalysts, alkali and acid catalysts are mostly used in biodiesel production. Recently the enzyme catalysts showed a high interest in their usage since they can prevent soap formation, and the purification process is straightforward. It has been found that the enzymes are not cost effective and had a high reaction time (Al-zuhair, Wei and Song, 2007; Lam, Lee and Mohamed, 2010; Samir Najem Aldeen Khurshid, 2014).

Homogeneous base catalyst or alkaline catalysts are mostly used catalysts in transesterification reaction, and this is mainly due to the high reaction rate. The mostly used base catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH), potassium hydroxide forms potassium methoxide (KOCH_3), and sodium hydroxide forms sodium methoxide (NaOCH_3) and sodium ethoxide ($\text{NaOCH}_2\text{CH}_3$). Potassium methoxide (KOCH_3) and Sodium methoxide (NaOCH_3) are more effective catalysts compare to sodium hydroxide (NaOH) and potassium hydroxide (KOH), this is because the methoxide has the facility to separate into CH_3O^- and Na^+ and CH_3O and K^+ increasing the biodiesel yield. According to (Silitonga *et al.*, 2014), the biodiesel production yield can go up to 98.53% with calophyllum inophyllum oil, 1 wt.% KOH and 9:1 methanol to oil ratio as feed.

Table 3-1: Common fatty Acids in Vegetable Oil (Shahidi, 2005)

| Fatty acid | Formula | Methyl ester |
|-------------------------------|--|---------------------|
| Palmitic acid (C16:0) | $\text{C}_{16}\text{H}_{32}\text{O}_2$ | Methyl Palmitate |
| Stearic acid (C18:0) | $\text{C}_{18}\text{H}_{36}\text{O}_2$ | Methyl Stearate |
| Oleic acid (C18:1) | $\text{C}_{18}\text{H}_{34}\text{O}_2$ | Methyl Oleate |
| Linoleic acid (C18:2) | $\text{C}_{18}\text{H}_{32}\text{O}_2$ | Methyl Linoleate |
| Linolenic acid (C18:3) | $\text{C}_{18}\text{H}_{30}\text{O}_2$ | Methyl Linoleate |

Sunflower oil is a combination of triacylglycerol, lipids, vitamins, steroid alcohols, and waxes. Linoleic acid and oleic acid are major fatty acids in sunflower oil. Saturated fatty acids are about 15% of the total fatty acid content (Shahidi, 2005). The composition specified by Codex Alimentarius (Codex-Stan 210-1999), saturated FFA content of sunflower oil reported lower than corn (22%), cottonseed oil (32%), peanut oil (28%) and soybean oil (20%). The linolenic acid content in sunflower oil is low, enhancing oxidative stability (Uriarte, 2010).

There are mainly four factors affecting the biodiesel production; methanol to oil ratio, catalyst ratio, reaction time and reaction temperature (Leung, Wu and Leung, 2010). However, in this work, the biodiesel production from sunflower oil using Sodium Hydroxide as a homogeneous catalyst was optimised by investigating the effects two parameters, namely methanol to oil ratio and catalyst ratio. The temperature and the time were kept constant, 60 °C and 60 minutes, respectively. Response Surface Methodology (RSM) using Central Composite Design was used in the optimisation process, and a quadratic mathematic model of the transesterification reaction was developed predicting the yield of biodiesel in the specified ranges of parameters.

3.3 Materials and methods

3.3.1 Materials

A multi-step Sunflower oil (triglyceride) was sourced from a local cooking oil supplier (Golden Fry). Chemicals; Methanol, Sodium Hydroxide were sourced from a local chemical supplier (labchem).

3.3.2 Experiment Design

The experimental design selected for this study was a central composite design (CCD) which helps in investigating linear, quadratic, cubic and cross-product effects of the four transesterification process variables (independent) on the yield of biodiesel (response) (Gunst, Myers and Montgomery, 2006). The four transesterification process variables studied were methanol to oil ratio (X_1) and catalyst weight (X_2), each variable been considered as two levels namely: low (-2) and high (+2). Table 3-2 shows the range, and the levels of the two transesterification variables studied. For each categorical variable, a 13-full factorial CCD for the two variables, consisting of 8 non-centre points and 5 replicates at the centre points was used. A full experimental design matrix is shown in Table 3-3.

Table 3-2: Factors and their values used for the experiment

| Coded values | Actual values for coded values | | | | |
|-----------------------------|--------------------------------|------|------|------|----|
| | -2 | -1 | 0 | 1 | 2 |
| A: X_1: | 3 | 6.75 | 10.5 | 14.3 | 18 |
| B: X_2 | 0.5 | 0.88 | 1.25 | 1.63 | 2 |

A: X_1 : Methanol to oil ratio (moles/mole); B: X_2 : Catalyst ratio (wt.%)

A mathematical model was developed to correlate the yield of methyl esters (biodiesel) to the transesterification process variables studied through a first order, second order and interaction terms according to the following third-order polynomial equation displayed in (3-1):

$$Y = \beta_0 + \sum_{j=1}^4 \beta_j X_j + \sum_{i,j=1}^4 \beta_{ij} X_i X_j + \sum_{j=1}^4 \beta_{jj} X_j^2 + \sum_{k,i,j=1}^4 \beta_{kij} X_k X_i X_j + \sum_{j=1}^4 \beta_{jjj} X_j^3 \quad (3-1)$$

Where Y is the predicted biodiesel yield, x_i and x_j represent the parameters, β_0 is the offset term, β_i is the linear effect, β_{ij} is the first-order interaction effect, β_{jj} is the squared effect and β_{jjj} is the second-order interaction effect.

Table 3-3: Experimental Design: Central Composite Design

| Experiments | A: | B | Yield (%) |
|-------------|------|-------|-----------|
| 1 | 6.75 | 0.875 | 33.69 |
| 2 | 14.3 | 0.875 | 37.74 |
| 3 | 6.75 | 1.63 | 34.82 |
| 4 | 14.3 | 1.63 | 33.72 |
| 5 | 3 | 1.25 | 9.11 |
| 6 | 18 | 1.25 | 36.92 |
| 7 | 10.5 | 0.5 | 50.64 |
| 8 | 10.5 | 2 | 28.89 |
| 9 | 10.5 | 1.25 | 37.91 |
| 10 | 10.5 | 1.25 | 37.87 |
| 11 | 10.5 | 1.25 | 37.92 |
| 12 | 10.5 | 1.25 | 37.89 |
| 13 | 10.5 | 1.25 | 37.91 |

A: Methanol to oil ratio (moles/mole); B: catalyst ratio (wt.%)

3.3.3 Experiment set-up

A flat bottom flask with a condenser was used as a laboratory-scale reactor for the experiments studied in this work, and a hot plate with magnetic stirrer arrangement was used for heating the mixture in the flask.

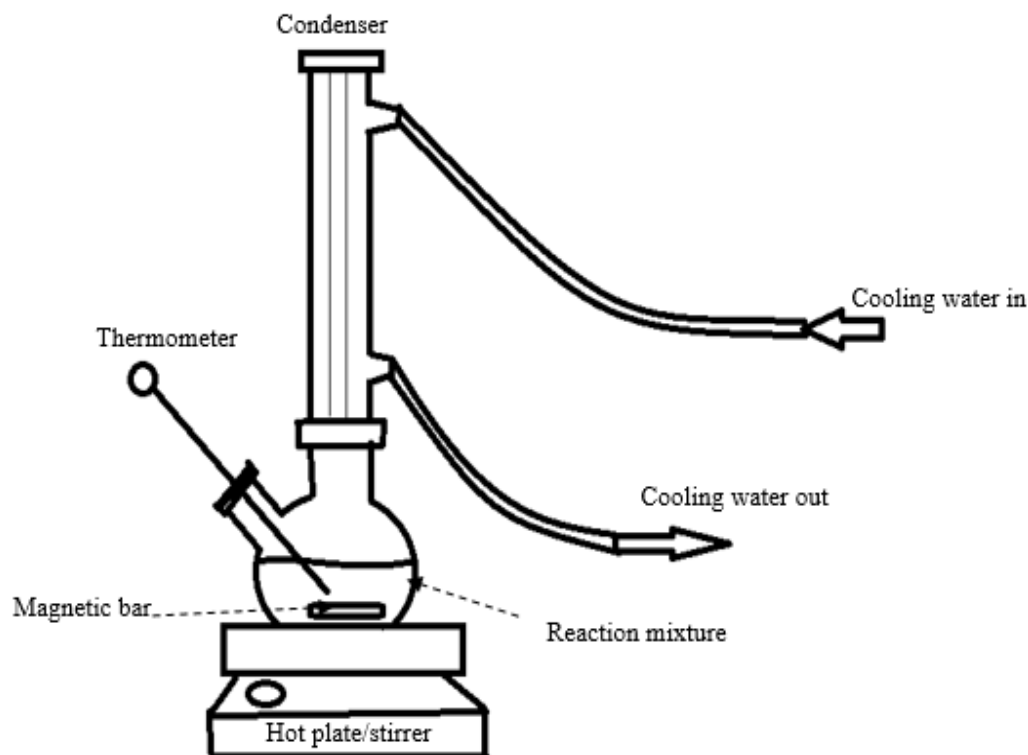


Fig. 3-2: Experiment set-up

3.3.4 Biodiesel Production

Sunflower oil was heated above 100°C to remove trace amounts of water using a hot plate. Heated oil removed from the hot plate and left to cool in a fume hood. The mass of catalyst calculated for each experimental run weighed in a beaker. The methanol added to the base catalyst (sodium hydroxide solid white pellets) and stirred using the magnetic stirrer unit until the sodium hydroxide fully dissolved. The purpose of stirring the methanol and catalyst is to activate the alcohol for the transesterification process. 50g of the heated sunflower oil weighed in a beaker then transferred into a 250 ml round-bottomed flask, which served as the reactor. The oil in the reactor heated to the desired temperature (60°C) using the temperature-controlled heating plate. The methanol and catalyst mixture added to the reactor containing the oil. A stirrer bar placed inside the reactor and the reactor placed in the warm bath supported on the magnetic stirrer. The total reflux condenser attached to the reactor. The agitation speed selected at 600 RPM. During the reaction, any evaporated methanol returned to the reactor by the condenser. After a reaction time of 60 minutes, the contents from the reactor transferred into a separating funnel. Once the reaction mixture settled in the separating funnel, there were two distinct noticeable layers (the top biodiesel layer and the bottom

glycerol layer). The bottom glycerol layer decanted into a bottle and massed. The top biodiesel layer displaced using a pipette and massed in a bottle. The top biodiesel layer characterised using a GC-MS. The GC-MS analysis confirmed FAME components.

FAME components were characterised via GC MS equipped with a polar DB wax column. FAME components identified against a mixture of FAME standard (1000ppm). Semi-quantification of FAME components calculated using external standard method. Total FAME content calculated by adding up the quantified components

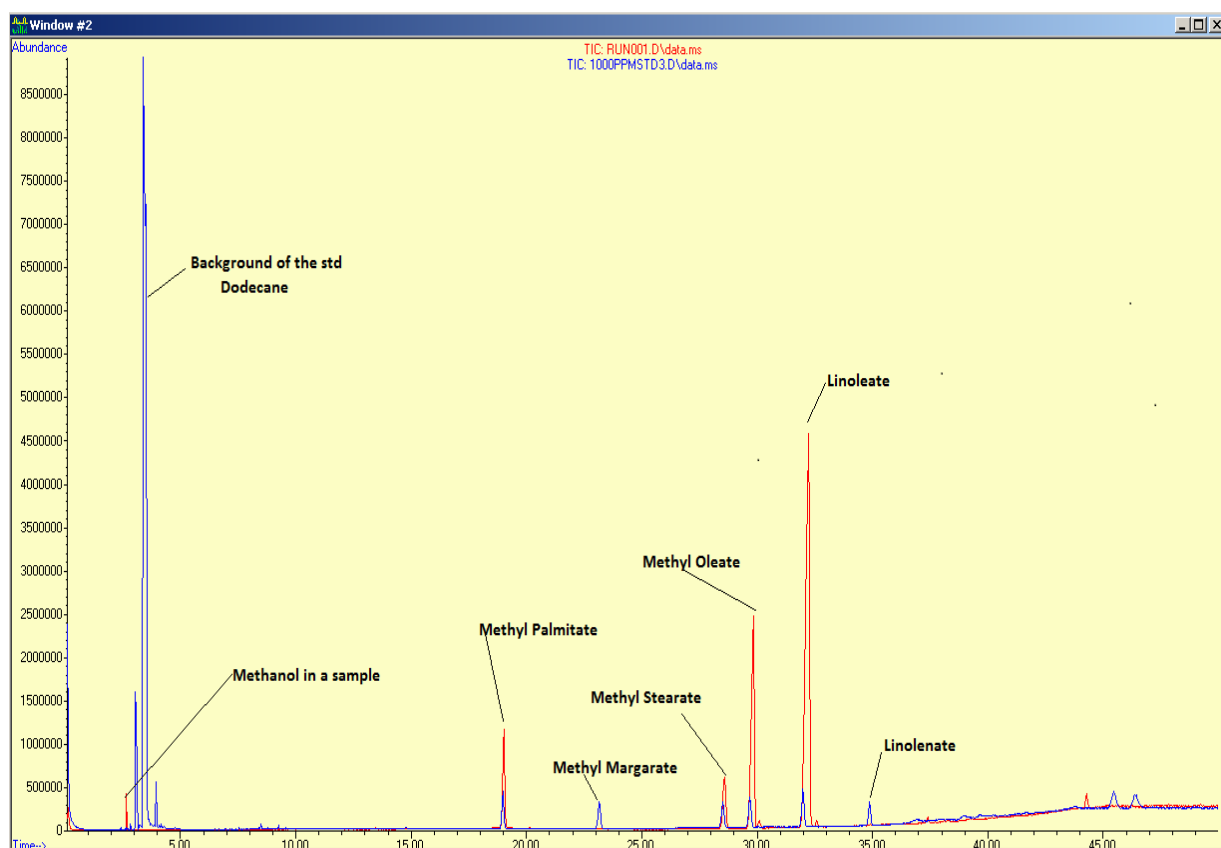


Fig.3-3: Chromatogram of sample Experiment 1 with 1000PPM FAME standard

3.3.5 Model fitting and statistical analysis

Design expert (10.0.7) software was used as regression analytical tool to fit experimental data to the third-order polynomial regression model. The evaluation of statistical significance of the model was developed.

3.4 Discussions

3.4.1 Development of regression model equation and the analysis of variance

The final equation in terms of actual values after excluding the insignificant terms was identified using Fisher's Test, and this is shown in (3-2) and (3-3). With (3-2) being the Final equation in terms of Coded Factors and (3-3) being the final equation in terms of actual factors.

$$\text{Yield} = +37.99 + 4.88A - 3.87B - 1.29AB - 3.71A^2 + 0.47B^2 \quad (3-2)$$

With, A: methanol to oil ratio (moles/mole) and B: catalyst ratio (wt. %)

The equation in terms of coded factors used to make predictions about the response for given levels of each factor. By default, the high levels of the factors coded as +2 and the low levels of the factors are coded as -2. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

$$\text{Yield} = +1.327 + 7.994A - 9.107B - 0.916AB - 0.264A^2 + 3.365B^2 \quad (3-3)$$

The equation in terms of actual factors used to make predictions about the response for given levels of each factor. Here, the levels specified in the original units for each factor. This equation not used to determine the relative impact of each factor because the coefficients scaled to accommodate the units of each factor and the intercept is not at the centre of the design space.

The negative sign in front of the terms indicates the antagonistic effect, while the positive sign indicates synergistic effect. The quality of the model could be evaluated from the coefficient correlation. The R^2 for (3-2) is 0.8387. This implies that 83.87 % of the total variation in the transesterification responses is explained by the model. Fig.3-4 shows the predicted versus the experimental values of biodiesel yield plotted against a unit slope. The results show that the regression model equation provided a very accurate description of the experimental data. $R^2=0.8387$ - R^2 is a statistical measure of how close the data is to the fitted regression line and is known as the coefficient of determination. 100% indicates that the model explains all the variability of the response data around the mean.

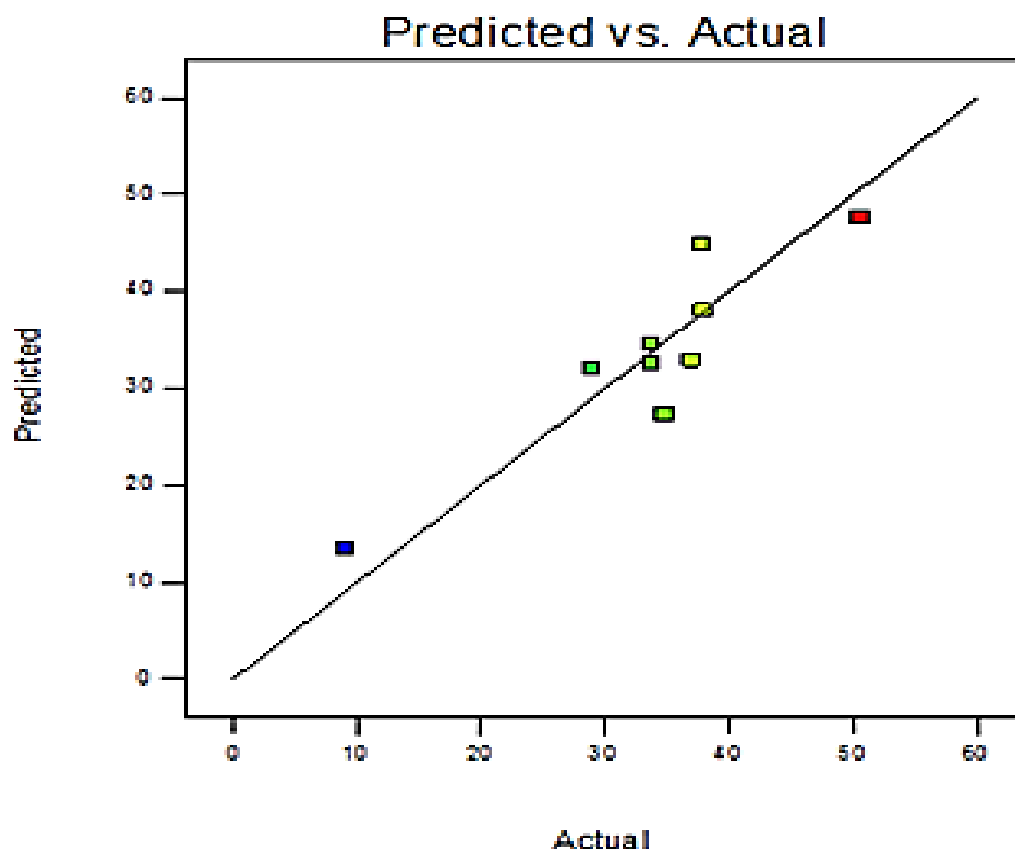


Fig.3-4: Linear representation of Actual versus the predicted biodiesel yield.

To test the capability of the model and to check the effectiveness of the predicted model, the experimental values compared to the predicted values by use of the parity plot confirms that the model fits the data equitably. The results show that the regression equation provides an accurate description of the experimental data using the minimum number of experiments

The Model F-value of 7.28 implies the model is significant; this is based on 83.87 % confidence level. Therefore, this indicates that the regression model can be reliable to predict the biodiesel yield. There is only a 1.07% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. There is only a 0.01% chance that a "Lack of Fit F-value" this large could occur due to noise.

It has been observed from Table 3-4, that the two variables (Methanol to oil ratio: A and catalyst ratio: B) have an impact on the biodiesel yield. Methanol to oil ratio has high influence than catalyst ratio.

Table 3-4: Analysis of variance ANOVA for the regression model equation and coefficients.

| Source | SOS | DOF | Mean Square | F-Value | p-value Prob > F |
|----------------------|--------|-----|-------------|----------|------------------|
| Model | 846.4 | 5 | 169.28 | 7.28 | 0.0107 |
| A | 285.96 | 1 | 285.96 | 12.3 | 0.0099 |
| B | 179.42 | 1 | 179.42 | 7.72 | 0.0274 |
| AB | 6.64 | 1 | 6.64 | 0.29 | 0.6097 |
| A² | 316.19 | 1 | 316.19 | 13.6 | 0.0078 |
| B² | 5.13 | 1 | 5.13 | 0.22 | 0.6528 |
| Residual | 162.75 | 7 | 23.25 | | |
| LOF | 162.75 | 3 | 54.25 | 1.30E+05 | < 0.0001 |

SOS=Sum of Squares; DOF= Degrees of Freedom; LOF =Lack of fit

3.4.2 Effects of transesterification variable

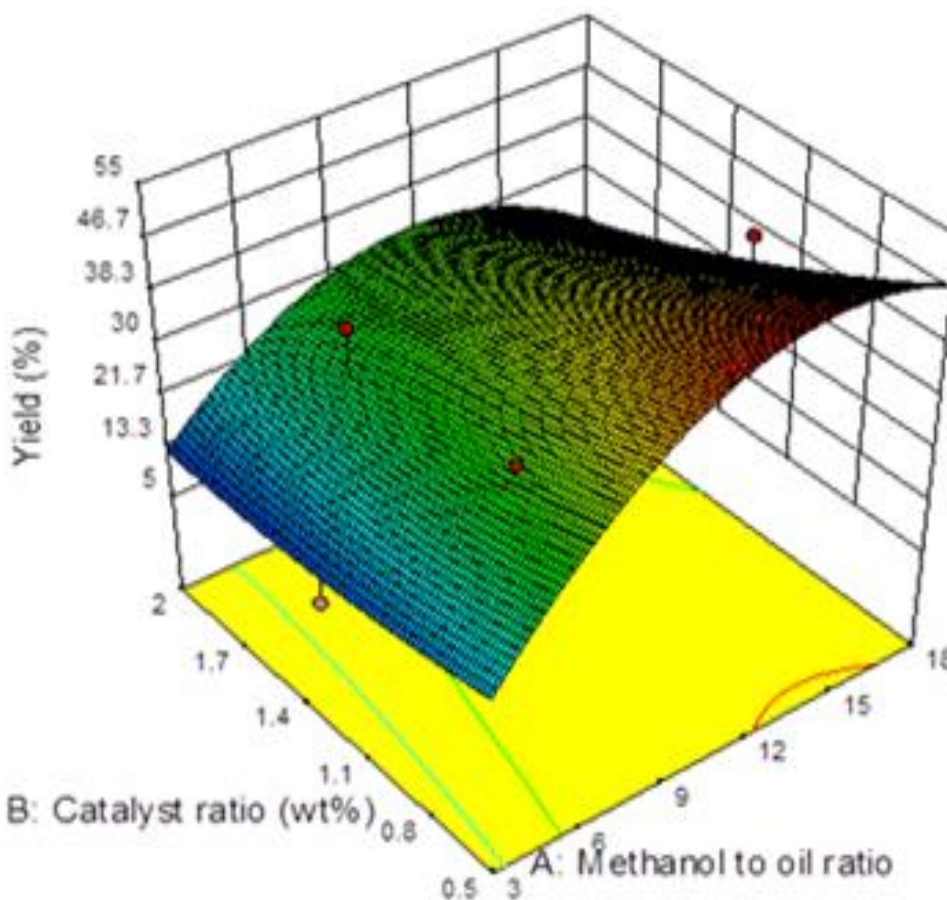


Fig. 3-5: Effect of Methanol to oil molar ratio and catalyst ratio

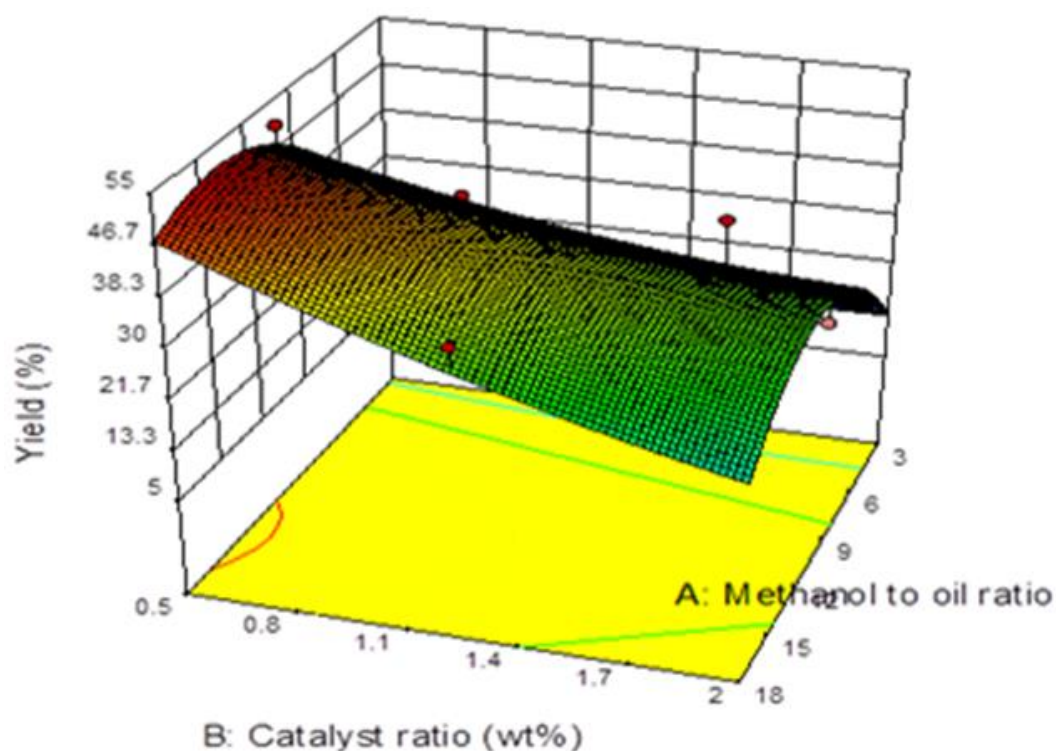


Fig.3-6: Effect of Methanol to oil molar ratio and catalyst ratio.

Fig. 3-5 and Fig.3-6 represent the response surface of biodiesel yield taken in a different angle from Design expert software. The methanol to oil ratio range studied was 3 to 18 molar ratios. By stoichiometry only three moles of methanol are needed to transesterify one mole of triglyceride, from the results it was seen that the low methanol ratio yields low biodiesel. This is explained by the fact that the transesterification reaction is a reversible reaction that needs excess of alcohol. By increasing the methanol to oil ratio, the forward reaction is favoured this is explained by the fact that at three mole methanol ratio the yield was very low, but as the methanol to oil ratio increase the yield increased up to 50.65 % which was the maximum yield obtained. This agrees with what reported by (Meher, Vidya Sagar and Naik, 2006). Excess methanol causes glycerolysis reaction to occur which lead to the production of monoglyceride instead of biodiesel (Lin *et al.*, 2009). (Meher, Vidya Sagar and Naik, 2006), further stated that when glycerol remains in the solution, it leads to the backward reaction, therefore reducing the yield of the esters. That is why beyond 10.5 molar ratio the yield decreased. The base catalyst Sodium Hydroxide studied in the range of 0.5 wt.% - 2 wt.%. The maximum yield of 50.65% of biodiesel was obtained at catalyst ratio of 0.5 wt.%. The higher catalyst ratio shows a decline in biodiesel yield. The highest yield of biodiesel

at 0.5 wt.% of catalyst is explained by the fact that 0.5 wt.% was enough to give the highest yield, the additional quantity of catalyst reacted to form soap, this explained the decrease in the biodiesel yield (Meher, Vidya Sagar and Naik, 2006).

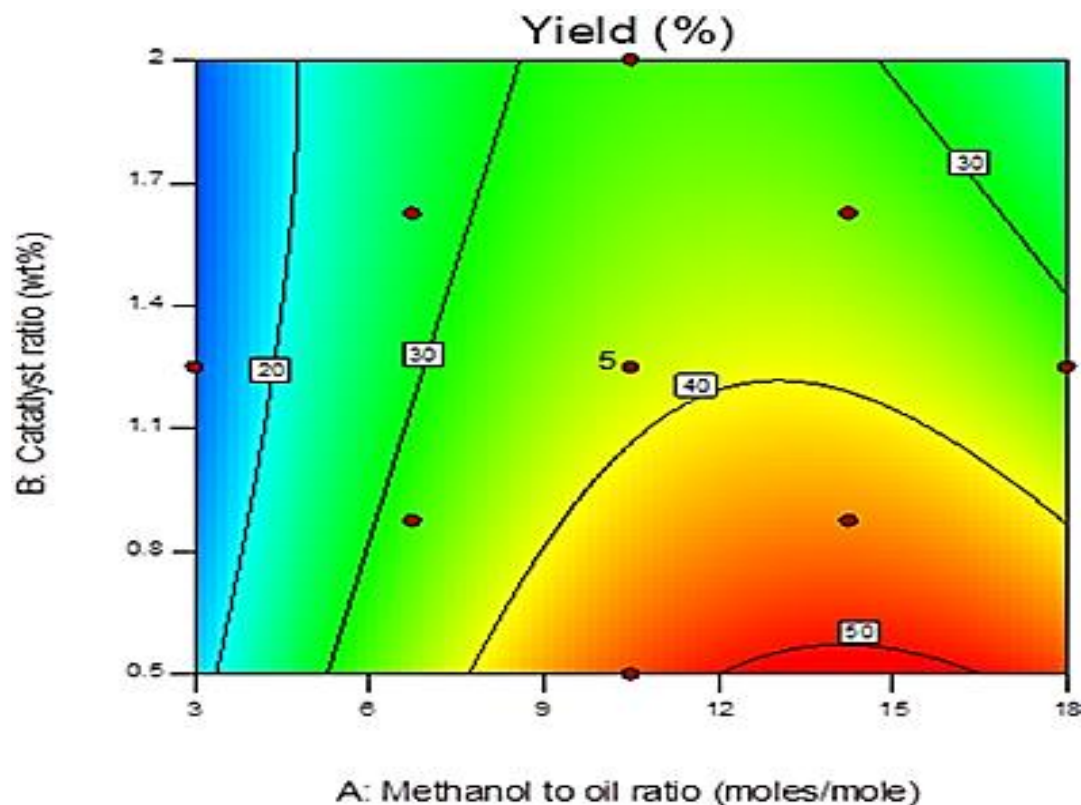


Fig.3-7: Contour Surface Plot of Biodiesel Yield.

The optimum biodiesel yield of 50.65% was obtained at 0.5 wt.% and methanol to oil ratio of 10.5; this can be seen in Fig.3-7. The red zone of the surface plot illustrates where the highest biodiesel yield obtained. As you move away from the red zone into the yellow and green zone, the biodiesel yields decrease. The blue zone represents the lowest biodiesel yield. This is due to increased catalyst concentration and low methanol to oil ratio not favouring the forward reaction as well as possible saponification.

3.5 Conclusion

Biodiesel is an environmentally friendly, renewable and biodegradable fuel and a potential substitute to conventional diesel, and can be produced using vegetable oil with short chains of alcohol. Therefore, this study aimed at optimising the biodiesel production from sunflower using

Sodium hydroxide as a homogeneous catalyst. The two parameters optimised were: methanol to oil ratio and catalyst ratio. A quadratic mathematic model using Central Composite Design from Response Surface Methodology was obtained. The highest yield of 50.65 % was obtained at methanol to oil ratio 10.5 and Catalyst ratio of 0.5 wt.% keeping the time, temperature, and stirring speed constant. The optimisation of the transesterification parameters of sunflower oil determined using Central Composite Design (CCD) shows that biodiesel yield is dependent on catalyst concentration and methanol to oil ratio. Analysis of variance (ANOVA) on biodiesel yield showed a $R^2=0.8387$. The results supported that sunflower oil can be used for biodiesel production.

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CHAPTER FOUR

4. BIODIESEL PRODUCTION FROM WASTE MARGARINE USING HOMOGENEOUS CATALYST POTASSIUM HYDROXIDE

4.1 Abstract

Biodiesel, an eco-friendly fuel is challenged by the high production cost mainly due to the cost of feedstocks. Waste margarine appears to be one of the alternatives. This work aimed at producing waste margarine biodiesel using a homogeneous catalyst potassium hydroxide (KOH). A laboratory-scale reactor consisting of flat bottom flask mounted with a reflux condenser, a hot plate as heating element equipped with temperature, timer and stirring rate regulator. The effects of four reaction parameters were studied, these were: methanol to oil ratio (3:1 to 15:1), catalyst ratio (0.3 to 1.5 wt. %), temperature (30 to 70 °C), time (20 to 80 minutes). The highest yield of 91.13 % was obtained at 60°C reaction temperature, 9:1 methanol to oil molar ratio, 0.9 wt. % catalyst ratio and 60 minutes. The important biodiesel fuel properties were found to be within specifications of the American Standard Test Method specifications (ASTM). It was concluded that waste margarine could be used to produce biodiesel as a low-cost feedstock.

Keywords: Biodiesel, Homogeneous catalyst, Transesterification and Waste Margarine.

4.2 Introduction

Biofuel ingenuity has been backed by many governments policies in the pursuit of lowering dependence on fossil fuels and the quest for energy security through partially replacing the limited fossil fuels and decreasing the threat to the environment from exhaust emissions (greenhouse gases) and global warming (Rice, Sanyal and Bata, 1991; Nigam and Singh, 2011; Bharathiraja *et al.*, 2014). Biodiesel is grander as compared to conventional diesel in terms of its lower Sulphur content, aromatic content and flashpoint. Biodiesel is basically Sulphur free and non-aromatic while conventional diesel can have up to 500ppm SO₂ and 20-40 wt. % aromatic compounds. These advantages could be a crucial solution in reducing urban pollution since the transport sector is the major contributor to the total gas emissions in the atmosphere (Utlü and Koçak, 2008).

The oils and fats used for biodiesel production range from edible oils to animal fat. These oils and fats are also used in the food industry. This is a stumbling block for the biodiesel industry to

overcome as it eats on the food sources. The use of edible oil for fuel is not a viable solution to the energy crisis, by using food to fuel motor vehicles is unethical, since there is starvation of majority of the global population (Ewing and Msangi, 2009). In the current day situation, biodiesel production cannot depend upon virgin vegetable oils; biodiesel ought to be produced in a way that does not cut into food supplies. An approach to resolve this problem is to use the waste from vegetable oils, collected from restaurants and food processing industries so to produce biodiesel. These oils can successively be more cost-effective to use as feedstock for biodiesel production (Gurunathan and Ravi, 2015). There are many losses during the production of butter and margarine, which averages 5tons of waste oils being produced in these factories every month. These wastes are flushed from production lines and disposed of by municipal utilities, such as sewage systems and landfills (Justino *et al.*, 2012).

Vegetable oils, unlike diesel fuel, comprise mainly of saturated hydrocarbons that are triglycerides. These triglycerides consist of esters and fatty acids. These fatty acids differ in the length of the carbon chain and the number of double bonds (Enweremadu and Mbarawa, 2009). The biodiesel synthesis has two main reactions, which are transesterification and esterification. The main product for both reactions is Fatty Acid Alkyl Esters (FAAE), despite that the main reactants differ. The main reactant for the transesterification reaction is triglyceride, while the reactant for the esterification reaction is free fatty acid. Transesterification is where an ester is formed from one form to the next (Santori *et al.*, 2012). Transesterification is the main used method of biodiesel production, which is a three steps reaction in which the triglyceride reacts with alcohol to produce an ester and diglyceride, followed by the diglyceride reacting with alcohol to produce another ester and a monoglyceride. And lastly, alcohol reacts with monoglyceride to form the third ester and glycerol (Abdullah *et al.*, 2007; Yusuf, Kamarudin and Yaakub, 2011).

A catalyst can be described as a substance that changes the rate of a reaction without being part of the reaction itself. Catalysts are used to speed up the rate of reaction; the catalyst changes the mechanism of the reaction. This mechanism lowers the activation energy and in turn, increasing the rate. A catalyst does not affect or shift the equilibrium of the reaction (Latchubugata *et al.*, 2018). There are two types of catalyst that can be used in the production of biodiesel; the catalysts can either be homogeneous, and heterogeneous (characterised as acid, alkaline and enzymatic). In earlier years of biodiesel production, more research was focused on the heterogeneous catalyst

with the hope of decreasing the production cost as the catalyst could be reused. The disadvantage of using the heterogeneous catalyst is that the operating temperature has to be quite high for the catalyst to work efficiently (Mittelbach and Trattnigg, 1990; Sivasamy *et al.*, 2009; Lam, Lee and Mohamed, 2010; Verma and M P Sharma, 2016), this then makes a homogeneous catalyst a viable option as the operational cost is far lower. Also, the reusability of the heterogeneous catalyst is not favourable, according to (Agarwal *et al.*, 2012), who reported there was a drop in the yield from 96.8% to 83.1% after just three cycles.

With increasing anxieties with regards to environmental impacts and the skyrocketing prices of petroleum has encouraged extensive studies to identify different fuel sources. Biofuels have attracted researchers' attention globally due to its renewability, biodegradability and low gas emission (Phan and Phan, 2008). Waste margarine has been known as a possible feedstock in the production of biodiesel. The waste margarine can be obtained at a low cost, which will, in turn, decrease the production cost. This study aimed at producing biodiesel from waste margarine using potassium hydroxide as a catalyst. In this study, the effects of process parameters on the biodiesel yield, such as methanol to oil ratio, catalyst ratio, reaction time and temperature, were investigated. The fuel properties, such as flash point, density, viscosity, sulphur and water content, were evaluated.

4.3 Materials and methods.

4.3.1 Materials and reagents

The waste margarine was sourced from a local margarine manufacturing plant. Potassium hydroxide (85%) used as a catalyst for the transesterification, Methanol (99.5%), Phenolphthalein Indicator used as an indicator, were sourced from ACE (Associate Chemical Enterprises) a local laboratory chemicals supplier.

4.3.2 Experimental Design

The experimental design used in this paper was one factor at a time (OFAT). The parameters were methanol to oil ratio, catalyst ratio to the oil ratio, temperature and reaction time.

Table 4-1: Experimental Design

| Parameter | Variable level | | | | |
|---|----------------|-----|-----|-----|-----|
| Methanol to oil ratio (mole/mole) | 3 | 6 | 9 | 12 | 15 |
| Catalyst ratio (wt. %) | 0.3 | 0.6 | 0.9 | 1.2 | 1.5 |
| Temperature (°C) | 30 | 40 | 50 | 60 | 70 |
| Time (minutes) | 20 | 35 | 50 | 60 | 80 |

4.3.3 Experiment Set-Up

The basic setup involves a reaction vessel that comprises a two-neck round-bottom flask that was fitted with a condenser and temperature controller. The condenser was fitted to make sure that any evaporated methanol does not leave the system when during the reaction at temperatures near or higher than the boiling point of methanol. The temperature controller was used to control the reaction temperature by automatically regulating the set reaction temperature. The reaction vessel was placed on a heating plate to retain the heat of the reaction. In the reaction vessel was also a magnetic stirrer to agitate the reaction mixture.

4.3.4 Experimental procedure

The waste margarine was heated at 110°C for an hour; then 1 gram of the heated margarine was placed in a conical flask. 10ml of isopropanol and three drops phenolphthalein were added to the flask. The mixture was heated for 10 minutes while using a magnetic stirrer to mix all the contents. After being cooled, the mixture was titrated with 0.1N KOH standard. The procedure was done in triplicate to get the average percentage. The Acid Value (AV) was calculated using (4-1), and the FFA percentage was obtained using (4-2). The FFA was found to be 1,79% which is below 2% which means the transesterification process could use KOH as the catalyst without forming an undesirable side reaction of saponification, which could decrease the ester content.

$$AV = \frac{ml\ of\ KOH \times N \times 56}{weight\ of\ sample} = mg\ of\ KOH \quad (4-1)$$

$$FFA\ \% = AV \times 0.503 \quad (4-2)$$

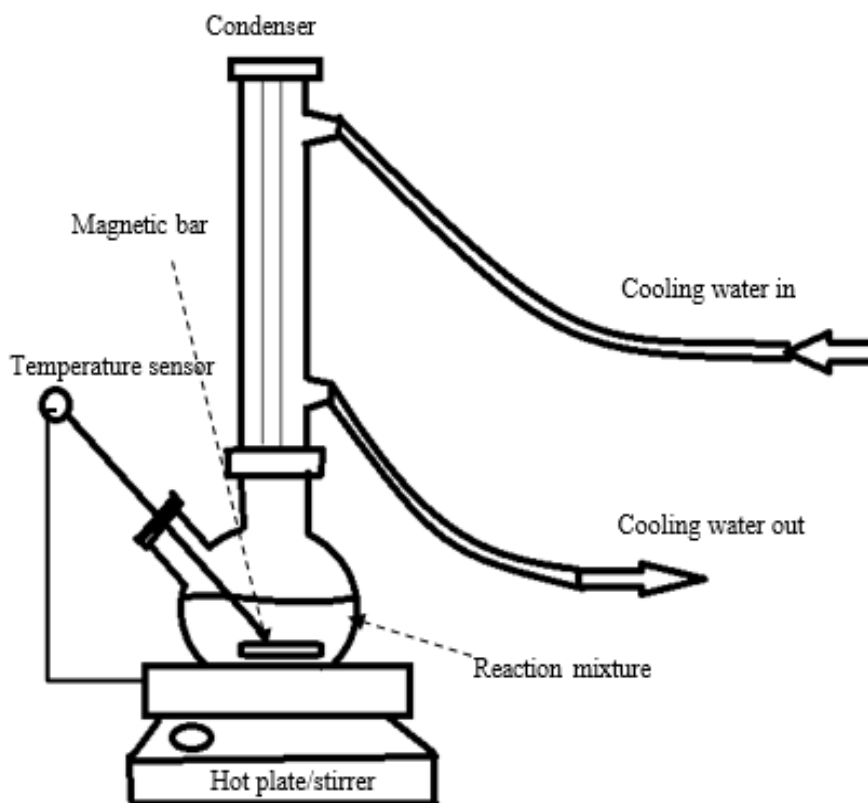


Fig. 4-1: Experiment set-up

The oil was heated at a temperature of 105 °C to ensure that little to no traces of water was present in the waste margarine, the reason of doing so is to prevent saponification reaction during the transesterification reaction, which is favoured by the presence of water. The condenser connected to the reactor vessel was cooled with tap water. Potassium methoxide was produced by mixing the required amount of methanol and potassium hydroxide. Oil was placed in the conical flask heated to the set temperature, once the set temperature was reached the methoxide was added to the reacting vessel and the timer was started. The methanol to oil molar ratio and catalyst ratio, reaction time and temperature were varied according to the experimental design. When the reaction time elapsed, the mixture was then emptied into a separating funnel where it separated into two layers the biodiesel and the glycerol layer. The glycerol layer the much denser fluid at the bottom was removed, leaving the biodiesel in the flask. The biodiesel was then washed with distilled water at 60°C; this was done to ensure that any traces of methanol and KOH are washed off from the biodiesel. The washed biodiesel was then dried using a heating plate at 105°C until no trace of

water was observed. The product was then cooled, and the biodiesel yield was calculated as per (4-3).

$$\text{Biodiesel yield} = \frac{\text{Mass of dry biodiesel}}{\text{Mass of oil}} \times 100 \quad (4-3)$$

4.4 Results and discussion

4.4.1 Effect of process parameters

The effect of methanol to oil molar ratio was evaluated at 0.9 wt. %, 60°C and 60 minutes, constant catalyst ratio, temperature and time, respectively. This is shown in fig.4 -2. Methanol to oil molar ratio was varied from 3:1 to 15:1 at 3:1 increment. The Influence of methanol to oil ratio is one of the most significant dynamics affecting the conversion efficiency of waste margarine to biodiesel yield. There was a steady increase in the conversion of the methyl esters content, and the highest yield was obtained at 12:1 (mole/mole) yielding 89.55%. The stoichiometric molar ratio of methanol to oil in the transesterification is 3:1, and the reaction is reversible, then higher molar ratios are required to increase the miscibility and to enhance the contact between the alcohol molecule and the triglyceride (Banerjee and Chakraborty, 2009). Meng, Chen and Wang (2008), obtained their highest yield at a ratio of 6:1. For the 15:1 molar ratio, the separation of glycerol became complex, and therefore the actual yield of biodiesel was reduced as a result of a fraction of the glycerol remaining in the biodiesel stage. The molar ratio of 9:1 seems to be the most suitable as there was no must difference in the yield as compared to the ratio of 12:1.

The effect of the catalyst was evaluated at 9:1, 60°C and 60 minutes, constant methanol to ratio, temperature and time, respectively. The catalyst was varied from 0.3 wt. % to 1.5wt. %. The effect of catalyst on the biodiesel yield is shown in fig. 4-3. There is an increase in biodiesel yield with an increase in catalyst concentration. Since the catalyst is there to speed up the reaction meaning it facilitates the forward reaction to reach equilibrium in a shorter space of time. The highest yield of 87.41% was obtained at 0.9 wt. %, but the catalyst load of from 0.9wt% to 1.5 wt. % lowered the percentage yield. The excess catalyst concentration increases the viscosity and also the formation of a gel and emulsion (Modiba, Osifo and Rutto, 2014a). It was also observed that the sample became dark in colour when the catalyst concentration was increased. Another explanation to why there is a retardation in the yield as the catalyst concentration is increased is since the KOH

may react with the FFA present in the glyceride during the transesterification, resulting in the formation of soap by saponification, this may consume the catalyst and reduce the efficiency.

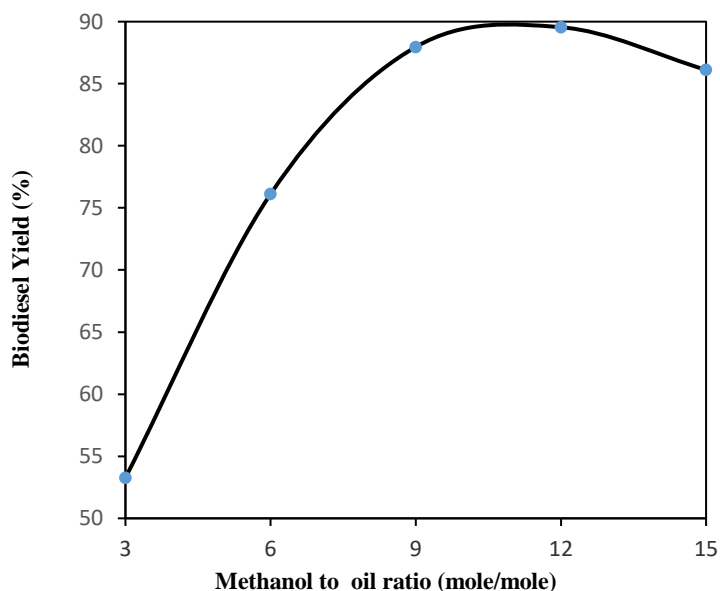


Fig. 4-2: Effect of methanol to oil ratio on the biodiesel yield.

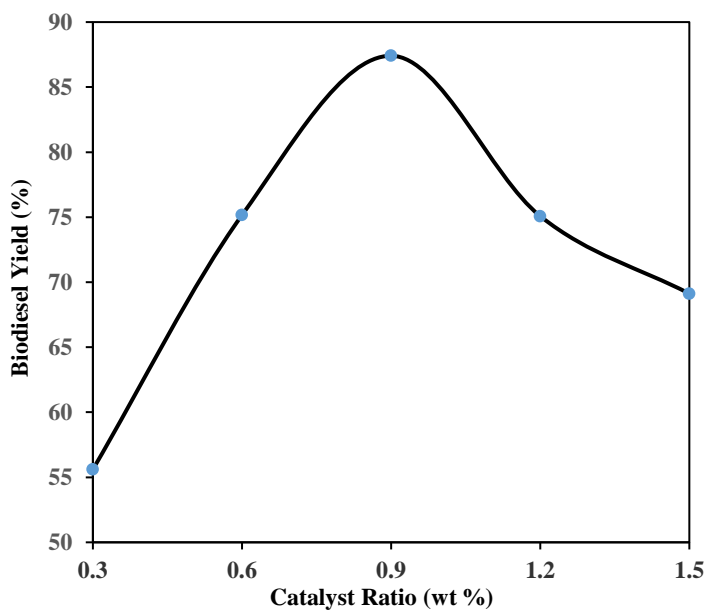


Fig. 4-3: Effect of catalyst ratio on the biodiesel yield

The effect of reaction temperature on the biodiesel yield was evaluated at 9:1, 0.9 wt. % and 60 minutes, constant methanol to ratio, catalyst ratio and time, respectively. The temperature was varied from 30°C to 70°C at 10°C increments. The effect of reaction temperature on the esters content is shown in fig. 4-4. There was an increase in the yield of the biodiesel from 30-60°C. The

highest yield of 87.85 % was obtained at 60 °C. According to (Cvengroš and Cvengrošová, 2004), the ideal reaction temperature is near the boiling point of the alcohol. Several studies reported that getting a high biodiesel yield the best reaction temperature must be in a range of 50°C- 70°C (Meng, Chen and Wang, 2008). The yield did not much drop above boiling temperature; this was due to the reflux, condenser that was placed. The decrease can be explained by the fact that the temperature is above the boiling point of methanol, and some of the methanol was in the vapour phase in the condenser, causing a reduction of methanol in the reaction media. The decrease of methanol concentration then shifts the reaction equilibrium to the left, which can decrease the yield.

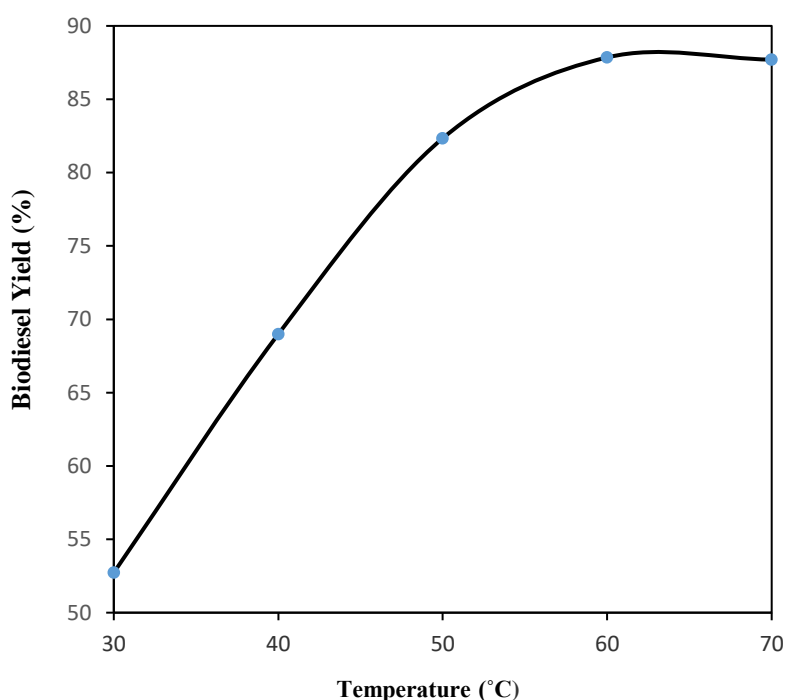


Fig. 4-4:Effect of temperature on biodiesel yield

The effect of reaction time on biodiesel yield was evaluated at 9:1, 0.9wt. % and 60°C, constant methanol to ratio, catalyst ratio and temperature, respectively. The effect of reaction time on the biodiesel yield was evaluated by varying time from 20 minutes to 80 minutes, as shown in fig. 4-5. As time was increased, an increase in the yield was also observed; this increase in yield is explained due to the fact that there was enough retention time for the reaction to occur. The maximum yield of 91.13 % was obtained at 60 minutes. The yield remained relatively constant as the time was increased to 80minutes, a very slight decrease was observed; this is explained by the

equilibrium reached. Further increase of time will cause a decrease in yield due reaction shifted to the left, causing loss of methyl esters and causing more fatty acids to form soaps (Leung, Wu and Leung, 2010).

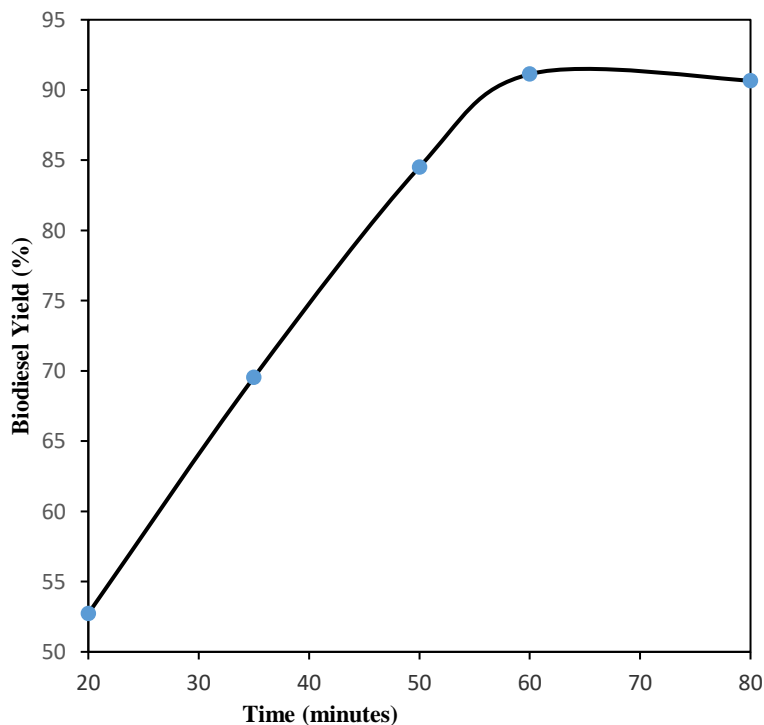


Fig. 4-5:Effect of time on the biodiesel yield

4.4.2 Fuel properties

The biodiesel sample produced at the optimum conditions was analysed to determine whether the biodiesel conforms to the ASTM standards. All the major fuel properties analysed were found to meet ASTM standards; these are summarised in Table 4-2

Table 4-2: Fuel properties of biodiesel from waste margarine

| Properties | ASTM D6751-02 | Results |
|--------------------------------------|---------------|---------|
| Flash Point (°C) | >130 | 148 |
| Density (g/cm ⁻³) | 0.86-0.9 | 0.8687 |
| Water Content % volume fraction, max | 0.05 | 0.0295 |
| Viscosity (mm ² /s) | 1.9 to 6.0 | 4.6503 |
| Sulphur content mg/kg, max | 10 | 8.32 |

4.5 Conclusion

The main objective of this study was to produce biodiesel from waste margarine, using waste margarine as a source of triglyceride, and the reaction was catalysed by Potassium hydroxide. The highest yield was obtained at 60 °C, alcohol to oil molar ratio of 9:1, catalyst load of 0.9wt%, and 60 minutes reaction time. An increase in the amount of alcohol to oil increases biodiesel yield and biodiesel purity; this increases the miscibility and enhances the contact between the alcohol molecule and the triglycerides. An increase in reaction temperature beyond 60°C decreased the yield, so a maximum point was determined. The optimal time was achieved, and it meant there was enough retention time to occur. The biodiesel produced met the ASTM standards. Further studies are recommended for the optimisation of biodiesel produced from margarine waste with different catalysts.

4.6 References

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CHAPTER FIVE

5. IN SITU REAL-TIME MULTIVARIATE ANALYSIS OF METHANOLYSIS MONITORING OF SUNFLOWER OIL USING FTIR

5.1 Abstract

The combination of the world population and the third industrial revolution led to high demand for fuels. On the other hand, the decrease of global fossil fuels deposits and the environmental air pollution caused by these fuels has compounded the challenges the world faces due to its need for energy. Therefore, new forms of environmentally friendly and renewable fuels such as biodiesel are needed. The primary analytical techniques for methanolysis yield monitoring have been chromatography and spectroscopy; these methods have been proven reliable but are more demanding, costly and do not provide real-time monitoring. In this work, the *in-situ* monitoring of biodiesel from sunflower oil using FTIR (Fourier Transform Infrared) has been studied; the study was performed using EasyMax Mettler Toledo reactor equipped with a DiComp (Diamond) probe. The quantitative monitoring of methanolysis was performed by building a quantitative model with multivariate calibration using iC Quant module from iC IR 7.0 software. Fourteen samples of known concentrations were used for the modelling which were taken in duplicate for model calibration and cross-validation, data were pre-processed using mean centring and variance scale, spectrum math square root and solvent subtraction. These pre-processing methods improved the performance indexes from 7.98 to 0.0096, 11.2 to 3.41, 6.32 to 2.72, 0.9416 to 0.9999, RMSEC, RMSECV, RMSEP and R^2 Cum, respectively. The R^2 value of 1 (training), 0.9918 (test), 0.9946 (cross-validation) indicated the fitness of the model built. The model was tested against univariate model; small discrepancies were observed at low concentration due to unmodelled intermediates but were quite close at concentrations above 18%. The software eliminated the complexity of the Partial Least Square (PLS) chemometrics. It was concluded that the model obtained could be used to monitor methanolysis of sunflower oil at industrial and lab scale.

Keywords: Biodiesel, calibration, chemometrics, FTIR, methanolysis, multivariate analysis, transesterification

5.2 Introduction

Global energy supply such as heating, transportation and power plants generally produced from fossil sources. The increase in the worldwide population and the industrialisation of the 21st century have caused a high demand for fuels. This increase in the consumption of fossil fuel resulted in the depletion of global fossil fuels deposits and the increase of environmental air pollution caused by these fuels. Therefore research has to focus on developing new forms of environmentally friendly and renewable forms of fuels (Marchetti, Miguel and Errazu, 2007; Leung, Wu and Leung, 2010; Atabani *et al.*, 2013; Avhad *et al.*, 2016; Pourzolfaghar *et al.*, 2016; Verma and Sharma, 2016b; Yusoff *et al.*, 2016; Amoah *et al.*, 2017; Baskar *et al.*, 2017; Muthukumaran *et al.*, 2017). Global energy consumption has doubled from 1973 to 2013; this is expected to increase by 34% from 2014 to 2035 for which the transportation sector is the leading CO₂ emitter accounting for 33.6%. Renewable energy comes from sources such as geothermal energy, solar, biomass and hydropower, for which solar is the most growing renewable energy. However, biomass is classified as the only green carbon (Ilmi *et al.*, 2017).

Biodiesel is defined as an alkyl ester; it is produced by reacting triglycerides with short-chain alcohols. The short-chain alcohols that are mostly used are methanol and ethanol (Zagonel, Peralta-Zamora and Ramos, 2004; Demirbas, 2009; Leung, Wu and Leung, 2010; Chouhan and Sarma, 2011; Richard *et al.*, 2011; Avhad and Marchetti, 2015; Avhad *et al.*, 2016). Among the advantages of biodiesel compared to its counterpart petroleum diesel are: low environmental impact, reduction of greenhouse gases effects due to less SO_x, NO_x and CO₂ gases emissions, biodegradability, high cetane number, high combustion efficiency; these advantages made biodiesel to be classified as a renewable fuel (Marchetti, Miguel and Errazu, 2007; Lukovi, Knežević and Bezbradica, 2011; Sani, Daud and Abdul, 2013; Avhad and Marchetti, 2015b; Mardhiah *et al.*, 2017). According to estimations, each kilogram of biodiesel produced reduces the CO₂ emission by 3.2 kilograms as compared to petroleum diesel (Kim *et al.*, 2004; Patil and Deng, 2009).

The transesterification reaction is the reaction of triglycerides and short-chain alcohol such as methanol or ethanol at a specific temperature in the presence of a catalyst; glycerol is also produced as a by-product. Transesterification is a reversible reaction; hence, the alcohol has to be in excess to favour the forward reaction (Al-zuhair, Wei and Song, 2007; Zhang *et al.*, 2010; Killner, Rohwedder and Pasquini, 2011; Sani, Daud and Abdul, 2013; Thinnakorn and Tscheikuna, 2014;

Amoah *et al.*, 2016; Firdaus, Guo and Fedosov, 2016; Knothe and Razon, 2017). The reaction conditions, feedstock compositional limits and post-separation requirements are determined by the nature of the catalyst (Zhang *et al.*, 2010; Killner, Rohwedder and Pasquini, 2011; Sani, Daud and Abdul, 2013; Khritsayaporn Thinnakorn and Tscheikuna, 2014; Amoah *et al.*, 2016; Firdaus, Guo and Fedosov, 2016; Knothe and Razon, 2017).

Generally, the catalysts used in biodiesel production are characterised in three categories namely: alkalis (heterogeneous and homogeneous), acids (heterogeneous and homogeneous) and enzymes. In comparison with enzyme catalysts, homogenous alkali and acid catalysts are the most used in biodiesel production (Al-zuhair, Wei and Song, 2007; Ejikeme *et al.*, 2010; Lam, Lee and Mohamed, 2010; Cossio *et al.*, 2012; Samir Najem Aldeen Khurshid, 2014; Guldhe *et al.*, 2015; Talha and Sulaiman, 2016). The mostly used homogenous base catalysts are sodium hydroxide, potassium hydroxide; the mostly used homogenous acid catalyst are Sulphuric acid, hydrochloric acid and phosphoric acid. Alkali catalysts are preferred due to their advantages such as low cost, the fast reactions and less energy requirement (60 °C is enough for high yield, while acid catalysts require more than 100 °C) (Killner, Rohwedder and Pasquini, 2011; Avhad and Marchetti, 2015). Heterogeneous alkali catalysts used in methanolysis are magnesium oxide (MgO), calcium oxide (CaO) and strontium oxide (SrO). Liquid and immobilised enzymes have attracted researchers' attention as they prevent soap formation and the product obtained is of good quality thus, reducing the purification processes (Al-zuhair, Wei and Song, 2007; Lam, Lee and Mohamed, 2010; Avhad and Marchetti, 2015; Talha and Sulaiman, 2016).

To ensure biodiesel quality, fuel properties and reaction monitoring transesterification, analytical methods have been used and reported by many scholars. The primary analytical method used to quantitatively and qualitatively monitor biodiesel yield has been Gas Chromatography (GC), this has the advantage to determine intermediate and other components. These components are; monoglycerides, diglycerides, glycerol moiety and unreacted triglyceride (Monteiro *et al.*, 2008; Zhang, 2012; Mahamuni *et al.*, 2017). Flame ionisation detection (FID) has been a widely used detector; the introduction of the mass spectrometer has increased the efficiency of the method (Monteiro *et al.*, 2008; Zhang, 2012; Mahamuni *et al.*, 2017). Numerous other methods have been employed such: Capillary Gas Chromatography (CGC) (Zagonel, Peralta-Zamora and Ramos, 2004; Yuan *et al.*, 2014), High Pressure Liquid Chromatography (HPLC) (Zagonel, Peralta-Zamora and Ramos, 2004; Monteiro *et al.*, 2008b; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017), Gel

Permeation Chromatography (GPC) (Dubé *et al.*, 2004; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017), FTIR Spectroscopy (Zagonel, Peralta-Zamora and Ramos, 2004; Knothe, 2006; Richard *et al.*, 2011b; Yuan *et al.*, 2014; Rabelo *et al.*, 2015; Cunha *et al.*, 2017a; Mahamuni *et al.*, 2017; Mohamed Shameer and Ramesh, 2017; Mowla, Kennedy and Stockenhuber, 2018; Purandaradas *et al.*, 2018), Ramon Spectroscopy (Richard *et al.*, 2011; Yuan *et al.*, 2014), Size Exclusion Chromatography (Zagonel, Peralta-Zamora and Ramos, 2004; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017), Nuclear Magnetic Resonance (NMR) (Dubé *et al.*, 2004; Zagonel, Peralta-Zamora and Ramos, 2004; De Lima *et al.*, 2014b; Yuan *et al.*, 2014), Ultra-sonication assisted spray ionization (UASI) spectroscopy, fluorescence spectroscopy (Zagonel, Peralta-Zamora and Ramos, 2004; Chand *et al.*, 2008; Yuan *et al.*, 2014b; Rabelo *et al.*, 2015; Mahamuni *et al.*, 2017; Mowla, Kennedy and Stockenhuber, 2018), UV spectroscopy (Richard *et al.*, 2011), Thin Layer Chromatography (TLC), thermogravimetric analysis (TGA)(Mahamuni *et al.*, 2017), Viscometry (Yuan *et al.*, 2014; Mahamuni *et al.*, 2017).

Chromatography and Spectroscopy are the most used methods of qualitative and quantitative methods of biodiesel are reputed for their accurateness. Nevertheless, they have disadvantages such as time-consuming (require extensive sample preparation), require highly qualified personnel, and their usage for in situ real-time monitoring transesterifications (fast reversible reactions) has not been feasible, except FTIR. FTIR spectroscopy has been reported as an accurate, fast and reliable method for quantitative and qualitative analysis of *in-situ* transesterification monitoring (Zagonel, Peralta-Zamora and Ramos, 2004; Yuan *et al.*, 2014; Rabelo *et al.*, 2015; Mahamuni *et al.*, 2017; Oleszko *et al.*, 2017). Many authors have reported the use Infrared Spectroscopy such as NIR (Near Infrared) spectroscopy, FTIR for real-time transesterification (Richard *et al.*, 2011; de Souza, Adriana Velloso, Cajaiba da Silva, 2012; Mueller *et al.*, 2013; De Lima *et al.*, 2014; Yuan *et al.*, 2014).

FTIR analysis uses infrared spectroscopy technique, in which the electromagnetic energy of the radiation spectrum is used, the energy used in spectroscopy has wavelengths between the visible light and radio waves (Zhang, 2012). The infrared region used in infrared spectroscopy is divided into three regions which are: Near-infrared (NIR) wavenumber ranging 12500-400 cm^{-1} , mid-infrared (MIR) wavenumber ranging 4000-400 cm^{-1} and far-infrared (FIR) wavenumber ranging 400 to 33 cm^{-1} (Zhang, 2012). MIR has been the most used region and used in this study. Infrared

spectroscopy has been in use for analysis for the past 70 years; infrared spectrums are classified as fingerprints of materials or samples, these fingerprints are constituted of absorption peaks that correspond to the frequencies of vibrations of atomic bonds constituting the material (Singh *et al.*, 2011).

Attenuated total reflection Fourier Transform Infrared (ATR-FTIR) coupled with PLS regression, has been reported by (Rabelo *et al.*, 2015) to be used in the multivariate calibration models for determining the content of biodiesel in its blend with petroleum diesel. The designed model was shown to be reliable for determining biodiesel-diesel blends. This same approach was used to determine the vegetable oil used in the transesterification by using FTIR in combination with soft independent modelling of class analogy (SIMCA), hierarchical cluster analysis (HCA), interval principal component analysis (iPCA) and principal component analysis (PCA). PLS combined with interval partial least squares (iPLS) and synergy partial least squares (siPLS) regressions were further used to determine the quality variables (amount, flash point, sulfur content and specific gravity) of diesel/biodiesel blends. These were further used to identify the most suitable region for each studied property (Rabelo *et al.*, 2015). Quantification of biodiesel yield using ATR-FTIR coupled with PLS regression was also used in microwave-assisted methanolysis of soybean oil by (Rabelo *et al.*, 2015). Zagonel, Peralta-Zamora and Ramos (2004), worked on the transesterification of degummed oil and ethanol, applying FTIR and multivariate analyses. Also, concluded that using FTIR to monitor transesterification was a fast and reliable analytical method. The above mentioned were confirmed by Richard *et al.* (2011) in their work on transesterification of high oleic sunflower oil with ethanol.

Transesterification monitoring of vegetable oils using FTIR being a fast and accurate analytical method needs the application of multivariate analysis to be successfully reliable and industrial quality control (Zagonel, Peralta-Zamora and Ramos, 2004; Yuan *et al.*, 2014; Cunha *et al.*, 2017a; Mahamuni *et al.*, 2017). FTIR, coupled with multivariate analysis for complex reaction attracted researchers since the late 90s (Zagonel, Peralta-Zamora and Ramos, 2004).

FTIR uses fibre-optic, which was developed to work in the mid and NIR regions (Zagonel, Peralta-Zamora and Ramos, 2004). Singh *et al.* (2011) used fibre optic and PLS to quantify methyl ester from transesterification of soybean oil, and he made use of the difference in NIR spectra between methyl esters at 6005 cm^{-1} and 4428 cm^{-1} . A cut band on a shoulder band of the oil (triglycerides)

was observed, also made use of the loss of OCH_2 groups in glycerol moiety, which resulted in a decrease in the 1378 cm^{-1} peak, this was analysed by FTIR (Dubé *et al.*, 2004).

Most of the multivariate calibration methods that have been developed use mainly PLS, Principal Component Regression (PCR) and PCA techniques. These methods have been reported to be tiresome as they necessitate simultaneous decomposition of absorption matrices and concentration in computing the spectral loading. The spectral loadings are afterwards used to determine the most impacting spectra to the calibration model. The multivariate calibration methods can be improved by increasing the number of calibration and validation samples (Mahamuni *et al.*, 2017). The regression calibration models can be improved by first using pre-processing methods such as mean centring technique (Cunha *et al.*, 2017; Mahamuni *et al.*, 2017) and baseline correction has been often used in as pre-processing method (Cunha *et al.*, 2017). Mean centring has been the most used pre-processing technique. Executing mean centring over numerous factors brings about the removal of the mean sample vector from all sample vectors in the data collection. Afterwards, the relative contrasts of the spectrum intensity at different wavelengths are more straightforward to recognise (Cunha *et al.*, 2017a). After a calibration model has been pre-processed, performance index algorithms are used to access the performance and accuracy of the model. These algorithms are Root Mean Square Error (RMSE), Root Mean Square Error of Calibration (RMSEC), Root Mean Square Error of Prediction (RMSEP) and Root Mean Square Error of Cross-Validation (RMSECV) (Mahamuni *et al.*, 2017). Though the use of PLS and PCA generate a reliable and robust model, they rely on Beer's law, which has high complex, mathematics (Mahamuni *et al.*, 2017). Therefore, the use of software becomes essential, as it was the case in this study, in which iC Quant Module Multivariate modelling was employed.

The most used analytical methods of biodiesel monitoring, namely Chromatography and Spectroscopy, offer information on the composition of the mixture. Though spectroscopy can be used for *in-situ* monitoring, they all offer some limitation for the fact that they can only be performed when the reaction had occurred or by an off-taking sample from the reaction mixture. FTIR spectroscopy offered the possibility of *in-situ* real-time monitoring of the process and had been found to be non-destructive, user-friendly and a rapid analytical technique. Therefore, this study aimed at developing *in-situ* real-time monitoring of the transesterification reaction using EasyMax 102 and the iC Quant module from iC IR 7.0 software, by simplifying the mathematical

complexity and time-consuming of taking spectra and transforming of multivariate analysis. Sample validation and performance index were performed to check the accuracy of the model built.

5.3 Materials and methods

5.3.1 Materials and reagents

Refined sunflower oil (triglyceride) was sourced from Golden Fry, a local cooking oil supplier. Sodium hydroxide (99.5%) used as a catalyst for the transesterification reaction and methanol (99%) used as an acyl acceptor for the transesterification reaction, hexane (99.5%) used as GC solvent and phosphoric acid (99.5%) used for washing biodiesel, were sourced from ACE (Associate Chemical Enterprises) a local laboratory chemicals supplier.

5.3.2 Standard Preparation

The biodiesel standard used in this work was obtained by transesterification reaction of sunflower with methanol in a laboratory-scale reactor composed of flat bottom flask mount with a reflux condenser and hot plate with magnetic stirrer equipped with a temperature controller. Sunflower oil was heated for 60 minutes at 105 °C for moisture removal. The transesterification reaction occurred under the following conditions: Atmospheric pressure, 60 °C, 12 methanol to oil mole ratio, 60 minutes reaction time, 1wt% (compared to oil) catalyst ratio and 600RPM stirring speed. The product obtained was separated by density difference using separating funnel, the bottom layer containing glycerol was then removed, and the remaining contained an excess of methanol. The excess methanol was removed by distillation. The biodiesel was vigorously washed with acidic water containing 3% phosphoric acid until the water was clear; the acidity had purpose to remove any soap and catalyst from the product (Abbaszadeh *et al.*, 2014). The washed biodiesel was heated at 105 °C for moisture removal, cooled and stored. A sample was collected for characterisation with GC-FID. The biodiesel standard produced was used to prepare 15 standard samples, for which one was methanol, and 14 were a mixture of biodiesel and sunflower oil at different concentrations for FTIR/PLS calibration using ReactIR 15 and data processing using iC IR software 7.0 and iC Quant Module from Mettler Toledo Easymax 102.

5.3.3 In-Situ Real-Time Transesterification

The *in-situ* transesterification methanolysis or transesterification of sunflower oil was performed in a Mettler Toledo Easymax 102 reactor. Mettler Toledo Easymax 102, as shown in Fig. 5-1, is equipped with two reactors of 100 ml each. The reactor was mounted with a reflux condenser and a mechanical stirrer. Easymax reactors have the advantage to simultaneously and independently controlling two reaction mixtures. The dosing mechanism has a purpose of allowing more accurate reactant addition to the system. Easymax 102 has the advantage to control the parameters such as temperature and pH in the specified range. The temperature is controlled by adjusting the heat of reaction and mixture by the heating and cooling system installed. All results timeously recorded for analysis at a further stage. EasyMax 102 is equipped with incorporated real-time *in-situ* instruments; this enables a depth process understanding and makes the determination of the kinetics easier. This instrument further allows the correction of parameters as they are quickly analytically detected (Guth, 2016).

A batch set up was carried by weighing approximately 50g of sunflower oil and transferred in the reactor, approximately 17g (approximating 9 moles) of methanol was weighed and mixed with approximately 0.5g (1wt % compared to oil) of Sodium Hydroxide and pumped in the reactor. A new batch transesterification reaction experiment was set using iControl software 5.0, with 55 °C, 200 RPM, 60 minutes; reaction temperature, stirring speed and reaction time, respectively. The reaction timing and stirring were set to start once the reaction mixture reached the set temperature, then using FTIR probe of the ReactIR spectrums were collected every 15 seconds by inserting the probe in the reaction mixture, this further produced a surface plot on the iC IR software for online quantification with the calibrated model. The overhead impeller was used as a stirring element.



Fig. 5-1: Mettler Toledo Easymax 102 equipped with a dosing system

5.3.4 GC analysis of the standard

The GC analysis of the standard was performed using flame ionisation (FID) on Trace 1310 Thermo Scientific (USA) Gas Chromatograph (GC) instrument, equipped with an automatic sampler and injector AI 1310. The separation was carried out in a BPX70-FAME optimised capillary column (Phase: BPX70, 0.25 μm film, Column: 25 m x 0.32 mm ID) from SGE (USA).

A constant flow of 2.2ml/l of the carrier (helium) was used, and the column head pressure was adjusted to 11.8 psi. The injection temperature was 250 °C; the injection mode was split with a ratio of 8:1, the detector temperature was 300 °C, and the injection volume was one μL . The initial temperature was 80 °C held for 2 minutes, firstly ramped to 130 °C at a rate of 50 °C/minutes held for 10min, secondly ramped to 172 at a rate of 2 °C/minutes and held for 6 minutes. The total run time was 33 minutes. Hexane was used as a solvent to prepare standard solutions. The methyl esters percentage was calculated by doing average the sum of triplicate surface areas of every methyl ester of the sample from the data of GC this was 99.57 % and used as standards.

5.3.5 FTIR spectrums collection

FTIR spectrums were collected on the 15 samples, for which one was pure methanol which was used for solvent subtraction on the multivariate data analysis. The probe was introduced in all the 14 biodiesel/sunflower oil mixture samples to collect samples in duplicate for multivariate

calibration; these are shown in Fig.5-2.

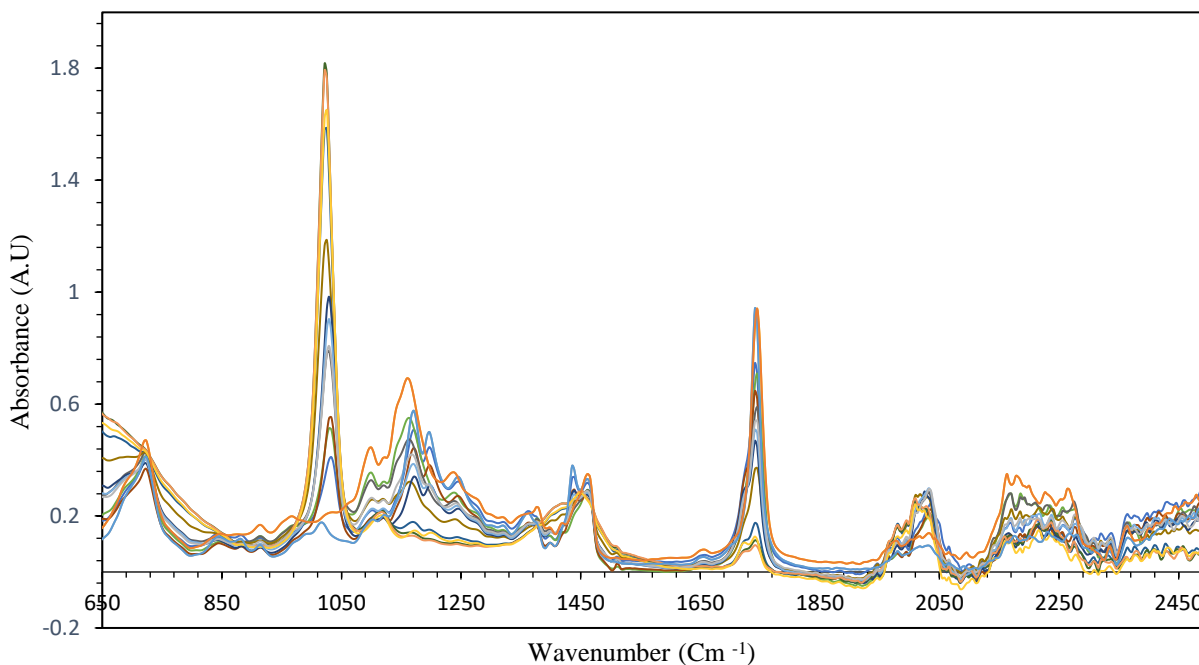


Fig. 5-2: Spectrums for multivariate analysis

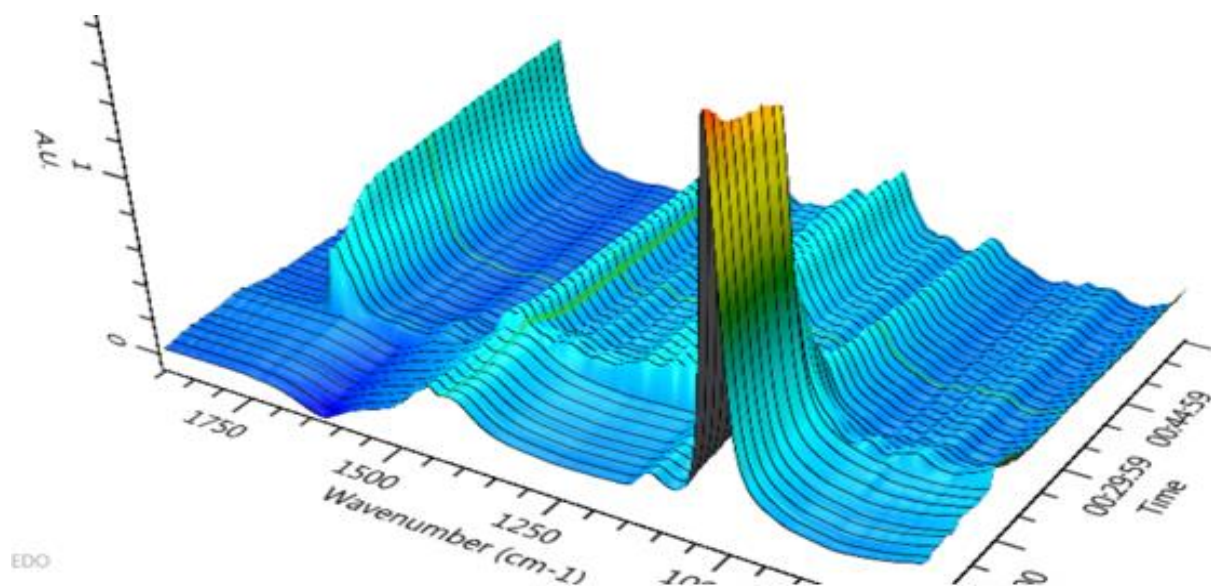


Fig. 5-3: Surface plot of the online monitoring of transesterification

For the real-time analysis, the inserted probe in the reaction mixture was collecting spectrums every 15 seconds, which was transferred to the iC IR software for interpretation. The spectrums recorded by averaging 128 scans in the wavenumber ranging from 2500 to 650 cm^{-1} using

ReactIR15 spectrometer from Mettler Toledo. The ReactIR15 spectrometer instrument operates with an MCT detector, 8 cm⁻¹ resolution, Happ-Genzel apodization DiComp (Diamond) probe and AgX 6mm x 2m Fiber (Silver Halide) interface.

5.3.6 Multivariate analysis

The multivariate analyses were performed on 14 samples of standards mixture containing different concentrations; the mixture concentrations were in a way that the entire range of conversion was covered. The multivariate analyses of the average FTIR spectra of the 14 samples were performed using PLS regression from iC Quant module of the iC IR 7.0 software of Metler Toledo. The region from 701 to 1822 cm⁻¹ was selected for data treatment. Uncontrolled sources of variation can lead to inter-batch differences. Therefore, all spectral data were pre-processed before performing multivariate analyses. Pre-processing methods such as mean centring, variance scaling, solvent subtraction and spectrum math square root were used. Cross-validation by a leave-one-out procedure was performed during the validation step to define the optimal number of factors that should be kept in the model to detect outliers. The spectrums were collected in duplicated and divided into two set for calibration and validation for calibration of the PLS regression model.

Table 5-1: Biodiesel and sunflower oil mixture for multivariate analyses

| Samples | Sunflower Biodiesel (%) | Sunflower Oil (%) |
|----------------|--------------------------------|--------------------------|
| 1 | 100 | 0 |
| 2 | 89.5 | 10.5 |
| 3 | 86.7 | 13.3 |
| 4 | 83.3 | 16.7 |
| 5 | 69.2 | 30.8 |
| 6 | 64.7 | 35.3 |
| 7 | 60 | 40 |
| 8 | 43.8 | 56.2 |
| 9 | 36.4 | 73.6 |
| 10 | 33.3 | 66.7 |
| 11 | 28.6 | 71.4 |
| 12 | 11.8 | 88.2 |
| 13 | 6.3 | 93.7 |
| 14 | 0 | 100 |

The performance index was used to evaluate the performance of the method. It indicates how well the calibrated method can classify the validation standards. As the performance index algorithm is

set to “RMSE”, the root mean square error is reported. The closer the RMSE value is to zero, the smaller are the differences between the calculated concentrations values and the actual values (Richard *et al.*, 2011). RMSEC, RMSECV and RMSEP have been calculated. Detection and elimination of outliers were carried out using score and leverage plots. The predictive ability of the model was evaluated according to the RMSEP obtained for the external validation set. An F-test at a confidence level of 95% was used to assess the statistical significance of differences between RMSE values. The F-values were calculated as the ratio of the squares of the largest and smallest RMSE values. Detection and elimination of outliers were performed using score, residual (X and Y) and leverage plots.

5.4 Results and Discussion

5.4.1 Multivariate calibration

It was observed from the results obtained that there are similarities in the spectra of sunflower oil and the biodiesel, this is due to the fact of the high chemical similarity between triglycerides and methyl esters, as it can be seen in Fig. 5-4. Nevertheless, some differences can be observed in the region of wavenumber from 900 to 1500 cm^{-1} ; this region is called the fingerprint region of biodiesel (Zagonel, Peralta-Zamora and Ramos, 2004; Rabelo *et al.*, 2015). As shown in Fig. 5-5 and Fig.5-6, another spectral region around 1740 cm^{-1} showed a difference this includes the stretching vibration of carbonyl groups and is due to the extent of glycerol substitution in the fatty acids by methoxy radicals.

There was an O-CH₂-C axial asymmetric stretching observed at the wavenumber of 1110 cm^{-1} in the oil spectra. Which was not observed in the methyl esters, an O-CH₃ stretching was also observed at 1195 cm^{-1} wavenumber in the biodiesel spectra which was absent in the one of oil, These were other factors considered for discrimination of oil and biodiesel, these were found to be similar to what (Mahamuni *et al.*, 2017) and (Rabelo *et al.*, 2015) reported. A region of wavenumber ranging from 1370 to 1400 cm^{-1} showed O-CH₂ groups glycerol moiety of triglycerides, diglycerides and monoglycerides present in the oil but absent in the biodiesel (Rabelo *et al.*, 2015; Mahamuni *et al.*, 2017b) but diglycerides and monoglycerides were very low to be considered for the multivariate modelling. Another region (see Fig.5-5) that clearly showed distinction and was also used as a crucial factor for differentiation was from wavenumber 1425

cm^{-1} to 1450 cm^{-1} , which represent an asymmetric bending of CH_3 (Zagonel, Peralta-Zamora and Ramos, 2004; Rabelo *et al.*, 2015; Mahamuni *et al.*, 2017).

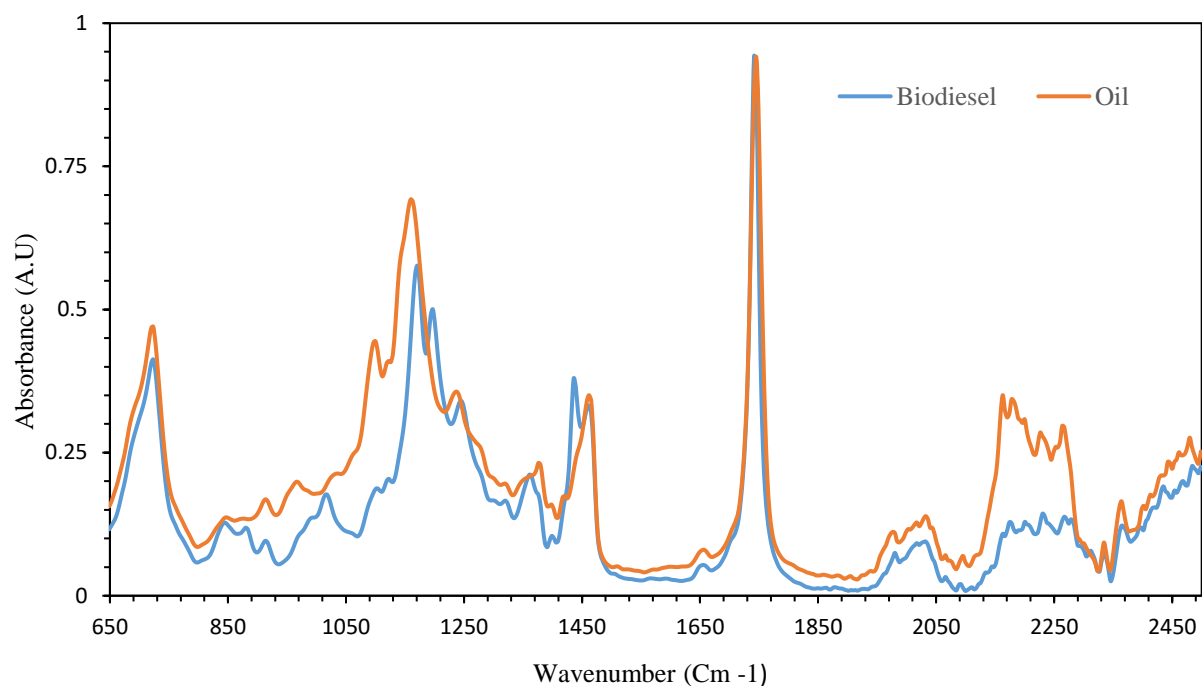


Fig. 5-4: FTIR spectra sunflower oil and biodiesel from 650 to 2500 cm^{-1}

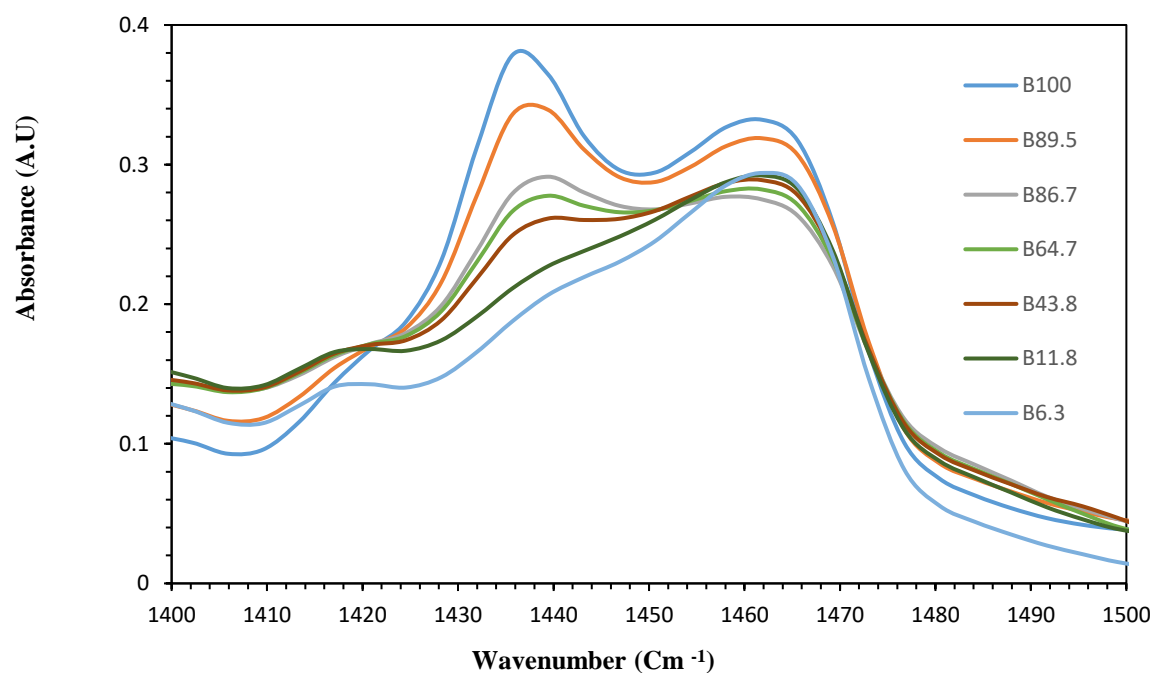


Fig. 5-5: FTIR spectra sunflower oil and biodiesel from 1400 to 1500 cm^{-1}

Fig. 5-6 and Fig. 5-7, showed that the stretching vibration of carbonyl groups was one of the critical factors for distinction among the set standard samples which contained different percentages of Sunflower oil and biodiesel. The obtained results confirmed the observation that the dislocation of the carbonyl signal, between the variables, was responsible for the spectral differentiation that occurred as a result of a gradual increase of sunflower concentration. That is, for the seven standard mixtures described in Table 1, there was a gradual migration of the C=O stretching vibration from a wavenumber of 1746 cm^{-1} in triglycerides to a wavenumber of 1738 cm^{-1} . Zagonel *et al.* (2004) reported a similar observation. In their work, they reported ethanolysis of degummed soybean oil in which the C=O stretching vibrations were observed at 1746.2 cm^{-1} and 1735.2 cm^{-1} for degummed soybean oil and ethyl esters, respectively.

Methanolysis of sunflower influences changes in the FTIR spectra of the reaction mixture, therefore, to allow the *in-situ* real-time monitoring of reaction yield a multivariate model was developed using PLS from iC Quant module from iC IR 7.0 software.

The FTIR/PLS calibration model was developed from the 14 samples (see Table 1), the region ranging from 701 to 1822 cm^{-1} (see Fig. 5-8) was selected this was motivated by the fact the most discrimination of the spectrum was found in that range, and the cumulative Root Mean square increased from 0.82 (on full-spectrum) to 0.89 (on selected range).

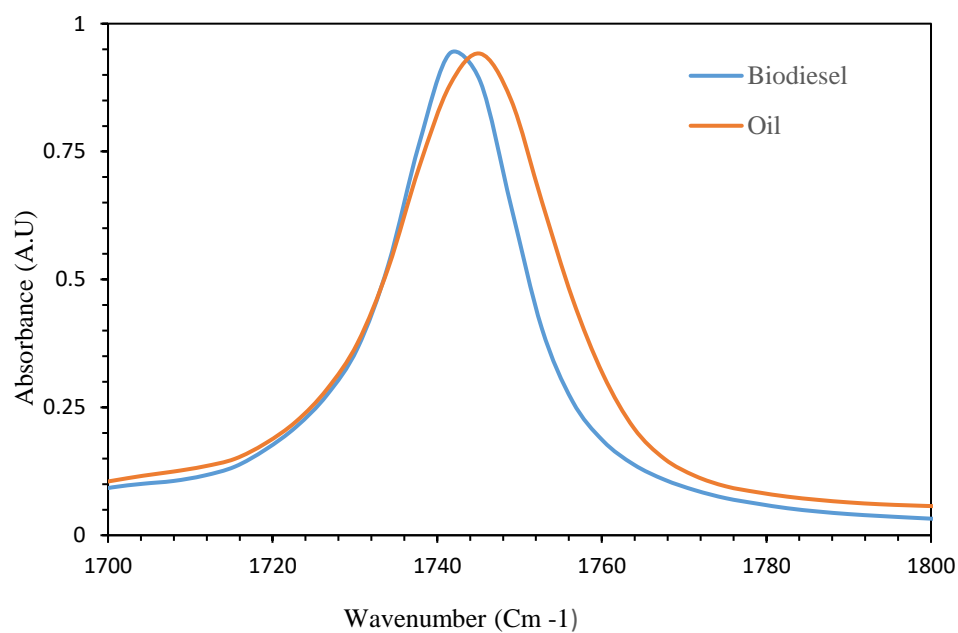


Fig. 5-6: FTIR spectra sunflower oil and biodiesel from 1700 to 1800 cm^{-1}

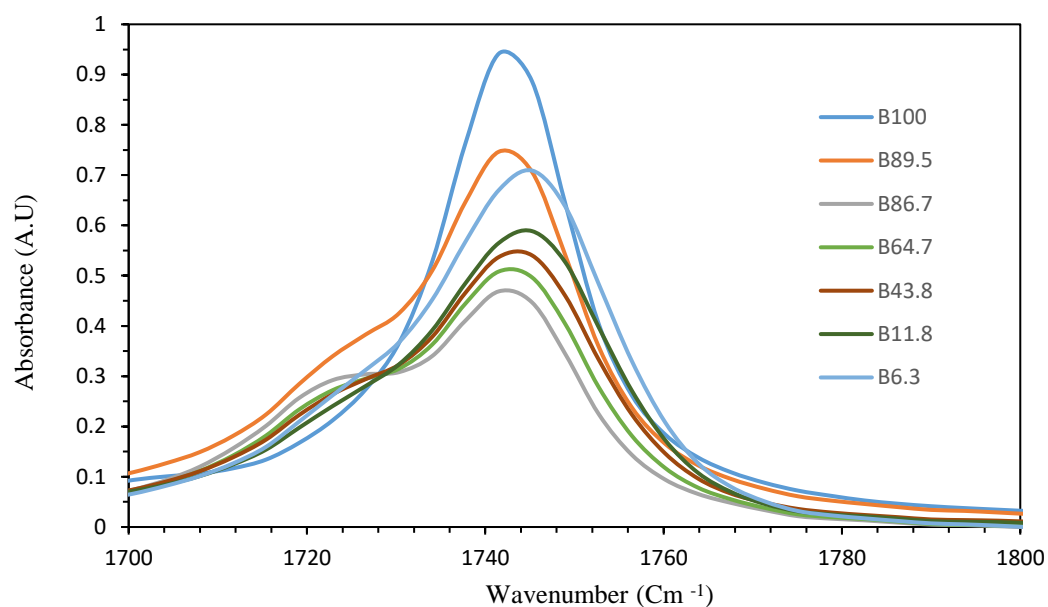


Fig. 5-7: FTIR spectra sunflower oil and biodiesel mixtures from 1700 to 1800 cm^{-1}

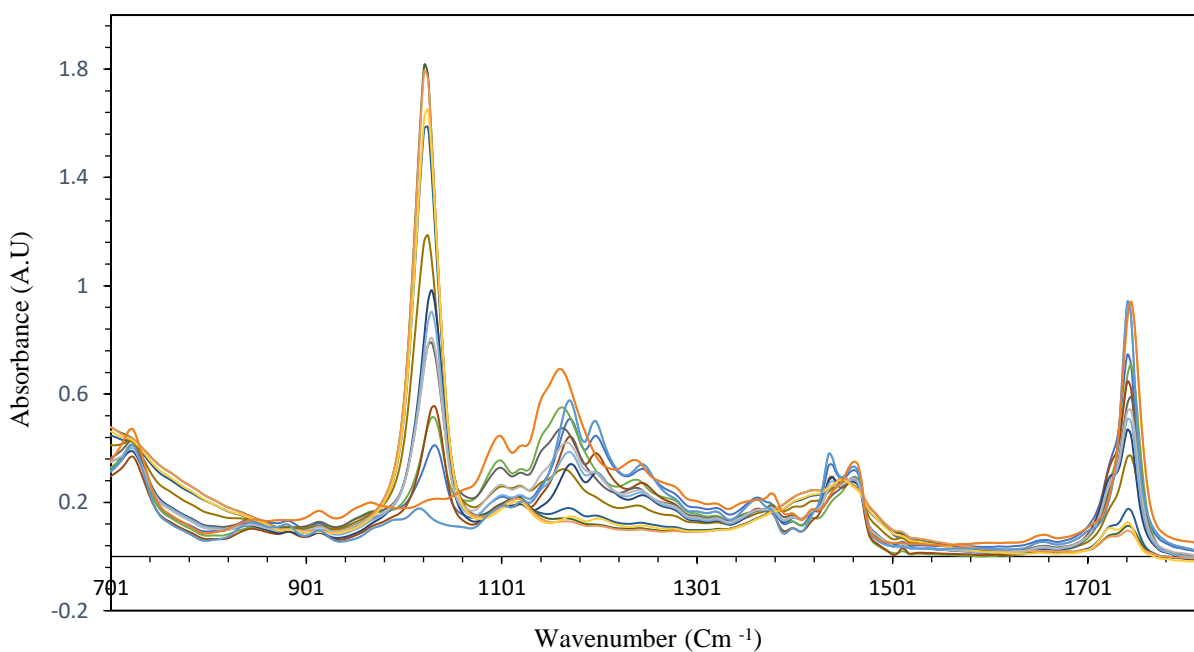


Fig. 5-8: Spectra range use for PLS/FTIR multivariate analysis

The same 14 samples were used for calibration (training data) and validation (test data); therefore, after calibration spectrums were taken, the validation spectrums were taken as well. Pre-processing methods (Variance Scale, Mean Centring, spectrum math square root and solvent subtraction) were

used. These resulted in the improvement of the performance index; this shows the predictive capability of the model (see Table 5-2). The improvement of the RMSEC, RMSECV, RMSEP and R^2 Cum showed the effect of perfecting the model by applying the pre-processing method. Cunha *et al.*, 2017; Mahamuni *et al.* (2017) in their works, reported the use of the performance index, as crucial tools to improve the performance of the model.

The predicted versus actual (see Fig. 5-9) illustrated how close the predicted results are to the actual values. The system calculated the best fit for the training set samples to the actual values, and the result of the training data is displayed in the chart. Since the model was adequately calibrated, almost all the training set samples fell on the 45° line. The chart also displays the number of factors used in calibrating the training set samples. Cross-validation by a leave-one-out procedure was performed during the validation step to define the optimal number of factors that should be kept in the model to detect outliers; this gave 11 optimum factors that were used in the model. By using score and leverage plot outliers were detected and eliminated. Detection and elimination of outliers were carried out using score and leverage plots.

The actual Predicted (Cross Validation) graph (see Fig. 5-10) represent cross-validation of the actual versus the predicted values in the model. In this study, the standards samples were taken as 28 samples each sample had two spectrums, one training set sample (standard) was removed from the calibration step at a time. For each standard removed, a new model was calculated, and this model was used to estimate the concentration of the omitted standard. For each standard, the maximum available data is included in the calibration model, but the model is not influenced by the inclusion of the standard to be estimated. This method provides a reliable estimate of the expected errors in using the calibration to estimate concentration in the unknowns.

Table 5-2: Performance index before and after applying pre-processing methods for multivariate calibration

| Index | before | after |
|----------------------------|---------------|--------------|
| RMSEC | 7.98 | 0.0096 |
| RMSECV | 11.2 | 3.41 |
| RMSEP | 6.32 | 2.72 |
| R^2Cum | 0.9416 | 0.9999 |

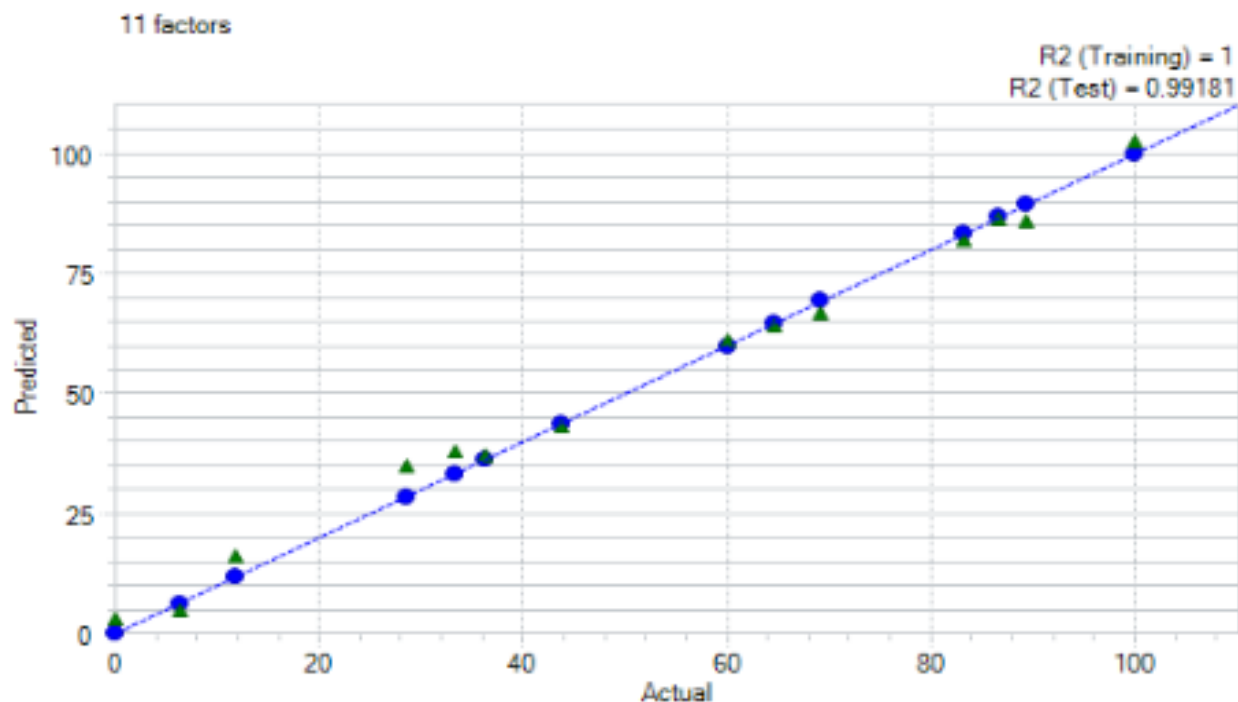


Fig. 5-9:: The predictive capability of the multivariate model for oil and biodiesel blend: Actual versus Predicted value of the model (blue: training data and green test data).

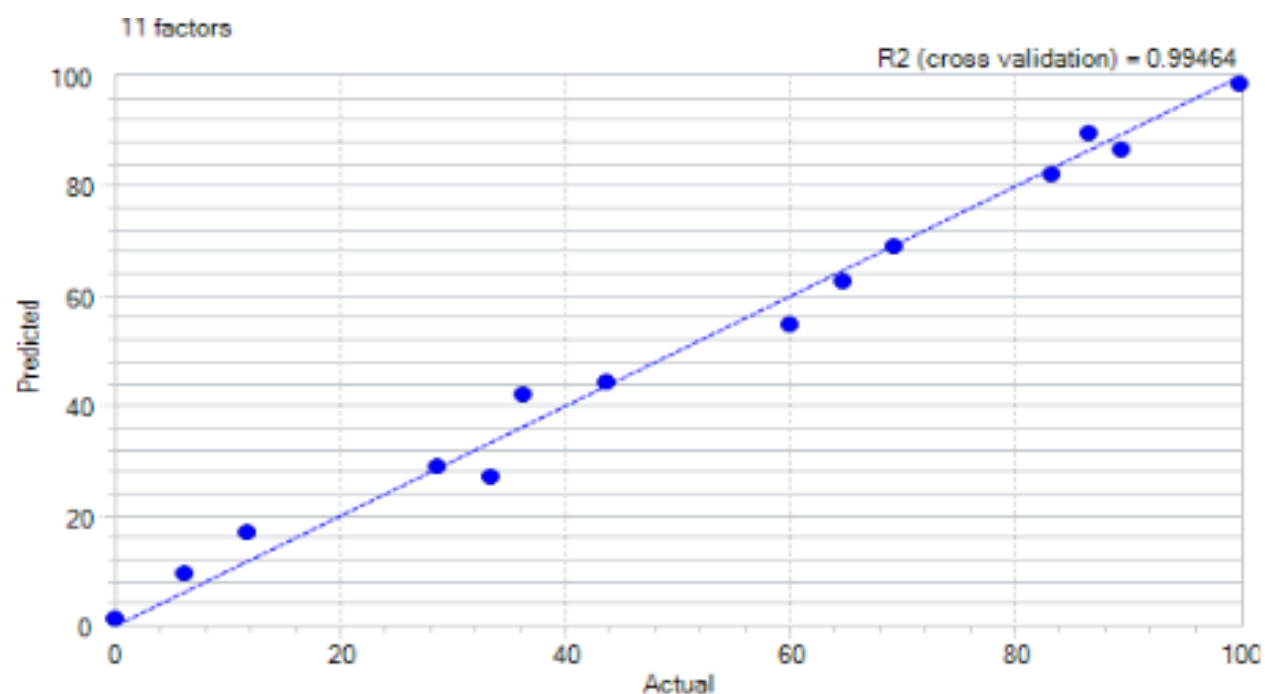


Fig. 5-10: Cross-Validation Predictive capability of the multivariate model for oil and biodiesel blend: Actual versus Predicted value of the model

The R^2 describes the fraction of the explained variations by each factor for each response variable. R^2 cumulative is cumulative explained variance by each factor for each response variable. The R^2 value of 1 (training), 0.9918 (test), 0.9946 (cross-validation) indicated that the degree to which the model fits the data. As seen in Fig. 5-11, the more optimum factors are used in the PLS model the cumulative R^2 approached 1; this indicated the number of optimum factors influences the cumulative R^2 positively. Hence the model became perfect.

The F Test Statistic Graph (see Fig. 5-12) plots the F-Ratio calculated for Residual Variance of each data sample in the Predictor variable space. The F-Ratio is the ratio of Residual variance for a sample versus the total variance of the training sample set. This ratio is an indication of how one sample is statistically similar to the training dataset of the model. The 95% confidence limit is displayed on the chart as a reference line. The sample's F-ratio being far below the 95% confidence limit, showed that there 95% possibility that the sample should not be considered an outlier.

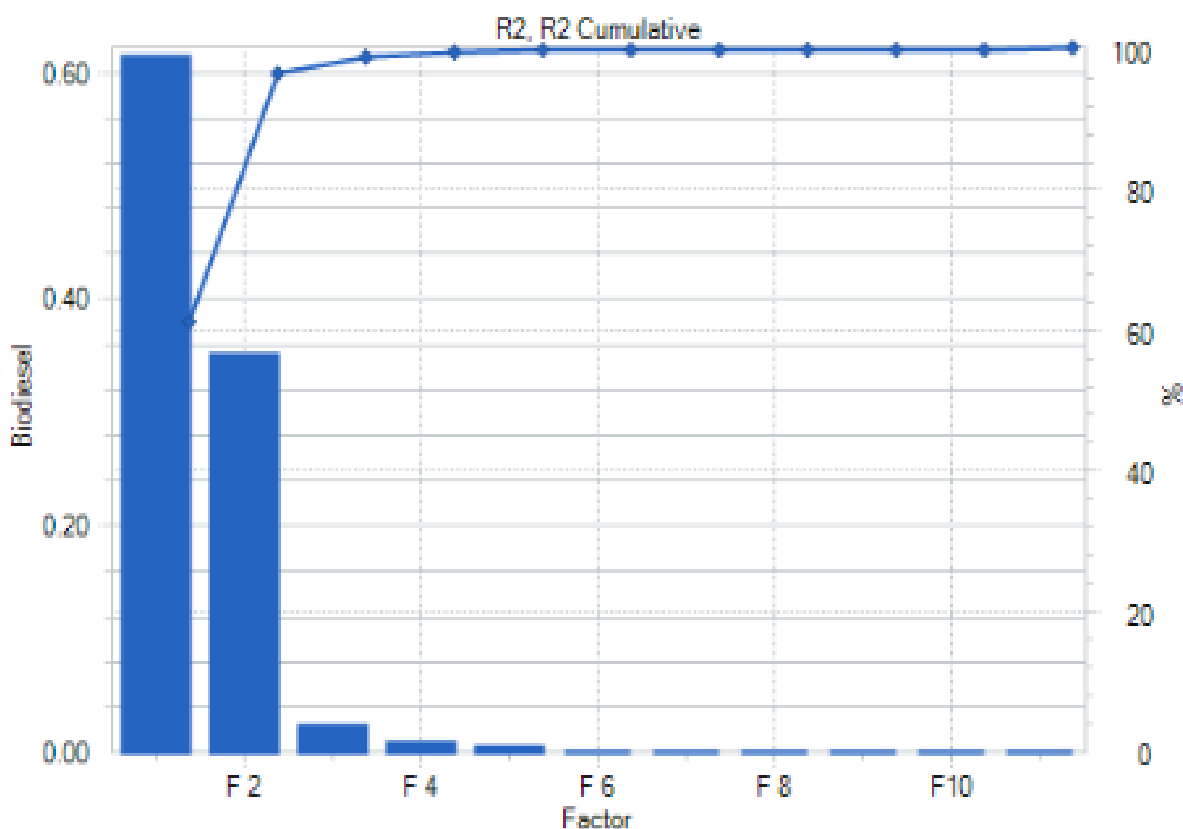


Fig. 5-11: R^2 , R^2 Cumulative graph of the model.

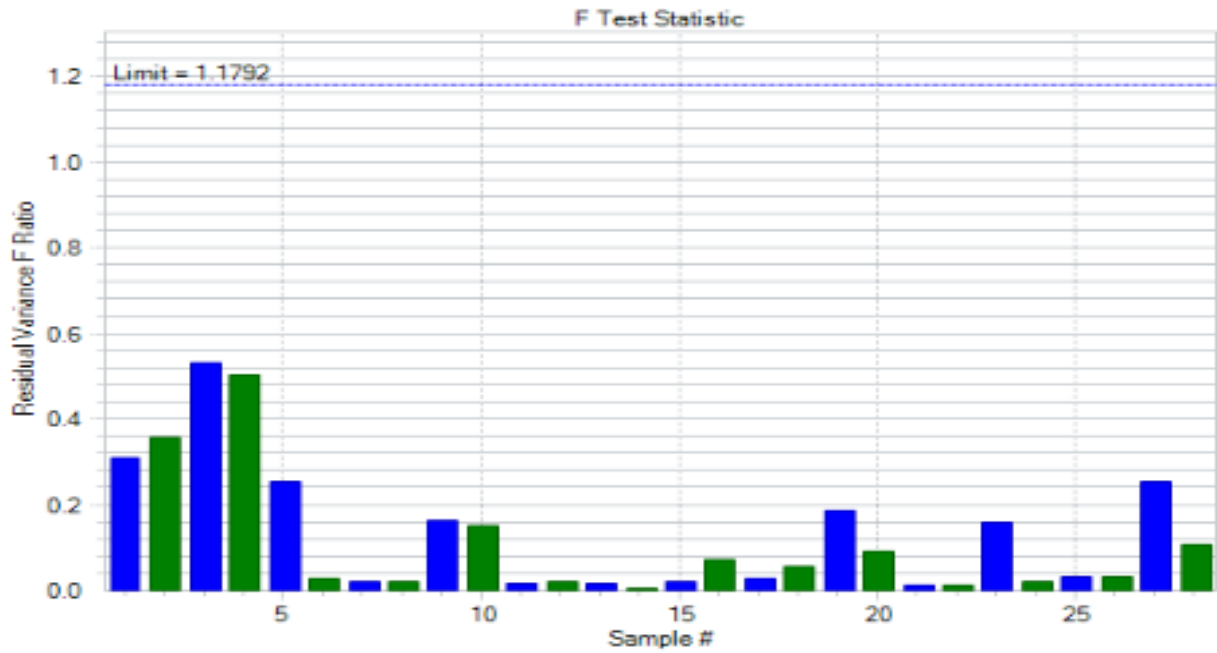


Fig. 5-12: F Test Statistic (blue training and green test)

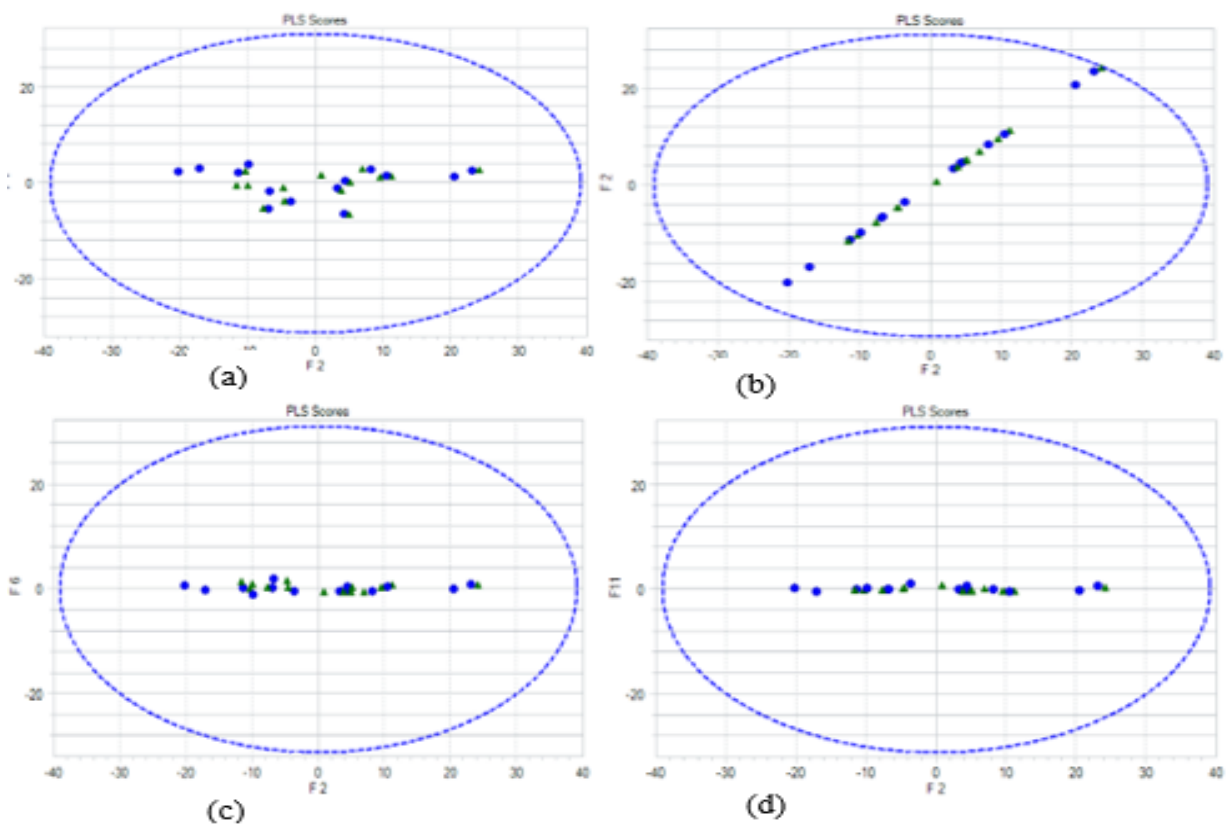


Fig. 5-13: PLS scores graphs: factor 1 vs factor 2 (a), factor 2 vs factor 2 (b), factor 6 vs factor 2 (c), and factor 11 vs factor 2 (d).

The scores are the projection of each spectrum onto the various PLS factors. The projection tells how much of a specific factor is used to model the given spectrum. The PLS score was used in conjunction with F-Test to detect outliers to classify samples and to obtain qualitative information about the calibration set. The circle describes the boundary using the two factors; this was done with a 95% confidence limit and helped identify if there are any potential outliers in the data set. Fig. 12, shows PLS scores graphs of factor 1 vs factor 2 (a), factor 2 vs factor 2 (b), factor 6 vs factor 2 (c), and factor 11 vs factor 2 (d), from the graphs it can be seen how the training data and very close to the test data and from the graph it was observed not no point was outside the ellipsoid, therefore, no potential outliers. The factor 2 versus factor is closed to the limit; this is explained as to why factor 2 is the highest in Fig. 5-13.

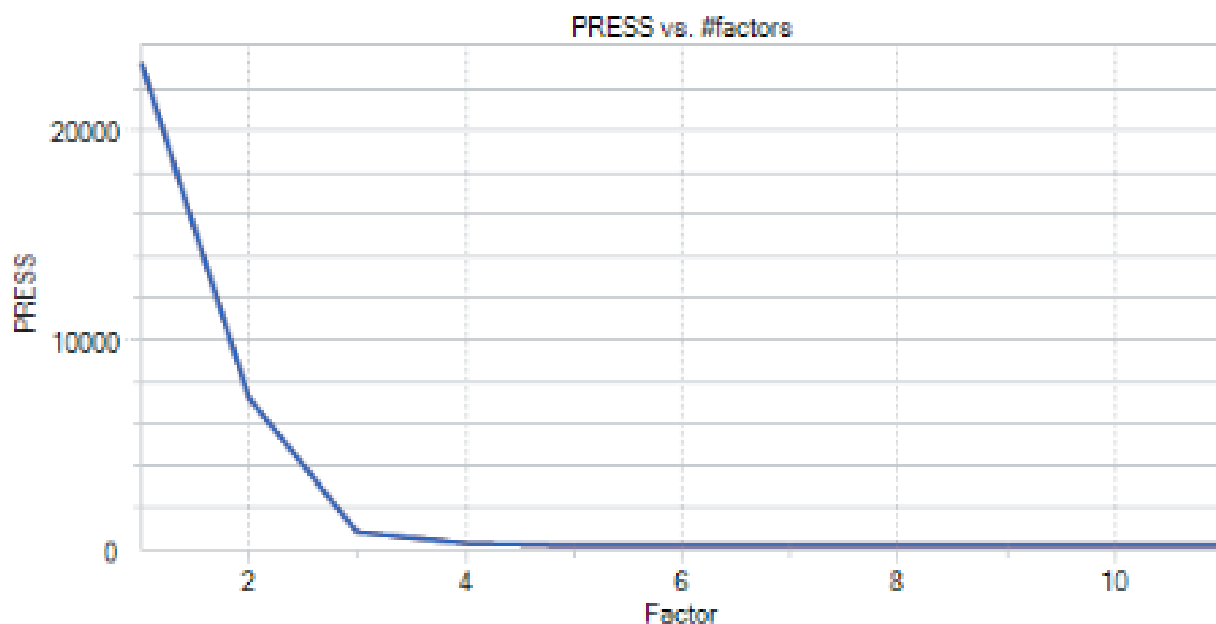


Fig. 5-14: Graph of PRESS vs number of Factors.

Fig. 5-14 shows how the press PRESS is affected by the increase in the number of factors; PRESS is the PRediction Error Sum of Squares (PRESS) versus the number of factors. PRESS is defined as the sum of the squared differences between actual and predicted Y values for the training data points that are left out in the Leave-N-out cross-validation process (Simon, no date). PRESS values are proper measures of the predictive power of the model. The system picks the number of factors that give the minimum PRESS value as the optimum number of factors. PRESS and RMSECV are closely related. RMSECV is the Root Mean Square of the PRESS.

The graph in Fig. 5-15 plots the value of RMSEC versus the number of factors used in the model. RMSEC values are calculated for all the training data points used in the model calibration and therefore are direct estimates of the modelling error. Each Y response variable has its own RMSEC series. Typically, the RMSEC value decreases when more factors are used in the model. PRESS and RMSEC are closely related.

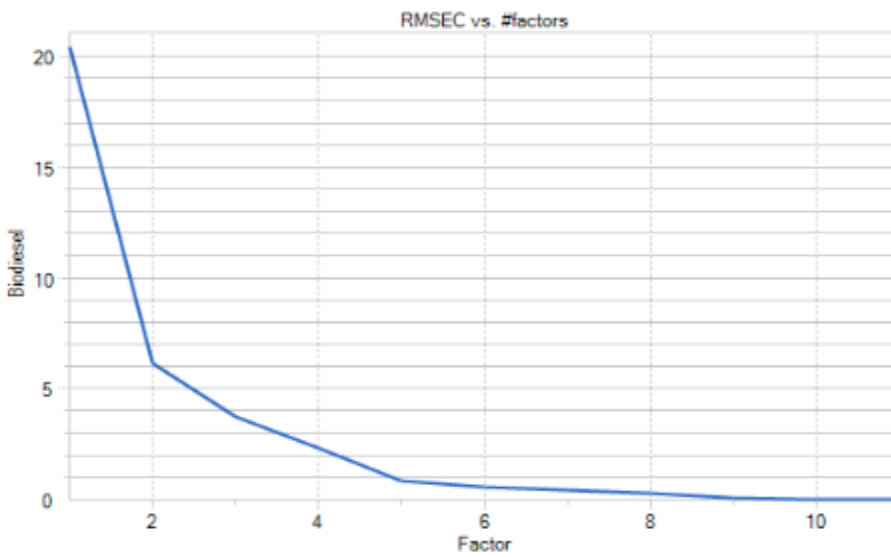


Fig. 5-15: Graph of RMSEC vs number of Factors

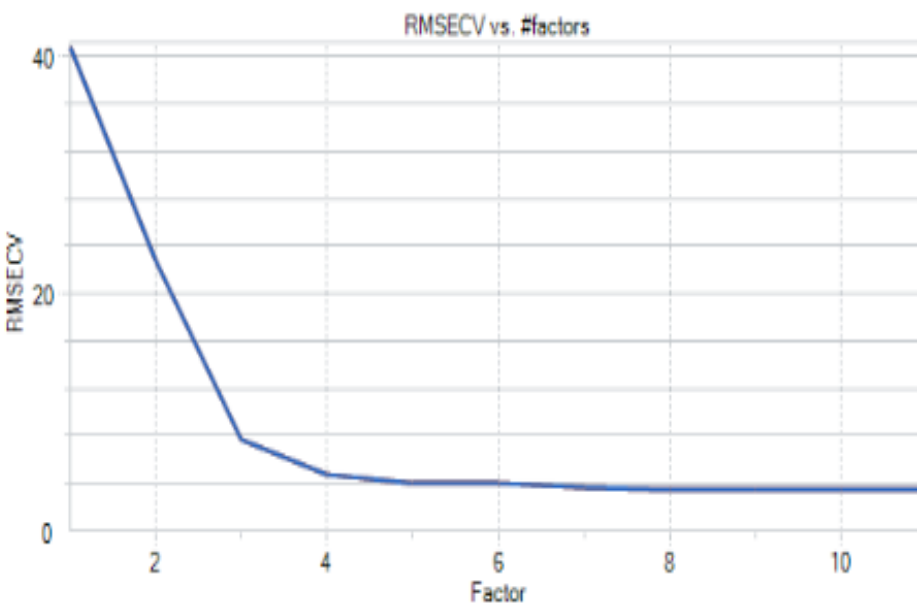


Fig. 5-16: Graph of RMSECV vs number of Factors

The graph in Fig. 5-16 plots the value of RMSECV versus the number of factors used in the model. RMSECV are calculated for the data points that are left out in the Leave-N-Out cross-validation during the model calibration. Each Y response variable has its own RMSECV series. Typically, RMSECV value decreases when more factors are used in the model.

The graph in Fig. 5-17 plots the value of RMSEP versus the number of factors used in the model. RMSEP is calculated for all the test data points using the calibrated model. RMSEP expresses the average error to be expected with future predictions. Typically, RMSEP values decrease when more factors are used in the model. RMSEP is a useful measure when the user compares different models, regardless of how the models were calibrated.

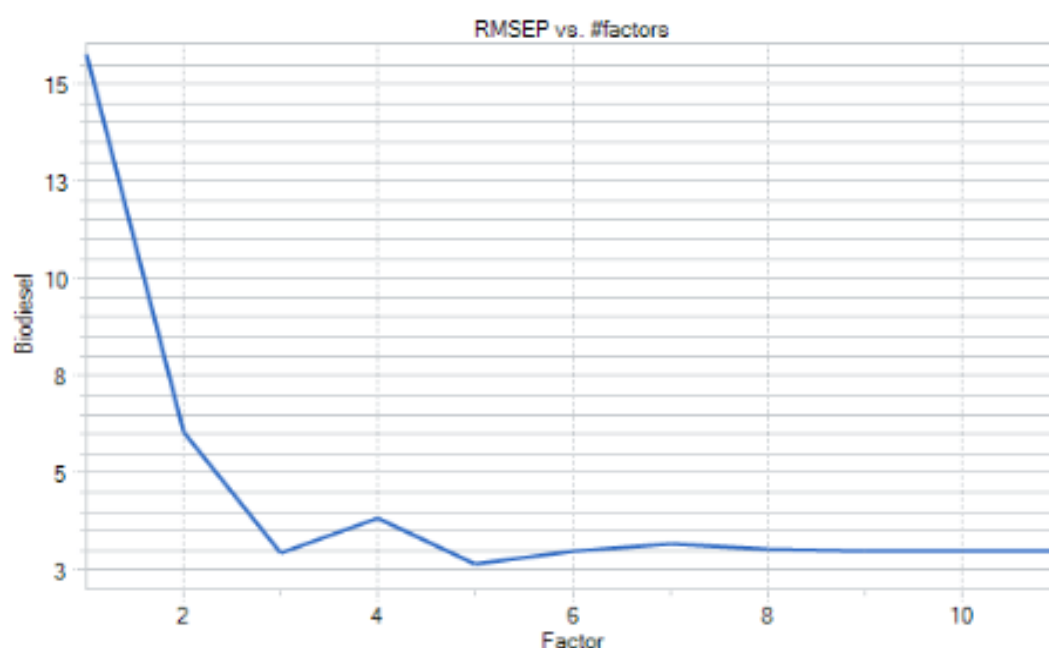


Fig. 5-17: Graph of RMSEP vs number of Factors

Fig. 5-18 plots the modelling residuals for the selected response variable for all samples. Residuals are the differences between the actual values and the predicted values. The residuals are what have not been modelled. A large residual for a sample indicates that this sample has not been well modelled (it may even be an outlier). The residuals should evenly be distributed meaning that the remaining unexplained variations in the data should be similar to white noise. A systematic pattern in the residuals indicates there might be some systematic variation in the data remains.

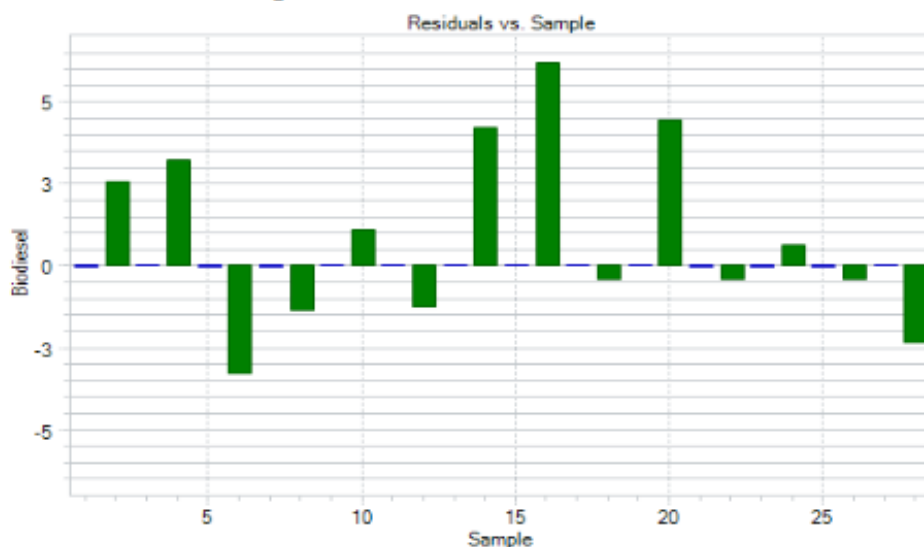


Fig. 5-18: Graph Residual vs sample.

Fig. 5-19, plots the Studentised residual versus leverage and can be used to detect possible outliers. An outlier is a standard which, due to either concentration error, is not similar to the rest of the calibration set and may be detrimental to the calculation. Ideally, no single standard should exert undue influence (leverage) on the calibration. Residuals are also ideally small. In practice, a high value for one or the other, notably leverage, does not automatically indicate an outlier. It may merely indicate an extreme standard in the calibration space, either in concentration or its spectrum. Those points with a significant residual and leverage may be outliers and therefore, should be removed from the calibration set before recalibration.

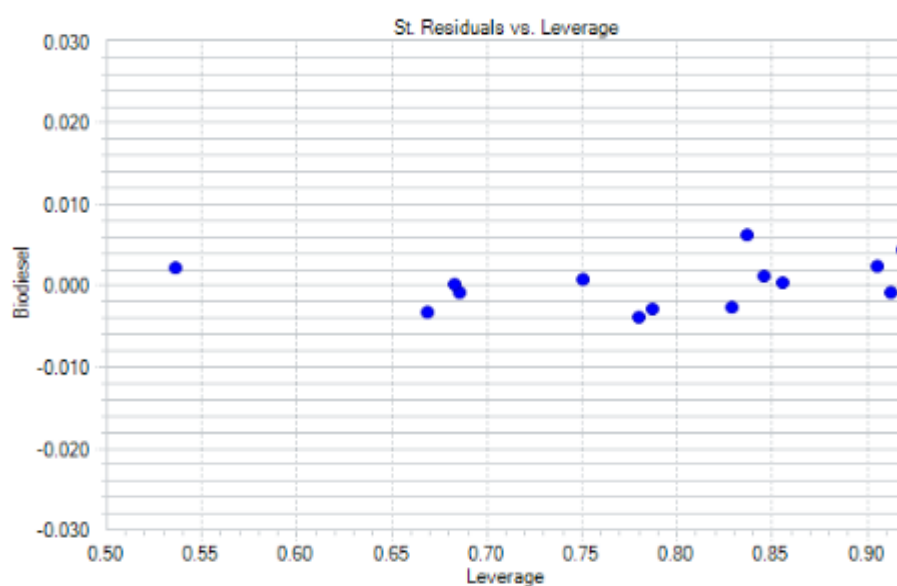


Fig. 5-19: St Residuals vs leverage.

5.4.2 *In-Situ* Real-time monitoring of transesterification.

The model hence obtained was then used to predict the biodiesel yield in real-time from an experiment run on an EasyMax 102 Mettler Toledo reactor. Using iC IR software 7.0, *in-situ* real-time monitoring was performed. Fig. 5-20 showed the results obtained; it can be seen that the model can be used to predicting the biodiesel yield in the transesterification of sunflower oil. It was also observed that the peak present in biodiesel (1437 cm^{-1} and 1744 cm^{-1}) was increasing with time and could be used to monitor the online transesterification of sunflower oil. As shown in Fig. 5-20, it was seen that there is a proportional increase of the peaks identified as peaks representing biodiesel, hence the model obtained is in line with what reported by (de Souza and Cajaiba da Silva, 2012), stating that single peaks can be used to monitor the biodiesel transesterification reaction. Considering a closed system, where no loss of methanol from the reaction, therefore, methanol (peak at 1023 cm^{-1}) consumption, which is observed to be decreasing, can be used as well to predict the biodiesel yield. The reaction monitoring of the biodiesel synthesis using methanol peak agrees with the work reported by (de Souza and Cajaiba da Silva, 2012).

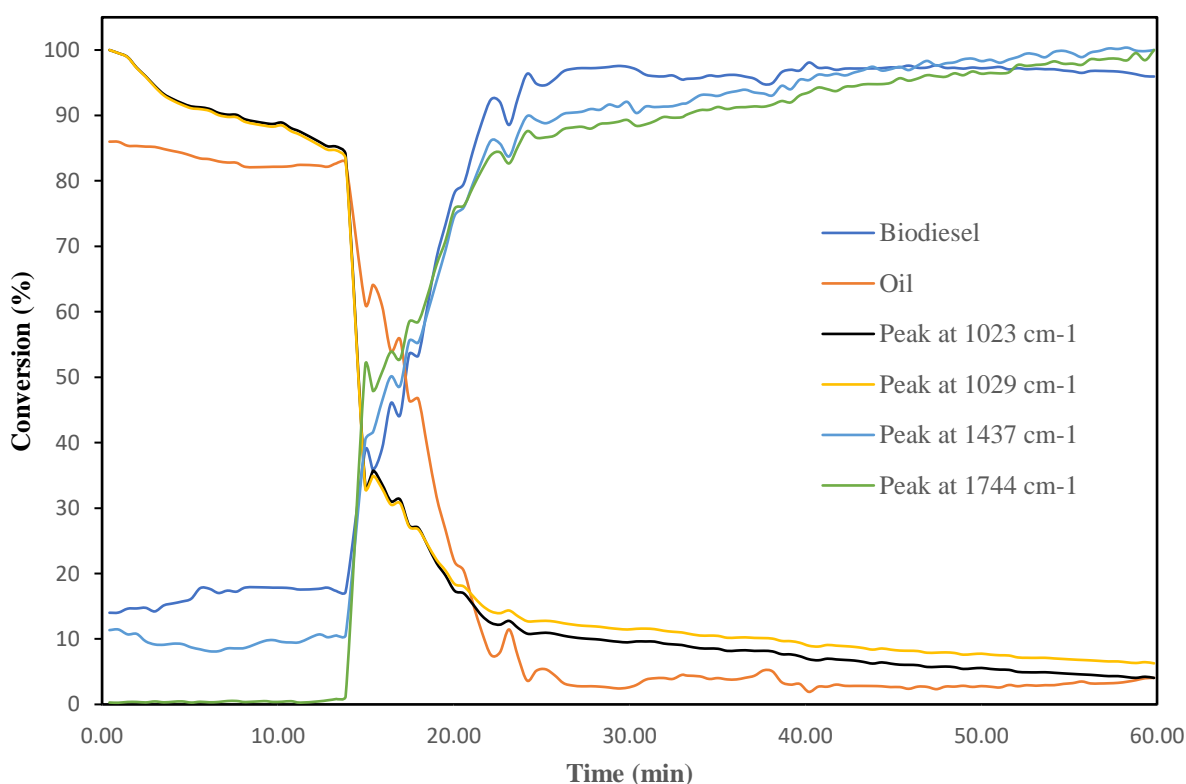


Fig. 5-20: In Situ Real-time monitoring of transesterification yield.

Fig. 5-20 indicates that the model obtained from iC IR software was quite reliable for predicting reaction yields at advanced reaction times in which conversions higher than 18 % were obtained. Small discrepancies were observed along with the linear regression, particularly at low conversion yields. This apparent uncertainty of the model was attributed to the interference caused by unmodelled reaction intermediates (unreacted mono- and diglycerides), which are particularly crucial at low reacting times. The matrix was significantly simplified towards the end of the reaction. Therefore, deviations at short reaction times were expected due to the occurrence of a higher amount of unmodelled reaction intermediates.

5.5 Conclusion

FTIR spectroscopy has been proven to potentially offer direct, non-destructive, rapid and real-time transesterification monitoring. The effectiveness of multivariate variation technique using FTIR technique lies in carefully performing calibration and model validation to be done with quite a high number of samples. Once this is done, there is no need for further validation as this can be used for years as long as the materials remain the same. This will give much more easiness to the operators, quality controllers and quality assurance operating the biodiesel plant to use the FTIR to determine the yield of biodiesel and to monitor the transesterification. The FTIR/PLS model was built to predict more advanced reaction yields of methanolysis Sunflower Oil, which is what matters to indicate the time in which the reaction should be stopped. The obtained model can be considered suitable for the quantification of Fatty Acid Methyl Ester in biodiesel produced in EasyMax 102 Mettler Toledo reactor and iC Quant module from iC IR 7.0 software. A more robust model can be built if non-converted mono and diglycerides are to be considered in the samples used for both calibration and validation. However, considering that using EasyMax Mettler Toledo equipped with ReactIR. FTIR probe does not require sampling for offline FTIR analysis, neither sample preparation for the analysis. As opposed to the GC reference method adopted by most of the conventional methods from regulating and monitoring agencies in the world, it can be concluded that it is a promising candidate for becoming a reference technique to be upgraded for industrial scale.

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CHAPTER SIX

6. KINETICS AND OPTIMISATION OF BIODIESEL PRODUCTION FROM SUNFLOWER OIL USING EASYMAX 102 METTLER TOLEDO REACTOR: REAL-TIME MONITORED BY FOURIER TRANSFORM INFRARED

6.1 Abstract

The increase in fuels consumption mainly caused by the third and fourth industrial revolution and the worldwide population growth led to the depletion of fossil fuels (the leading supplier of fuels) and has caused environmental pollution. Therefore, research emanates from the challenge mentioned above to come up with a solution for new eco-friendly and renewable fuels such as biodiesel. Most reported biodiesel analysis has been done using Gas Chromatography though accurate it is costly, requires qualified personal, samples preparation, time-consuming and does not provide *in-situ* real-time monitoring. Fourier Transform Infrared (FTIR) has mainly been used for qualitative analysis of biodiesel, but few works have been reported in *in-situ* real-time monitoring. This work aimed and optimising and modelling the kinetics of biodiesel production from sunflower oil real-time monitored using FTIR catalysed by Sodium Hydroxide. The study was performed in a batch reactor setup, EasyMax Mettler Toledo reactor was used which was equipped with an FTIR DiCom (Diamond) probe, the experiments were designed and monitored using iControl software. The results were recorded and quantified using iC IR software based on a biodiesel calibrated model built. The optimisation of the biodiesel was performed using three key parameters (methanol to oil ratio, catalyst ratio and temperature) while keeping time at 60 minutes and mixing rate at 150RPM. The highest yield of 97.85 % was obtained at 60 °C, 0.85 wt % catalyst ratio and 10.5 methanol to oil mole ratio. The analysis of variances of biodiesel production showed the values of 0.9847, 0.9674 and 0.8749, for R-squared, adjusted R-squared and predicted R-squared, respectively. A quadratic mathematical model was developed to predict the biodiesel conversion in the specified parameters ranges. Using the Arrhenius equation, activation energy (E_a) and frequency factor were found to be 41.279 kJ.mole⁻¹, $1.08 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$, respectively. The proposed kinetic model was a pseudo-first-order reaction.

Keywords—Biodiesel, Fourier Transform Infrared (FTIR), Kinetics, Optimization, Real-time monitoring, Transesterification.

6.2 Introduction

The third and four industrial revolutions have brought significance change by improving the industrial sector and daily lifestyles. However, this has come with a considerable demand for fossil fuels as the primary source of energy and chemicals. The high demand for fossil fuel has significantly increased with the global population growth (Mwenge, Pilusa and Seodigeng, 2018). This high demand of fuels is proportional to high energy consumption which expected to increase by a third from 2014 to 2035, for which transportation is the most demanding of about a third (Ilmi *et al.*, 2017). As consequences of the above mentioned are the decrease of global fossil fuels reserves, to that added the environmental pollution (Atabani *et al.*, 2013; Avhad *et al.*, 2016; Pourzolfaghar *et al.*, 2016; Amoah *et al.*, 2017). Energy is considered as the most crucial element for human life sustainability; the primary sources of energy is being at threat and need to be replaced by other forms of fuels. Therefore, liquid fuel such as biodiesel received close attention from researchers. Biodiesel a fuel that can replace petroleum diesel, biodiesel has the advantage of being produced from bio-renewable sources, eco-friendly, low environmental impact, high cetane number, low emission of SO_x, NO_x and CO₂ gases emissions, high combustion efficiency (Marchetti, Miguel and Errazu, 2007; Lukovi, Knežević and Bezbradica, 2011; Sani, Daud and Abdul, 2013; Avhad and Marchetti, 2015; Mardhiah *et al.*, 2017; Purandaradas *et al.*, 2018). In 2012 the European Union estimated the biodiesel consumption of 11.41 Mega tonnes, this has paved a way to establish a sustainable criterion for biofuels in the framework of the EU Directives 2009/28/EC and 2009/30/EC (Reyero *et al.*, 2015).

Biodiesel, a non-petroleum liquid fuel is defined alkyl esters derived from biological feedstocks such as plants oils and animal fats (Avhad and Marchetti, 2015; Avhad *et al.*, 2016; Purandaradas *et al.*, 2018). The principal used process of biodiesel production has been transesterification also known as alcoholysis in which the plant oils or animals' fats (triglycerides) react with short chains of alcohol such as methanol and ethanol in the presence of a catalyst. The transesterification reaction generally involves three steps reversible reactions, in which the triglyceride reacts with alcohol to yield first diglyceride and alkyl ester, diglyceride reacts with alcohol to yield monoglyceride and alkyl ester, and lastly monoglyceride reacts with alcohol to yield alkyl ester and glycerol; the alcohol is always in excess to favour the forward reaction which is the reaction yielding the alkyl ester (Zhang *et al.*, 2010; Killner, Rohwedder and Pasquini, 2011; Thinnakorn and Tscheikuna, 2014; Amoah

et al., 2016; Firdaus, Guo and Fedosov, 2016; Purandaradas *et al.*, 2018). The reaction parameters generally depend on the feedstock composition, type of catalyst and post-separation processes (Knothe and Razon, 2017). The transesterification reaction uses mainly two types of catalysts, chemical (alkali and acid) catalysts, enzymatic catalysts. Homogenous catalysts such as Potassium Hydroxide (KOH) and Sodium Hydroxide (NaOH) are the most used in industrial biodiesel production (Guldhe *et al.*, 2015; Talha and Sulaiman, 2016; Purandaradas *et al.*, 2018).

In order to certify the quality of biodiesel fuel properties and reaction monitoring, many analytical methods have been reported in the literature. A number of analytical methods has been used for biodiesel analysis such as: Capillary Gas Chromatography (CGC), High Pressure Liquid Chromatography (HPLC), Gel Permeation Chromatography (GPC), Fourier Transform Infrared (FTIR) Spectroscopy, Ramon Spectroscopy, Size Exclusion Chromatography, Nuclear Magnetic Resonance (NMR), Ultra-sonication assisted spray ionization (UASI) spectroscopy, fluorescence spectroscopy, Viscometry (Yuan *et al.*, 2014), UV spectroscopy (Richard *et al.*, 2011), Thin Layer Chromatography (TLC), thermogravimetric analysis (TGA) (Mahamuni *et al.*, 2017). The most used method for biodiesel analysis has been Gas Chromatography (GC), this has the advantage of determining the concentration of other intermediate such as diglycerine, monoglyceride and glycerol (Monteiro *et al.*, 2008; Zhang, 2012; Yuan *et al.*, 2014; Mahamuni *et al.*, 2017). Though chromatography and spectroscopy are known to be accurate; however, they have some limitations such as they require sample preparations and analytical time required is considerable, require internal standards, required high qualified personnel, solvents and their usages in *in-situ* real-time transesterification have not been possible (Rabelo *et al.*, 2015; Mahamuni *et al.*, 2017). However, FTIR spectroscopy has been found as a reliable analytical method and reported by many authors to be used in *in-situ* monitoring of transesterification reaction (Richard *et al.*, 2011; De Souza and Cajaiba Da Silva, 2013; Mueller *et al.*, 2013; De Lima *et al.*, 2014; Yuan *et al.*, 2014).

FTIR spectroscopy is based on a technique that uses electromagnetic radiation spectrum which passes through a material and give a corresponding molecular spectrum reason why it is classified as a fingerprint technique for the fact that every molecule has a specific spectrum, and this electromagnetic energy is found in the region of infrared light region (Zhang, 2012). De Souza and Cajaiba Da Silva, (2013) used real-time univariate analysis principle in which peaks were used to evaluate the synthesis of biodiesel. However, this approach becomes

challenging in transesterification reaction in which there are overlapping of spectrums (Zagonel, Peralta-Zamora and Ramos, 2004). To overcome the above-mentioned challenge, FTIR was reported been used coupled with partial least squares (PLS) regression for multivariate calibration models, which allows the use of FTIR for quantitative analysis. It has meanly been used to determine the blend of biodiesel and petroleum diesel (Rabelo *et al.*, 2015). PLS is a method that is based on Beer's law principle for quantification (Yuan *et al.*, 2014). FTIR was reported to be used in combination with other technique such as: hierarchical cluster analysis (HCA), principal component analysis (PCA) soft independent modelling of class analogy (SIMCA) and interval principal component analysis (iPCA), Principal Component Regression (PCR) and Principal Component Analysis (PCA) (Rabelo *et al.*, 2015). Pre-processing methods such as mean centring technique (Mahamuni *et al.*, 2017) and baseline correction (Cunha *et al.*, 2017) have been used to improve the calibrated model. The pre-processing techniques, performance index algorithms have been used to assess the robustness of the models, some of this performance index algorithms are: Root-Mean-Square-Error (RMSE), Root Mean Square Error of Calibration (RMSEC), Root Mean Square Error of Prediction (RMSEP) and Root Mean Square Error of Cross-Validation (RMSECV) (Mahamuni *et al.*, 2017). There are very few works that reported the *in-situ* real-time monitoring of biodiesel production, and quantitative analysis of biodiesel production using FTIR.

In this paper, the focus was on the production of biodiesel from sunflower oil *in-situ* real-time monitored using FTIR produced in an EasyMax Mettler Toledo reactor. Also, the optimisation of the biodiesel production by investigating the effect of variables, namely: methanol to oil ratio, catalyst ratio and temperature using a factorial design aided by Design-Expert software 11.04, while keeping time, and stirring rate constant. The reaction constants, the activation energy and the reaction order were determined.

6.3 Material and methods

6.3.1 Material and reagents

Sunflower oil triglyceride used in this work was sourced from Golden Fry, a local cooking oil supplier. The transesterification catalyst Sodium Hydroxide (99.5%) and the transesterification acyl acceptor Methanol (99%) were sourced from ACE (Associate Chemical Enterprises) a local laboratory chemicals supplier.

6.3.2 Experimental setup



Fig. 6-1: Mettler Toledo Easymax 102 equipped with a dosing system.

The setup used for the transesterification was Mettler Toledo Easymax 102 which is equipped with two reactors of 100ml each, with reflux condensers can be mount on each of them. The setup equipment can allow two reactions taking place at the same time, and both reactions can be monitored independently. The dosing mechanism has as purpose to allow a more accurate addition of reactants to the system. EasyMax 102 has the advantage to control the parameters in the specified range. This is made possible by the fact that the heat of reaction and mixing are removed more effectively by the heating and the cooling system. All results are timeously recorded for analysis at a further stage. Equipped with an incorporated real-time *in-situ* instrument, the equipment allows a depth understanding of the process and makes the determination of the kinetics easier. Correction of parameters can quickly be corrected as soon as they are analytical detected, the above-mentioned is made possible by the flexibility of the equipment (Mettler Toledo, 2014; Guth, 2016).

6.3.3 Experimental Design

The experimental design used in this work was the response surface methodology (RSM). This is a more effective method as it reduces the number of experiments and thereby saving in time (Kuo *et al.*, 2014). Expert Design 11.0.4.0 was used to determine the set of an experiment for the RSM using central composite design (CCD). Transesterification of sunflower oil mathematical model of the experiments was determined and can be used to determine the yield

in the specified range of parameters. The parameters were alcohol to oil mole ratio, catalyst ratio and temperature, as can be seen in Table 6-1 and Table 6-2.

Table 6-1: Experimental design using RSM CCD: Level of transesterification parameters used

| Number of factors | Variable | Parameter | Variable level | | | | |
|-------------------|--------------------|-----------------------------------|----------------|-------|------|-------|-----|
| | | | -2 | -1 | 0 | +1 | +2 |
| 1 | x ₁ : A | Alcohol to oil ratio (moles/mole) | 3 | 6.75 | 10.5 | 14.25 | 18 |
| 2 | x ₂ : B | Catalyst ratio (wt %) | 0.2 | 0.525 | 0.85 | 1.175 | 1.5 |
| 3 | x ₃ : C | temperature (°C) | 30 | 37.5 | 45 | 52.5 | 60 |

6.3.4 Experimental Procedure

The experimental procedure followed a batch setup in which approximately 50g of sunflower oil was weight and place in a 100ml Mettler Toledo reactor. Sodium methoxide was prepared by dissolving the designed amount of Sodium hydroxide (0.2 to 1.5 wt % with respect to oil) in methanol (3 to 18 moles ratio with respect to oil). An experimental design was programmed for each reaction using iControl 5.0 software in which time of the reaction was set for 60min, and the reaction temperature was set as per experimental design (30 to 60°C), the stirring rate was set for 150RPM. The methoxide was then mixed to the oil. The reaction timing and stirring were started when the mixture reached the set temperature. Using FTIR probe, spectrums were collected every 15 seconds, and these collected spectrums were directly converted to transesterification conversion. The collection of spectrums was performed by using the ReactIR 15 spectrometer instrument, which uses an MCT detector, 8 cm⁻¹ resolution, Happ-Genzel apodization, DiComp (Diamond) probe and AgX 6mm x 2m Fiber (Silver Halide) interface. The recording was done by averaging 128 scans in the region of wavenumber of 2500 to 650 cm⁻¹.

6.3.5 Transesterification mechanism

The mechanism of the transesterification of sunflower oil using sodium hydroxide is shown in Fig. 6-2. The outline of the mechanism is: Sodium hydride reacts with one mole of methanol to produce sodium methoxide (NaCH₃O), hydrogen ion (H⁺) and hydroxyl ions (OH⁻) are as well produced. The sodium methoxide, in turn, dissociates to form Sodium ion (Na⁺) and

methoxide ion (CH_3O^-). Methoxide a strong organic base catalyst has high catalytic active sites which speed up the transesterification reaction (Modiba, Enweremadu and Rutto, 2015). The strong nucleophilic affinities of the methoxide ease the methoxide ability to attack the trigonal planar of the triglyceride to produce a tetrahedral intermediate from which the diglyceride ion and methyl ester are produced. The diglyceride molecule is produced by the reaction of hydrogen ion (H^+) and diglyceride ion; the diglyceride ion reacts with the second molecule of methanol to produce a glyceride molecule and methoxide ion. The methoxide ion, in turn, starts an another catalytic to produce monoglyceride ion and a second molecule of methyl ester, the same trend continues until three molecules of methyl esters, and one molecule of glycerol is produced. The catalyst is also regenerated by the reaction of sodium ion (Na^+) and hydroxyl ion (OH^-).

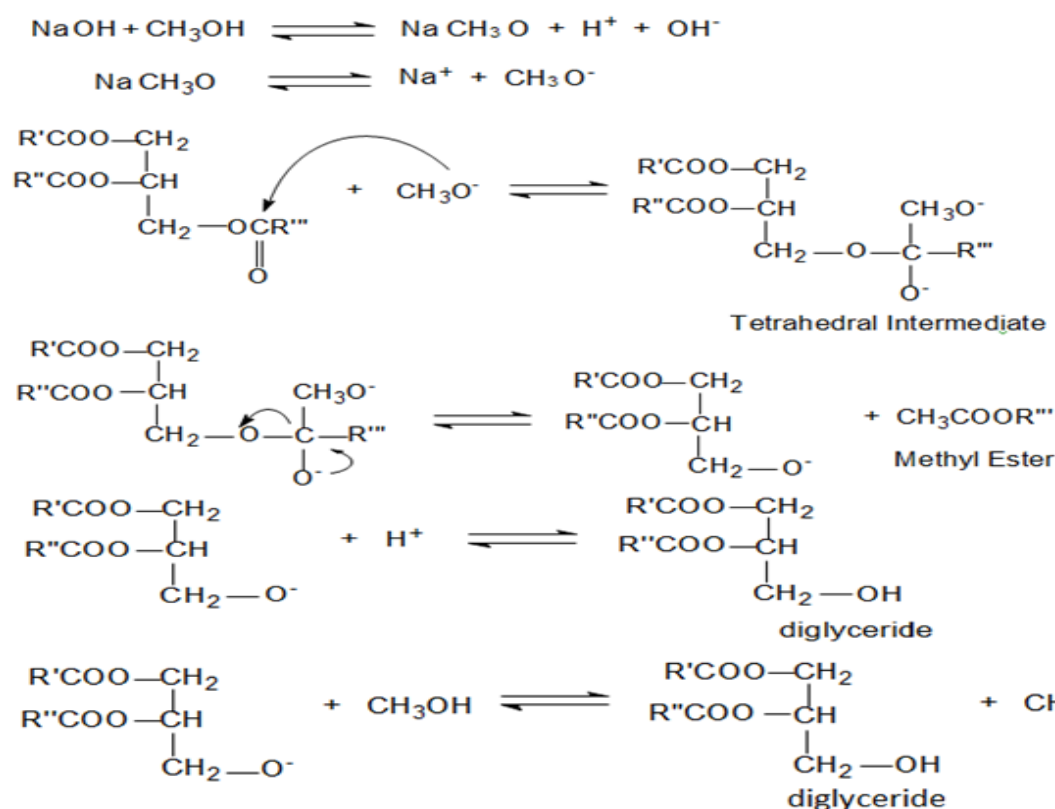


Fig. 6-2: Reaction mechanism of transesterification using NaOH as catalyst.

6.3.6 Kinetic analysis

For the reaction kinetics, the reaction was considered isothermal, and since the methanol was in excess, the assumption of irreversible was used in this work. The conversion or yield of the biodiesel produced was real-time monitored using FTIR, which gave data every 15 seconds.

The production of methyl esters and consumption of triglyceride was observed and measured. The reaction conditions used for the kinetics was taken at one of the optimum conditions, which were: methanol to oil ratio of 9, catalyst ratio of 1 wt% and, temperature of 60 °C. The time was 60 min and stirring rate of 150RPM.

The transesterification of sunflower oil follows a single-step reaction, as shown in (6-1).



Where, TG for glyceride, MeOH for methanol, ME for methyl ester and G for glycerol.

From the above equation, the rate of the reaction can be expressed (6-2).

$$r = \frac{d[TG]}{dt} = k[TG][MeOH]^3 \quad (6-2)$$

Where, r is the rate of the transesterification reaction in $M.s^{-1}$, $[TG]$ concentration of triglyceride in M , $[MeOH]$ concentration of methanol in M and k the rate constant in $M^{-1}.s^{-1}$.

Methanol molecular weight used was 32.044 g/mole, and the one of Sunflower oil find in the literature (Sánchez *et al.*, 2012) was 876.16 g/mole. Molecular weights were inserted in the iC Kinetics 5.0, and the data from iC IR were imported to the iC Kinetics 5.0 for the rate of reaction calculations, and the graph for the rate was plotted. The iC kinetics software is a product of Mettler Toledo. The reaction kinetics followed a pseudo-first (6-2) can be rewritten as (6-3).

$$-r_{TG} - \frac{dC_{TG}}{dt} = k \times C_{TG}^{\alpha} \times (C_{MeOH}^{\beta})^3 \quad (6-3)$$

Where C_{TG}^{α} is the concentration of triglyceride; C_{MeOH}^{β} is the concentration of methanol, and α and β are unknown. Stoichiometrically three moles of methanol is required to convert one mole of triglyceride, excess of methanol was used, and the methanol concentration was taken as constant. Therefore $k (C_{MeOH}^{\beta})^3$ was equated to k' then the equation became

$$-r_{TG} = - \frac{dC_{TG}}{dt} = k' \times C_{TG}^{\alpha} \quad (6-4)$$

Apply ln on both sides of (6-4),

$$\ln \left(\frac{dC_{TG}}{dt} \right) = \ln k' + \alpha \ln C_{TG} \quad (6-5)$$

Let assume initial concentration of triglyceride at time zero to be C_{TG_i} and final concentration to be C_{TG_f} , generated (6-6) as seen below.

$$C_{TG} = C_{TGi} - C_{TGf} \quad (6-6)$$

Replacing equation (6-6) in (6-5) and rearranging

$$\left[\frac{\ln\left(\frac{dC_{TG}}{dt}\right)}{\ln k'} \right] = -\alpha \left[\ln\left(\frac{C_{TGi}}{C_{TGf}}\right) \right] \quad (6-7)$$

The conversion of methyl ester X_{ME} can be express as:

$$X_{ME} = 1 - \frac{C_{TGf}}{C_{TGi}} \quad (6-8)$$

By deriving

$$\left[\frac{\ln\left(\frac{dC_{TG}}{dt}\right)}{\ln k'} \right] = -k't \quad (6-9)$$

Replacing (6-8) and (6-9) in (6-7), and rearranging gives:

$$k't = -\ln(1 - X_{ME}) \quad (6-10)$$

Therefore, the equilibrium rate constant can be express as:

$$k' = \frac{-\ln(1-X_{ME})}{t} \quad (6-11)$$

$$k = A \times e^{\left(\frac{E_a}{RT}\right)} \quad (6-12)$$

Where k is the rate coefficient, A is a constant known as the frequency factor in $M^{-1} \cdot s^{-1}$, E_a is the activation energy $J \cdot mole^{-1}$, R is the universal gas constant, and T is the temperature (in kelvin). The universal gas constant R has a value of $8.314 J \cdot mole^{-1} \cdot K^{-1}$. The Arrhenius equation was used to calculate the activation energy.

The rate of the reaction was calculated and provided by iC Kinetics 5.0. The algebraic method was used to determine the activation energy by applying \ln on Arrhenius (6-12) and using (6-11) to calculate the k value at different temperatures.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (6-13)$$

$$\text{At temperature 1: } \ln k_1 = \ln A - \frac{E_a}{RT_1} \quad (6-14)$$

$$\text{At temperature 2: } \ln k_2 = \ln A - \frac{E_a}{RT_2} \quad (6-15)$$

Subtracting (15) in (14) gave (16) from which after simplification gave an expression of activation energy see (17)

$$\ln k_1 - \ln k_2 = -\left(\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right) \quad (6-16)$$

$$E_a = \left(\ln \frac{k_1}{k_2}\right) R \left(\frac{T_2 T_1}{T_1 - T_2}\right) \quad (6-17)$$

6.4 Results and discussion

6.4.1 Biodiesel Quantification

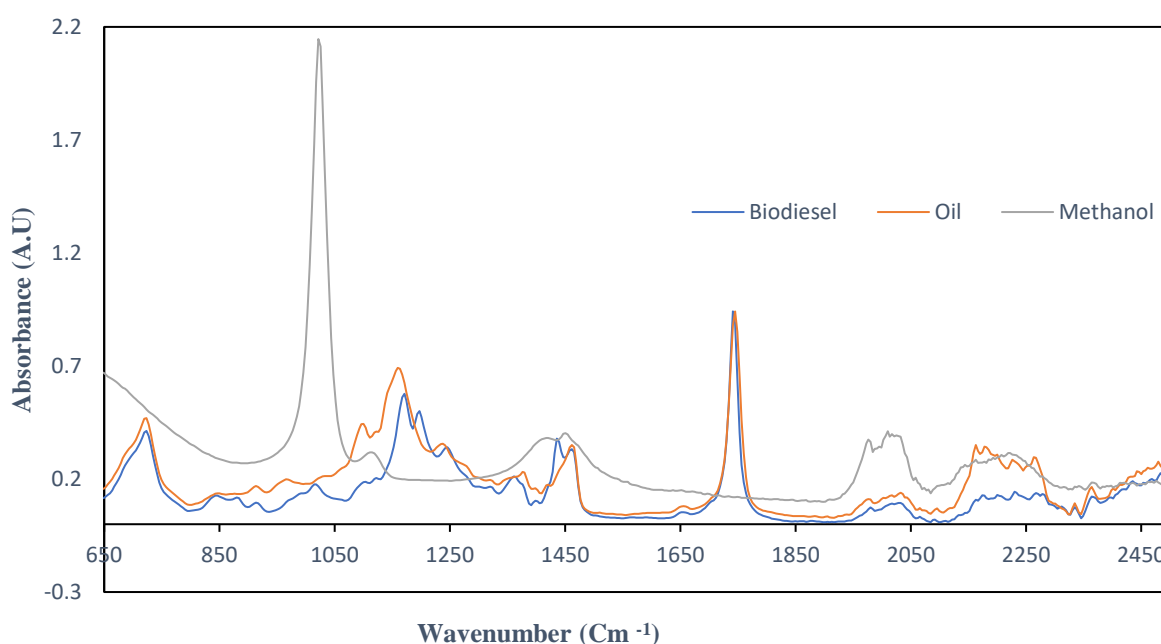


Fig. 6-3. FTIR spectra of methanol, sunflower oil and biodiesel from 650 to 2500 cm⁻¹.

Fig. 6-3 is a representation of three spectrums of three different components of the mixture, namely: methanol, sunflower oil and biodiesel. The spectrums thus collected could only be used for qualitative analysis using their peaks. The authors in their earlier work (Mwenge and Tumisang) performed a quantitative analysis to build a model that was used to quantify the conversion of sunflower oil to biodiesel produced. Thus, online monitoring was performed in which spectrums were collected every 15 seconds for 60 minutes, thus producing a 3D surface plot from the iC IR software as can be seen in Fig. 6-4. Using iC IR software 7.0, *in-situ* real-time monitoring was performed. Fig. 6-5 showed the results obtained; it can be seen that the model can be used to predicting the biodiesel yield in the transesterification of sunflower oil. It was also observed that the peak present in biodiesel (1437 cm⁻¹ and 1744 cm⁻¹) was

increasing with time and could be used to monitor the online transesterification of sunflower oil.

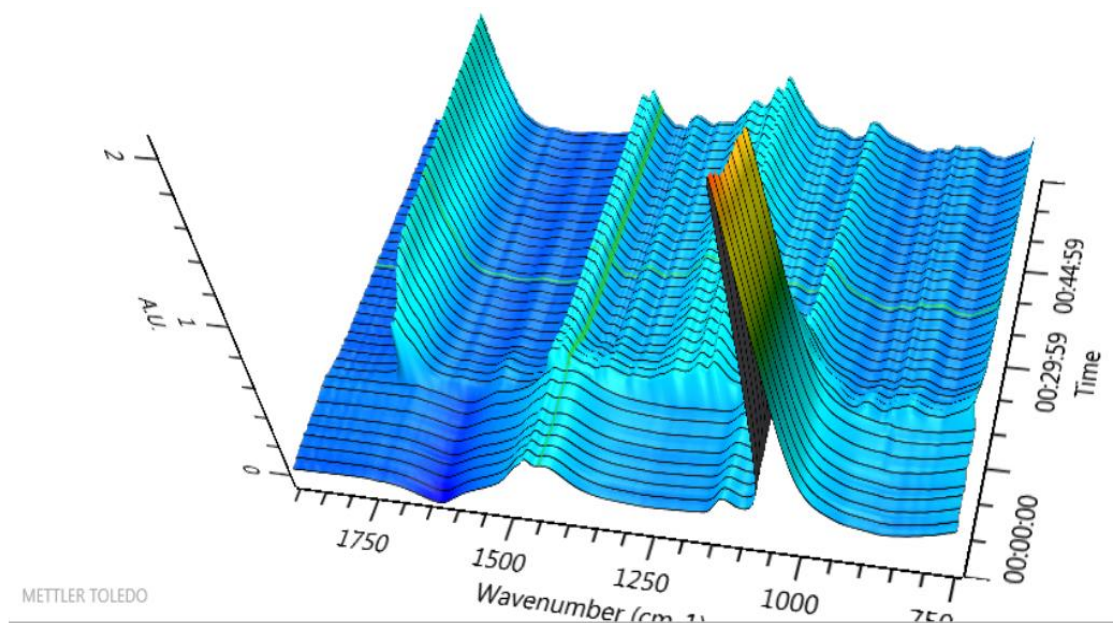


Fig. 6-4: Surface plot of sunflower oil transesterification

Table 6-2: Experimental results

| Run | Methanol to oil ratio (moles/mole) | Catalyst ratio (wt%) | Temperature (°C) | Yield (%) |
|-----|------------------------------------|----------------------|------------------|-----------|
| 1 | 10.5 | 0.85 | 45 | 92.12 |
| 2 | 6.75 | 1.175 | 52.5 | 79.56 |
| 3 | 10.5 | 0.85 | 45 | 92.51 |
| 4 | 10.5 | 0.2 | 45 | 52.37 |
| 5 | 10.5 | 0.85 | 30 | 77.29 |
| 6 | 14.25 | 0.525 | 52.5 | 75.29 |
| 7 | 10.5 | 0.85 | 45 | 91.76 |
| 8 | 10.5 | 0.85 | 45 | 92.56 |
| 9 | 6.75 | 0.525 | 52.5 | 66.82 |
| 10 | 14.25 | 0.525 | 37.5 | 72.91 |
| 11 | 14.25 | 1.175 | 37.5 | 82.58 |
| 12 | 6.75 | 0.525 | 37.5 | 61.12 |
| 13 | 14.25 | 1.175 | 52.5 | 94.18 |
| 14 | 10.5 | 0.85 | 60 | 97.85 |
| 15 | 6.75 | 1.175 | 37.5 | 67.56 |
| 16 | 18 | 0.85 | 45 | 80.98 |
| 17 | 10.5 | 1.5 | 45 | 79.15 |
| 18 | 3 | 0.85 | 45 | 45.34 |

Table 6-2, shows the quantitative results obtained according to experimental design, this results were quatified from using FTIR.

6.4.2 Transesterification kinetics

The reaction was considered isothermal for kinetics purposes, and since the methanol was in excess, the assumption of irreversible reaction was considered. The conversion or yield of the biodiesel produced was real-time monitored using FTIR, which gave data every 15 seconds. The reaction conditions used for the kinetics was taken at one of the optimum conditions which were: methanol to oil ratio of 9, catalyst ratio of 1 wt% and, temperature of 60 °C, the time was 60 min and stirring rate of 150 RPM.

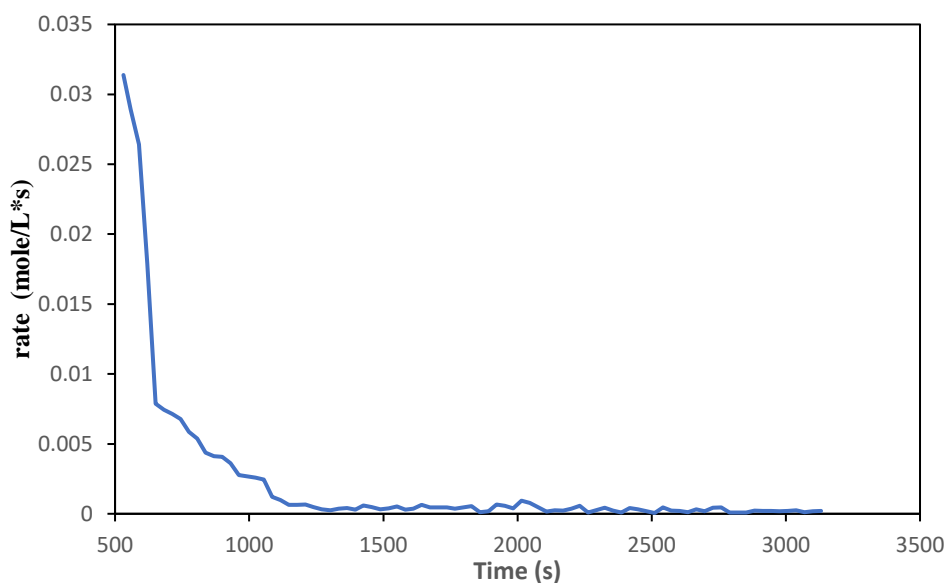


Fig 6-5: Rate of reaction vs time

From the data imported to the iC Kinetics, the rate of reaction was calculated and graph for the rate of reaction vs time was plotted, as shown in Fig. 6-5. The reaction kinetics was suggested to follow a pseudo-first order reaction kinetics. The rate of the reaction was calculated and provided by iC Kinetics 5.0 software. It is demonstrated that the reaction was stable from 500 seconds the rate reaches its peak, then decreases to 1300 seconds, where the reaction rate reaches a lower point where there was no reaction taking place as the rate was 0.

Fig. 6-6, shows the plot of the logarithm of the rate vs time, from the plot, the assumption of the pseudo-first-order can be confirmed with and coefficient of regression of 0.9501.

Using runs 6 and 10 from Table 6-2 as point 1 and 2, the concentration of methanol was calculated based on the experimental design and data obtained from the iC Kinetics. Using equation (11) the values of k' were calculated at the two different temperatures as shown in Table 6-3. Once the values of k' were obtained using the expression $k' = k [MeOH]^3$, k values

were calculated. The activation energy was calculated using algebraic method from the Arrhenius equation simplified (17) and found to be 41.279 kJ.mole⁻¹. The activation energy was found to be low; however, it was found to be in the range determined by Freedman, Butterfield and Pryde, (1986), who found activation energy ranging from 33.472 kJmol⁻¹ – 83.68 kJmol⁻¹. Once the activation energy calculated, the frequency factor was calculated and was found to be 1.08 x10⁻⁴ M⁻¹. s⁻¹.

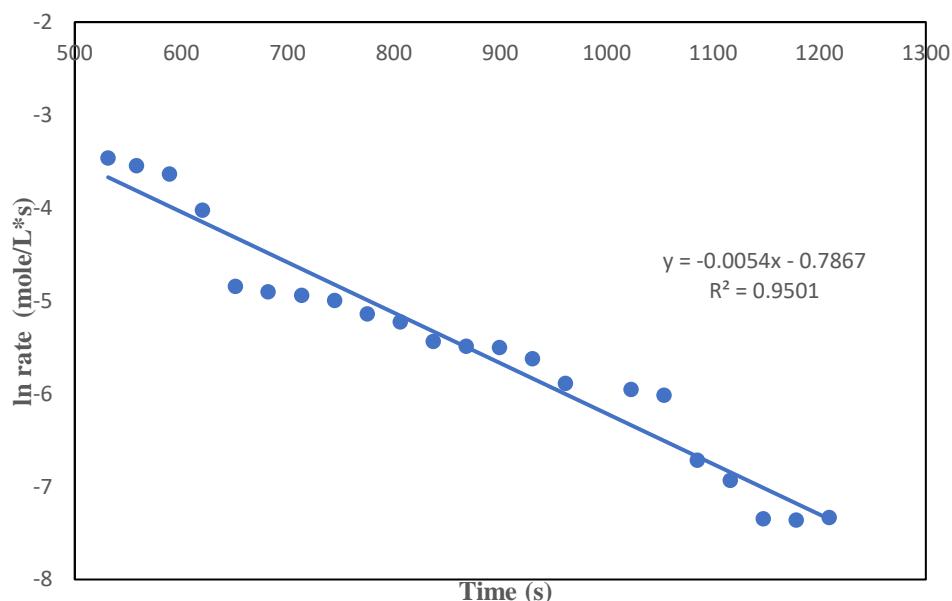


Fig. 6-6: ln rate of reaction vs time

Table 6-3: Kinetics data

| | 1 | 2 |
|------------------------|------------------------|------------------------|
| T (K) | 325.5 | 310.5 |
| [MeOH] (M) | 5.753 | 5.444 |
| k' (M ⁴ /s) | 4.118*10 ⁻⁴ | 7.058*10 ⁻⁴ |
| k (M/s) | 2.163*10 ⁻⁶ | 4.374*10 ⁻⁶ |

6.4.3 Optimisation

6.4.3.1 Development of Regression Model Equation and the Analysis of Variance

A regression model was developed by excluding insignificant terms and by the use of Fisher's Test (Modiba, Enweremadu and Rutto, 2015), (Onukwuli *et al.*, 2017). As shown in (3) and

(4). Equation (3) is the final equation in terms of Coded Factors and (4) is the final equation in terms of Actual Factors.

$$\text{Yield} = +87.85 + 4.14A + 6.53B + 9.54C - 4.63AB + 1.1AC + 3.62BC - 6.1A^2 - 7.97B^2 - 2.52C^2 \quad (6-18)$$

Where, A is methanol to oil ratio (moles/mole), B is catalyst ratio (wt. %) and C is Temperature.

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +2, and the low levels are coded as -2. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

$$\text{Yield} = +91.66 + 7.57A + 6.33B + 4.55C + 1.17AB - 0.4625AC + 1.94BC - 7.41A^2 - 6.76B^2 - 1.31C^2 \quad (6-19)$$

The equation in terms of actual factors can be used to make predictions about the biodiesel yield for given levels of each factor. Hence, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor, and the intercept is not at the centre of the design space. The antagonistic effect is indicated by the negative sign in front of the terms, while the synergic effect is indicated by the positive sign.

The effectiveness of the model was evaluated by the coefficient correlations, the R-Squared of 0.9847, adjusted R-Squared 0.9674 and Predicted R-Squared 0.8749. The high R-Squared of 0.9847 indicated that 98.47 % of the total variation of the outcome would be explained by the model (Modiba, Enweremadu and Rutto, 2015).

To test the capability of the model and to check the effectiveness of the predicted model, the experimental values are compared to the predicted values by use of the parity plot confirms that model fits the data equitably. The results showed that the regression equation provides an accurate description of the experimental data using the minimum number of experiments. As shown in Table 6-4, the actual (experimental) values are compared to the predicted values, which were found to be in good agreement. This result is graphically shown in Fig. 6-4, displaying the correlation between the experimental and actual biodiesel yield. It is shown that the suggested model can be used to predict the yield of biodiesel within the range of methanol to oil ratio, catalyst ratio and temperature used in the study (Alshaibani *et al.*, 2014). The results

of this study have demonstrated an adequate adjusted and predicted R-squared of 0.9674 and 0.8749, respectively, which is in the reasonable agreement since the difference is less than 0.2 as suggested by Design expert.

Table 6-4: Actual and predicted biodiesel yield from the quadratic model.

| Run Order | Actual Value | Predicted Value | Residual | Leverage | Internally Studentized Residuals |
|-----------|--------------|-----------------|----------|----------|----------------------------------|
| 1 | 92.12 | 91.66 | 0.4630 | 0.233 | 0.197 |
| 2 | 79.56 | 80.70 | -1.14 | 0.621 | -0.690 |
| 3 | 92.51 | 91.66 | 0.8530 | 0.233 | 0.362 |
| 4 | 52.37 | 51.94 | 0.4310 | 0.683 | 0.285 |
| 5 | 77.29 | 77.31 | -0.0165 | 0.683 | -0.011 |
| 6 | 75.31 | 78.39 | -3.08 | 0.621 | -1.861 |
| 7 | 91.76 | 91.66 | 0.1030 | 0.233 | 0.044 |
| 8 | 92.56 | 91.66 | 0.9030 | 0.233 | 0.383 |
| 9 | 66.82 | 66.51 | 0.3128 | 0.621 | 0.189 |
| 10 | 72.91 | 74.09 | -1.18 | 0.621 | -0.712 |
| 11 | 82.58 | 85.21 | -2.63 | 0.621 | -1.591 |
| 12 | 61.12 | 60.35 | 0.7652 | 0.621 | 0.462 |
| 13 | 94.18 | 97.27 | -3.09 | 0.621 | -1.864 |
| 14 | 97.85 | 95.51 | 2.34 | 0.683 | 1.545 |
| 15 | 67.56 | 66.80 | 0.7602 | 0.621 | 0.459 |
| 16 | 80.98 | 77.15 | 3.83 | 0.683 | 2.531 |
| 17 | 79.15 | 77.26 | 1.89 | 0.683 | 1.249 |
| 18 | 45.34 | 46.85 | -1.51 | 0.683 | -0.997 |

The adjusted R-Squared is explained by the fact that there is a change in the biodiesel yield closed to the mean, which is explained by the model and adjusted terms in the model, this can be seen in Table 6-4. In case the number of terms does not sum-up to the model according to the model improvement, this, in turn, affects the value of adjusted R-Squared negatively. As a result, it is the poor indication of the model that can be alleviated by decreasing the number of terms and searching to eliminate the outliers. Hence, it is desired to have high adjusted R-Squared. The predicted R-squared is defined as the deviation from the mean in the new data explained by the model. In case the value of predicted R-squared is negative; it is an indication of an outlier in the data. Hence it is desired to have a high predicted R-squared (Fahim, Elhaggar and Elayat, 2012).

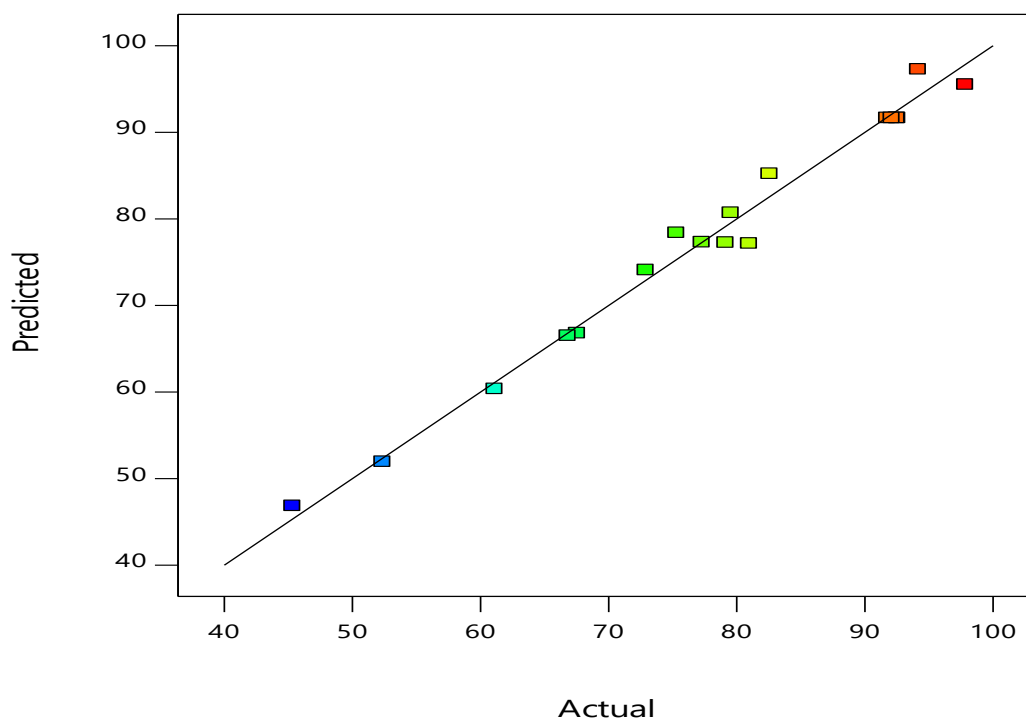


Fig. 6-7: Linear representation of actual versus the predicted biodiesel yield.

Table 6-5: R-squared obtained from design-expert.

| | | | |
|------------------|--------|--------------------------------|---------|
| Std. Dev. | 2.69 | R² | 0.9847 |
| Mean | 77.89 | Adjusted R² | 0.9674 |
| C.V. % | 3.45 | Predicted R² | 0.8749 |
| PRESS | 472.32 | Adeq Precision | 25.1473 |

Adequate precision is the measurement signal to noise ratio. It is desired to have a ratio greater than 4. The ratio of 25.1473 as shown in Table 6-5 indicated an adequate signal, implying that the model can be used to navigate the design space.

The interpretation of the contribution of each factor was done using ANOVA, R^2 , predicted R^2 and adjusted R^2 were used to analyse the effectiveness of the model. Predicted R^2 and adjusted R^2 were used to assess the system, R^2 was not selected since R^2 can be improved by adding terms to the model, the significance of the terms does not affect the R^2 , and therefore R^2 could not be used to access the model. Predicted R^2 decreases with the increase of the insignificant terms; on the other hand, the adjusted R^2 plateaus with the increase of insignificance terms. The effectiveness of the model was based on the significance of the p-value, insignificant lack of fit test, good agreement between adjusted and predicted R^2 and adequate precision over four and well-behaved residuals. It is preferred to have insignificance lack of fit as a significant lack

of fit, and this implies that replicates variation of the mean values is lower compared to one of the predicted design point values. (Ejikeme, Onukwuli and Ejikeme, 2014)

The significance of the model is shown by the F-value of 57.11, implying that there is only a 0.01% chance that an F-value this large could occur due to noise. The significance of the model is also indicated by P-values less than 0.05. Therefore; A, B, C, A², B² are significant model terms as they have P-values less than 0.05 and AB, BC, AC and C² are not significant model terms by their high P-values (Gunst, Myers and Montgomery, 2006). The Lack of Fit F-value of 82.08 implies the Lack of Fit is significant. There is only a 0.21% chance that a Lack of Fit F-value this large could occur due to noise.

Table 6-6: Coefficients in Terms of actual Factors

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|----------------------|----------------|----|-------------|---------|---------|-------------|
| Model | 3718.70 | 9 | 413.19 | 57.11 | <0.0001 | significant |
| A | 918.09 | 1 | 918.09 | 126.89 | <0.0001 | |
| B | 641.10 | 1 | 641.10 | 88.61 | <0.0001 | |
| C | 331.42 | 1 | 331.42 | 45.81 | 0.0001 | |
| AB | 10.95 | 1 | 10.95 | 1.51 | 0.2535 | |
| AC | 1.71 | 1 | 1.71 | 0.2365 | 0.6398 | |
| BC | 30.03 | 1 | 30.03 | 4.15 | 0.0760 | |
| A² | 1199.45 | 1 | 1199.45 | 165.77 | <0.0001 | |
| B² | 998.37 | 1 | 998.37 | 137.98 | <0.0001 | |
| C² | 37.56 | 1 | 37.56 | 5.19 | 0.0522 | |
| Lack of Fit | 57.46 | 5 | 11.49 | 82.08 | 0.0021 | significant |

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-collinearity, the higher the VIF, the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable. Therefore, the VIFs values of less than 1.5 are in an acceptable range. From the data presented in Table 6-6 and Table 6-7, methanol to oil ratio has the most effect on the biodiesel production, followed by catalyst ratio and lastly temperature. The P-value for both models is less than 0.05, which implies that the model is significant for 95% confidence intervals for the biodiesel production prediction. The “Lack of Fit F-value” of the response indicates the insignificance of the Lack of Fit relatively to the pure error. Hence, a nonsignificant “Lack of Fit” is acceptable. The accuracy and reliability of the

experiments were confirmed by the coefficient of variation (CV), which was 3.45 (Alshaibani *et al.*, 2014).

Analyses of Variance (ANOVA) showed quadratic effects of methanol to oil ratio, catalyst ratio and temperature affecting the biodiesel yield. It was clearly shown from the Sum of Squares that methanol to oil ratio has the highest effect; this is followed by catalyst ratio and lastly temperature. It can also be said that all the three factors used in the transesterification reaction have significant effect on the biodiesel transesterification of sunflower oil.

Table 6-7: Coefficients in Terms of Coded Factors

| Factor | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|----------------------|----------------------|----|----------------|------------|-------------|--------|
| Intercept | 91.66 | 1 | 1.30 | 88.66 | 94.65 | |
| A | 7.58 | 1 | 0.6725 | 6.02 | 9.13 | 1.0000 |
| B | 6.33 | 1 | 0.6725 | 4.78 | 7.88 | 1.0000 |
| C | 4.55 | 1 | 0.6725 | 3.00 | 6.10 | 1.0000 |
| AB | 1.17 | 1 | 0.9510 | -1.02 | 3.36 | 1.0000 |
| AC | -0.4625 | 1 | 0.9510 | -2.66 | 1.73 | 1.0000 |
| BC | 1.94 | 1 | 0.9510 | -0.2555 | 4.13 | 1.0000 |
| A² | -7.41 | 1 | 0.5759 | -8.74 | -6.09 | 1.18 |
| B² | -6.76 | 1 | 0.5759 | -8.09 | -5.44 | 1.18 |
| C² | -1.31 | 1 | 0.5759 | -2.64 | 0.0160 | 1.18 |

Table 6-8: Sequential Model Sum of Squares

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---------------------------|----------------|----------|---------------|--------------|-------------------|------------------|
| Mean vs Total | 1.092E+05 | 1 | 1.092E+05 | | | |
| Linear vs Mean | 1890.61 | 3 | 630.20 | 4.68 | 0.0182 | |
| 2FI vs Linear | 42.69 | 3 | 14.23 | 0.0849 | 0.9669 | |
| Quadratic vs 2FI | 1785.39 | 3 | 595.13 | 82.25 | <0.0001 | Suggested |
| Cubic vs Quadratic | 37.24 | 4 | 9.31 | 1.80 | 0.2907 | Aliased |
| Residual | 20.64 | 4 | 5.16 | | | |
| Total | 1.130E+05 | 1 | 6276.23 | | | |
| | | 8 | | | | |

The highest-order polynomial was selected where the additional terms are significant, and the model is not aliased as it can be seen in Table 6-8. The quadratic vs 2FI was suggested by the software.

The focus was on the model maximising the Adjusted R² and the Predicted R², looking at the two, the results showed that quadratic model has high value for both Adjusted and Predicted R², therefore it was selected as the best fit model.

Table 6-9: Model Summary Statistics

| Source | Std. Dev. | R ² | Adjusted R ² | Predicted R ² | PRESS | |
|---------------|-------------|----------------|-------------------------|--------------------------|---------------|------------------|
| Linear | 11.61 | 0.5006 | 0.3936 | 0.1835 | 3083.64 | |
| 2FI | 12.94 | 0.5119 | 0.2457 | 0.0874 | 3446.53 | |
| Quadratic | 2.69 | 0.9847 | 0.9674 | 0.8749 | 472.32 | Suggested |
| Cubic | 2.27 | 0.9945 | 0.9768 | -0.1251 | 4248.96 | Aliased |

Table 6-10: Lack of Fit Tests

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|-------------------|----------------|----------|--------------|--------------|---------------|------------------|
| Linear | 1885.55 | 11 | 171.41 | 1224.17 | < 0.0001 | |
| 2FI | 1842.86 | 8 | 230.36 | 1645.11 | < 0.0001 | |
| Quadratic | 57.46 | 5 | 11.49 | 82.08 | 0.0021 | Suggested |
| Cubic | 20.22 | 1 | 20.22 | 144.39 | 0.0012 | Aliased |
| Pure Error | 0.4201 | 3 | 0.1400 | | | |

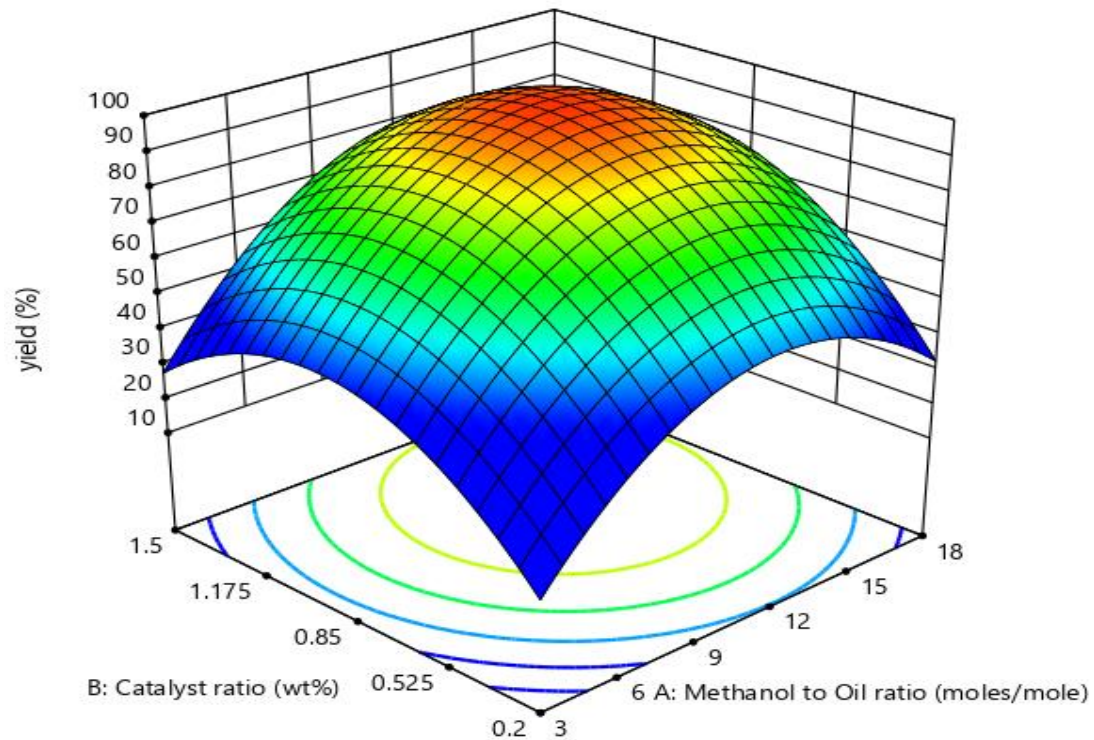
Table 6-10 compares the lack of fit of the models by looking at the F-values, the selected model should have insignificant lack-of-fit, and the quadratic model had a less F-value and was suggested.

The models were also compared by the use of the sequential model sum of square, as shown in Table 6-10. The sequential model sum of square demonstrated the statistical significance of stepwise addition of new model terms. It helps in explaining the variation associated with P-values (Prob>F) in order to predict the worthiness of the model and perceiving how far it merits going in the level of a polynomial (Ejikeme, Onukwuli and Ejikeme, 2014).

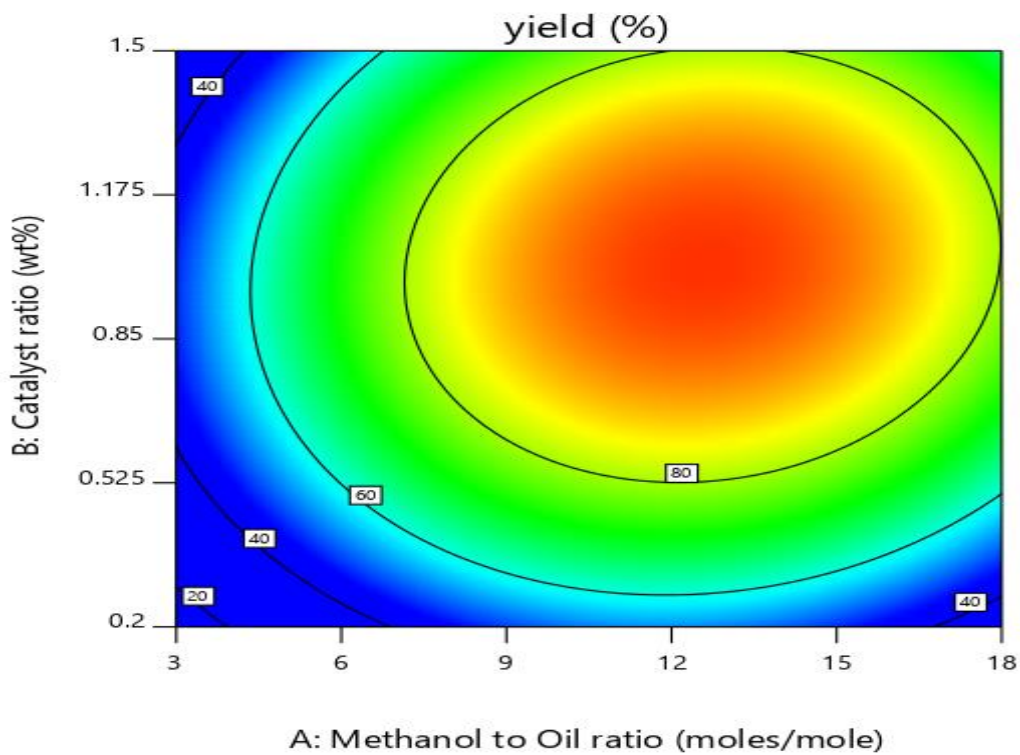
6.4.3.2 Effect of Transesterification variables on the biodiesel yield.

The effect of process variables on the transesterification of sunflower oil was assessed using three process variables, methanol to oil ratio (3 to 18 moles/mole), catalyst ratio (0.2 to 1.5 wt. %) and temperature (30 to 60 °C). Time and stirring rate were kept constant to 60 minutes and 150RPM, respectively. The Central Composite Design (CCD) from Response Surface Methodology (RSM) was used to access the effect of the three studied process variables. The CCD shows three-dimensional plots and contour plots in which the response is presented in function of two variables and keeping the other constant, and two-dimension plot in which, the

response is presented in term of one variable, holding another variable at two points and keeping one variable constant. The RSM illustration of the biodiesel yield is shown in Fig. 6-8 to Fig. 6-10.



(a)



(b)

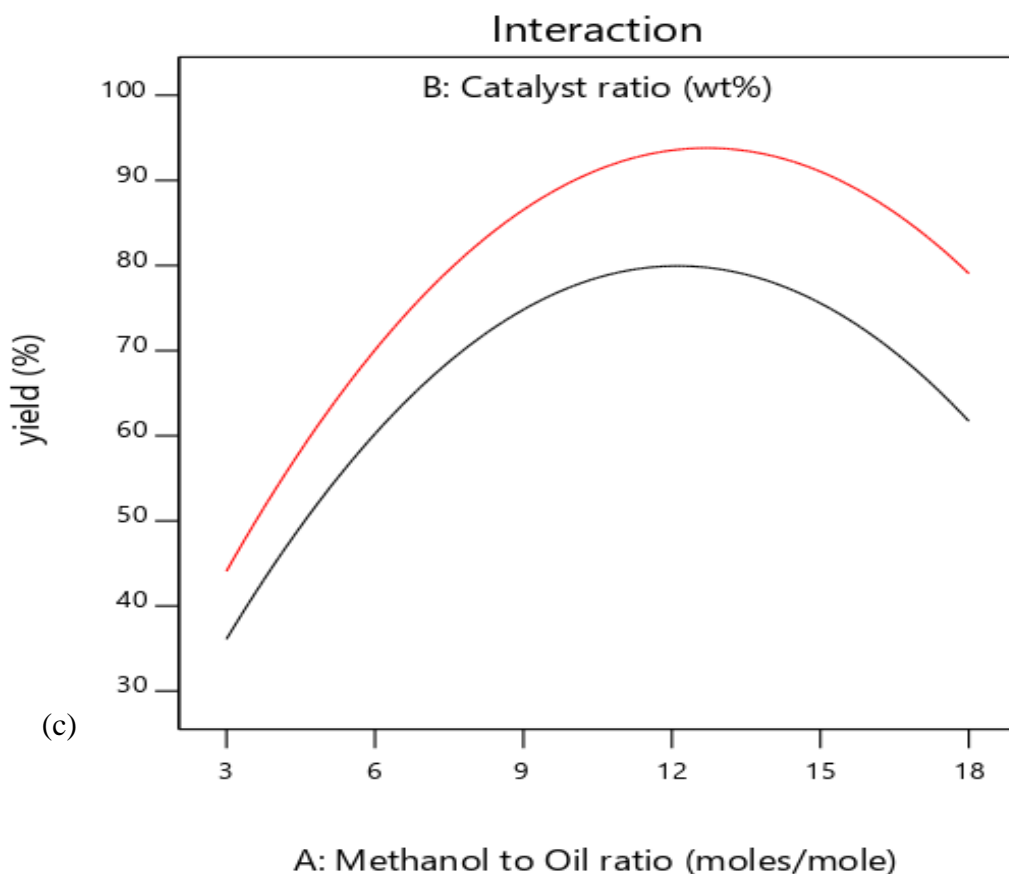


Fig. 6-8: Effect of methanol to oil ratio and temperature at a catalyst ratio of 0.85 wt%: (a) response surface, (b) contour plot and (c) two-dimension plot with temperature at (-) 37.5°C and (+) 52.5 °C.

Fig. 6-8 shows the effect of catalyst ratio and methanol to oil ratio at a temperature of 45 °C in which (a) is a three- dimensional response surface, (b) contour plot and (c) two-dimension plot with catalyst ratio held at at (-) 0.525 wt % and (+) 1.175wt %. In this, the interaction of methanol to oil ratio and catalyst ratio are illustrated at a constant temperature of 45 °C. As the catalyst ratio and the methanol to oil ratio are increasing, there is an increase in the yield reaching an optimum range where a decrease in yield is observed. This mean methanol to oil ratio affects the yield proportionally, though the two variables are influencing the yield on the same proportion.

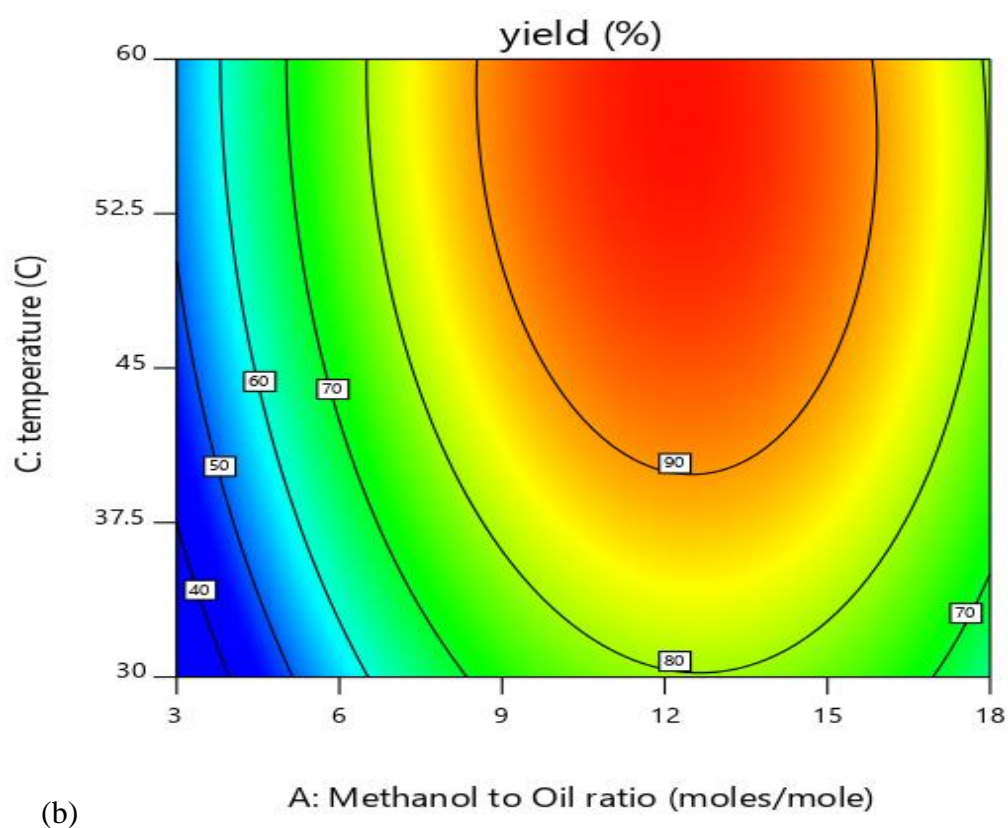
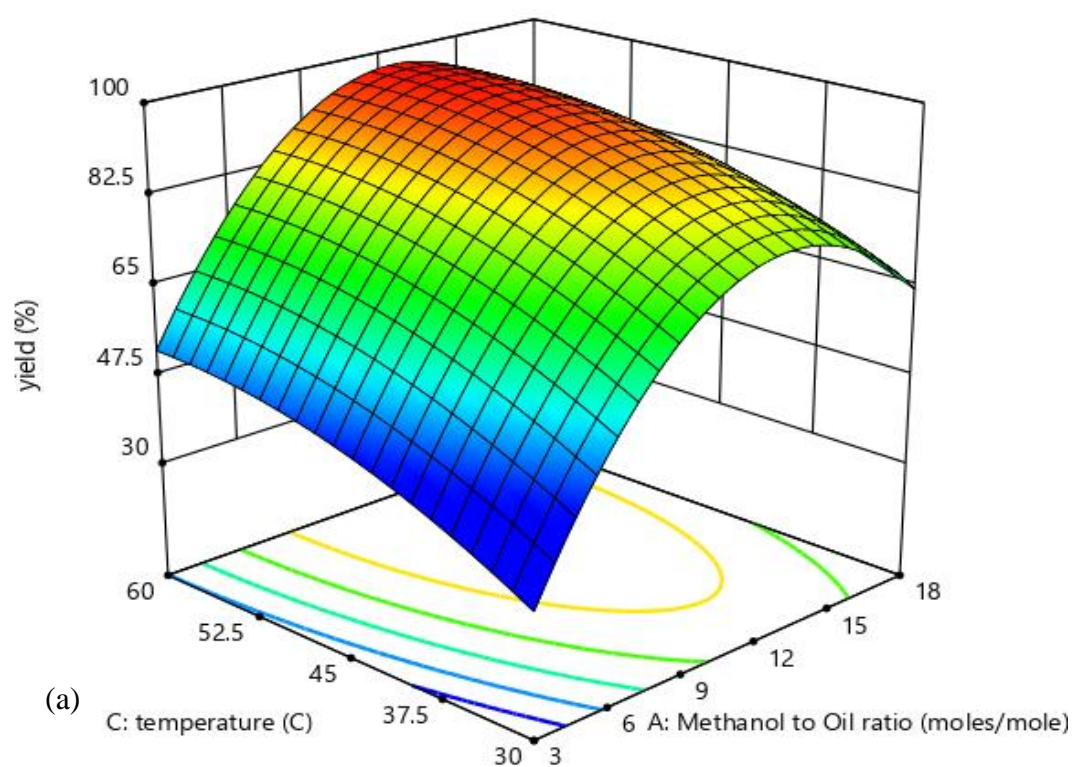
Fig. 6-9 shows the effect of methanol to oil ratio and temperature at a catalyst ratio of 0.85 wt% in which (a) response surface, (b) contour plot and (c) two-dimension plot with the temperature at (-) 37.5°C and (+) 52.5 °C. The interaction of methanol and temperature is clearly illustrated at a constant catalyst ratio of 0.85 wt%. It is seen that the increase of both variables affects positively affect the yield, however at a temperature of 60 °C being the maximum temperature

was enough to reach the highest yield, but there was a need for increasing the methanol to oil ratio that could give a high yield at a lower temperature.

In Fig. 6-10, the interaction of the effect of catalyst ratio and temperature is illustrated by keeping the methanol to oil ratio at 10.5 moles/mole. It is seen that the increase of both variables affects positively the yield, however at a temperature of 45 °C, a high yield could be obtained, but that depends on catalyst ratio.

The effect of methanol to oil ratio on biodiesel yield, as shown in Fig. 6-8 and Fig. 6-9. At low methanol to oil ratio, there is a low yield, but this increases with the increase of methanol to oil ratio, the starting ratio being three moles per mole as the required stoichiometrical ratio, though three moles/mole ratio is required to theoretically fully convert triglyceride, experimentally this was not observed. It is explained by the fact that, the transesterification is a reversible reaction; therefore, excess methanol will favour the forward reaction, being the biodiesel production. However, by increasing methanol to a certain ratio there is a decrease of biodiesel formation, this can explain the fact that exceeding a specific ratio of methanol causes glycerolysis reaction to occur, this reaction consequently leads to the formation of monoglyceride instead of methyl ester (biodiesel) (Meher, Vidya Sagar and Naik, 2006). Increasing methanol to high ratio leads the OH group from the oil to react with the triglyceride to a hydrolysis reaction which will subsequently lead to soap formation (Mansourpoor and Shariati, 2012). The same observation has been reported in the studies of Baskar and Soumiya (2016)

The effect of catalyst ratio is shown in Fig. 6-8 and Fig. 6-10, it was experimental demonstrated that the yield is affected by the catalyst ratio. At low ratio, the yield was low until it reached a certain point where the yield decreased, as the catalyst ratio increased, the increase in the yield is explained by the fact that there was not enough catalyst to speed up the reaction rate but as the catalyst increase the reaction rate increased as well this was demonstrated by the increase in the yield, there decrease in the yield was explain by the fact that Sodium hydroxide used as catalyst, caused gelled mixture causing soap formation thereby decrease the yield and caused separation problem. (Zhang *et al.*, 2010; Leung, Wu and Leung, 2010; Modiba, Osifo and Rutto, 2014) reported in their studies similar results.



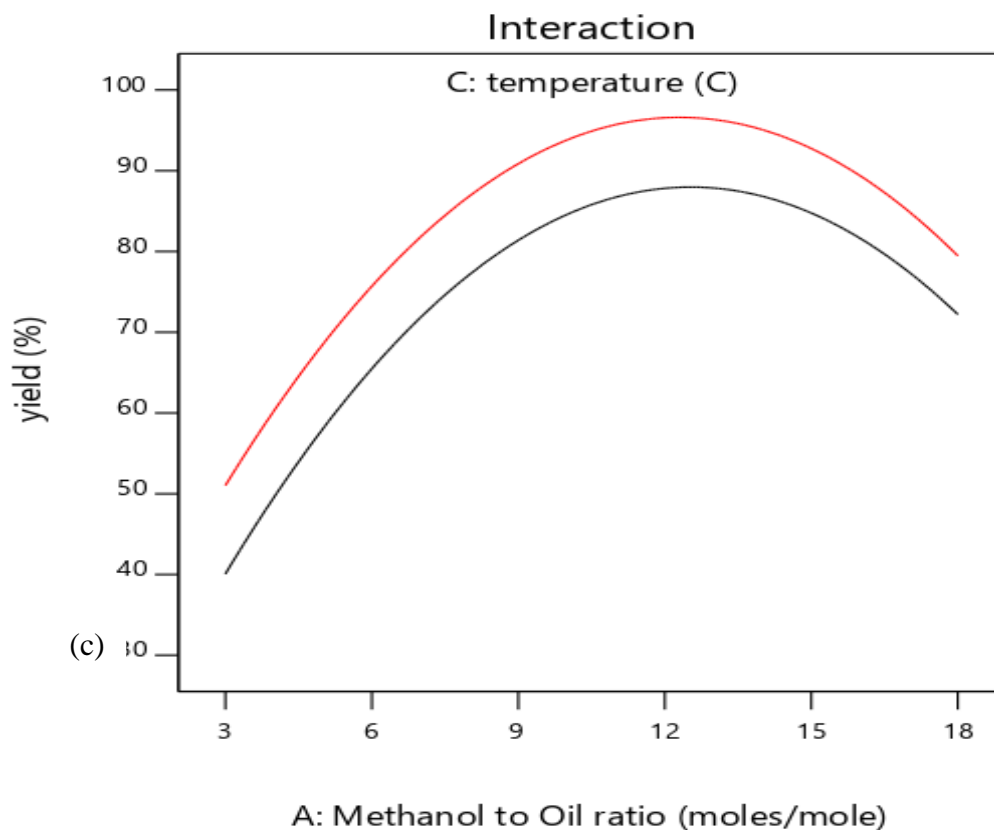
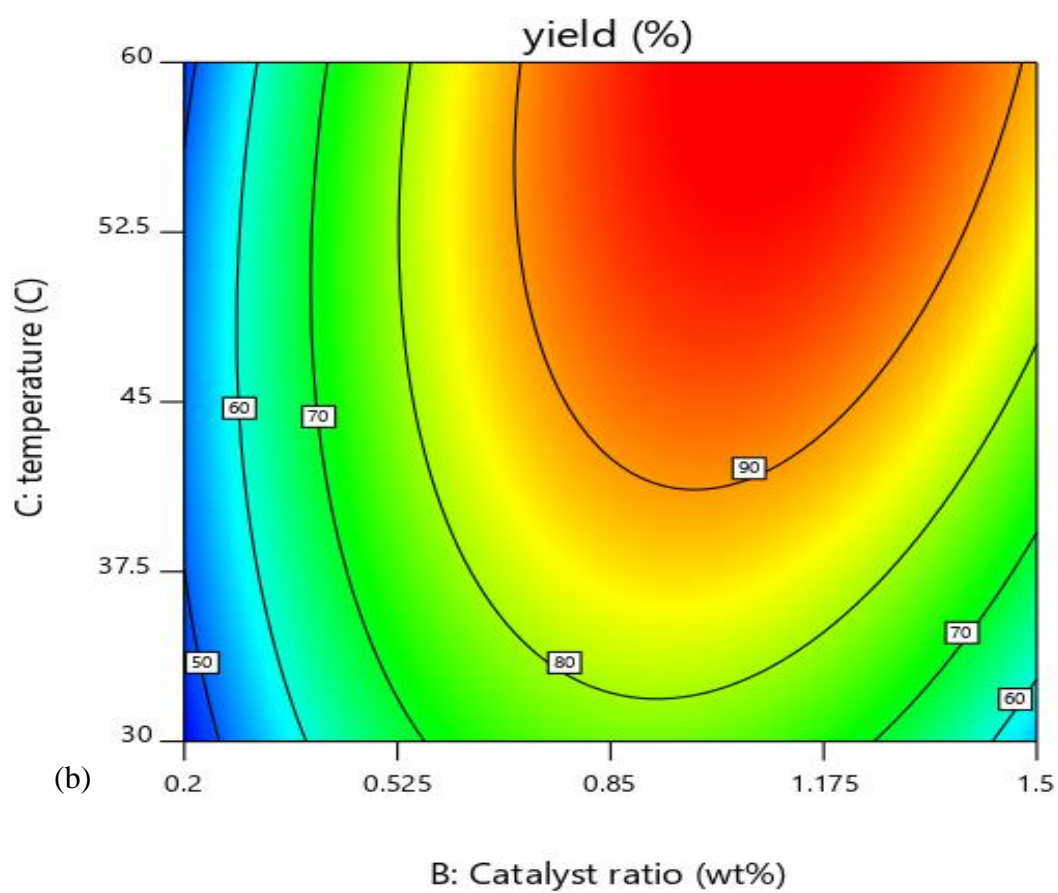
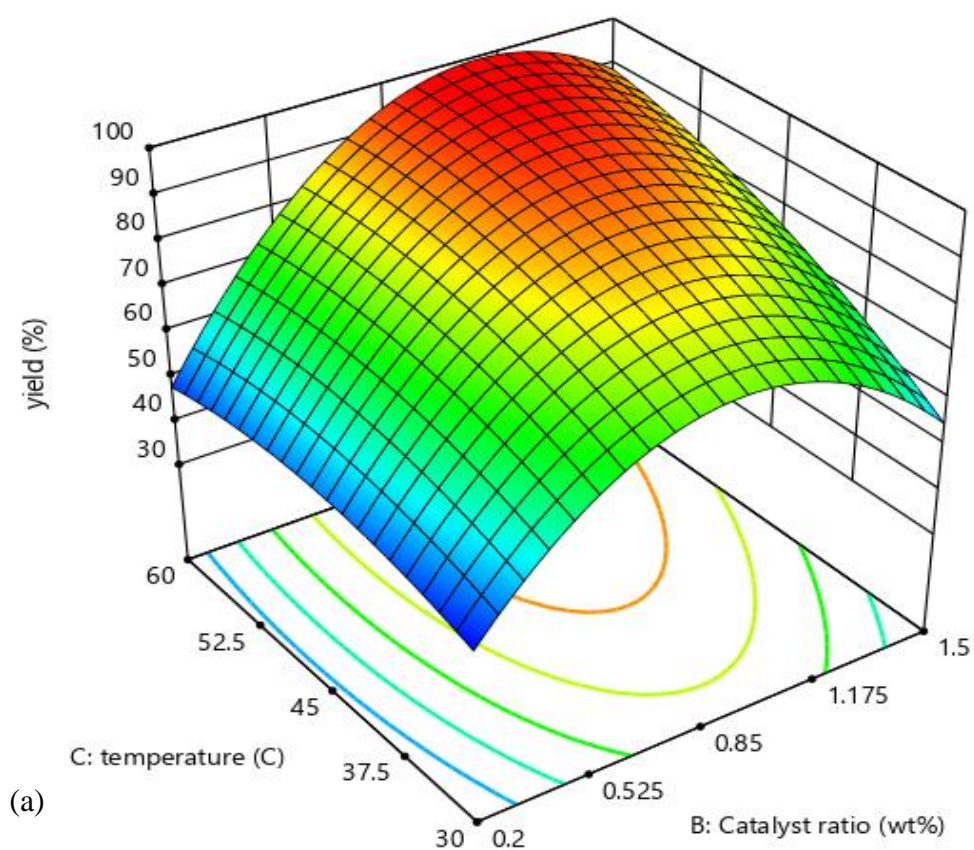


Fig. 6-9: Effect of methanol to oil ratio and temperature at a catalyst ratio of 0.85 wt%: (a) response surface, (b) contour plot and (c) two-dimension plot with temperature at (-) 37.5°C and (+) 52.5 °C.

The effect of temperature is shown in Fig. 6-9 and Fig. 6-10, it was observed that there was an increase in yield with the increase in temperature. The increase in yield with the increase in temperature is explained that at low temperature the reaction rate was low, it can further be explained that the dispersion and mixing of methanol in the alcohol were low due to the methanol subcritical condition, but as the temperature increased the dispersion and mixing was favoured (Leung, Wu and Leung, 2010). At high temperature, the mass transfer coefficients and the reaction kinetics are intensified (Blaž Likozar and Levec, 2014). A decrease in the yield was not observed this was due to the fact that the highest temperature selected was 60 °C. The evaporation of methanol would occur and at high temperature above 60 °C reducing the molecular interaction residence time between methanol-oil-catalyst causing thermal degradation which will decrease the yield (Leung and Guo, 2006; Zhang et al., 2010; Leung, Wu and Leung, 2010). The same observation was reported by (Kostić et al., 2016).



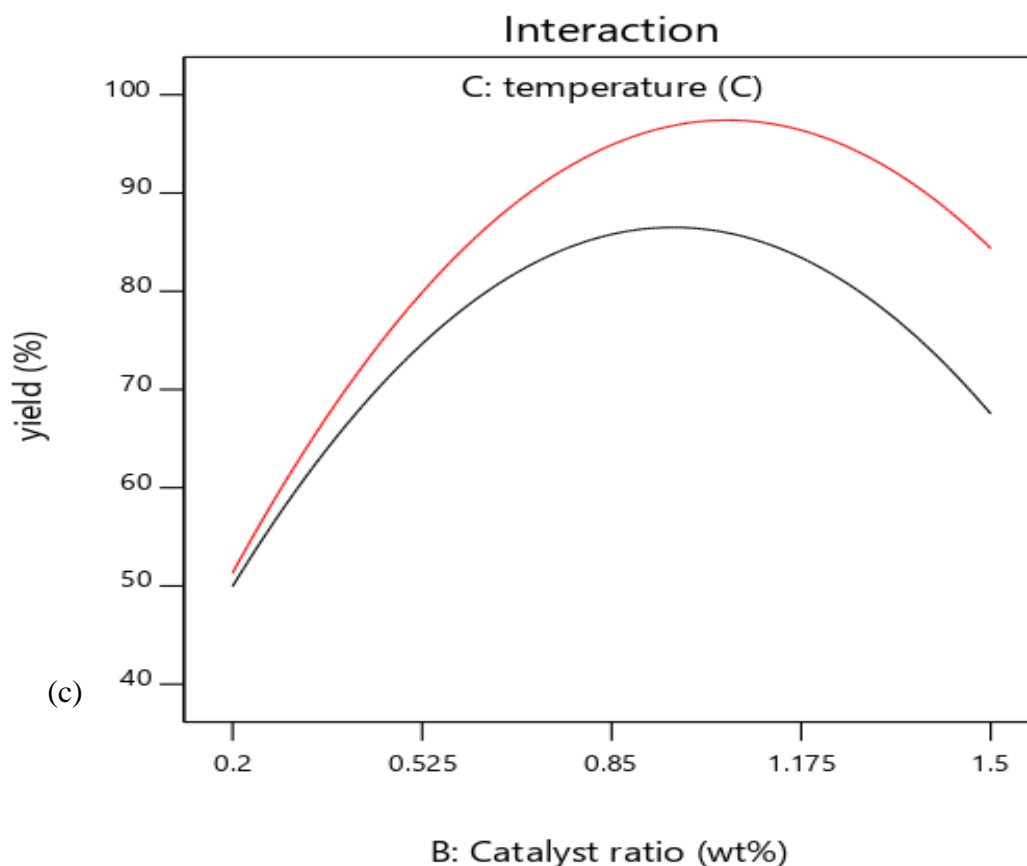


Fig. 6-10: Effect of catalyst ratio and temperature at a mole ratio of 10.5 moles/mole: (a) response surface, (b) contour plot and (c) two-dimension plot with temperature held at (-) 37.5°C and (+) 52.5 °C.

Fig. 6-11 shows the perturbation plot in which the effect of the three transesterification variables studies can be discussed at a point in the design space. The influence of each variable is evaluated and plotted against the yield by keeping the other variables constant. It is shown that methanol to oil ratio and catalyst ratio have a higher effect on the transesterification compare to the reaction temperature. This observation entirely agrees with the results from the analysis of variance. The general observation was that the further increase in methanol to oil ratio and catalyst ratio causes a slight decrease of the yield while a further increase of yield is observed with increase in the temperature is due to the highest temperature reported in the literature that gives high yield is 60 °C.

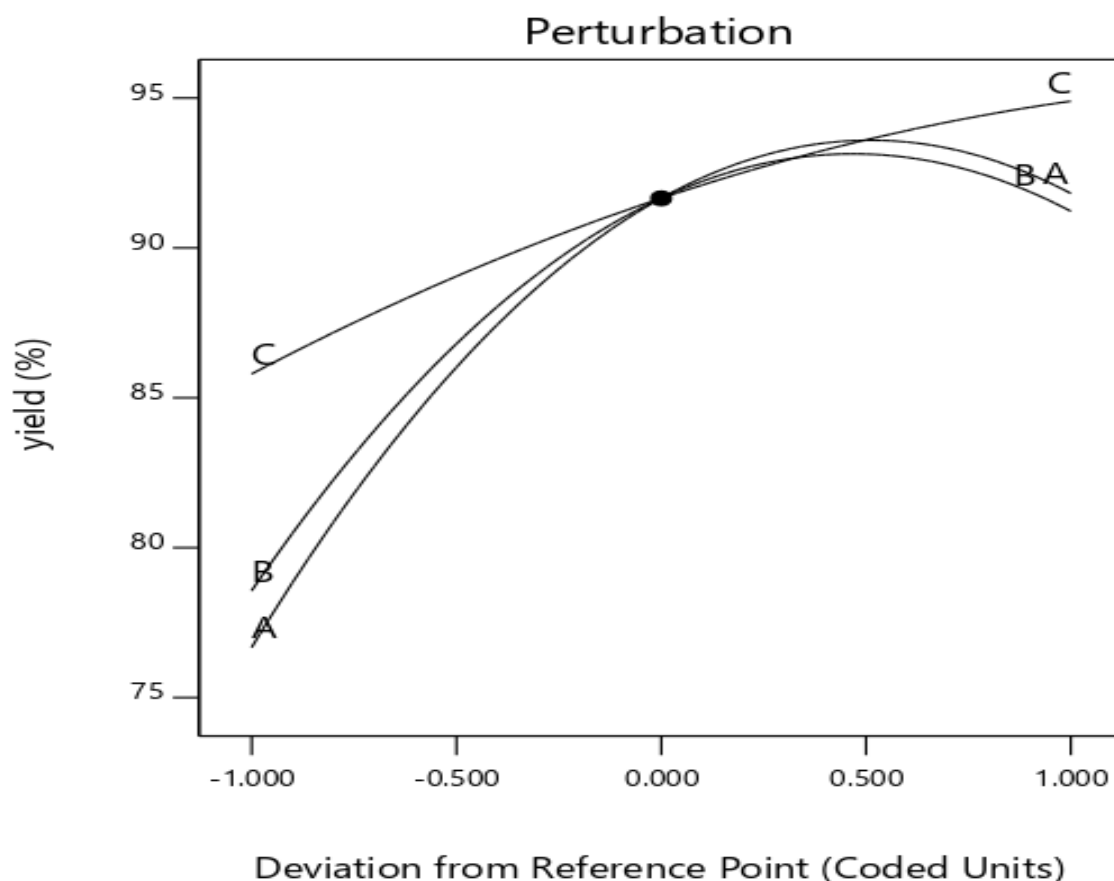


Fig. 6-11: Effects of individual variables on transesterification of sunflower oil to biodiesel.
A: Methanol to oil ratio; B: Catalyst to oil ratio; C: Reaction temperature.

6.4.3.3 Optimisation of biodiesel production

The optimisation of the biodiesel production condition was given by Design Expert for which 100 solutions were found. From the 100 solutions, the aim was to reduce to outmost ten solutions as shown in Table 11; for which desirability, yield and standard yield error were used in order to screen the best ten solutions. The desirability being 1.0 for all the solutions could not be considered as a criterion; therefore, only yield and standard yield error were used for the screening. To reduce the number of solutions to ten, solutions with yields of less than 90 % and standard yield error higher than 1.3 were discarded. The highest optimum yield solution was 97.29 % obtained at 12.22 moles/mole, 1.00 wt % and 48.17 °C and 1.28, methanol to oil ratio, catalyst ratio, temperature and standard yield error, respectively. The highest yield obtained in this work was closed to what obtained by (Mansourpoor and Shariati, 2012), a yield of 98.181 was obtained at methanol to oil ratio of 6.825, catalyst ratio of 0.679%wt, the temperature of 48°C, 290 RPM of stirring rate, 2h reaction time. Considering the design point

of view (reactor sizing, the energy required), yield and the standard yield error, solution seven was suggested as the optimum solution amongst the ten solutions.

Table 6-11: Optimisation solutions from Design experts

| Number | Methanol to Oil ratio | Catalyst ratio | temperature | yield | StdErr(yield) | Desirability |
|-----------|-----------------------|----------------|-------------|-------|---------------|--------------|
| 1 | 12.75 | 1.03 | 45.68 | 95.83 | 1.24 | 1.000 |
| 2 | 11.30 | 0.92 | 48.21 | 95.80 | 1.26 | 1.000 |
| 3 | 12.423 | 0.78 | 46.563 | 92.63 | 1.25 | 1.000 |
| 4 | 12.22 | 1.00 | 48.17 | 97.29 | 1.28 | 1.000 |
| 5 | 11.70 | 1.08 | 45.37 | 94.98 | 1.24 | 1.000 |
| 6 | 10.34 | 0.85 | 51.34 | 94.13 | 1.22 | 1.000 |
| 7 | 10.96 | 1.02 | 47.43 | 95.64 | 1.25 | 1.000 |
| 8 | 13.15 | 0.90 | 47.29 | 95.55 | 1.24 | 1.000 |
| 9 | 10.44 | 1.00 | 45.17 | 93.13 | 1.26 | 1.000 |
| 10 | 9.12 | 1.03 | 49.57 | 92.11 | 1.26 | 1.000 |

6.5 Conclusion

Biodiesel a renewable fuel has been produced worldwide, and it is mainly blended with petroleum diesel. The mainly used analytical method has been GC, which is a time-consuming method; its requirement led to the search for a friendly analytical method such as FTIR. This work focused on the optimisation and kinetics of biodiesel produced in an EasyMax Mettler Toledo reactor, with real-time quantification using FTIR. FTIR being a spectroscopy method, has the advantage of being fast and offer real-time monitoring. Biodiesel was produced using methanol as an alkyl acceptor, sodium hydroxide as catalyst and sunflower oil as a triglyceride. Three parameters were used for the optimisation of the biodiesel production, namely: temperature, catalyst ratio and methanol to oil ratio, time and mixing rate were kept constant. CCD from RSM was used as a statistical tool for the optimisation of biodiesel produced the values of R-squared, adjusted R-squared and predicted R-squared obtained from ANOVA were found to be satisfactory. The rate of the reaction was obtained from the iC Kinetics 5.0 with data obtained from iC IR. Using the Arrhenius equation, activation energy and frequency factor were calculated. Based on the results obtained it could be concluded that iC Kinetics is a tool that simplifies the mathematics, therefore, it was recommended that further kinetics

studies be performed on the catalysed biodiesel production produced in a Mettler Toledo reactor using iC Kinetics software.

6.6 References

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CHAPTER SEVEN

7. GENERAL CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusion

The study aimed at developing a model for *in-situ* real-time monitoring transesterification (biodiesel production) of sunflower oil using FTIR produced in a Mettler Toledo Easymax 102 reactor. Very few works reported the investigation of the real-time monitoring of biodiesel and the use of FTIR to quantify the biodiesel produced. There was a characterisation of the biodiesel that was performed using GC this was a long process as it necessitated the need of highly qualified personnel, time-consuming as extensive sample preparation was needed, though biodiesel was also produced from margarine waste the samples' characterisation challenge was posed. There it necessitated the used of FTIR as an alternative which was used, and the probe constituted of a DiCom probe with wave number ranging from 650 to 2500 cm^{-1} .

Biodiesel was firstly produced and optimised using methanol to oil ration and catalyst ratio. Temperature and time were kept constant; the low yield was reported and could be explained by the setup and type of analysis used; the reaction was catalysed using sodium hydroxide. The optimisation was performed using CCD, an analysis of variance was performed and confirmed that methanol to oil ration and catalyst ration are influencing parameters. A quadratic mathematical model was obtained, which could help to determine the yield in the specified range of variables used in the study.

The biodiesel from margarine waste was produced using potassium hydroxide as a catalyst, and the results showed that margarine waste could be used as a feedstock of the biodiesel production, margarine waste can be used as a low-cost feedstock in the biodiesel production. Waste margarine mainly contained sunflower oil as the water has been removed from its emulsion. Four parameters were used; these were mainly; methanol to oil ratio, catalyst ratio, time and temperature. The biodiesel produced was tested if it conforms with the ASTM standard; the properties tested were found to be in the ASTM specifications.

The model was build using EasyMax Mettler Toledo reactor equipped with a DiComp (Diamond) probe. The quantitative monitoring of the biodiesel production was performed using iC Quant module from IC IR Software, 14 samples of known concentrations were used for model calibration, and cross-validation, data were pre-processed using mean centring and

variance scale, spectrum math square root and solvent subtraction. The pre-processing methods improved the performance indexes from 7.98 to 0.0096, 11.2 to 3.41, 6.32 to 2.72 and 0.9416 to 0.9999, RMSEC, RMSECV, RMSEP and R-squared Cumulative, respectively. The R-squared value of 1 (training), 0.9918 (test), 0.9946 (cross-validation) indicated the fitness of the model built. The model thus obtained was tested against univariate and also was used to optimise the process using three key parameters (methanol to oil ratio, catalyst ratio and temperature) by keeping time at 60 minutes and mixing rate at 200RPM. The obtained model was considered suitable for the quantification of Fatty Acid Methyl Ester in biodiesel produced in EasyMax 102 Mettler Toledo reactor and iC Quant module from iC IR 7.0 software. The effectiveness of multivariate variation technique using FTIR technique lies in carefully performing calibration and model validation to be done with quite several samples. Once this is done, there was no need for further validation as this can be used for years as long as the materials remain the same. The FTIR/PLS model was built to predict more advanced reaction yields of transesterification of Sunflower Oil, which is what matters to indicate the time in which the reaction should be stopped.

The model built was used to optimised and developed kinetics of biodiesel produced in an EasyMax Mettler Toledo reactor; sodium hydroxide was used as a catalyst. Temperature, catalyst ratio and methanol to oil ratio were used as optimisation parameters, time and mixing rate were kept constant. The statistical tool used was CCD from RSM, the values of R-squared, adjusted R-squared and predicted R-squared obtained from ANOVA were found to be satisfactory. The rate of the reaction was obtained from the iC Kinetics 5.0 with data obtained from iC IR. Using the Arrhenius equation, activation energy and frequency factor were calculated. Based on the results obtained, it could be concluded that iC Kinetics is a tool that simplifies the mathematics, thereof. The order of the reaction was reported to follow pseudo-first-order.

EasyMax Mettler Toledo equipped with ReactIR FTIR probe does not require sampling for offline FTIR analysis, neither sample preparation for the analysis as opposed to the GC reference method adopted by most of the conventional methods from regulating and monitoring agencies. It can be concluded that it is a promising candidate for becoming a reference technique to be upgraded for industrial scale.

7.2 Recommendations

Based on the results obtained, it was therefore recommended that:

- The model built can be adapted for industrial purposes of the biodiesel production.
- For a more robust model that will lead to a more accurate and give better understanding of the process, mono and diglycerides to be included in the modelling.
- To decrease the operational cost for industrial purposed other types of probe can be investigated and used as the DiCom (diamond) probe is costly.
- iC Kinetics software (a package of Easymax Mettler Toledo Reactor) to be used to performed further kinetics studies using different types of feedstocks and catalysts.