KINETICS AND THERMODYNAMIC STUDIES ON THE PRODUCTION OF BIODIESEL FROM *Balanites aegyptiaca* OIL USING ITS SHELL AS CO-CATALYST

By

HAGGAI, Disho
M.TECH/CHM/16/0714

A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, SCHOOL OF PHYSICAL SCIENCES, MODDIBO ADAMA UNIVERSITY OF TECHNOLOGY, YOLA, IN FULFULMENT OF THE REQUIREMENT FOR THE AWARD OF MASTER OF TECHNOLOGY IN PHYSICAL CHEMISTRY

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April, 2019

DECLARATION

I hereby declare that this thesis was written by me and it is a record of my own research work. This work has not been presented in any previous application for a higher degree. All references have been duly acknowledged.

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Haggai, Disho Date

CERTIFICATION

This thesis entitled "**Kinetics and Thermodynamic Studies on the Production of Biodiesel from B*alanites aegyptiaca* oil using its shell as co-catalyst**" meets the Regulation Governing the Award of Master's Degree in Physical Chemistry of Moddibo Adama University of Technology, Yola and is approved for its Contribution to Knowledge and the Literary Presentation.

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(Head of Department)

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(Dean, School of Postgraduate Studies) Date

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(Internal Examiner) Date

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…….

(External Examiner) Date

DEDICATION

This work is dedicated to my wife Lisami, and my children, Douram, Monopo and Giliki.

ACKOWLEDGEMENTS

I acknowledge God Almighty for providing me life and ability, the knowledge and wisdom for this work. I appreciate Dr. Peter M. Dass who efficiently supervised this work. I appreciate the HOD Dr. I. I. Nkafamiya and the outgoing HOD Dr. O. N. Maitera, for their immense support, and the entire members of staff of the Department of Chemistry for their co-operation and assistance to me in various ways.

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ABSTRACT

Activated carbon from the waste fruit shell of *Balanites aegyptiaca* plant was generated. Oil from the kernel of the fruit was extracted and biodiesel produced. In the course of the biodiesel production, the experimental values of temperature, time of stirring, volumes of reactants and products, concentration of catalyst, ratios of quantities of materials were monitored and recorded. The optimum values of the results obtained were used to determine the values of the kinetic and thermodynamic parameters governing the biodiesel production from the seed oil. The activated carbon was used to catalyze the trans-esterification of the oil and methanol to produce the biodiesel. The biodiesel yield obtained was appreciable, (72.5%). The values of the kinetic and thermodynamic parameters governing the process have been determined. The reaction followed a second order kinetic with rate constant $\boldsymbol{k}$ = **0.017239ml/min** at **303K**. The change in entropy, Δ**S = 62.4JK^{-1}**, heat of reaction, $\Delta\boldsymbol{H}$ **= 29,207Jmol^{-1}** and energy of activation, $\boldsymbol{E_a}$ **= 29,207Jmol^{-1}**. The positive value of the ΔH showed the reaction to be endothermic, taking in heat from the surrounding, and due to the large value of the E_a the reaction could not have occurred without the catalyst. It is recommended that further research be carried out to find out the reaction order for the forward reaction of the trans-esterification and not finalize conclusion on the order of reaction obtained by mirror image of the process.

CHAPTER ONE

INTRODUCTION

Despite the widespread use of fossil petroleum-derived diesel fuels, Engineers and Scientists have been experimenting with vegetable oils as fuel for diesel engine since 1900, and it is only recently that the necessary fuel properties and engine parameters for reliable operation have become apparent (Corsini, A. *et al.,* 2015). In their research they reported some operational problems associated with the use of vegetable oils as fuel for diesel engine. These problems include high viscosity of vegetable oils compared to petroleum diesel fuel, which results in poor atomization of the fuel in the fuel tray and often leads to deposits and coking of the injectors and valves. To lower the viscosity of vegetable oil, chemical and thermal processes were tried to make vegetable oil compatible to compression ignition engines. Attempts to overcome these problems included heating of the vegetable oil, blending it with petroleum-derived diesel fuel or ethanol, pyrolysis, cracking of the oils, micro-emulsification and trans-esterification, where glycerides from vegetable oils react with a lower alcohol to produce fatty acid alkyl esters possessing properties similar to mineral diesel (Ramandhas *et. al.*, 2005). Trans-esterification turned out to be a better solution to the problem. In this research, oil was extracted from *Balanites aegyptiaca* fruit, and the oil was trans-esterified using methanol. The reaction was co-catalysed with carbonized material of the fruit pericarp to produce biodiesel. The thermodynamic and kinetic parameters involved in the process were investigated.

1.1 Background of the study

In 1895, when Dr. Rudolf Diesel invented the Diesel Engine, he used only biofuel in his engine and made a visionary statement which says, “The use of vegetable oils for engine fuel may seem insignificant today, but such oils may become in course of time, as important as petroleum and coal tar products of the present time.” This prediction is becoming a reality today as more and more biodiesel is being used all over the world. (Arumugam *et al.,* 2009). The tilt toward the use of biofuel shall increase as time proceeds. This is because environmental scientists have found that fossil fuels pose environmental concerns. Therefore an alternative fuel that will be environmentally friendly will be gladly welcomed. Even though today fossil fuel may have its place in running our automobiles and industrial machines, shortage of it in the

future has been predicted. The above issues have attracted significant attention to scientific and technological research concerning conversion of biomass into biofuels to replace fossil fuel. An important step toward the realization of this is the trans-esterification of vegetable oils. Trans-esterification is a chemical reaction in which an ester group reacts with an alcohol that has a carbon structure that is not the same as the carbon structure of the original alcohol that formed the ester, such that a new ester group is formed in which the original alcohol carbon structure is exchanged with that of the reacting alcohol. In the case of the trans-esterification of triglycerides (vegetable oils) with methanol (classical biodiesel production process), the three ester groups of a triglyceride molecule, in which three fatty acid components are attached to a carbon back-bone of a trihydric alcohol (i.e. that of glycerol) react with three molecules of methanol to yield three molecules of esters each containing single fatty acid and methanol components and one molecule of glycerol. Therefore, the general chemical name of biodiesel produced by the trans-esterification of vegetable oils is fatty acid methyl esters (i.e. FAME biodiesel).

1.2 Statement of the problem

In recent times, due to the realization that crude oil is limited and poses a threat to well-being of mankind from emissions of exhaust gases, vegetable oil has been revisited for its scope as a fuel in compression ignition engines. But if the use of vegetable oil as fuel for engines is to compete with its consumption as food then the problem is not really solved. Therefore it becomes necessary to seek for feedstocks which are considered as waste and non-edible by man and animals and convert them to forms that will be of advantage technologically. The shell of *Balanites aegyptiaca* fruit is thrown away as waste, and the oil extracted from its nut is not so much edible, especially in Northern Nigeria. It is therefore reasoned that carbonization of the fruit shell of the desert date tree can produce a catalyst to optimize the trans-esterification reaction between oil extracted from the *Balanites aegyptiaca* fruit kernel and methanol for biodiesel production.

Many research works on acid and base-catalyzed trans-esterification of vegetable oils exist, but virtually little or no work is done on its catalysis by activated carbon from waste fruit shells. While the general features of the reaction mechanism of acid and base-catalyzed trans-esterification are well known, not many studies have been

directed towards a better understanding of the principles and parameters governing the kinetics and thermodynamics of the trans-esterification of vegetable oils, which is instrumental in improving the commercial performance of the process. An accurate analysis of kinetic and thermodynamic data on the trans-esterification process can be very helpful for process optimization; however, the thermodynamic and kinetic details and models describing the kinetics of specific processes can be drastically dependent on some other reaction parameters, such as the nature of the solvent, catalyst, and substrate (Arumugam *et al*., 2009) as well as temperature.

1.3 Significance of the study

This research is significant in the following ways:

(i) As the oil from the nut of *Balanites aegyptiaca* tree is not consumed as food in Northern Nigeria, and its fruit shell is usually discarded as waste, the production of biodiesel from it as feedstock does not interfere with the local food economy.

(ii) The continuing growth in demand of biodiesel globally has been a challenge for scientists to develop innovative and more efficient processes for producing biodiesel from vegetable oils.

(iii) From the kinetic and thermodynamic studies made on the reaction for the biodiesel production, the rate law and the values of the rate coefficient (k), order of reaction (n), activation energy (E_a), Arrhenius constant (A), Gibbs free energy (ΔG), enthalpy of activation (ΔH) and entropy of activation (ΔS) that were determined, will serve as reaction properties and conditions necessary for the possible optimization of the biodiesel production on an industrial scale.

1.4 Aim and objectives

This research aimed at determining the Kinetic and Thermodynamic properties of the trans-esterification of desert date (*Balanites aegyptiaca)* oil and methanol for biodiesel production, using activated carbon from the shell of the fruit of the *Balanites aegyptiaca* as heterogeneous co-catalyst for the reaction.

The research was based on the following objectives:

- Production of activated carbon from the shell of desert date nut, and use of it as heterogeneous catalyst for trans-esterification;
- Proximate analysis for the catalyst prepared in terms of percentage yield, moisture content and pH;
- Experimental determination of the separate effects of the activated carbon produced, as a catalyst alone and as a co-catalyst, in the trans-esterification to generate biodiesel from *Balanites aegyptiaca* oil;
- Investigation of the effects of temperature, time of stirring, catalyst concentration and molar ratio of reactants on the yield of biodiesel;
- Proffering the optimum conditions for maximum biodiesel yield from *Balanites aegyptiaca* oil.

1.5 Scope and limitation of the research

The scope of this work was dedicated to laboratory trans-esterification reaction for biodiesel production from *Balanites aegyptiaca* oil using heterogeneous catalysts and the analysis of the accompanying kinetic and thermodynamic parameters.

CHAPTER TWO

LITERATURE REVIEW

2.0 General background

2.1 *Fatty acid alkyl esters as biodiesel*

With exception of hydroelectricity and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted in the near future (Arzamendi *et al.*, 2008). Thus, looking for alternative sources of energy is of vital importance.

Vegetable oils are a renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel (Zaher, 2009). Historically, it is believed that Rudolf Diesel himself started research with respect to the use of vegetable oils as fuel for diesel engines. In the decades that followed, the studies became more systematic and, nowadays, much is known about its use as fuel. Despite energetically favorable, the direct use of vegetable oils in fuel engines is problematic. Due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely. They form deposits in the fuel injector of diesel engines. Furthermore, acrolein (a highly toxic substance) is formed through thermal decomposition of glycerol (Schwab *et al.,* 2007). Different ways have been considered to reduce the high viscosity of vegetable oils:

- dilution of 25 parts of vegetable oil with 75 parts of diesel fuel (Schwab *et al.,* 2007);
- microemulsions with short chain alcohols (*e.g*. ethanol or methanol) (Schwab *et al.,* 2007);
- thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds (Schwab *et. al.,* 2009);
- catalytic cracking, which produces alkanes, cycloalkanes and alkylbenzenes (Rocha *et al.,* 2009), and
- trans-esterification with ethanol or methanol (Freedman *et al.,* 2007).

Among all these alternatives, the trans-esterification seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel (Schwab *et. al.,* 2007) and the process is relatively simple.

The predicted shortage of fossil fuels and related environmental concerns have been the reason drawing significant attention to scientific and technological issues concerning the conversion of biomass into fuels.

The production of biodiesel has been strongly developed in some countries as a substitute for addition in conventional diesel fuel. At levels of 1 – 2% of it has the beneficial effect of restoring lubricity lost due to the restricted sulfur content. The drawbacks that biodiesel emits more NO_X than conventional fuel and is competing with food production for land use have been the last point that supports the recent development of second and third generation biofuels. Biodiesel consists of alkyl esters of fatty acids produced by trans-esterification of vegetable oil by methanol or ethanol. Vegetable oils are triglycerides obtained from plants (Portha *et al*., 2012).

2.2 Desert date (*Balanites aegyptiaca)*

Balanites aegyptiaca is a species of tree, classified either as a member of the Zygophyllaceae or the Balanitaceae. It is spiny shrub or tree up to l0 m tall, native to and widely distributed in dry land areas of much of Africa, South Asia and parts of the Middle East. It is commonly known as 'desert date.' Other names are soapberry tree (Dalziel); thorn tree (Dalziel); Egyptian myrobalan (the unripe fruit, Dalziel); Zachun oil (the seed kernel oil, Dalziel). It is traditionally used in treatment of various ailments i.e. jaundice, intestinal worm infection, wounds, malaria, syphilis, epilepsy, dysentery, and constipation. It is mostly found in most arid, semiarid to sub-humid tropical savannahs, and hot dry areas, along watercourses and in woodlands. It borders seasonally inundated black clay plains and grows well in valleys and on river banks in depressions, and on the slopes of rocky hills. It has edible leaves, fruit and nut when young. Its leaves are used as animal fodder. Its oil rich seed is useful for cooking and industrial purposes. Its oil is traditionally used in Egypt for perfumes. Soap is made from the ashes of its bark and roots. Its wood is used to make handles for tools.

2.2.1 Oil from Balanites aegyptiaca

Balanites kernels contain a high percentage of oil, sometimes known as zachun oil or betu oil, which is highly familiar and prized in most part of Africa. Its culinary quality

is comparable to that of good-quality vegetable oil. The seed kernel oil is reported to be rich in saturated fatty acids and is used as cooking oil in some parts of African countries (NRC, 2006). It also contains steroids (saponins, sapogenins, diosgenins) as raw material for industrial production of contraceptive pills, corticoids, anabolisants and other sexual hormones (UNIDO, 2000). Reports on studies of *B. aegyptiaca* kernel oil (Mohammed *et al.*, 2012) indicate that the kernel oil consists of four major fatty acids; linolein, olein, stearic and palmitic acids but in varying proportions across study sites. Some studies, for example, (Deshmuhk and Bhuyar, 2009 and Chapagain *et al.*, 2008) have demonstrated and recommended the use of *Balanites* oil for biodiesel production. There is therefore a growing interest in understanding the development potential of *B. aegyptiaca* as a resource for improving livelihood of dry land communities.

Seer *et al*. (2016) studied the potentials of *B. aegyptiaca* seed oil for production of biodiesel, the results obtained from the preliminary investigation carried out showed that the seed oil was an economically viable oil source because its oil content was found to be high. Also, the oil parameters showed that the oil was composed of moderately long chain fatty acids with a degree of unsaturation, making it a good feedstock for biodiesel production. It was observed from the results that the seed had low moisture content, which was an indication that the shelf life of the seed oil is high, because there is little or no water for hydrolysis to take place. The average oil content obtained from the desert date seed of 0.6mm was found to be higher than that of 1.8mm; meaning that the smaller the particle size the higher the yield of oil obtainable from that seed.

2.3 Use of vegetable oil for production of biodiesel

Apart from the significant role of sound practices in feedstock exploitation and cultivation in meeting global environmental goals and in stabilizing the socio-economic balance of the biodiesel industry, the further development of the biodiesel industry also lies in scientific and technological innovation (Meher *et al*., 2006 and Vasudevan *et al*., 2008). In this regard, there is a significant interest in improving the existing biodiesel production methods from both economic and environmental viewpoints, as well as in alternative and innovative production processes. The direct

use of straight vegetable oils (SVOs) as fuels in diesel engines were investigated well before the energy crisis of the 1970s (Knothe *et al.*, 2005). However, the high viscosity of straight vegetable oils (Demirbas, 2003 and Srivastava, 2000) causes a range of problems and leads to poor fuel characteristics. Among possible solutions, such as engine modifications, blending straight vegetable oils with fossil diesel, micro-emulsification, trans-esterification, or thermal cracking, the trans-esterification of oils to the corresponding fatty acid methyl esters (FAMEs) has seen wider application owing to its easy, cost-effective technology as well as because of the favorable physicochemical parameters of the fuel (Meher *et. al.*, 2006).

Another promising approach to convert vegetable oils and fats into quality fuel is hydro-treating/cracking technology, which produces the diesel fuel with a chemical composition similar to that of conventional diesel (hydrocarbons). Both types of biodiesel can replace petroleum diesel without the need for modification or adjustment of engines. In addition to reducing CO_2 emissions, biodiesel offers significant environmental benefits such as the lack of SOx emissions as a result of the virtual absence of sulfur in the feedstock. In the case of FAME biodiesel, the higher oxygen content with respect to petroleum diesel ensures more complete combustion and a lower content of CO, hydrocarbons, and particulate in emissions. In addition, FAME biodiesel is non-toxic and biodegradable, though its biodegradability results in lower stability of the fuel. Sometimes, its oxidation should be prevented by adding additives, which is particularly the case of biodiesel obtained from vegetable oils which have been previously subjected to extraction procedures to recover high-value components, such as vitamins, which have antioxidant properties (Dunn, 2006 and Knothe, 2007). The continuing growth in demand of biodiesel following several legislations in a number of countries that have mandated biodiesel blends in transportation fuels has been a challenge for scientists to develop innovative and more efficient processes for producing biodiesel from vegetable oils. In this context, the development of new catalytic systems for the trans-esterification and hydrocracking of oils remains a challenging research frontier.

2.4 Kinetics and thermodynamics of triglyceride trans-esterification

The trans-esterification of vegetable oil is a complex process; the reaction rate and equilibrium yields are affected by numerous chemical and physical factors. Vegetable oil is composed from over 100 substances, and different oils have different compositions that can vary even for the same oil. In addition, the most common industrial trans-esterification of triglycerides with methanol is normally a heterogeneous process, which involves at least two immiscible liquid phases (oil and methanol phases) or even one solid phase if a solid catalyst is used. Mass-transfer processes over liquid–liquid and liquid–solid interfaces often complicate the understanding of the true reactivity by kinetic analysis. In fact, several authors indicated that the trans-esterification of vegetable oil with methanol represents a two-phase system in the first few minutes of the reaction then becomes a single phase as a sufficient amount of methyl esters is accumulated which act as a mutual solvent (Noureddini *et al*., 2003); however, it was also noted that after some glycerol is formed, the phase-separation phenomenon takes place again (Mittelbach *et al*., 2004). Side reactions, such as hydrolysis, also often take place. All these phenomena make the equilibrium and rate constants as well as the general kinetic behavior very dependent on the particular system (Arumugam *et al*., 2009).

Generally, for either an acid- or base-catalyzed mechanism, the trans-esterification of a triglyceride is a reversible process, where the overall process is composed of a sequence of three equilibrium steps involving the formation of intermediate di- and mono-glycerides, and finally of a glycerol molecule. Most studies show that the equilibrium constant (K3) for the third step of the conversion of the mono-glyceride into the corresponding ester is one to two orders of magnitude higher than those of the preceding steps. In most cases, second-order kinetics has been observed at 6:1 methanol/oil molar ratio (double excess of alcohol per reacting ester group in the triglyceride). Depending on the systems, second-order (Noureddini *et. al*., 2004), pseudo-second-order (Darnoko *et. al*., 2000 and Leevijit *et al*., 2004) or, at higher excess of MeOH, pseudo-first-order kinetic models have been successfully applied for data fitting. Several mechanistic models have been proposed, all of which resulted in quite suitable fitting of the experimental data by the respective mathematical models; namely, a simple sequence of reversible trans-esterification steps, consecutive steps

with contribution of the shunt mechanism (simultaneous reaction of all three ester groups in the triglyceride) (Noureddini, 2004) and competitive hydrolysis–trans-esterification (Komers *et al.*, 2002). In most cases, the authors claim that the observed reaction rates and calculated constants are indeed reflecting the chemical processes and not mass-transfer processes. For example, activation energies in the range of 5–20 $kcalmol^{-1}$ have been observed for separate trans-esterification steps (Darnoko *et al.*, 2000). In some studies, induction periods have been observed on the kinetic curves which were attributed to the mass-transfer limitations in the initial reaction phase (Darnoko *et al*., 2000). In particular, mixing has been outlined as critical for the reaction to proceed in the kinetic regime from the beginning. At optimal mixing intensity (600 rpm), the lag, which was observed on kinetic curves at lower stirring rates, disappeared. The authors indicated that the mass-transfer contribution to the kinetic behavior is felt at the beginning of reaction because of the phase-transfer limitations. As the methyl ester is accumulated, it acts as a mutual solvent and ultimately a single-phase system is formed which is favorable for a kinetically controlled process.

An accurate analysis of kinetic data on the trans-esterification process can be very helpful for process optimization; however, the kinetic details and models describing the kinetics of specific processes can be drastically dependent on some other reaction parameters, such as the nature of the solvent, catalyst, and substrate (Arumugam *et al*., 2009).

2.5 Feedstocks

Any vegetable oil or animal fat can be used to prepare biodiesel; however, a careful choice of feedstock should be made. Currently, biodiesel is mostly produced from edible and non-edible vegetable oils obtained from rapeseed (Gryglewicz *et al*., 1999, Leclercq *et al*., 2001 and Yuan *et al*., 2008), soybean [Abreu *et al*., (2003), Furuta *et al*., (2006), Guerreiro *et al*., (2006), 47–57], oil palm, coconut, sunflower and *Jatropha curcas*. The use of oils from andiroba, babassu, camelina, cumaru, cynara cardunculus, groundnut, karanja, algae, poppy seed, rice bran, rubber seed, sesame, tobacco seed, palm kernel, fish, and others for the preparation of biodiesel has been reported also.

The source of feedstock for the production of biodiesel should fulfil two requirements: price (low feedstock and production costs; more than 80% of the production cost corresponds to the feedstock cost) and local availability (large and constant production volume). It is also necessary to take into consideration the oil content of the seeds and the yield of oil per hectare. Detailed data regarding the oil-yielding capacity of different plants has been reported, from which it emerges that oil palm, under commercial planting conditions, can give an excellent oil yield per hectare of about 4000 kg. Trans-esterification technology for "used" cooking oils and animal fats is more complex as compared to fresh vegetable oils. The free fatty acids (FFAs) contained in waste oils can react with the commonly used alkaline catalysts resulting in deactivation of the catalyst and in unfavorable saponification phenomenon. The high FFA content and other low quality of vegetable oils are usually the result of their exposure to heating, moisture, and oxygen. The latter causes hydrolysis and cracking of oils to FFAs, as well as their oxidation and biodegradation. As a rule, used cooking oils, oils produced in summer, and oils stored for a long time exhibit a higher FFA content. For example, the FFA content of used oil from food processing is reported to be in the range of 5 to 30%. Generally, conventional trans-esterification technology requires that the reagents be free of moisture and the FFA content does not exceed 0.1–0.5 wt%. The use of oils with a high amount of FFAs significantly decreases the biodiesel yield owing to FFAs reacting with the alkaline catalysts forming soaps and water, both of which must be removed during the subsequent ester purification step. Notably, the presence of soap and water also reduces the efficiency of the catalyst and renders product separation difficult. Vegetable oils with a high FFA content should be refined; otherwise they require a combined acid-catalyzed esterification–base-catalyzed trans-esterification process. In this case, use is made of FFAs as both reactions result in the formation of FAME biodiesel.

It is important to point out that the properties of biodiesel are strongly influenced by the nature of the fatty acid chains in the triglyceride, such as their length, degree of unsaturation, and presence of other chemical functional groups, which also strongly depends on the source of the feedstock. In general, the cetane number, cloud point, heat of combustion, melting point, and viscosity of the biodiesel increase with

increasing chain length of the component fatty acid and decrease with increasing unsaturation. In addition, esters with unsaturated fatty acid chains are less stable as a result of relatively fast oxidation. The melting point of vegetable oils is a key property, as the trans-esterification process is carried in the liquid phase and oils with a high melting point may require heating to higher temperatures, which ultimately increases the energy requirements and production costs. Furthermore, the trans-esterification process does not alter the fatty acid chain composition and therefore the biodiesel made from feedstocks containing higher concentrations of high-melting-point saturated long- chain fatty acid chains tends to have relatively poor cold flow properties. The presence of impurities and calorific value content of the feedstock also affects the quality of the biodiesel.

2.6 Alcohols for production of biofuel

Methanol is commonly used in industrial biodiesel production as a result of its relatively low cost and easy availability. Ethanol is not commonly used owing to a high cost related to the removal of the final 4% water. As the non-catalytic trans-esterification is too slow and energetically unfavorable, acid or base catalysts are used. Various catalysts can be used, such as alkaline hydroxides and methoxides, inorganic acids and their salts, transition-metal compounds, silicates, and lipases. The classical reaction protocol for the trans-esterification of triglycerides with methanol using homogeneous catalysts such as sodium methoxide requires mixing and stirring the reagents in a batch reactor. The excess of methanol recovered from the glycerol phase is usually reused, and the byproduct glycerol can also be valorized to improve the economics of the process.

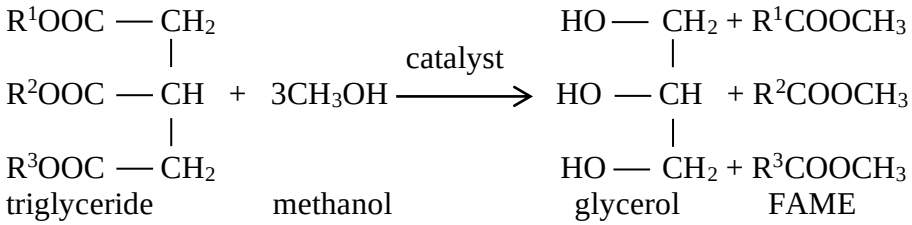
2.7 Trans-esterification of vegetable oils

Biodiesel as an alternative fuel for diesel engines is produced chemically by reacting a vegetable oil or animal fat with an alcohol such as methanol or ethanol through a process known as trans-esterification. In words, the reaction is:

Oil + alcohol → biodiesel + glycerin

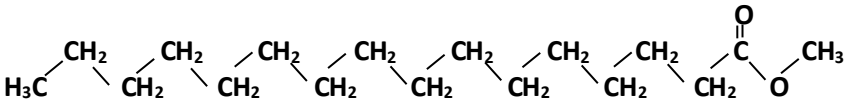
In the trans-esterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol (Wright *et al*., 2001) (Scheme 1). An ester group reacts with an alcohol that

has a structure different from that of the original alcohol moiety of the ester, such that a new ester group is formed in which the original alcohol moiety is exchanged with that of the reacting alcohol. In the case of the trans-esterification of triglycerides of fatty acids (vegetable oils) with methanol (classical biodiesel production process), the three ester groups of a triglyceride molecule in which three fatty acid moieties are attached to a single alcohol moiety (i.e. that of glycerol) react with three molecules of methanol to yield three molecules of esters each containing single fatty acid and methanol moieties and one molecule of glycerol. Trans-esterification is called alcoholysis. It is represented by the general equation: (Scheme 1).



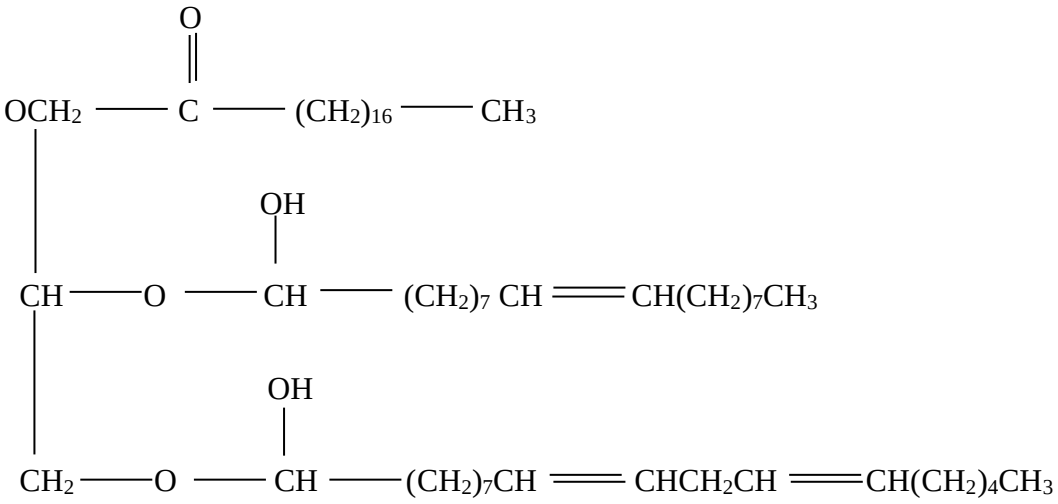
Scheme 1. Trans-esterification reaction of triglyceride with methanol

The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol. of a triglyceride and 3 mol. of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. The process of trans-esterification is employed in organic chemistry to convert one ester into another, in the presence of a strong base (NaOH or KOH). Chemically, the biodiesel produced can be a methyl or ethyl ester depending upon the type of alcohol used in trans-esterification process. One such molecule of bio-diesel comes from green energy source – algae (Levine, *et al*., 2010). Actually, the substance extracted from the algae is a glyceride which is trans-esterified into the biodiesel. This bio-diesel molecule produced in the reaction is used to produce energy through combustion in machines. Given the bond energies and chemical structure of the biodiesel, one can calculate the amount of energy released on the complete combustion of one molecule of biodiesel (methyl ester).



Scheme 2. Structure of Biodiesel molecule

Animal and plant fats and oils are composed of triglycerides, which are esters formed by the reactions of three free fatty and the trihydric alcohol, glycerol. The alcohol reacts with the fatty acids to form the mono-alkyl ester (biodiesel) and crude glycerol. The reaction between the biolipid (fat or oil) and the alcohol is a reversible reaction so excess alcohol must be added to ensure complete conversion.



Scheme 3. Structure of a triglyceride molecule (Gao, *et. al.*, 2009)

The reaction of oils of vegetables or fats with alcohols for biodiesel production should be with short-chain low molecular weight alcohols (typically methanol or ethanol). These alcohols are the most used because of their low cost. However, greater conversions into biodiesel can be reached using methanol. Although the trans-esterification reaction can be catalyzed by either acids or bases the most common means of production is base-catalyzed trans-esterification. This path has lower reaction times and catalyst cost than those posed by acid catalysis. The alkaline catalysis has the disadvantage of its high sensitivity to both water and free fatty acids present in the oils. The presence of water during base-catalyzed trans-esterification causes the triglycerides to hydrolyze, which is undesirable as it gives salts of the fatty acids (soaps) instead of producing biodiesel. So the reaction must be kept dry. Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal

alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. This undesirable saponification reaction reduces the ester yields and considerably makes the recovery of the glycerol difficult due to the formation of emulsions (Freedman *et. al.*, 2007).

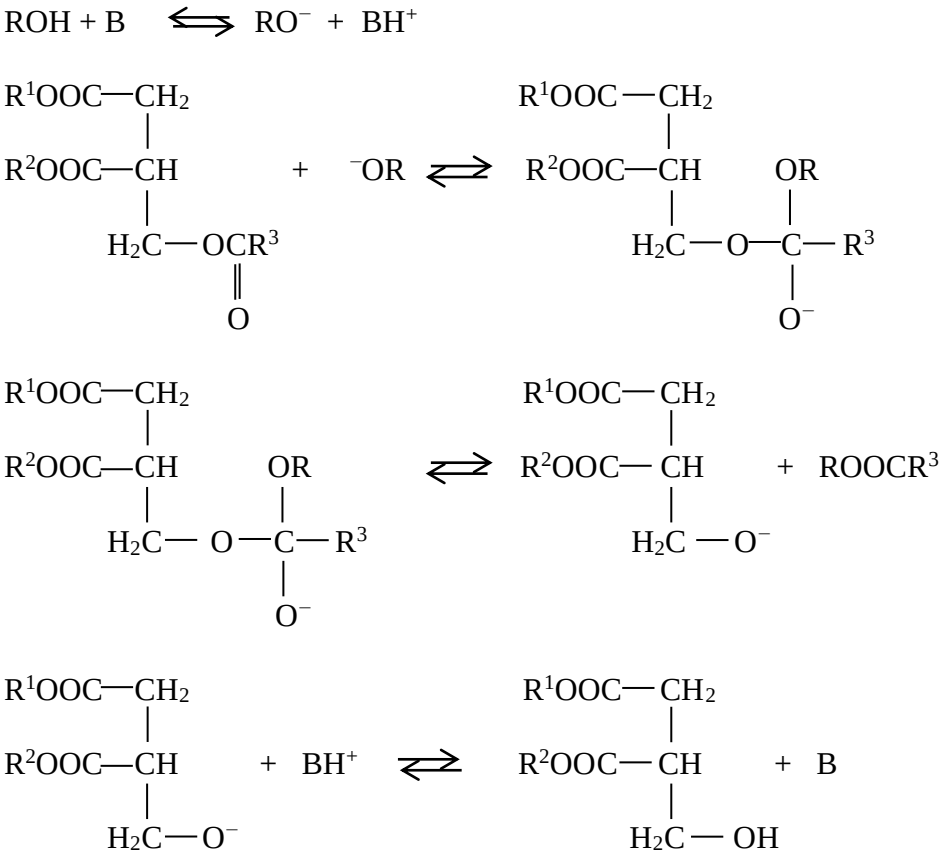
$$R'OOR + H_2O \rightleftharpoons R'OOH + ROH$$

$$R'OOH + NaOH \rightleftharpoons R'OONa + H_2O$$

R' = carbon chain of the fatty acid; R = alkyl group of the alcohol

2.8 Mechanism of based-catalyzed trans-esterification

In the trans-esterification process, the added alcohol is deprotonated with a base to make it a stronger nucleophile. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol. Under normal conditions, this reaction will proceed either exceedingly slowly or not at all, so heat, as well as catalysts (acid and/or base) are used to speed the reaction. It is important to note that the acid or base are not consumed by the trans-esterification reaction, thus they are not reactants, but catalysts. Common catalysts for trans-esterification include sodium hydroxide, potassium hydroxide, and sodium methoxide. In the base-catalyzed trans-esterification mechanism, the first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst (Scheme 4). Next the carbonyl carbon of the starting ester ($-CH_2COOR^3$) undergoes nucleophilic attack by the incoming alkoxide (RO^-) to give a tetrahedral intermediate, which either reverts to the starting material, or proceeds to the trans-esterified product (the alkyl ester, $RCOOR^3$) and the corresponding anion of the diglyceride. The latter deprotonates the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. The various species exist in equilibrium, and the product distribution depends on the relative energies of the reactant and product.



Scheme 4. General reaction mechanism of trans-esterification of triglycerides with base catalysts.

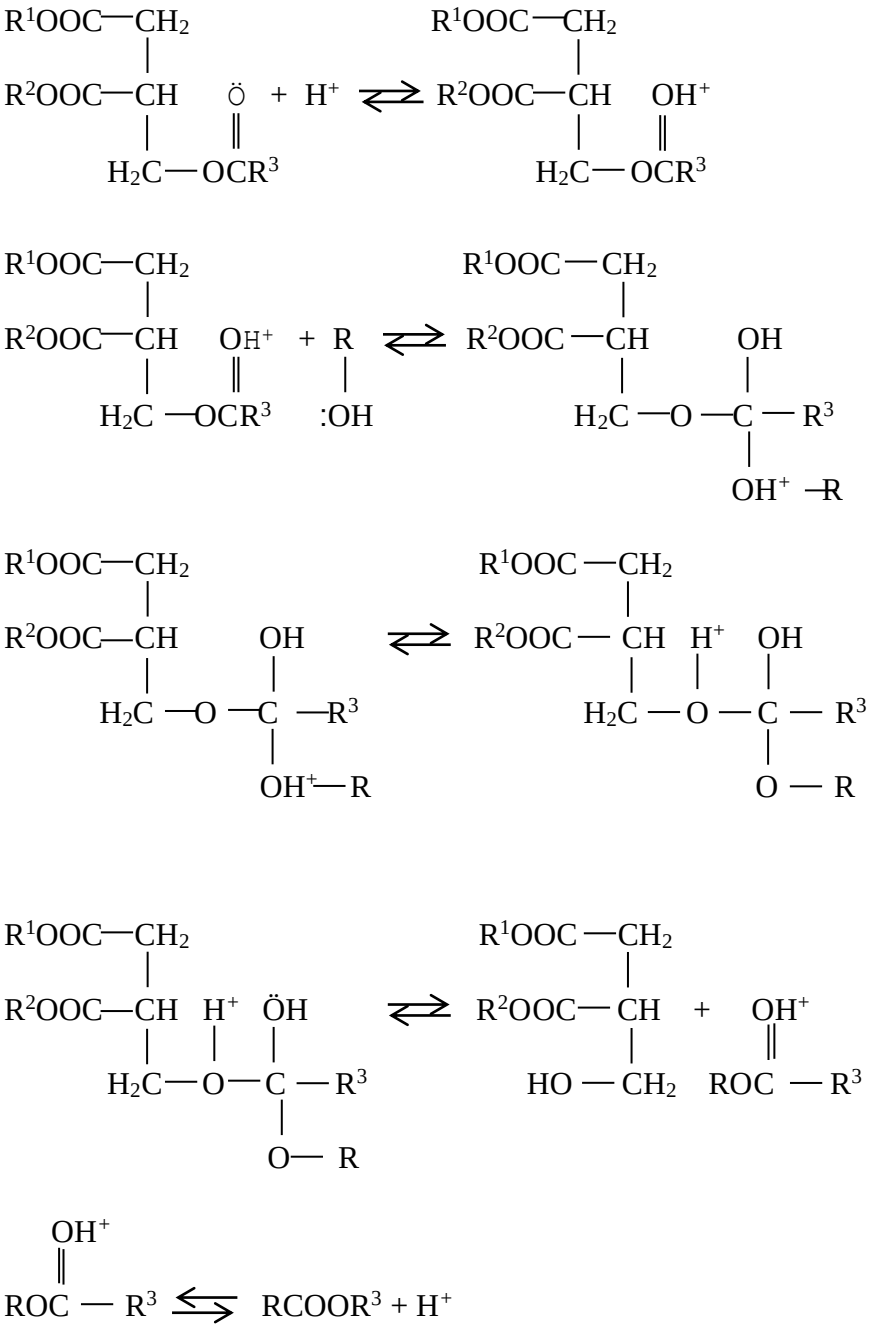
2.9 Mechanism of acid-catalyzed trans-esterification

The trans-esterification process is reported to be catalyzed by BrØnsted acids, preferably by sulfonic (Stern *et. al.* 2012) and sulfuric acids (Jacobson *et. al.* 2008). These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 h to reach complete conversion (Sivasamy *et. al.,* 2009). Freedman *et. al.* (2009) showed that the methanolysis of soybean oil, in the presence of 1 mol% of H_2SO_4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and ethanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively.

The mechanism of the acid-catalyzed trans-esterification of vegetable oils is shown in Scheme 4 (Sivasamy *et al.,* 2009). The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV,

and to regenerate the catalyst H^+. According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed trans-esterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters. (Schuchardt *et al.*, 2001).

In the acid-catalyzed mechanism of the reaction, the $ROOR^3$ is protonated.



Scheme 5. General reaction mechanism of trans-esterification of triglycerides with acid catalysts.

Generally, for either an acid- or base-catalyzed mechanism, the trans-esterification of a triglyceride is a reversible process, where the overall process is composed of a sequence of three equilibrium steps involving the formation of intermediate di- and monoglycerides, and finally of a glycerol molecule. (Sivasamy *et. al.*, 2009).

Almost all biodiesel is produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids). The base-catalyzed technique is the predominant method for commercial-scale production.

Trans-esterification of vegetable oil is a suitable approach to completely fulfilling the kinematics viscosity specifications for renewable diesel. This is because the high value of the viscosity of the pure vegetable oil observed give rise to a number of technological and operational issues. To address these issues, trans-esterification of the oils was carried out; this is a very important step, since it strongly affects the kinematics viscosity (Babagana *et al.*, 2012).

As the non-catalytic trans-esterification is too slow and energetically unfavorable, acid or base catalysts are used. Various catalysts can be used, such as alkaline hydroxides and methoxides, inorganic acids and their salts, transition-metal compounds, silicates, and lipases. The classical reaction protocol for the trans-esterification of triglycerides with methanol using homogeneous catalysts such as sodium methoxide requires mixing and stirring the reagents in a batch reactor. The excess of methanol recovered from the glycerol phase is usually reused, and the byproduct glycerol can also be valorized to improve the economics of the process.

2.10 Choice of catalyst for trans-esterification

The selection of an appropriate catalyst is of fundamental importance for the design of a sustainable trans-esterification process. Homogeneous, heterogeneous, and enzymatic (Watanabe *et al.*, 2000 and Fukuda *et al.*, 2001) catalysts have been investigated. Currently, homogeneous alkaline catalysts, such as sodium hydroxide and potassium hydroxide, are most commonly used in industrial trans-esterification processes for biodiesel production, mainly because they are able to efficiently

promote the reaction at relatively low temperatures. Homogeneous acid catalysts and heterogeneous (solid) catalysts are used to a lesser extent.

While the main advantages in the use of homogeneous acid and base catalysts are their cost-effectiveness and good performance, both catalysts require the use of an excess of alcohol, can provoke various problems, and are associated to technical difficulties. The use of homogeneous catalysts is normally limited to batch-mode processing followed by a catalyst separation step. The immiscible glycerol phase, which accumulates during the course of the reaction, solubilizes the homogeneous base catalyst and, therefore, withdraws it from the reaction medium. Moreover, other difficulties of using homogeneous base catalysts relate to their sensitivity to FFAs and water and the resulting saponification phenomenon. Usually, base catalysts are better suited to the trans-esterification of triglycerides, whereas acid catalysts are better suited for the esterification of FFAs. Therefore, feedstocks containing FFAs may require two different types of catalysts (acid and base catalysts) that are usually employed in a two-stage process, which means that the acid catalyst from the first stage has to be removed before the base catalyst is added in the second stage. A disadvantage of homogeneous acid catalysts is also their increased corrosiveness. Alternatively, the esterification and trans-esterification can be combined in a consecutive continuous process, which would require the combination of acid and base heterogeneous catalysts. Solid bifunctional catalysts that are able to effectively catalyze both processes simultaneously (one pot or in continuous mode) have been reported. Another cost-effective solution for the conversion of feedstocks with high FFA content into FAMEs lies in the consecutive hydrolysis–esterification process (hydro-esterification). In the first step, the triglyceride content of the oil is stoichiometrically hydrolyzed into the corresponding FFAs
using a well-known industrial steam hydrolysis process. The FFAs formed then undergo selective esterification over an acid catalyst.

Heterogeneous catalysts have the general advantage of being reusable and easy to separate from the reaction products (generally cleaner process). In addition and more specifically, they do not form soaps, are more selective to biodiesel (purer product), and simplify the glycerol purification (99% purity glycerol can be produced against 75% in the homogeneous process). They are in general much more tolerant to water and FFAs in the feedstock. Nevertheless, heterogeneous catalysts for biodiesel

production generally require more severe working conditions than those for homogeneous catalysts, in particular, higher temperatures and pressures. Those on solid supports tend to be less active than the active species in solution. Finally, there is always the possibility of leaching, which might contaminate the biodiesel and reduce the lifetime of the catalyst. The growing attention to develop biodiesel production processes based on an enzymatic approach is justified by the use of more moderate reaction conditions, a lower alcohol-to-oil ratio, easier product recovery, and higher environmental compatibility than chemical catalysts (homogeneous or heterogeneous). Furthermore, FFAs present in oils/fats can be completely converted into alkyl esters using enzyme catalysts. Notably, new immobilization technology indicates that enzyme catalysts can become cost-effective as compared to chemical processing. However, the production cost of lipases, which is the most investigated and promising class of enzyme catalysts for trans-esterification, is still significantly higher than that of alkaline catalysts. Enzyme-based technology is still at a stage of intensive research and process optimization.

2.11 Homogeneous base catalysts

The trans-esterification of triglycerides with low-molecular weight alcohols catalyzed by homogeneous alkali catalysts is the most common process in the biodiesel industry because of the low cost of the catalyst and the good conversions that can be achieved in short reaction times and at moderate temperatures. Catalysts such as alkaline metal hydroxides, alkoxides, and carbonates are most often used. Commercially, NaOH and KOH are preferred because of their availability and low cost. The alkoxides are more expensive than the hydroxides and are more difficult to handle because they are hygroscopic. However, as the hydroxide ion is present only as an impurity in alkoxides, (Meher *et al.*, 2006) they do not produce soap through triglyceride saponification. However, the general limitation for the use of homogeneous alkaline catalysts is the total FFA content associated with the feedstock, which must not exceed 0.5 wt%; otherwise, soap formation seriously hinders the production of fuel-grade biodiesel (Meher *et al*., 2006).

Ma *et al*. (2016) investigated the effect of alkaline catalysts on the trans-esterification of beef tallow. NaOH was found to perform significantly better than NaOMe. Furthermore, a slightly

higher concentration of NaOMe with respect to NaOH (0.5 vs. 0.3% w/w) was needed to obtain the maximum conversion of the oil into the corresponding esters. Singh *et al*., (2006) studied the reaction of methanol with canola oil at different concentrations of alkaline catalyst (NaOH, KOH, NaOMe, and KOMe), reaction temperatures, and methanol-to-oil molar ratios. A preliminary analysis of the variance performed on the four process variables and their possible two-way interactions showed that only the catalyst formulation–concentration and catalyst formulation–reaction temperature had significant contributions among the two-way interactions. The results showed that there were significant differences in the product yields among the four catalyst formulations. Potassium-based catalysts gave better yields than the sodium-based catalysts, and methoxide catalysts gave higher yields than the corresponding hydroxide catalysts. On the other hand, potassium-based catalysts resulted in a larger extent of soap formation than the corresponding sodium-based catalysts. Notably, the cost of potassium and sodium methoxides is five to six times higher than potassium and sodium hydroxides. An increase in reaction temperature had a positive effect on both trans-esterification and saponification reactions. Increasing the MeOH/oil molar ratio had a positive effect on the reaction yields as it helped to drive the reaction equilibrium forward. The molar ratio of methanol to oil, however, had an unpredicted effect on the saponification. The amount of soap formed decreased with an increase in the molar ratio from 3:1 to 4.5:1 but increased when the molar ratio increased from 4.5:1 to 6:1. On the other hand, as the catalyst concentration in the methanol phase was relatively high at lower MeOH/oil ratios, higher reaction rates were observed. Potassium and sodium hydroxides and methoxides were also investigated as catalysts by Vicente *et al*. (2004) in the trans-esterification of sunflower oil using a methanol-to-oil molar ratio of 6:1 and 1% catalyst. The yields of esters were reported to be higher than 98% for the methoxide catalysts, and 85.9 and 91.67 wt% for the sodium and potassium hydroxides, respectively, because the saponification resulted in more substantial decreases in yield.

Leadbeater *et al*. (2006) showed that the use of microwave heating allows an efficient and easy preparation of biodiesel with the advantage of a short reaction time. The process can be effectively adapted for both batch and continuous-flow preparation of biodiesel and in the presence of either homogeneous acid or base catalysts. Azcan *et al*. (2008) studied the effect of microwave heating on the trans-esterification of

cottonseed oil using NaOH and KOH as catalysts. The results indicated that microwave heating effectively reduced the reaction time from 30 min (for a conventional heating system) to 7 min.

Tang *et al*. (2008) studied the catalytic activity of triethylamine, diethylamine, ethylenediamine, and monoethanolamine in the trans-esterification reaction of rapeseed oil in supercritical methanol. The catalytic activity decreased in the order: diethylamine> triethylamine>monoethanolamine>ethylenediamine. With triethylamine as catalyst, it was observed that an increase in pressure has a positive effect on the trans-esterification reaction. Furthermore, the use of an appropriate co-solvent, such as ethyl acetate, can improve yields.

Arzamendi *et al*. (2008) investigated the catalytic activity and selectivity of hydroxides of Li, Na, K, Rb, Cs, and Ca in the trans-esterification of refined sunflower oil with methanol at 50^{o}C. The activity was compared to that of a heterogeneous system, such as carbonates of Na, K, Ca, and Mg, bicarbonates of N and K, and oxides of Ca and Mg. Notably, the catalytic experiments were conducted using a large excess of methanol (methanol/oil molar ratio of 12:1). The alkaline metals hydroxides were the most active catalysts, although potassium and sodium carbonates showed appreciable performances also. In the case of K_2CO_3, its significant solubility in methanol suggests that the contribution of homogeneous reaction routes can be important.

Schuchardt *et al*. (2001) investigated the trans-esterification of rapeseed oil with methanol using substituted cyclic and acyclic guanidines and compared the results with the unsubstituted guanidine. The catalytic activity of the guanidines depended mainly on their intrinsic base strength. No lipophilic effect was observed with a long alkyl chain on the guanidine. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene showed the best performance. In fact, when used at 1 mol %, the methyl esters were obtained in 90% yield after 1 h of reaction. Schuchardt and co-workers also investigated many other non-ionic bases, especially with the goal to make them heterogeneous. Very recently, Cerro *et al*. (2008) reported the promising performances of non-ionic triamino(imino)-phosphoranes (phosphazenes) as base catalysts for the water-free alcoholysis of vegetable fatty esters. The use of two catalysts, with different intrinsic

basicity, allowed the direct correlation of the activity to the basicity of the catalyst. Very high yields (93–95% mol) of biodiesel were achieved under rather mild reaction conditions. Furthermore, the study indicated that the catalyst could be recovered and recycled.

2.12 Homogeneous Acid Catalysts

Homogenous acid catalysts are significantly more effective than base catalysts in the esterification of FFAs but are not as effective as the base catalysts in the trans-esterification of triglycerides. Acid-catalyzed trans-esterification proceeds approximately 4000 times slower than that catalyzed by the same amount of an alkali catalyst (Srivastava *et al*., 2000) and also needs harsher temperature and pressure conditions. However, the advantages of acid catalysts include their low sensitivity to moisture and absence of soap formation. Acid catalysts can be used in the trans-esterification of feedstocks containing a high content of FFAs, such as waste cooking oils, where the use of base catalysts is undesirable because of the formation of soap. Acid catalysts can be used also in a two-stage process, in which the first stage involves the esterification of FFAs into biodiesel in the presence of the acid catalyst followed by base-catalyzed trans-esterification.

The trans-esterification of different triglycerides in the presence of hydrochloric, sulfuric, phosphoric, and organic sulfonic acids have been extensively studied by Freedman, *et al*. (2007). He investigated the conversion of soybean oil into its methyl ester in the presence of 1% sulfuric acid with an alcohol/oil ratio of 30:1 at 65^{o}C and observed that a reaction time of 50 h was required to obtain yields over 99%. Butanolysis at 117^{o}C and ethanolysis at 78^{o}C using the same quantities of catalyst and alcohol required 3 and 18 h, respectively. Different types of feedstocks, such as rice bran oil and waste cooking oil, have been successfully trans-esterified with methanol using sulfuric acid as catalyst in the temperature range 60–80^{o}C. In particular, Zullaikah *et al*. (2005) investigated the acid-catalyzed methanolysis of dewaxed/degummed rice bran oil with varying FFA contents at atmospheric pressure and 60^{o}C using 1:10 molar ratio of oil/methanol and 2 wt% sulfuric acid as catalyst. The initial FFA content appreciably influences the rate of methanolysis and the final methyl ester content in the product. A methyl ester content of about 96% in the product could be obtained in 8 h for rice bran oil with an initial FFA content of 76 %.

Notably, analysis of the reaction products showed constant residual acid content (2–3 wt%), which might be attributed to the presence of phenolic compounds such as oryzanol, tocols, and/or other minor components in the rice bran oil. Consistent with the fact that acid-catalyzed alcoholysis of triglycerides is a slow reaction, a substantial amount of unreacted triglyceride was detected even after 24 h if the starting oil contained more than 20% FFAs. A further increase in reaction time or methanol concentration had a negligible effect on the trans-esterification of the triglycerides. To overcome these problems, a two-step acid-catalyzed methanolysis process was adopted to obtain good conversions in reasonably short times using rice bran oil with a high FFA content (>20%) as feedstock. The first step was performed at 60^{o}C using 2 wt% sulfuric acid and an oil/methanol molar ratio of 1:5. At a reaction time of 2 h, when more than 98% of the FFAs were converted into the corresponding methyl esters, the organic phase containing the reaction product was removed and used as the substrate for the second methanolysis reaction at 100^{o}C. At the end of the first step, the reaction product contained 62% FAMEs, 3.2% FFAs, and 34.8% acylglycerides. Methanolysis of this product at 100^{o}C resulted in a FAME content of more than 96% in the final mixture for a total reaction time of 8 h.

Zheng *et al*. (2006) showed that, in a large excess of methanol, the acid-catalyzed trans-esterification reaction of waste cooking oils is essentially a pseudo-first-order reaction. The oil/methanol/acid molar ratio and temperature were the most significant factors affecting the yield of FAMEs. At 70^{o}C with an oil/methanol/acid molar ratio of 1:245:3.8, and at 80^{o}C with oil/methanol/acid molar ratios in the range from 1:74:1.9 to 1:245:3.8, the trans-esterification was essentially a pseudo-first-order reaction as a result of the large excess of methanol which drove the reaction to completion (99% at 4 h). In the presence of the large excess of methanol, the FFAs present in the waste cooking oil were very rapidly converted into methyl esters in the first few minutes under the above conditions. Little or no monoglycerides were detected during the course of the reaction, and the diglycerides present in the initial waste cooking oil were rapidly converted into FAMEs.

Recently, Aranda *et al*. (2008) investigated the acid-catalyzed homogeneous esterification of palm fatty acids with anhydrous and hydrated methanol and ethanol. With anhydrous methanol, it was noted that sulfuric and methanesulfonic acids were

the best catalysts, with conversions higher than 90% obtained after 1 h reaction at 130ºC. The esterification reaction using anhydrous ethanol showed similar results. On the other hand, trichloroacetic acid did not accelerate the reaction, and phosphoric acid yielded minor improvements in conversion. Notably, even a small amount of sulfuric acid (0.01% w/w) proved to appreciably promote the reaction. A water inhibition effect was observed mainly in the ethanolic reaction. Abreu *et al*., (2003) studied the trans-esterification of different types of Brazilian native oils using organometallic catalysts such as Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$, Pb(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$, and Zn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$ at alcohol/vegetable oil/catalyst molar ratios of 400:100:1. These bivalent metal complexes can homogeneously catalyze the trans-esterification reaction by acting as Lewis acid sites. It was noted that the tin complex was the most active for all the vegetable oils tested. Furthermore, the catalysts showed an increased activity when vegetable oils with short-chain fatty acids or with a high degree of unsaturation and short linear alcohols were used.

2.13 Heterogeneous Catalysts

High energy consumption and costly separation of the catalyst from the reaction mixture have inspired the development of heterogeneous catalysts. The use of heterogeneous catalysts does not lead to the formation of soaps through neutralization of FFAs or saponification of triglycerides. Furthermore, solid acid catalysts can indeed improve the sustainability of the biodiesel production process, eliminating the corrosion problems associated with their use and consequent environmental hazards posed by them. However, the performance of heterogeneous catalysts is generally lower than that of the commonly used homogeneous catalysts. Moreover, heterogeneously catalyzed trans-esterifications require relatively elevated temperatures and pressures. Notably, diffusional limitations might sometimes drastically reduce the surface of the solid that is available for promoting the trans-esterification reaction. Therefore, a careful design of the pore structure of these materials is important. In this respect, zeolites are ideal systems. Furthermore, to improve the performance of these catalysts, it is essential to understand the correlations between acid and base strength and catalytic activity. It is clear that the surface of these heterogeneous materials should display some hydrophobic character to promote the preferential adsorption of triglycerides and to avoid deactivation of

catalytic sites by strong adsorption of polar by-products such as glycerol and water. As in the case of homogeneous catalysts, microwaves have shown superior performance than traditional heating methods for biodiesel production, with heterogeneous catalysis leading to better yields and conversions of triglycerides into FAMEs in a short time and, consequently, less energy consumption. One of the main problems with heterogeneous catalysts is their deactivation with time owing to many possible phenomena, such as poisoning, coking, sintering, and leaching. The problem of poisoning is particularly evident when the process involves used oils. More general and dramatic is catalyst leaching, which not only can increase the operational cost as a result of replacing the catalyst but also leads to product contamination. While purification of the reaction substrates, optimization of process parameters, and inclusion of catalyst-regeneration steps can minimize the deactivation of heterogeneous catalysts, leaching phenomena can be minimized only by altering the catalyst formulation. In particular, it is essential to use robust materials that are able to resist attrition. Furthermore, it is important to enhance the interaction between the active phase and the support. This enhancement can be obtained by tuning the synthesis parameters, for instance, by designing embedded catalysts. Finally, partial dissolution of the catalyst opens up the serious possibility of co-existing homogeneously catalyzed reaction pathways. Several heterogeneous catalysts have been reported for the trans-esterification of vegetable oils.

2.14 Acid Zeolites

Among numerous other applications, zeolites are probably the most investigated inorganic solid acid catalysts for the production of biodiesel by trans-esterification, as these materials can be synthesized with extensive control of acidic/basic and textural properties. The acidic properties of zeolites are usually improved by protonation, that is, by exchange of the cations contained in the positively charged aluminosilicate cage with protons. Furthermore, it is possible to induce some hydrophobicity of zeolites by the elimination of water of hydration. Koh *et al.* (2008) studied the trans-esterification of waste cooking oil using various zeolite catalysts with different acidities and pore structures. Proton-exchanged MOR, MFI, FAU, and BEA zeolites were employed in the reaction with silicalite, which has no strong acid sites. The yields were found to be independent of the pore structure of the zeolites. The authors found that the yield increased linearly with enhancing the acid strength and with increasing the amount of

strong acid sites. Consistently, proton-exchanged MOR(10) zeolite, which has more acid sites and greater acid strength than other zeolites, induced the highest yield of methyl esters (95 %). The stability of zeolites, especially at moderate/high temperatures and in the presence of water, must be carefully considered. In fact, the consequent dealumination process can lead to a serious decrease in the quantity of acid sites and the acid strength, with consequent deactivation of the catalyst.

Shu *et al*. (2007) prepared a La/zeolite beta catalyst by the ion-exchange method and used it in the batch trans-esterification of soybean oil with methanol. The prepared La/zeolite beta catalyst showed higher conversions and better stability than zeolite beta which was correlated to the larger quantity of external Brønsted acid sites.

2.15 Basic Metal Oxides

Alkaline earth oxides can act as solid base catalysts in the trans-esterification of triglycerides. Among these, Ca bases are the most promising as they are inexpensive, exhibit low solubility in methanol, and are the least toxic.

Leclercq *et al*. (2001) showed that the trans-esterification of rapeseed oil with methanol could be efficiently performed over a high-surface-area (300 m^2g) magnesium oxide to give a high conversion of the vegetable oil and a high yield of methyl esters, particularly when the hydroxide precursor was calcined at 550^oC. In addition, preliminary results with barium hydroxide showed a high activity of the catalyst and a high yield of esters was obtained. This catalyst was particularly effective: at a methanol-to-oil ratio of 6 and under reflux of methanol, a conversion of about 80% of the oil was observed after 1 h, and the ester was obtained in near-quantitative yield. Reddy *et al*. (2006) showed that nanocrystalline CaO was an efficient catalyst in the trans-esterification of soybean oil owing to the high surface area associated with the presence of small crystallites and lattice defects.

Kawashima *et al*. (2009) studied the catalytic activity of calcium oxide for the trans-esterification of rapeseed oil with methanol. The authors highlighted the need for an optimal catalyst activation protocol. In fact, by retreating CaO with methanol, a small amount of CaO was converted into $Ca(OCH_3)_2$, which acted as the initiating reagent for trans-esterification. Subsequently, the calcium-glycerol complex formed in the

reaction of CaO with glycerol functioned as the main catalyst in trans-esterification. Under optimal reaction conditions (0.1 g CaO, 3.9 g methanol, 15 g oil, and 1.5 h activation time at room temperature), the methyl ester was obtained in approximately 90% yield within 3 h at 60^{o}C.

Xie *et al*. (2006) used ZnO loaded with KF as a solid base catalyst in the trans-esterification of soybean oil with methanol which showed good activity. In this case, the activity of the catalyst correlated well with their basicity. The best performances were observed with a KF loading of 15 wt%. Xie and co-workers also investigated the trans-esterification of soybean oil using a Ba-ZnO catalyst. The results showed that with an increase in the calcination temperature from 400 to 600^{o}C, the basicity of the catalysts increased which resulted in an improvement in the conversion. However, at calcination temperatures higher than 600^{o}C, there was a decrease both in the basicity of the Ba-ZnO catalysts as well as in the conversion of the soybean oil.

2.16 Insoluble/Immobilized Metal Salts and Hydroxides

The catalytic activity of basic alkali-metal-containing species immobilized on alumina has also been the subject of studies focused on the trans-esterification of vegetable oils. For example, alumina loaded with KI was shown to be an active solid base catalyst. The optimal KI loading was found to be 35 wt%, which ensured a good basicity and, therefore, a good catalytic activity. Under optimized reaction conditions, a conversion of 96% was achieved.

Kim *et al*. (2004) investigated the trans-esterification of soybean oil using Na/NaOH-Al_2O_3 catalysts, which showed rather similar activity to a conventional homogeneous NaOH catalyst. Using the common methanol/oil molar ratio of 6:1, the yields of biodiesel obtained after 1 h were slightly below 80% and slightly above 90% for the heterogeneous and homogenous catalytic systems, respectively. However, at a methanol-to-oil molar ratio of 9:1 and using n-hexane as a co-solvent, biodiesel was obtained in over 90% yield after 2 h at 60^{o}C with Na/NaOH-Al_2O_3.

Ebiura *et al*. (2005) reported that selective trans-esterification of triolein with methanol could be achieved at around 60^{o}C using alumina loaded with alkali-metal salts as a solid base catalyst. The catalytic activities were shown to be relatively insensitive to the presence of water. The most favorable performance was observed

with K_2CO_3 on alumina, with which methyl oleate and glycerol were obtained in up to 94 and 89% yield, respectively, after 1 h reaction at 60°C.

Suppes *et al.* (2001) showed that a satisfactory performance of calcium carbonate catalysts in selected alcoholysis reactions was achieved even at high temperatures (over 200°C), where complete conversion was observed after reaction times as short as 18 min. No decrease in the activity of calcium carbonate was noted after several weeks of utilization.

2.17 Solid organic bases

Immobilized organic bases, such as guanidines anchored on polymers or encapsulated in a zeolite cage, can also act as catalysts for the trans-esterification of vegetable oils. A number of supported guanidines have shown turnover frequencies of 12–15 h_1 at 5–9 cycles of repeated use in the trans-esterification of soybean oil with MeOH (oil/methanol ratio: 1:7) at 70°C. Encapsulated bases were not very efficient owing to diffusion limitations to the transfer of bulky triglycerides. Salts of amino acids that are insoluble in monovalent alcohols, glycerol, and fatty acids esters were investigated as catalysts for the methanolysis of triglycerides. It was shown that Ni, Cu, Cd, La, Fe, and Zn salts of 2-amino-5-guanidinovaleric acid, carnitine, betaine, and taurine, and especially those containing quaternary ammonium or guanidino groups, displayed good catalytic activity. For example, in the methanolysis of palm oil with zinc arginate as a catalyst, nearly 90% yields of the ester were achieved within 200 min at 135°C and 5 bar.

2.18 Alkali earth alkoxides

Gryglewicz showed that alkaline earth metal alkoxides can catalyze the trans-esterification reaction (Gryglewicz *et al*., 1999). Liu *et al*., (2007) investigated the trans-esterification of rapeseed oil to biodiesel with methanol using calcium methoxide as a solid base catalyst. Calcium methoxide exhibits strong basicity and good thermal stability. Furthermore, calcium methoxide displayed excellent catalytic activity and stability in the trans-esterification of soybean oil to biodiesel with methanol, under optimal conditions of 1:1 (v/v) ratio of methanol to oil, addition of 2% $Ca(OCH_3)_2$ catalyst, 65°C, and a reaction time of about 2 h. Calcium methoxide has a moderate surface area, relatively broad particle size distribution, narrower pore

size distribution, strong basicity, long catalyst lifetime, and good stability in organic solvents. A recycling experiment revealed a long lifetime of the catalyst, which maintained its activity even after being reused for 20 cycles. Calcium ethoxide has also been proposed as a catalyst for the trans-esterification of soybean oil with methanol and ethanol. The results showed that the optimum conditions were 12:1 molar ratio of methanol to oil, 3% $Ca(OCH_2CH_3)_2$ catalyst, and a reaction temperature of 65°C. A biodiesel yield of 95.0% was obtained within 1.5 h under these conditions.

Recently, Martyanov *et al*. (2008) investigated the trans-esterification of tributyrine in the presence of calcium methoxide as a solid catalyst. The observed kinetic curves pointed at a sequential reaction process. The reaction started significantly slower than with homogeneous sodium and magnesium methoxides, but then the rate increased to surpass that observed with magnesium methoxide. Even though the reaction in the presence of $Ca(OCH_3)_2$ appeared to be a typical heterogeneous process, a careful investigation indicated a considerable contribution of the homogenous reaction. The loss of calcium methoxide during the reaction followed by its washing and drying was close to 35 wt%. In addition, the pH of the liquid surrounding $Ca(OCH_3)_2$ at the end of the first run was pH 12–13. This liquid part of the reaction mixture recovered after the first run was by itself catalytically active for the trans-esterification of tributyrin. The authors correlated the interaction between $Ca(OCH_3)_2$ and glycerol as a major factor governing the formation of catalytically active homogeneous species. The authors also pointed at the weak heterogeneous catalytic activity of $MgO_x(OCH_3)_{2-2x}$, where a fast deactivation of the catalyst was observed owing to accumulation of the butyric salt species on the catalyst surface.

2.19 Influence of reaction time, mixing intensity, and temperature

It is necessary to mention some important process variables of biodiesel production from vegetable oils such as the methanol/oil ratio, reaction time, mixing intensity, and temperature. The molar ratio of alcohol to triglycerides is an important variable that affects the yield of biodiesel in the trans-esterification reaction. Most systems for trans-esterification employ an alcohol/triglyceride molar ratio of 6:1. The excess of methanol with respect to the reaction stoichiometry is needed to shift the reaction equilibrium to the right (product side). Clearly, the conversion of the oil into the ester is also strongly dependent on the reaction time and temperature. Typically, the trans-

esterification reaction is complete within around 1 h using a methanol/oil molar ratio of 6:1 at a reaction temperature of 60 ^{o}C (Knothe *et al*., (2005). The trans-esterification of peanut, cottonseed, sunflower, and soybean oil were compared using a methanol:oil molar ratio of 6:1, 0.5% sodium methoxide as catalyst, and a reaction temperature of 60^{o}C. A biodiesel yield of around 80% was observed after already 1 min for the soybean and sunflower oils. After 1 h, a conversion of 93–98% was reached for all four oils. Even if some oils can be efficiently converted into their esters at ambient temperature, such as castor oil into methyl ricinoleae, most systems are designed to operate between 60 and 70^{o}C. Refaat *et al*. (2008) found that the optimum temperature for the trans-esterification of various types of oils is 65^{o}C, with most reactions being complete within 30 min at this temperature, whereas at 25^{o}C significantly lower yields were obtained even after 1 h of reaction. In the study by Freedman *et al*. (2007) after 6 min of reaction the corresponding esters were obtained in yields of 94, 87, and 64% at 60, 45 and 32^{o}C. In the latter case (reaction at 32^{o}C) nearly 4 h reaction time was required to reach 99% yield. The rate of the trans-esterification reaction of vegetable oil with alkaline methanol solution strongly depends on the rate of mass transfer at the interface between glycerol–methanol and oil–ester phases. Generally, low reaction rates are observed in trans-esterification as a result of a poor dispersion of the methanol and oil phases, and an induction period can be often seen on the kinetic curves (slow initial reaction before steady-state concentrations are reached). Therefore, intense mixing is very important for the trans-esterification process. Noureddini *et al*. (2004) investigated the effect of variations in mixing intensity during the trans-esterification of triglycerides to methyl esters in a pilot plant. The optimum stirring rates were in the range of 1000 rpm using both motionless and high-shear mixers. Singh *et al*. (2006) using a statistical approach, were able to optimize the operating conditions to maximize the biodiesel yield and minimize the formation of soap. The following set of optimized conditions was indicated: potassium methoxide concentration of 0.2 molL^{-1}, a reaction temperature of 50^{o}C, and a methanol/oil molar ratio of 4.5:1.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Sample collection

Desert date (*Balanites aegyptiaca*) fruits which were hand-picked by local people from the uncultivated desert date trees in the bush was purchased from them in the local markets in Adamawa State.

3.2 Chemicals and reagents

All the chemicals that were used were of analytical grade. These included anhydrous methanol (CH_3OH), hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium hydroxide (KOH), ethanol (C_2H_5OH), diethyl ether ($(C_2H_5)_2O$), phenolphthalein, potassium carbonate (K_2CO_3), and calcium oxide (CaO),

3.3 Equipment/Apparatus

The following equipment/apparatus were employed in the course of this research: weighing balance, muffle furnace, crucible, water bath, oven, hot plate, heating mantle, soxlet extractor, mechanical grinder, tray, heating pan, separating funnel, 300mm sieve, beakers, conical flasks, round-bottom flask, measuring cylinders, pipette, magnetic stirrer, thermometer, watch clock, and calorimeter, desiccator, sample containers, metal mortar and pestle, Whatman 42 filter paper (125 mm diameter and a pore size of 2.5 μm), titration setup.

3.4 Methods

3.4.1 Collection and preparation of raw materials

Fruits of *Balanites aegyptiaca* was purchased from the local markets in Adamawa State. The fruits were sorted to remove the ones that have defects and unwanted materials and contaminants. The sorted fruits were tied in sacks and pounded to get the exocarp (epicarp) removed. The fruits now stripped of the exocarp were soaked in water and allowed to remain there for 24 hours, so that the mesocarp got softened, after which it was washed off by scrubbing and rinsing with clean water. The cleaned nuts were emptied out of the water and spread in the sun for 12 hours to dry.

3.4.2 Pre-treatment of raw materials

The pericarp or shell of the cleaned *Balanites aegytiaca* nuts were cracked with pebble, split open and the kernels removed. The kernels were put in clean polythene bags, sealed and kept ready for extraction of the *Balanites aegytiaca* oil. The shells were sorted and any unwanted parts and contaminants were removed. The sorted shells were washed and rinsed with distilled water again and again so that no trace of colour showed in the water. The washed shells were sun-dried for two days and then crushed to small particle sizes in metal mortar and pestle. This pre-treated shell was kept in a stoppered sample container ready for carbonization and activation process. The kernels or the contents of the nut were packed together and kept in clean polythene bags for extraction of the oil.

3.5 Carbonization (physical activation) of *Balanites aegyptiaca* shell

Carbonization, otherwise known as physical activation or pyrolysis of carbonaceous substances is their breakdown into elemental carbon and chemical compounds by process of heating. The carbonization was carried out according to the method used by Abdul *et al.* (2008). The pre-treated *Balanites aegyptiaca* shell was placed in a crucible and carbonized at the standard temperature for the carbonization of the plant fruit shell (300 - 1000^{o}C) for an activation duration of 2 hours. During the carbonization it was ensured that little or no oxygen was allowed to penetrate the sample, which otherwise would allow it to burst into flames and burn away into ash. The absence of oxygen forced the *Balanites aegyptiaca* shell material to decompose into various substances, the main of which is a black porous solid consisting mainly of elemental carbon. At the end of 2 hours the sample was left to cool down to room temperature in a desiccator. It was then be removed, ground, sieved with a 300mm sieve and stored in an air-tight bottle which was labelled as AC (activated carbon). This activated carbon was used as catalyst for trans-esterification of *Balanites aegyptiaca* oil to generate biodiesel.

For the catalyst that was prepared above, the percentage yield, moisture content and pH were determined.

3.6 Proximate analysis of catalyst

3.6.1 Determination of the effect of temperature on the percentage yield (%) of catalyst produced by physical activation of Balanites aegyptiaca shell

The total yield (%) of catalyst that was produced by physical activation of *Balanites aegyptiaca* shell at varying temperatures was determined relative to the mass of the sample of material that was pre-treated, by using the formula:

$$Y_{ac} = (\overline{m}\ x100)/m_o$$

where Y_{ac} is the activated carbon yield (%) obtained; m īs the final mass of the catalyst that was produced at a given temperature; m_o is the initial mass of the of sample that was pre-treated and used in the carbonization (Verla *et al.,* 2012).

3.6.2 Determination of percentage (%) of moisture in catalyst produced by physical activation of Balanites aegyptiaca shell

For the determination of the moisture content of the catalyst the method adopted was the one by Donni *et al*. (2005). A sample mass of the catalyst was weighed in a crucible and dried in an oven set at a temperature of 110^{o}C. The drying sample was constantly re-weighed at 10 minutes interval until constant mass was obtained. The crucible and its content were then retrieved from the oven and cooled in a desiccator. The difference in mass was recorded and the moisture content was calculated from the relation:

$$MC = [(m_i - m_f)\ x\ 100]/m_i$$

where m_i is the initial mass before heating and m_f is the final mass after heating of the activated carbon sample.

3.6.3 Determination of pH of catalyst produced by physical activation of Balanites aegyptiaca shell

The pH of the catalyst produced by physical activation of *Balanites aegyptiaca* shell was determined as follows. A sample mass of 1.0g of the catalyst obtained was weighed in a 250ml-beaker, 100ml of distilled water was added and stirred for 1 hour. The sample was allowed to stabilize and the pH measured by using a hand-held pH-meter, Jenway 430 model.

3.7 Extraction of oil from *Balanites aegyptiaca* seed

The kernels of the *Balanites aegyptiaca* seeds were spread on heated coarse sand in a pan, and briskly and continuously were turned round and round until it was lightly fried. The fried kernels were shaken and gathered together, and then separated from the sand in a tray. They were allowed to cool down. The cooled kernels were gently rubbed with palm in a tray to remove any burned parts. Unwanted parts were either hand-picked or blown away. The cleaned kernels were weighed and subjected to both cold-pressed extraction and soxlet extractor method to obtain the oil. The oil was received in clean vessels. The cold pressed procedure employed the use of a mechanical extractor or presser.

3.8 Preliminary procedures for biodiesel production

3.8.1 Pre-reatment of Balanites aegyptiaca seed oil

The extracted *Balanites aegyptiaca* seed oil was screened to remove any suspended particles that might be in it using a fine micro-sieve. It was then heated in oven at a temperature of 110^{o}C to ensure that every trace of moisture in it was driven away. It was allowed to cool while in the oven and then transferred to a sample container, closed tightly and kept ready for further treatment and trans-esterification.

3.8.2 Determination of free fatty acid in Balanites aegyptiaca oil

A sample of the cleaned feedstock oil was titrated with a standardized base solution in order to determine the acid value, i.e. concentration of free fatty acids (carboxylic acids) present in the vegetable oil sample. Chemical titration method was used. This acid value was defined as the number of mg of KOH required to neutralize the fatty acids contained in 1 g of the fat. The results were expressed in units of mg fatty acids per g of sample or mmoles per Kg.

The procedure used was as follows:

0.1 to 10 g of oil or fat was weighed in a glass vial and dissolved in at least 50 ml of the solvent mixture.

The resulting solution was titrated, with shaking, with the KOH solution in a 25 ml burette graduated in 0.1 ml to the end point of the indicator (5 drops of indicator), the pink color persisting for at least 10 s. The acid value was calculated by the formula:

$$56.1 \times N \times V / m$$

where V is the number of ml of KOH solution used and N is the exact normality, m is the mass in g of the sample. Other expressions of calculations were carried out considering an average molecular weight of 282 for fatty acids.

3.8.3 Pre-treatment of methanol

The methanol used was poured into a round-bottom flask that was fitted with soxhlet apparatus, and was moderately heated and received in its pure form at its boiling point of 64.7^{o}C.

3.9 Biodiesel production from *Balanites aegyptiaca* seed oil

Single stage step by step trans-esterification was used in the production of biodiesel catalyzed first by the heterogeneous catalyst of CaO, then by the physically activated carbon from the *Balanites aegyptiaca* shell, and finally by both of them combined as co-catalyst. The following steps were followed:

i. About 7.8ml of the *Balanites aegyptiaca* seed oil was measured in 100ml measuring cylinder, and 30ml of methanol in a 100ml beaker, and their initial temperatures were measured and recorded.

ii. 0.5g CaO catalyst was added to the beaker of 30ml of methanol and properly stirred using a magnetic stirrer until the catalyst dissolved, making a solution of methoxide.

iii. The initial temperatures of the methoxide solution and *Balanites aegyptiaca* seed oil were measured and recorded.

iv. The *Balanites aegyptiaca* seed oil was gradually poured into the methanol in the beaker. The beaker and its contents were placed on the magnetic stirrer and a thermometer was mounted into the mixture. The temperature was taken as T1. The speed of the stirrer was adjusted to degree 1 and a stop-clock was set at 0. Both stirrer and stop-clock were started simultaneously and allowed to run for 30 minutes during which the temperature was monitored for any changes.

v. At the end of the period the time t, and the temperature T2 were taken and recorded. The resulting mixture in the beaker was carefully transferred to a separating funnel and allowed to cool and settle for 2 hours.

vi. The lower layer (the polar phase which comprises of glycerol, catalyst, the excess of methanol and soap) was collected from the bottom of the separating funnel in a beaker. The upper layer, the non-polar part contained the ester (biodiesel).

vii After the biodiesel was separated, warm water was used to wash it to remove any trace of glycerol and soap that might have remained in the funnel.

ix. The sample of biodiesel was dried by placing it on a warm-plate so that any excess water still remaining in it was driven away.

x. The quantity (volume) of biodiesel produced was collected, measured and recorded.

The above procedures were repeated using activated carbon of *Balanites aegyptiaca* shell and CaO as co-catalyst, for each of varying:

i. molar ratio of catalyst to oil;

ii. temperature;

iii. molar ratio of alcohol to vegetable oil

iv. stirring time; and

v. stirring intensity.

The results were recorded in a tabular form.

3.10 Determination of kinetic parameters of trans-esterification

The reaction time or time of stirring, *t* to form the volume of biodiesel, V_{BD} , at a given temperature, T was determined using a stop-clock. From the stoichiometric equation of the reaction:

$$TG(l) + 3MeOH(l) \rightleftharpoons glycerol(l) + BD(l)$$

The rate of the reaction (taken as rate of formation of biodiesel), r was evaluated as

$$r = d\,V_{BD}/dt = k(V_{TG})^x\,(V_{MeOH})^y$$

where V_{BD} is volume of biodiesel formed; V_{TG} is the volume of the vegetable oil (*B. aegyptiaca* oil) and V_{MeOH} is the volume of methanol that were used up to form the volume of biodiesel, V_{BD} in time t; k is the rate coefficient of the reaction; x and y are the orders of the reaction with respect to the vegetable oil (triglyceride) and methanol (MeOH) respectively. Since the reaction between a biolipid (fat or oil or vegetable oil) and alcohol is always a reversible reaction, the alcohol was added in excess to ensure complete conversion. The rate of the reaction was measured as the rate of formation of biodiesel and therefore determined as follows:

$$r = (V_{BD\,2} - V_{BD\,1})/(t_2 - t_1)$$

where $V_{BD\ 1}$ is biodiesel yield in time t_1, and $V_{BD\ 2}$ is biodiesel yield in time t_2. A number of runs of the reaction at constant temperature, T and varying volume of vegetable oil, V_{TG} to yield a corresponding volume of biodiesel, $V_{BD,}$ at excess volume of methanol, V_{MeOH} using the ultimate time, t permitted the calculation of the values of the rate constant k, partial order of reaction x with respect to V_{TG}, and y with respect to V_{MeOH} algebraically.

The values of x, y and k for the trans-esterification were experimentally determined by employing two experimental situations. The first situation is the one in which the volume of the vegetable oil was varied while the volume of the alcohol was kept constant. The second situation is the reverse of the case above in which the volume of the alcohol was varied while the volume of the vegetable oil was kept constant. In each of these situations the optimum values of temperature, catalyst and time of stirring were used. Series of runs of the experiment gave results that permitted the calculations of the kinetic parameters.

3.11 Determination of thermodynamic parameters of trans-esterification for biodiesel production

3.11.1 Determination of ΔH, ΔS, and E_a *of biodiesel formation*

Since trans-esterification is a reversible reaction, the free energy, ΔG = 0. But the energy of activation E_a was calculated using Arrhenius equation $k = Aexp(-E_a/RT)$. Rate constants *k*, were calculated as the slopes of the kinetic graphs of production of biodiesel $V_{BD}^{-1} = kt$ at temperatures T = 25ºC (298K), 30ºC (303K) and 40ºC (313K). By taking the logarithm of both sides of the Arrhenius equation, $ln(k) = -E_a/RT + ln(A)$ it was related to the straight line plot of the logarithm of the rate constants versus reciprocal of temperatures ($ln(k)$ vs $1/T$), where the slope , $m = -E_a$, and the intercept $b = ln(A)$

To determine the ΔH and ΔS of the trans-esterification the equation

$\Delta G = \Delta G^o + RT\ ln\ (k)$ was used,

where,

ΔG is Gibb's free energy at non-standard states, and

ΔG^o is Gibb's free energy at standard states.

But $\Delta G = 0$ for systems at equilibrium

so $0 = \Delta G^o + RT \ln (k)$

and $\Delta G^o = - RT \ln (k)$

But $\Delta G^o = \Delta H^o - T\Delta S^o$

Therefore, $\Delta H^o - T\Delta S^o = - RT \ln (k)$.

At non-standard states it becomes

$$\Delta H - T\Delta S = - RT \ln (k)$$

$$\ln (k) = \frac{-\Delta H + T\Delta S}{RT}$$

$$\ln (k) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

Relating this equation to the graph of *ln(k)* vs *1/T* , $\frac{-\Delta H}{R}$ is the slope, *m* and $\frac{\Delta S}{R}$ is the intercept *b* on the *ln(k)* axis, from which ΔH and ΔS were calculated.

3.12 Expected outcome of the research

The following are expected as the outcome of the research:

i. Production of biodiesel from *Balanites aegyptiaca* oil using activated carbon from its shell as catalyst;

ii. The establishment of the optimum conditions in terms of temperature, time and catalyst to oil ratio for maximum production of biodiesel from *Balanites aegyptiaca* oil.

iii. The establishment of the kinetic parameter of rate law that shall be specific for the production of biodiesel from *Balanites aegyptiaca* oil. The rate law is the mathematical expression which shows how, for a given duration and temperature of reaction, the concentrations of the reactants, and of products, along with the order of the reaction, interact to determine the speed with which the reaction proceeds. The order of the reaction shows the class of the reaction based on the mathematical

relationship between the rate of the reaction and the concentration of the reacting chemical species.

iv. The establishment of kinetic parameters of order of reaction, *n* and rate constant k for the trans-esterification of *Balanites aegyptiaca* oil.

iv. The establishment of thermodynamic parameters of enthalpy (heat) of reaction, ΔH, entropy ΔS, and energy of activation E_a, specific for the trans-esterification of *Balanites aegyptiaca* oil.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Determination of the effect of temperature on the percentage yield (%) of catalyst produced by physical activation of *Balanites aegyptiaca* shell

For a given carbonization temperature three separate 13g samples were fed into the furnace. The mass of carbon obtained for each was measured and the average calculated. The Efficiency is expressed as a percentage yield of carbon catalyst produced from the mass of the fruit shell used to produce it at the specified temperature (Booth, H. E., 1983). The result of the percentage yield (%) at varying temperatures is presented on Table 1.

T (°C)	Y_{ac} (%)
300	3.9
400	5.6
500	27.4
600	63.5
700	83.5
800	78
900	18
1000	2.6

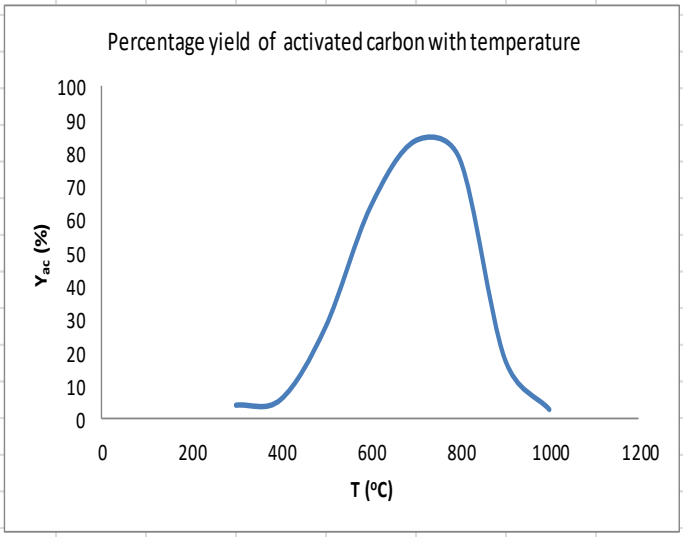


Figure 1: Graph showing the effect of temperature on the percentage yield of catalyst produced by physical activation of *Balanites aegyptiaca* shell

During the carbonization, a steady and considerable amount of heat was allowed into and out of the fruit shell. First, the shell dried up. At a furnace temperature of about 270-300°C spontaneous pyrolysis occurred, so there was little carbon formed. At temperatures from 500°C decomposition occurred to form carbon and other substances. The amount of carbon produced increased with temperature to about 700°C after which it dropped due to expel of substances as vapours or due to ashing.

4.2 Proximate analysis of catalyst

4.2.1 Determination of percentage (%) of moisture in catalyst produced by physical activation of Balanites aegyptiaca shell

The thermogravimetric method was used as described by Donni *et al*. (2005). 13g of the shell was weighed (as m_i) and heated at a constant temperature for a defined period of time after which it was weighed again (as m_f). The moisture content was determined by the difference between m_i and m_f. The loss of moisture content of the catalyst with time is shown on Table 2.

The moisture content was calculated as:

$$MC = [(m_i - m_f) \times 100]/m_i$$
$$= [(13 - 10.7) \times 100]/13$$
$$= 17.7\%$$

4.2.2 Determination of pH of catalyst produced by physical activation of Balanites aegyptiaca shell

The pH of the catalyst produced by physical activation of *Balanites aegyptiaca shell* at varying temperatures was found to be 9.5.

4.3 Determination of free fatty acid in *Balanites aegyptiaca* oil

For the determination of the free fatty acid in the *Balanites aegyptiaca* oil that was extracted, the titration method described by (Mahesar *et al.*, 2014) was used. 0.7g of the oil was dissolved in 20cm^3 of diethylether/ethanol (1/1, v/v) and titrated against 0.1 M solution of KOH that was prepared in ethanol. The result of the titration is shown in Table 3.

Average volume, V of KOH used = ⅓ (1.2 + 1.0 + 1.1)

$$= 1.1 \text{ ml}$$
$$\text{Acid value of oil} = 56.1\text{g} \times N \times V/m$$
$$= 56.1 \times 1 \times 1.1/0.7$$
$$= 88.157\text{mg of FFA/g of sample}$$
$$= (88.157 \times 10^{-3})/1\text{g} \times 100$$
$$= 8.82\%$$

Results of the titration to determine the percentage of free fatty acid in *Balanites aegyptiaca* oil showed that about 9% of the oil used was free fatty acid. This meant that along with the biodiesel and glycerol that was produced as products there was by-products of water and soap. So the percentage of biodiesel obtained could not have

been as it should when the oil has zero free fatty acid. This was what added to the difficulty encountered in trying to separate any unused oil left in the lower layer that settled from the post reaction mixture at the bottom of the separating funnel. It was even more difficult when the amount of oil left was small. This difficulty and shortage of equipment for delicate separation of the constituents of the lower layer informed the researcher to adopt the method of measuring the rate of the reaction by the formation of biodiesel (formed as a clear upper layer in the separating) instead of the rate of consumption of the vegetable oil in the trans-esterification.

4.4 Determination of the yield of Biodiesel in its production from *Balanites aegyptiaca* seed oil

The yields of biodiesel in different runs using varying catalyst concentrations and time of stirring, temperature, molar ratio of alcohol to vegetable oil, varying volumes of vegetable oil, and varying volumes of methanol are presented on Tables 4, 5, 6, 7, 8 and 9.

4.4.1 Determination of the quantitative proportions of B. aegyptiaca oil to methanol in Biodiesel production

The equation of reaction in trans-esterification of vegetable oils shows that the proportion of triglyceride to alcohol is 1:3. 30ml of methanol which weighed 23.3g was taken as reference point. One-third the mass of the ethanol should be the required mass of the oil, i.e. 7.77g to give complete reaction. This mass of the oil is equivalent to 8.3ml. Table 4 shows the result of the investigation of the approximate volume of the oil that would react with 30 ml of methanol at ambient temperature, using 0.5g of CaO as catalyst and 20 minutes run time.

8.3ml of the oil happened to give the highest yield of biodiesel when it was reacted with 30 ml of methanol. Additional volume of the oil seemed to give little difference.

4.4.2 Effect of catalyst concentration on Biodiesel yield

The catalyst employed for the trans-esterification was either CaO, the activated carbon from the *Balanites aegyptiaca* shell or the combination of the two as co-catalyst. From the results in Table 5 it is observed that the maximum yield of biodiesel obtained was when the concentration of the catalyst was 0.3g for any of

catalysts CaO, C-act and CaO/C-act. There was not much difference in the yield of biodiesel when CaO, C-act or CaO/C-act was used.

4.4.3 Effect of time of stirring on biodiesel yield

Time of stirring ranged between 25-30 minutes. But within 15 minutes of stirring, the trans-esterification was completed. This timing of course corresponded to the quantities of the reactants used. Higher quantities would definitely require longer time of stirring.

4.4.4 Effect of temperature on biodiesel yield

The temperature range that was considered in this investigation was from 25 – 45^{o}C. At 30 ^{o}C high yield of biodiesel was obtained using 0.3g of either activated carbon (C-act) as catalyst or the co-catalyst (C-act/CaO). Higher yield of biodiesel was obtained at 40 - 45 ^{o}C, but the biodiesel appeared cloudy or milky. The increase in temperature must have caused some changes in the biodiesel. 25 ^{o}C gave a lower yield of biodiesel.

4.4.5 Effect of mole ratio of alcohol to vegetable oil on Biodiesel yield

As can be seen on Table 7, the ratio of alcohol to vegetable oil that gave the highest yield of Biodiesel yield was 8.3**:**30 when stirred for 15 minutes at 30^{o}C.

4.5 Determination of kinetic parameters of trans-esterification

The reaction time or time of stirring, *t* to form the volume of biodiesel, V_{BD} , at a given temperature, T was determined using a stop-clock. From the stoichiometric equation of the reaction;

$$TG(l) + 3MeOH(l) \rightleftharpoons \text{glycerol}(l) + BD(l)$$

the rate of the reaction (taken as rate of formation of biodiesel), r was evaluated using the rate law:

$$r = d\,V_{BD}/dt = k(V_{TG})^{x}\,(V_{MeOH})^{y}$$

where V_{BD} is volume of biodiesel formed; V_{TG} is the volume of the vegetable oil (*B. aegyptiaca* oil) and V_{MeOH} is the volume of methanol that were used up to form the volume of biodiesel, V_{BD} in time t; k is the rate coefficient of the reaction; x and y are the orders of the reaction with respect to the vegetable oil (triglyceride) and methanol

(MeOH) respectively. The rate of the reaction was measured as the rate of formation of biodiesel and therefore determined as follows:

$$r = (V_{BD\,2} - V_{BD\,1})/(t_2 - t_1)$$

where $V_{BD\,1}$ is biodiesel yield in time t_1, and $V_{BD\,2}$ is biodiesel yield in time t_2. A number of runs of the reaction at constant temperature, T and varying volume of vegetable oil, V_{TG} and varying volume of methanol, V_{MeOH} to yield a corresponding volume of biodiesel, $V_{BD,}$ using the ultimate time, t permitted the calculation of the values of the rate constant k, partial order of reaction x with respect to V_{TG}, and y with respect to V_{MeOH}.

To determine the partial orders of the reaction and the rate constants, as well as the overall order of the reaction and its rate constant, the methods of differential rate law and the integrated rate law were used described by Davis, 2019. The experimental values that enabled the calculation of these kinetic parameters are presented on Tables 8, 9 and 10.

4.5.1 Determination of the partial orders of reaction with respect to triglyceride and methanol with corresponding rate constants

To experimentally determine the partial orders of the reaction x and y and the corresponding partial rate constant with respect to TG and MeOH for the trans-esterification of *Balanites aegyptiaca* oil using activated carbon from its shell mixed with CaO as co-catalyst, two experimental situations were employed. The first situation is the one in which the volume of the vegetable oil was varied while the volume of the alcohol was kept constant. The second situation is the reverse of the case above in which the volume of the alcohol was varied while the volume of the vegetable oil was kept constant. In each of these situations the optimum temperature of 30^{o}C was chosen, 0.3g of catalyst was used, and the time of stirring fluctuated between 15 and 20 minutes based on the range of the volumes of the vegetable oil chosen. In fact, from the repeated runs of the experiment (Table 5, 6 and 7), in most of the times the trans-esterification was complete in 15 minutes for the quantities of the reactants used.

4.5.1.1 Effect of varying amounts of vegetable oil versus constant/excess amount of alcohol on biodiesel yield at T = 30°C

Table 8 shows the volumes of biodiesel obtained when the amount of vegetable oil was varied while that of alcohol was kept constant and/or in excess, at T = 30°C and relatively constant time of stirring. The corresponding volumes of biodiesel (V_{BD}), vegetable oil (V_{TG}) and methanol (V_{MeOH}) in the trans-esterification can be and are kinetically related by the rate equation:

$$r = d(V_{BD})/dt = k(V_{TG})^x (V_{MeOH})^y$$

This rate equation is the differential rate law for the kinetics of a reaction where two different substances react to form products. Normally the equation should have been

$$r = d[BD]/dt = k[TG]^x[MeOH]^y$$

when concentration of the species are used. But in this experiment, volumes have been used because the actual composition of *Balanites aegyptiaca* oil is not known and the definite triglyceride in the oil that reacted with methanol to form biodiesel is not known, talk less of its molecular formula or molecular mass. By using the data of volumes of the species (instead of their concentrations) in the reaction at a fixed temperature, the values of x, y and k were calculated. The volumes in each run of the experiment on Table 7 were substituted into the rate equation to determine the partial orders of the reaction x and y with respect to vegetable oil and methanol, as well as the rate constant, k. Therefore, it follows that

$$r_1 = 19/15 = k_1(5)^x(30)^y$$
$$r_2 = 24.3/15 = k_1(6.4)^x(30)^y$$
$$r_3 = 30.4/15 = k_1(8)^x(30)^y$$
$$r_4 = 43/17 = k_1(10)^x(40)^y$$
$$r_5 = 45/18 = k_1(12)^x(45)^y$$
$$r_6 = 58/20 = k_1(14)^x(50)^y$$

where k_1 is the rate constant for this first situation

We can arbitrarily take the ratio of any two of the substituted rate equations and algebraically calculate the values of x, y and k.

Thus, by taking the ratio of r_1 to r_2, we have

$$r_1/r_2 = 19/24.3 = (5/6.4)^x$$
$$0.7819 = 0.7813^x$$
$$x = \log 0.7819/\log 0.7813$$
$$= 0.9967$$
$$\approx 1$$

The value of x obtained as 1 means that the partial order of reaction with respect to the triglyceride as reactant is first-order. This means that the reaction rate is directly proportional to the concentration (or amount) of the triglyceride in the reaction.

Taking the ratio of r_1 to r_4, we have

$r_1/r_4 = 19/15x17/47 = (5/10)^x (30/40)^y$

$0.4582 = (0.5^x)(0.75^y)$

But x = 1 from above, therefore

$0.4582 = (0.5^x)(0.75^y)$ … … (1)

$= 0.5(0.75^y)$

$\log 0.4582 = \log 0.5 + y\log 0.75$

$y = (\log 0.4582 - \log 0.5)/ \log 0.75$

$= 0.303$

≈ 0

The value of y obtained as 0 means that the partial order of the reaction with respect to the methanol as reactant is zeroth-order. As zeroth-order it means the rate of the reaction was independent of the concentration (or amount) of the methanol as a reactant. This can be accepted to be true because the amount of the methanol was provided in excess, which has a consequence of being kept constant.

Or by taking the ratio of r_3 to r_5, we have

$r_3/r_5 = 30.4/15x18/45 = (8/12)^x (30/45)^y$

$0.8107 = (0.67^x)(0.67)^y$ … … (2)

By taking the logarithms of equations (1) and (2) they can be solved simultaneously as follows:

eqn (1): $0.4582 = (0.5^x)(0.75^y)$

$\log 0.4582 = x\log 0.5 + y\log 0.75$

$–0.3390 = –0.3010x – 0.1250$ … … (3)

eqn (2): $0.8107 = (0.67^x)(0.67)^y$

$\log 0.8107 = \log (0.67^x) + \log(0.67)^y$

$–0.0911 = –0.1740x – 0.1740y$ … … (4)

eqn (3)x7: $–2.373 = –2.107x – 0.875y$ … … … (5)

eqn (4)x5: $–0.456 = –0.870x – 0.870y$ … … … (6)

$–1.917 = –1.237x$

$x = 1.55 \approx 1$

By taking equation (5) or (6) and substituting the value of x we can y as

$–2.373 = – 2.107 (1.55) – 0.875y$

$y = –0.55 \approx 0$

Again these values of x = 1 and y = 0 indicate that under this condition, the reaction proceeded with first-order and zeroth-order with respect to the triglyceride and methanol respectively.

To prove further the relationship of the data on the rate law, if we take the ratio of r_1/r_4, it will be

$$r_1/r_4 = (24.3/15)x(20/58) = (6.4/14)^x . (30/50)^y$$
$$0.5586 = (0.4571)^x . (0.6)^y \ldots \quad \ldots \quad (7)$$

By taking the logarithm of equation (7) and substituting the value of x = 1, it becomes

$$\log 0.5586 = \log (0.4571) + y\log (0.6)$$
$$\text{so, } y = -0.39$$
$$\approx 0.$$

If y = 0, the logarithm of eqn (7) becomes

$$\log 0.5586 = x\log (0.4571)$$
$$\text{Therefore, } x = 0.7438$$
$$\approx 1.$$

Taking r_3 arbitrarily and substituting for the values of x and y obtained, k_1 is calculated as

$$r_3 = 30.4/15 = k_1(8)^x(30)^y$$
$$2.03 = 8k_1$$
$$k_1 = 0.2533\text{ml/min.}$$

With k_1 = 0.2533ml/min it means that 0.2533ml of the triglyceride was being consume in every one minute in the course of the reaction.

Hence, it can be seen that in the trans-esterification of *Balanites aegyptiaca* oil, the order with respect to methanol as a reactant is zero-order. One or both of these two propositions can account for this. The first proposition is that the volume of alcohol (methanol) here was provided in excess compared to the volume of the vegetable oil. If the amount of the alcohol used is not significant compared to the unreacted amount left in the vessel, the reaction would tend toward zero-order. The proposition is that the volume of alcohol was not only in excess, it has the implication of being kept constant, as if little or nothing was changing in it compared to the vegetable oil. The excess volume of methanol ensured complete conversion to products as it is the case with reversible reactions, the reaction between vegetable oil and alcohol being one. In chemical kinetics, keeping the concentration of a reactant constant (or in excess) can make the order of reaction with respect to the reactant to be zero-order, or be independent of the rate of the reaction.

4.5.1.2 Effect of constant/excess amount of vegetable oil versus varying amounts of alcohol on biodiesel yield at T = 30°C

On the other way round when the volume of the vegetable oil (V_{TG}) was provided in excess and the volume of methanol (V_{MeOH}) varied at T = 30°C, the result is as shown on Table 9.

V_{MeOH} (ml)	V_{BD} (ml)
15	16
20	21
25	25
30	32
33	35
35	37
37	39
40	43

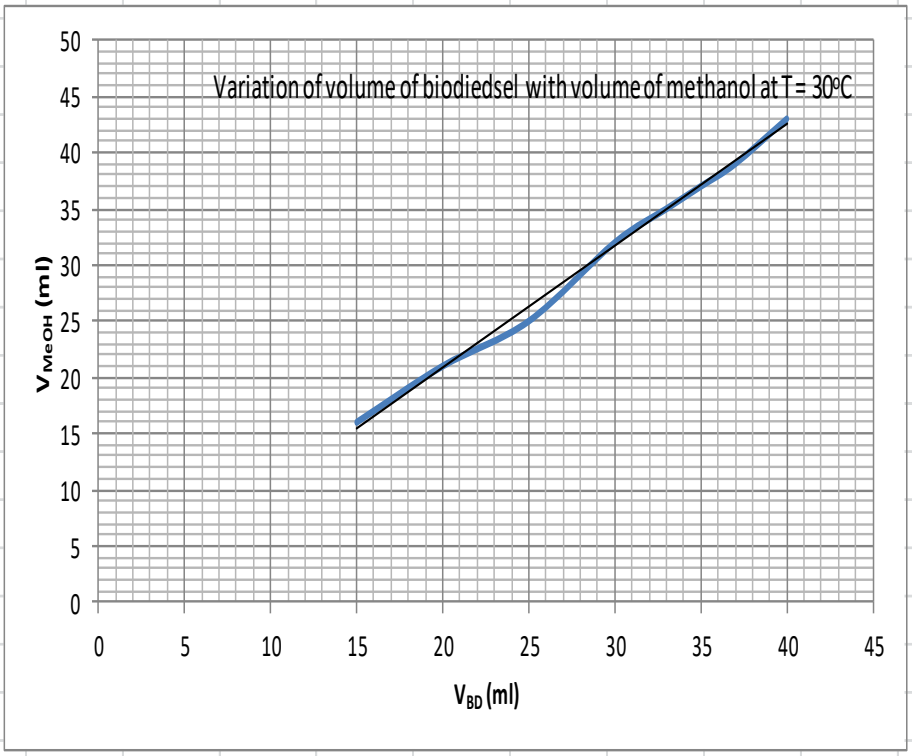


Figure 2: Graph of volume of biodiesel obtained against volume of methanol used

In Table 9, volume of triglyceride was kept constant (or in excess) and volume of methanol was varied throughout.

As before, using the rate equation,

$$r = d\,V_{BD}/dt = k(V_{TG})^x\,(V_{MeOH})^y$$

and substituting values obtained at the various experimental runs, we have

$$r_7 = 16/15 = k_2\,(10)^x(15)^y$$
$$r_8 = 21/15 = k_2\,(10)^x(20)^y$$
$$r_9 = 25/15 = k_2\,(10)^x(25)^y$$
$$r_{10} = 32/15 = k_2\,(10)^x(30)^y$$
$$r_{11} = 35/15 = k_2\,(10)^x(33)^y$$

$r_{12} = 37/15 = k_2 (10)^x(37)^y$
$r_{13} = 39/15 = k_2 (10)^x(39)^y$
$r_{14} = 40/15 = k_2 (10)^x(40)^y$
$r_{15} = 40/15 = k_2 (10)^x(45)^y$
$r_{16} = 40/15 = k_2 (10)^x(50)^y$

where k_2 is the rate constant for this second situation.

By taking the ratio of r_7 to r_8, we have

$$r_7/r_8 = 16/21 = (15/20)^y$$
$$0.7619 = 0.75^y$$
$$y = \log 0.7619/\log 0.75$$
$$= 0.9453$$
$$\approx 1$$

In this situation, the order with respect to methanol is first-order, which means that the reaction rate was directly proportional to the amount of the methanol.

Similarly, by taking the ratio of r_{13} to r_{10}, we have

$$r_{13}/r_{10} = 39/32 = (39/30)^y$$
$$1.2188 = 1.3^y$$
$$y = \log 1.2188/\log 1.3$$
$$= 0.7542$$
$$\approx 1$$

Also $r_7/r_{16} = 16/40 = (15/50)^y$
$$0.4 = 0.3^y$$
$$y = \log 0.4/\log 0.3$$
$$= 0.7611$$
$$\approx 1$$

This still confirms that the reaction order with respect to methanol here is first-order.

In this situation, keeping the volume of vegetable oil, $\mathbf{V_{TG}}$ constant (or in excess) and varying the volume of methanol V_{MeOH}, the order of the reaction y with respect to V_{MeOH} is first order.

The excess of V_{TG} here implied that the order x with respect to the V_{TG} must be zero-order as earlier explained.

Substituting these values of x and y in any of the runs, e.g. r_{11}, k is calculated also as

$$r_{11} = 35/15 = k_2(10)^x(33)^y$$
$$2.3333 = k_2 (33)$$
$$k_2 = 0.0707\text{ml/min.}$$

k_1 and k_2, even though controlled by the same temperature, are not expected to be the same because different conditions were imposed in the two situations. The rate at which the trans-esterification could go in any of the situations was governed by the

constraint placed on it. One can see some degree of agreement between the stoichiometric proportion of the reactants (triglyceride and methanol) and the rate constants obtained in varying their amounts in the two cases above.

The ratio of triglyceride to methanol is

triglyceride : methanol = 1: 3

That is, for every one mole of triglyceride that reacted, it required three moles of methanol. So the relative rates must have been that the rate of consumption of the triglyceride must be three times that of methanol for it to catch up.

Hence,

$k_1 : k_2 = 0.2533ml/min : 0.0707ml/min$

Dividing the two values by the smaller one gives

$$k_1 : k_2 = \frac{0.2533ml/min : 0.0707ml/min}{0.0707ml/min : 0.0707ml/min}$$

= 3.6 : 1 (giving room to experimental error of 20%)

4.5.2 Determination of the overall order and the rate constant of the reaction

The overall order and the rate constant for the reaction were obtained from the combined effect of allowing the trans-esterification to occur freely. Time was the only independent variable that was monitored to get the corresponding volume of biodiesel produced.

If no constraint were placed on any of the quantities of the reactants in the trans-esterification, such that the reaction was allowed to proceed in its natural course to completion and any limiting quantity was not externally imposed, the reaction for the production of biodiesel by the trans-esterification of *Balanites aegyptiaca* oil using its shell as co-catalyst would obey the rate law of the form

$$r = k[A][B]$$

where $[A] = V_{TG}$ and $[B] = V_{MeOH}$ the volumes of the two reactants, k is the rate constant, and the overall order of the reaction would be second order. The equation states that the rate of the reaction is directly proportional to both the amounts of reactants TG and MeOH.

Since the volume of triglyceride and volume of methanol initially were present in stoichiometric proportions (1:3), they must have remained so throughout the free reaction,

i.e. $V_{TG}/V_{MeOH} = ⅓$ at any time t; [From: TG(*l*) + 3MeOH(*l*) $\rightleftharpoons$ glycerol(*l*) + BD(*l*)].

Focusing on the TG alone and considering the reaction to occur at second order, the rate of the reaction becomes

$$r = -⅓dV_{TG}/dt = k(V_{TG})^2$$ (i.e. the rate of use up of TG with time.)

But $-⅓dV_{TG}/dt = dV_{BD}/dt = k(V_{BD})^2$ (i.e. the rate of formation of BD is equal to ⅓ the rate of use up of TG with time.)

Experimentally it was easier to measure the rate of formation of biodiesel, $\mathbf{V_{BD}}$ than the rate of disappearance of vegetable oil, $\mathbf{V_{TG}}$. Therefore the rate law for the formation of biodiesel as a second order of reaction would take the form:

$r = dV_{BD}/dt = k(V_{BD})^2$, and when we integrate, we have

$$\int (V_{BD})^{-2} dV_{BD} = k\int dt$$

$$V_{BD}^{-1} = -kt$$

This is the integrated rate law for a second order reaction. If a reaction were second-order, a plot of its data using this integrated rate equation would give a straight line graph with a negative slope. The value of the slope or *k* would depend on the temperature at which the experiment was carried out.

4.5.2.1 Effect of no constraint on the amount of vegetable oil versus amount of alcohol on Biodiesel yield at different temperatures and times

Experimentally it was established that 8.3ml of *Balanites aegyptiaca* oil required 30mls of ethanol to react completely in 15 minutes for the temperatures 25 - 40^{o}C. So to determine the kinetic parameters for the trans-esterification of *Balanites aegyptiaca* oil, the initial volume of vegetable oil $\mathbf{V_{TG}}$ = 8.3ml, initial volume of methanol $\mathbf{V_{MeOH}}$ = 30mls and mass of catalyst **m-cat** = 0.3 were used for the reaction to generate biodiesel. The volume of biodiesel $\mathbf{V_{BD}}$ formed at varying times **t** were recorded at three temperatures **T** = 25^{o}C, **T** = 30^{o}C and **T** = 40^{o}C. The results obtained have been entered in tables 9, 11 and 13.

But none of the set of values obtained at the three temperatures could fit into second order kinetic plot. Perhaps it was because the rate of the reaction was measured by monitoring the rate of formation of biodiesel instead of rate of rate of consumption of vegetable oil. To get round the problem it was reasoned that since trans-esterification is a reversible reaction, the path followed by the forward reaction must be the path followed by the reverse reaction. Therefore the corresponding values for the reverse reaction were obtained by mirror-imaging. The results obtained are presented on Tables 10, 12 and 14. Surprisingly the data obtained fit into the second order kinetic plot. The pair of curves for both the forward and reverse cases for the three temperatures are shown on Figures 3, 4 and 5.

t (min)	V_{BD} (ml)	V_{BD}* (ml)
0	0	
2	0.3	35.5
5	15.8	14.2
8	21.2	8.8
10	23	7
12	24.2	5.8
15	25.3	4.7

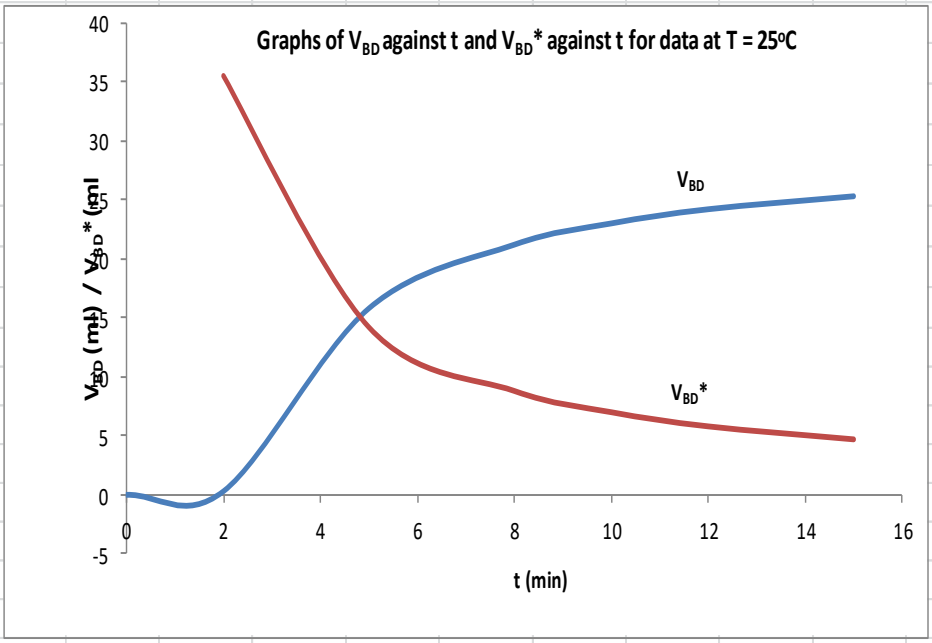


Figure 3: Graphs of volume of biodiesel for forward reaction (**V_{BD}**) against time and volume of biodiesel for the backward reaction (**V_{BD}***) against time for data at **T** = 25°C

Figure 3 shows the variation in the volume of biodiesel with time for the forward reaction (**V_{BD}**) and for the backward reaction (**V_{BD}***) at 25°C. The data used for the curves are from Tables 9 and 10.

t (min)	V_{BD} (ml)	V_{BD}* (ml)
0	0	30
2	14	16
5	20	10
8	24	6
10	25	5
12	25.8	4.2
15	26.3	3.6

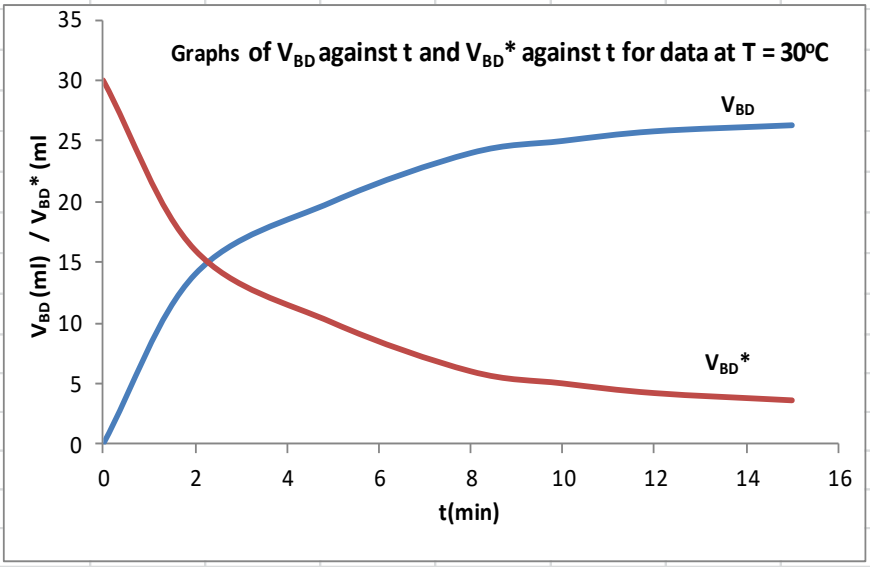


Figure 4: Graphs of volume of biodiesel for forward reaction (V_{BD}) against time and volume of biodiesel for the backward reaction (V_{BD}*) against time for data at **T** = 30°C

Figure 4 shows the pair of curves for the variation in the volume of biodiesel with time for the forward reaction (V_{BD}) and for the backward reaction (V_{BD}*) at 30°C. The data used for the curves are from Tables 11 and 12.

t (min)	V_{BD} (ml)	V_{BD}* (ml)
0	0	30.3
2	17.5	12.5
5	23.5	6.5
8	25.7	4.3
10	26.4	3.6
12	27	3

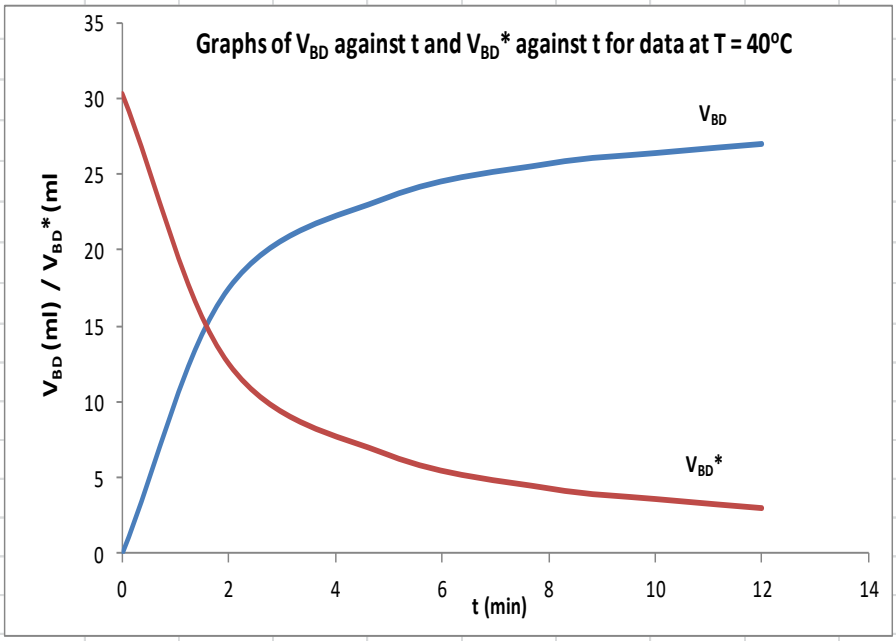


Figure 5: Graphs of volume of biodiesel for forward reaction (**V_{BD}**) against time and volume of biodiesel for the backward reaction (**V_{BD}***) against time for data at **T** = 40°C

Figure 5 shows the pair of curves obtained for the variation in the volume of biodiesel with time for the forward reaction (**V_{BD}**) and for the backward reaction (**V_{BD}***) at 40°C. The data used for the curves are from Tables 13 and 14.

The data for the forward reactions for T = 25°C, 30°C and 40°C in Tables 9, 11, and 13 above could not fit into second order kinetic plots (**V_{BD}^{-1}** against **t**) but the ones for the backward reactions (**V_{BD}*$^{-1}$** against **t**) in Tables 10, 12 and 14 did. These are shown in figure 6.

t (min)	VBD*-1	VBD*-1	VBD*-1
0		0.03	0.03
2	0.028	0.0625	0.08
5	0.071	0.1	0.155
8	0.114	0.166	0.23
10	0.142	0.2	0.28
12	0.171	0.25	0.33
15	0.214	0.275	

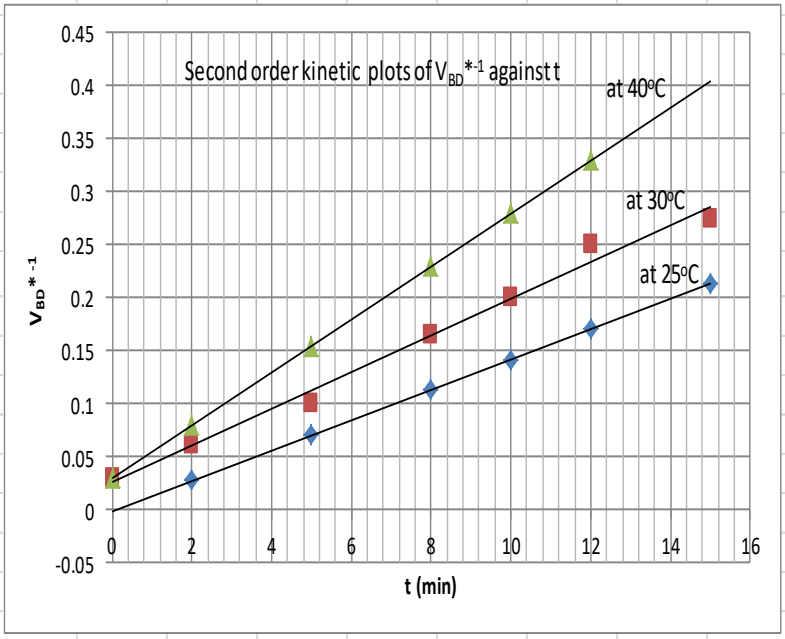


Figure 6: Second order kinetic plots of the reciprocal of volume of biodiesel for reverse reaction ($\mathbf{V_{BD}^{*-1}}$) against time (**t)** for the production of biodiesel at temperatures of 25°C, 30°C and 40°C

The straight line plots obtained for the $\mathbf{V_{BD}^{*-1}}$ against **t** graphs show that the trans-esterification of *Balanites aegyptiaca* oil obeyed the second-order rate law. Darnoko *et al*. (2000) had carried out the kinetics of trans-esterification of palm oil and has reported that the conversion of triglycerides (TG) appeared to be second order up to 30 min of reaction time.

4.6 Determination of the rate constants for the second order kinetics for the production of biodiesel at temperatures of 25°C, 30°C and 40°C

From the straight line graphs of $\mathbf{V_{BD}^{*-1}}$ vs **t** for temperatures of 25°C, 30°C and 40°C in figure 6, the rate constants were determined by taking the slopes of the straight lines (by least square method). The values are presented on table 16. The rate constant of a reaction is known to change when there is a change in temperature. The rate constants k_1 and k_2 that were obtained for the separate experimental situations in

sections 4.5.1.1 and 4.5.1.2 at 30°C seem to have the following relationship with the rate constant, *k* for the overall reaction at 30°C. k_1 = 0.2533ml/min; k_2 = 0.0707ml/min; k = 0.017239 ml/min.

$$k = (k_2/ k_1)^3$$

$$0.017239 = (0.0707/0.2533)^3$$

$$0.017239 = 0.021744$$

By rounding to two decimal places we have

$$0.02 = 0.02$$

Hence, *k* is the ratio of *(k_2 to k_1)* raised to the power of three.

T-1	ln(k)
0.003356	-4.25
0.0033	-4.117
0.003194	-3.68

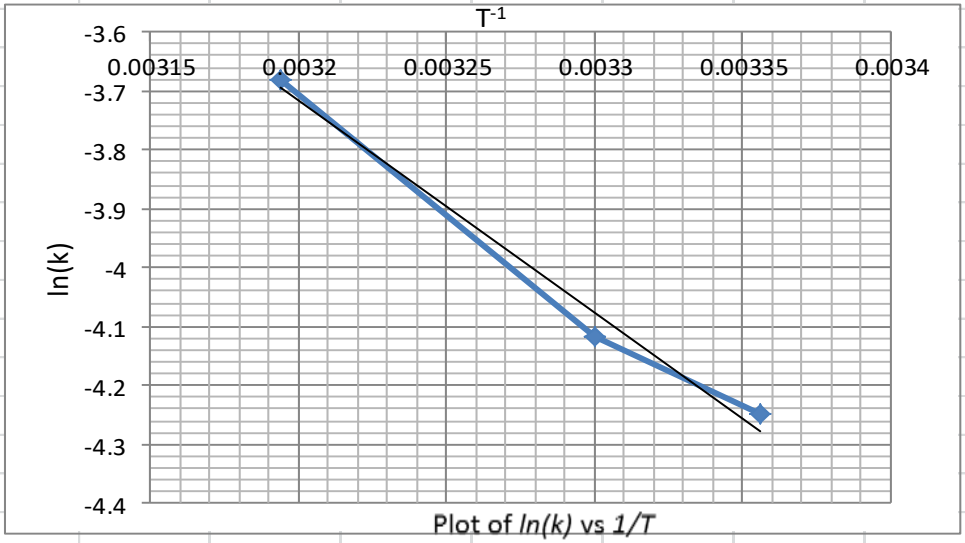


Figure 7: Plot of logarithm of rate constant, *ln(k)* against inverse of temperature, *1/T*

4.7 Determination of thermodynamic parameters for the trans-esterification reaction for biodiesel production

In determining the parameters of enthalpy (heat) of reaction, ΔH, entropy ΔS, and Gibb's free energy of activation, ΔG of trans-esterification of *Balanites aegyptiaca* oil, Arrhenius equation was used.

$$k = Aexp(-E_a/RT) \ldots \quad \ldots \quad \ldots \quad (1)$$

where

k is the rate constant

A is the Arrhenius pre-factor whose value depends on the reactants, and

E_a is the activation energy of the reaction.

By taking the logarithm of both sides of the equation, it gives

$$ln(k) = -E_a/RT + ln(A) \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

This equation is linear when $ln(k)$ is plotted against 1/T. k was determined for the varying temperatures. The plot of $ln(k)$ *vs.* $1/T$ gave a straight line of slope, $m = -E_a/R$ and an intercept $b = ln(A)$.

The slope m, and the intercept b on the $ln(k)$ axis have been calculated using Least Square Method where

$$m = \frac{\sum_{i=1}^{n} (x_i - \overline{X})(y_i - \overline{Y})}{\sum_{i=1}^{n} (x_i - \overline{X})^2} = -3513\text{K}, \text{ and}$$

$$b = \overline{Y} - m\overline{X} = 7.5$$

The slope, m of the graph is $-E_a/R$ [From equation (2)]

$m = -3513\text{K} = -E_a/R$

$E_a = 3513\text{K} \times R = 3513\text{K} \times 8.314\text{Jmol}^{-1}\text{K}^{-1}$

$= 29207\ \text{Jmol}^{-1}$

This is the energy of activation E_a, which also is the Gibbs free energy, ΔG. The positive and high value of it shows that the energy barrier between the reactants and the products was great, such that it was practically impossible to transform vegetable oil and ethanol to biodiesel without a catalyst for the reaction. But the catalyst employed, being activated carbon from the shells of *Balanites aegyptiaca* kernel, was able to lower the activation energy, so that the reaction began and proceeded to equilibrium where $\Delta G = 0$.

The intercept $b = ln(A)$

$= 7.5$

$A = e^{7.5} = 1808$

A is Arrhenius factor a constant whose value depends on the reactants of a reaction. 1880 is the value of *A* when *Balanites aegyptiaca* oil reacted with methanol.

4.7.1 Determination of ΔH, entropy ΔS

To determine the ΔH and ΔS of the trans-esterification of *Balanites aegyptiaca* oil in biodiesel production the equation

$$\Delta G = \Delta G^o + RT \ln (k) \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

was used, where,

ΔG is Gibb's free energy at non-standard states, and

ΔG^o is Gibb's free energy at standard states.

R is the universal gas constant. It functions here as a constant that relates energy to temperature in a reaction.

Since trans-esterification is a reversible reaction, at equilibrium

$\Delta G = 0$

so $0 = \Delta G^o + RT \ln (k)$

$\Delta G^o = - RT \ln (k)$

But $\Delta G^o = \Delta H^o - T\Delta S^o$

Therefore, $\Delta H^o - T\Delta S^o = - RT \ln (k)$.

At non-standard states it becomes

$\Delta H - T\Delta S = - RT \ln (k)$

$$\ln (k) = \frac{-\Delta H + T\Delta S}{RT}$$

$$ln\,(k) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

Relating this equation to the graph of *ln(k)* vs *1/T* , $\frac{-\Delta H}{R}$ is the slope, *m* and $\frac{\Delta S}{R}$ is the intercept *b* on the *ln(k)* axis.

Therefore, $\frac{-\Delta H}{R} = m$

$= -3513K$

and $\Delta H = 3513K \times R = 3513K^{-1} \times 8.314Jmol^{-1}K^{-1}$

$= 29{,}207Jmol^{-1}$

This value of ΔH shows that the trans-esterification is an endothermic reaction. It drew heat from the surrounding.

The intercept, $b = \frac{\Delta S}{R}$. It is a constant that relates the change in entropy to the gas constant, giving.

$\Delta S = b \times R = 7.5 \times 8.314$
$= 62.4JK^{-1}$

This value of ΔS shows that the entropy increased by 62.4J per every rise in Kelvin during the trans-esterification.

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

Biodiesel was produced by trans-esterification of oil extracted from *Balanites aegyptiaca* seed. The reaction process was catalyzed by activated carbon which was generated from the fruit shell using carbonization by physical activation. In the course of the biodiesel production, the experimental values of temperature, time of stirring, volumes of reactants and products, concentration of catalyst, ratios of quantities of materials were monitored and recorded. The optimum values of the results obtained were used to determine the values of the kinetic and thermodynamic parameters governing the biodiesel production from the seed oil.

5.2 Conclusion

Biodiesel can be generated from the oil of *Balanites aegyptiaca* seed. Activated carbon from the shell of its fruit can serve as catalyst or co-catalyst. 30ml of methanol mixed with 0.3g of catalyst and 8.3ml of the oil and stirred for 15minutes at 30^{o}C yielded 28 ml of biodiesel. The generation of the biodiesel followed the partial first order kinetics for methanol and oil respectively, giving an overall second order for the process, with a rate constant of k = 0.017239ml/min at 30^{o}C. The activation energy of the process is E_a = 29,207Jmol^{-1}. The process is endothermic with ΔH = 29,207Jmol^{-1} and leads to increase in entropy with $\Delta S = 62.4 JK^{-1}$. The trans-esterification could not have been possible without the catalyst.

5.3 Recommendation

It is recommended that FTIR and MS of *Balanites aegyptiaca* oil be carried out to know the specific triglyceride component of it that reacts with methanol to form the biodiesel. It is also recommended that further research be carried out to find out the reaction order for the forward reaction of the trans-esterification and not finalize conclusion on the order of reaction obtained by mirror image of the process.

5.4 Contribution to knowledge

It has been established that the activated carbon from the shell of *Balanites aegyptiaca* is a catalyst for the trans-esterification of its oil to form biodiesel. The values of the kinetic and thermodynamic parameters for the trans-esterification specific for the production of biodiesel from *Balanites aegyptiaca* oil have been found. The values of the kinetic parameters can be

used to predict the extent of the reaction at any time under particular conditions. Those of the thermodynamic provide the energy consideration and the temperatures to be used.

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APPENDICES

Appendix I: Table for percentage yield (%) of catalyst produced by physical activation of *Balanites aegyptiaca* shell at varying temperatures

T (°C)	m_o (g)	m (g)	$\bar{m}$ (g)	Y_{ac} (%)
300	13.04	0.43		
	12.56	0.51	0.503	3.9
	13.20	0.57		
400	12.98	0.72		
	13.08	0.77	0.740	5.6
	13.01	0.73		
500	13.05	3.42		
	13.10	3.66	3.573	27.4
	12.97	3.64		
600	13.00	8.22		
	13.02	8.32	8.28	63.5
	13.08	8.30		
700	12.96	10.80		
	13.20	11.01	10.93	83.5
	13.12	10.93		
800	13.11	9.88		
	13.02	10.42	10.2	78.0
	13.10	10.30		
900	13.04	2.40		
	13.03	2.20	2.38	18.0
	13.00	2.54		
1000	13.03	0.40		
	13.10	0.37	0.34	2.6
	13.05	0.25		

Appendix II: Table for loss of moisture content of the catalyst with time

t (mins)	m (g)
0	13
10	11.6
20	11.2
30	11.0
40	10.8
50	10.8
60	10.7
70	10.7

Appendix III: Table for determination of percentage of free fatty acid in *Balanites aegyptiaca* oil

Titration / Vol. of KOH	1st	2nd	3rd
Final vol. (ml)	16.3	17.3	18.5
Initial vol. (ml)	15.1	16.3	17.4
Vol. added (ml)	1.2	1.0	1.1

Appendix IV: Table for volumes of biodiesel obtained using varying volumes of *Balanites aegyptiaca* oil with constant volume of methanol

Run	V-Oil (ml)	V-meOH (ml)	V-biodiesel (ml)
1	3.6	30	24
2	5	30	25.3
3	6.4	30	26
4	8.3	30	28
5	10	30	28
6	12	30	27.5

Appendix V: Table for effect of catalyst concentration and time of stirring on Biodiesel yield

Run	Cat	m-Cat (g)	V-meOH (ml)	V-Oil	T (°C)	t (mins)	V-biodiesel (ml)
1	CaO	0.1	30	8.3	30	30	25
2	CaO	0.1	30	8.3	30	20	24
3	CaO	0.1	30	8.3	30	15	24
4	CaO	0.3	30	8.3	30	30	29
5	CaO	0.3	30	8.3	30	20	30
6	CaO	0.3	30	8.3	30	15	30
7	CaO	0.5	30	8.3	30	30	24
8	CaO	0.5	30	8.3	30	20	23
9	CaO	0.5	30	8.3	30	15	24
10	C-act	0.1	30	8.3	30	30	26
11	C-act	0.1	30	8.3	30	20	26
12	C-act	0.1	30	8.3	30	15	24
13	C-act	0.3	30	8.3	30	30	28
14	C-act	0.3	30	8.3	30	20	29
15	C-act	0.3	30	8.3	30	15	28
16	C-act	0.5	30	8.3	30	30	24
17	C-act	0.5	30	8.3	30	20	23
18	C-act	0.5	30	8.3	30	15	23
19	C-act/CaO	0.1	30	8.3	30	30	25
20	C-act/CaO	0.1	30	8.3	30	20	26
21	C-act/CaO	0.1	30	8.3	30	15	24
22	C-act/CaO	0.3	30	8.3	30	30	28
23	C-act/CaO	0.3	30	8.3	30	20	29
24	C-act/CaO	0.3	30	8.3	30	15	28
25	C-act/CaO	0.5	30	8.3	30	30	23
26	C-act/CaO	0.5	30	8.3	30	20	23
27	C-act/CaO	0.5	30	8.3	30	15	24

Appendix VI: Table for effect of temperature on Biodiesel yield

Run	Cat	m-Cat(g)	V-meOH (ml)	V-Oil	T (°C)	t (mins)	V-biodiesel (ml)
1	C-act	0.3	30	8.3	25	30	23
2	C-act	0.3	30	8.3	30	30	29
3	C-act	0.3	30	8.3	35	30	32
4	C-act	0.3	30	8.3	40	30	33 (cloudy)
5	C-act	0.3	30	8.3	45	30	33 (cloudy)
6	C-act/CaO	0.3	30	8.3	25	30	22
7	C-act/CaO	0.3	30	8.3	30	30	30
8	C-act/CaO	0.3	30	8.3	35	30	31
9	C-act/CaO	0.3	30	8.3	40	20	32 (cloudy)
10	C-act/CaO	0.3	30	8.3	45	15	33 (cloudy)

Appendix VII: Table for effect of mole ratio of alcohol to vegetable oil on Biodiesel yield

Run	Cat	m-Cat (g)	V-meOH (ml)	V-oil	T (°C)	t (mins)	V-biodiesel (ml)
1	C-act	0.3	30	5.0	30	15	25
2	C-act	0.3	30	6.4	30	15	26
3	C-act	0.3	30	8.3	30	15	29
4	C-act	0.3	30	10.0	30	15	28
5	C-act	0.3	30	15.0	30	15	28
6	C-act	0.3	30	20.0	30	15	28
7	C-act	0.3	10	8.3	30	15	14
8	C-act	0.3	15	8.3	30	15	16
9	C-act	0.3	20	8.3	30	15	21
10	C-act	0.3	25	8.3	30	15	26
11	C-act	0.3	30	8.3	30	15	29
12	C-act/CaO	0.3	30	5.0	30	15	22
13	C-act/CaO	0.3	30	6.4	30	15	24
14	C-act/CaO	0.3	30	8.3	30	15	29
15	C-act/CaO	0.3	30	10.0	30	15	29
16	C-act/CaO	0.3	30	15.0	30	15	29
17	C-act/CaO	0.3	30	20.0	30	15	29
18	C-act/CaO	0.3	10	8.3	30	15	15
19	C-act/CaO	0.3	15	8.3	30	15	15
20	C-act/CaO	0.3	20	8.3	30	15	21
21	C-act/CaO	0.3	25	8.3	30	15	26
22	C-act/CaO	0.3	30	8.3	30	15	30

Appendix VIII: Table for volumes of biodiesel, $\mathbf{V_{BD}}$ obtained in different runs at T = 30°C with varying volumes of vegetable oil, $\mathbf{V_{TG}}$ and excess volumes of methanol using the ultimate time

Run	V_{TG} ((ml)	V_{MeOH} (ml)	V_{BD} (ml)	t (min)
1.	5	30	19	15
2.	6.4	30	24.3	15
3.	8	30	30.4	15
4.	10	40	43	17
5.	12	45	55	18
6.	14	50	58	20

Appendix IX: Table for volumes of biodiesel, $\mathbf{V_{BD}}$ obtained in different runs at T = 30°C with excess volume of vegetable oil $\mathbf{V_{TG}}$ and varying volumes of methanol using the ultimate time

Run	V_{TG} (ml)	V_{MeOH} (ml)	V_{BD} (ml)	t (min)
7.	10	15	16	16
8.	10	20	21	16
9.	10	25	25	16
10.	10	30	32	17
11.	10	33	35	16
12.	10	35	37	16
13.	10	37	39	17
14.	10	40	43	17

Appendix X: Table for volume of biodiesel $\mathbf{V_{BD}}$ generated at varying time, **t** and temperature **T** = 25^{o}C for the forward reaction

t (min)	$\mathbf{V_{BD}}$ **(ml)**	$\mathbf{V_{BD}^{-1}}$
0	0	0.0
2	0.3	0.1540
5	15.8	0.05714
8	21.2	0.04484
10	23	0.04167
12	24.2	0.04032
15	25.3	0.03846

Appendix XI: Table for volume of biodiesel V_{BD}* generated at varying time, **t** and temperature **T** = 25^{o}C for the backward reaction (obtained by mirror-imaging)

t (min)	V_{BD}* (ml)	V_{BD}^{*-1}
0	-	-
2	35.7	0.028
5	14.2	0.071
8	8.8	0.114
10	7.0	0.142
12	5.8	0.171
15	4.7	0.214

Appendix XII: Table for volume of biodiesel $\mathbf{V_{BD}}$ generated at varying time, **t** and temperature **T** = 30°C for the forward reaction

t (min)	$\mathbf{V_{BD}}$ **(ml)**	$\mathbf{V_{BD}^{-1}}$
0	0	0.0
2	14	0.071
5	20	0.050
8	24	0.042
10	25	0.04
12	25.8	0.039
15	26.3	0.037

Appendix XIII: Table for volume of biodiesel V_{BD}^* generated at varying time, **t** and temperature **T** = 30°C for the backward reaction

t (min)	V_{BD}^* (ml)	V_{BD}^{*-1}
0	30	0.03
2	16	0.0625
5	10	0.1
8	6	0.166
10	5	0.2
12	4.2	0.25
15	3.6	0.275

Appendix XIV: Table for volume of biodiesel $\mathbf{V_{BD}}$ generated at varying time, **t** and temperature **T** = 40°C for the forward reaction

t (min)	$\mathbf{V_{BD}}$ **(ml)**	$\mathbf{V_{BD}^{-1}}$
0	0.00	0.0000
2	17.5	0.0571
5	23.5	0.0426
8	25.7	0.0389
10	26.4	0.0379
12	27.0	0.0370

Appendix XV: Table for volume of biodiesel V_{BD}^* generated at varying time, **t** and temperature **T** = 40°C for the backward reaction

t (min)	V_{BD}^* (ml)	V_{BD}^{*-1}
0	30.3	0.03
2	12.5	0.08
5	6.5	0.155
8	4.3	0.23
10	3.6	0.28
12	3	0.33

Appendix XVI: Table for rate constants, *k* for the production of biodiesel at temperatures T = 25°C (298K), 30°C (303K) and 40°C (313K).

k	**T (K)**	**ln(k)**	**T^{-1}**
0.014272	298	-4.250	0.0033557
0.017239	303	-4.117	0.0033003
0.025	313	-3.689	0.0031944