EVALUATION OF THE BIOFUEL PROPERTIES OF THE METHYL, ETHYL ESTERS AND ESTER/DIESEL BLENDS OF THREE SEEDS OILS.

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CERTIFICATION

I, **ANEKWE, OZIOMA JULIANA** hereby certify that this dissertation was written by me. The work embodied in this dissertation is original and to the best of my knowledge has not been submitted in part or full to this university or any other institution for the award of a degree or diploma.

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APPROVAL PAGE

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DEDICATION

This work is dedicated to Almighty God and My children Frances, Marie, Andrea and Pio-Mario.

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ABSTRACT

The depletion and price fluctuations of fossil fuel in the international market have been a major source of concern in total dependence on diesel fuel hence use of biodiesel produced from vegetable oil is a good substitute or additive fuel. Studies were carried out to investigate the fuel properties of *Cyperus esculentus*, *Colocynthus vulgaris*, *Sesamum indicum* ethylesters, methylesters and their corresponding methyl/ethyl ester blends. Ethylesters and methylesters of these oils were prepared by H_2SO_4 catalyzed transesterification reaction between the oils and ethanol/methanol. The fuel properties such as kinematic viscosity, flash points, pour point and water crackle were determined using ASTM methods. GC-MS was used to determine the fatty acid profile of the transesterified oils. Fourier Transform Infra Red (FTIR) was used to identify the chemical bond functional groups on all the biodiesel, their blends and petrodiesel was carried out at different temperatures 28^oC, 100^oC, 150^oC and 200^oC to determine the bond stability. The heavy metal present in the samples were analyzed using atomic absorption spectrometer and flame absorption spectrometry. The kinetics of transesterification was tested using zero order, 1st order and second order kinetic models on the methyl/ethyl esters. Engine emission / performance tests were carried out on a TECHNO R175A diesel engine. Pearson correlation was used to measure the linear relationship between the biofuel properties and fatty acid variables of the biofuel samples. It was observed that the density of most of the ethyl/methyl esters and their blends were higher than that of the petrodiesel, this is as a result of the fatty acid composition and molecular weight of the oil and the biodiesel. The flash points and pour points of all the samples were within ASTM limits. The FFA results showed that the oils were rich in saturated fatty acids (66.67%), appreciable value of monounsaturated fatty acids (33.33%) and (33.33%) polyunsaturated fatty acids. The fatty acid chain lengths that were predominant in *Cyperus esculentus*, *Colocynthus vulgaris*, *Sesamum indicum* were C16, C17, C18 and C20 for the ethylesters while those in the methylesters were C16, C17, C18, C19 and C21. From the FTIR results, it was observed that the wavenumbers slightly increased with increase in temperature which showed that the esters, ester blends and the petrodiesel were thermally stable at those temperatures and had good resistance to thermal degradation and polymerisation. The heavy metal compositions of the esters were lower than that of the corresponding oils which showed that the esters were purified during the esterification process. The optimum temperature for the ethylation and methylation of the samples was 40^oC except for *Cyperus esculentus* methyl ester and *Colocynthus vulgaris* ethyl ester that had 70^oC as the optimum temperature. The values of correlation coefficients R^2 obtained from trend line indicated that the experimental data in this study fitted well with the pseudo second order kinetic model. The engine emission / performance tests carried out showed that the biofuels and the oils could power a TECHNO R175A diesel engine used for the test and the fumes from the biofuels were less acidic than the hydrocarbon diesel hence more environmentally friendly. It was observed from the pearson correlation that %MUFAs had strong correlations with pour point and relative density r = 0.984 and 0.885 respectively. The kinematic viscosities at various temperatures had very strong correlations between each other, the viscosity at 70^0C had strong correlations with the viscosity at 100^0C (r=0.970), Weak correlations was also observed between %PUFAs and pour point, %MUFAs and viscosities at different temperatures. Transeserification of these vegetable oils enhanced the fuel properties of the oils and these esterified oils can be better alternatives to fossil diesel.

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CHAPTER ONE

INTRODUCTION

1.1 Background of study

Escalation of crude oil prices and environmental awareness has increased interest in the use of renewable fuel sources. One area of attention is the upgrading of vegetable oils for use as a fuel or fuel additive. Besides being a renewable source, the use of vegetable oils has benefits economically and environmentally. The possibility also exists for the reuse of current vegetable oil wastes such as wastes from fast food restaurants. Since the world's accessible oil reservoirs are gradually depleting, it is important to develop suitable long-term strategies based on utilization of renewable fuel that would gradually substitute the declining fossil fuel production. In addition, the production and consumption of fossil fuels have caused the environmental damage by increasing the CO_2 concentration in the atmosphere (Westermann *et al*., 2007).

The overdependence on crude oil for energy sources and the future fear that the continuous use of fossil fuel would soon be depleted with no possibilities of being replenished easily pose a negative impact to the many economy (Footprint to Africa.,2017**)**. This has called for more research on renewable energy sources which can replace fossil fuel and may even at present be a substitute to the available energy sources. The need to protect the environment has also influenced the search for a sustainable alternative energy source that would be more environmental friendly. Research, development and industrialization of renewable energy are currently moving at a rapid pace worldwide. Biofuel play significant roles in our future energy needs and act to mitigate deleterious impact of greenhouse gas emissions. National government obligations and international directives are mandating the blending of biofuels in petrol (gasoline) and diesel and these are acting as great stimuli to the industrial sector (Walker., 2010, Altin *et al.*, 2001) showed that vegetable oil methyl esters gave performance and emission characteristics close to petroleum diesel. The main problems associated with the increased use of this fuel are the costs of the oil and its processing. Also, the marketing of this product is limited to diesel engine applications.

It is common knowledge that vegetable oils can be cracked into lighter fuel fractions by the use of catalysts. There is however a number of problems associated with this process with cost being one of the major ones. (Altin *et al.,* 2001) noted that at present vegetable oils are more expensive than diesel fuels.

Another problem with the use of vegetable oils for conversion to fuels is that the composition of such oils varies drastically between types. This means that a particular set of reaction conditions and catalyst type will give different products according to the starting oil.

Biodiesel refers to any diesel-equivalent biofuel made from renewable biological materials such as vegetable oils or animal fats consisting of long-chain saturated hydrocarbons. (Pinto *et al.*, 2005). It can be used in pure form (B100) or may be blended with petrodiesel at any concentration. Biodiesel made from crops such as corn and soybeans is one such alternative that most people are aware of.

Biodiesel is formed through a chemical process called “transesterification” that occurs when an alcohol (such as methanol or ethanol) is added to the plant oil together with an alkaline reactant such as caustic soda (sodium hydroxide) or potassium hydroxide – this acts as a catalyst. The glyceride molecule is “cracked” and replaced with an alcohol molecule, forming an alkaline ester chain.

The need for alternative fuel, which can solve the problems of finite nature of fossil fuels and their environmental concerns, is imperative. About 98% of carbon emissions result from fossil fuel combustion (Balat, 2010). The continued and increasing use of diesel derived from fossil oil intensifies air pollution and magnifies the global warming problem caused by CO_2 and other particulate matters (Shay, 1993). Biodiesel, which is renewable in nature, non-toxic, and environmentally friendly with higher cetane number than diesel, is the most promising candidate. It can be defined as the alkyl esters of long-chain fatty acids derived from renewable feedstock like vegetable oils or animal fats, obtained by transesterifying oil or fat with an alcohol (Knothe, 2010). Despite the food versus fuel challenge facing the world, both edible and non-edible vegetable oil have been successfully used to produce biodiesel with superior qualities to diesel.

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fats. “Bio” represents its renewable and biological source in contrast to traditional petroleum-based diesel fuel; “diesel” refers to its use in diesel engines (Zhang *et al*., 2003).The most common method to produce biodiesel is through a process called “transesterification”, which involves altering the chemical properties of the oil by using alcohol. Transesterification of plant oils with methanol is a relatively simple process that yields high conversion with only glycerin as a byproduct (Shawn, 2006). In continuation for search for better alternative biofuel feedstock, the oil seeds *Cyperus esculentus L., Colocynthus vulgaris and Sesamum indicum* seed oils have been chosen for this research.

1.2 Statement of problem

The unpredictable price fluctuations of crude oil in the international market have been a major source of concern in total dependence on diesel fuel.

All countries including Nigeria are grappling with the problem of meeting the ever increasing demand of transport fuel within the constraints of international commitments, environmental concerns regarding the emissions responsible for climate change**,** alongside other harmful substances such as SO_X, NO_X and methane released during fossil fuel combustion. The growth in energy demand in all form is expected to continue unabated owing to increasing urbanization, standard of living and expanding population. The increasing gap between the demand and production of petroleum based energy resource is a matter of serious concern. The depletion of the world's petroleum deposit and the attendant pollution caused by combustion of these non renewable energy sources has necessitated the need for an alternative source of energy (Petchmala *et al*., 2008).

Hence there need to diversify sources of fuel and solve energy security problem created by increasing demand, depletion of fossil fuels and also create a positive impact on the environment. Hence, biodiesel produced from vegetable oil is a good substitute or additive fuel and can also extend the longevity of the use of diesel.

Variation in quality of biodiesel as biodiesel is made from variety of vegetable oil crops. There are little or no information on the fuel properties and kinetics paramaters of transeterification reactions of these vegetable oil seeds and the performance of these vegetable oil crops for their utilisation.

The economic values of these vegetable crops used for biodiesel production will increase through their utilisation for biodiesel production.

1.3 Aim and objectives of the study

The aim of this research is to determine the biofuel properties of the oils, methyl, ethyl esters and ester/diesel blends of the oils from *Cyperus esculentus L., Colocynthus vulgaris and Sesamum indicum L.* seeds with a view of utilising them in diesel engines for reduction of emission of air pollutant gases.

The objectives of the study include to:

1. Extract oils from the oil seeds (*Cyperus esculentus L., Colocynthus vulgaris and Sesamum indicum L.)*
2. Prepare methyl and ethyl esters of the three seed oils
3. Blend the oil esters with fossil diesel
4. Determine the biodiesel properties of the oils, methyl, ethyl esters and ester/diesel blends and diesel using American society of testing materials standards methods.
5. Determine the kinetic parameters and their effects on transesterification of the oils.
6. Demonstrate the usuability of the biodiesels and their diesel blends in diesel engine.
7. Evaluate the emission reduction ability of the biodiesels/blends in comparison to petroleum diesel.
8. Determine the heavy metals using atomic absorption spectroscopy
9. Determine the fatty acids profile of the esters using gas chromatography-mass spectroscopy (GC-MS).

10. Determine the bond structure and stability of the esters and esters/diesel blends in comparison with petroleum diesel at different temperatures (28 - 200^{0}C) using Fourier Transform Infrared spectroscopy (FTIR).

1.4 Scope of the study

The study covered the following:

Selection of seed, Oil extraction from the oil seeds (*Cyperus esculentus L.*, *Colocynthus vulgaris and Sesamum indicum L.)*, physicochemical characterization of the extracted oil and their esters (methyl and ethyl), Verification of kinetic parameters on the transesterified oil samples and determination of the rate of reactions, order of reactions, rate constants and activation energies from the results of kinetic analyses. Preparation of esters (methyl and ethyl esters) and their esters/diesel blends, determination of fuel properties of the oil, methyl/ethyl esters and the biodiesel blends in comparison with petroleum diesel, comparison of produced biodiesel with American society of testing and materials standards. Investigation of engine performance and engine emission reduction effect of the fuel samples in a diesel engine, heavy metal composition analyses using atomic absorption spectrophotometer, determination of fatty acids profile of the esters by gas chromatography-mass spectroscopy (GC-MS) and Fourier Transform Infrared spectroscopy (FTIR) analysis of the esters and esters/diesel blends in comparison with petroleum diesel at different temperatures (28 - 200^{0}C).

Justification for the study

This research will provide knowledge and solution in developing alternative fuel from the three seed oils as an alternative to combustion of hydrocarbon fuel that contribute to more than half of all greenhouse emissions.

The research will provide information on the optimal conditions for biodiesel production from *Cyperus esculentus L., Colocynthus vulgaris and Sesamum indicum L.* seeds oils.

The results obtained at the end of this research, will offer more valuable insight into production process of biodiesel from the three seed oils.

The research will also create reliable correlations of the fuel properties of the feedstock for optimal blending.

The social and economic values of *Cyperus esculentus L., Colocynthus vulgaris and Sesamum indicum L.* seeds will increase through their utilization for biodiesel production.

CHAPTER TWO

LITERATURE REVIEW

Transesterification reactions have been studied for many vegetable oils such as soybean, rapeseed, palm, cotton seed, canola, coconut seed, olive, peanut oil etc. (Cervero *et al.*, 2008; Kubamarawa *et al.,* 2007; May *et al* 2005; Ajiwe *et al.,* 2001; Ajiwe *et al.,* 2006; Ezekwe and Ajiwe, 2011). Biodiesel production from soybean oil is very popular. It has five fatty acids: approximately equal amount of palmitic acid, oleic acid and linolenic acid (about 13% each). Linoleic acid (approximately 55%) and stearic acid (approximately 4%). A useful industrial application of soybean oil is in biodiesel blends. Biodiesel from Soybean oil possess enhanced biodegradation, increased flash point, reduced toxicity, lower emissions and increased lubricity. (Kinney and Clemente, 2005). Vegetable oils have long been promoted as possible alternatives for mineral Diesel. In fact, Rudolph Diesel, the inventor of the Diesel engine, used peanut oil as the fuel for its demonstration at the 1900 world exhibition in Paris and said, The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time (Shailendra *et al*., 2008).

Sendžikienė *et al*., (2011) reported that *Cyperus esculentus* seeds have potential for the production of biodiesel fuel, since the seeds contain not only a significant amount of oil (28.1 %), the fatty acid methyl esters of *Cyperus esculentus* oil meet the equirements of the Standard that defines biodiesel fuel quality, except for the cold filter plugging point, which is only +1.4 ^{o}C. The cold filter plugging point of fatty acid methyl esters produced from *Cyperus esculentus* oil can be reduced to -5.5 °C by adding 1250 ppm of the depressant Wintron XC-30 or 1800 ppm of Infineum R-442. In Lithuania, such a product can be used as fuel during the summer period. Methanolysis of a related species of *colocynthus vulgaris* Muskmelon (*Cucumis melo*) seed oil by Umer *et al.,* (2011) found that *Cucumis melo* gave yield 89.5% of the methyl esters at the following reaction conditions; 5.8:1 methanol-to-oil ratio, 0.79% catalyst concentration, 55 °C reaction temperature and 72.5-min reaction time. The biodiesel was analyzed using GC/MS (gas chromatography/mass spectrometry) which indicated four FAMEs (fatty acid methyl esters) (linoleic-, oleic-, palmitic- and stearic acids) as its major components. In this current study the fatty acid present in *colocynthus vulgaris* were (palmitic acid, linoleic acid, stearic acid) in the methyl ester and (linoleic acid and stearic acid) in the ethyl esters, they optimum catalyst concentration was 10ml for both methyl and ethyl esters, 40^{o}C and 70^{o}C reaction temperature respectively for methyl and ethyl esters and 40 and 60 min reaction time respectively for its ethyl and methyl esers, In a study, sesame *(Sesamum indicum L.*) seed was investigated as an alternative feedstock for the production of a biodiesel fuel. The methylester of sesame (*Sesamum indicum L.*) seed oil was prepared by transesterification of the crude oil. Transesterification showed improvement in fuel properties of sesame seed oil. This study supports the production of biodiesel from sesame seed oil as a viable alternative to the diesel fuel (Abdurrahman *et al*., 2008). Various esters ranging from methyl, ethyl, propyl to butyl esters have been produced from the oils using different reaction conditions. (Ogbu and Ajiwe, 2013).

2.1 Facts on vegetable seeds used for the research

2.1.1 *Cyperus esculentus*

Cyperus esculentus is commonly known as earth almond, tiger nut, chufa, yellow nutsedge and zulu nuts. It is known in Nigeria as Aya in Hausa, Ofio in Yoruba and Akihausa in Ibo where three varieties (black, brown and yellow) are cultivated (Umerie *et al*., 1997). Among these, only two varieties, yellow and brown are readily available in the market. The yellow variety is preferred to all other varieties because of its inherent properties like its bigger size, attractive colour and fleshier body (Belewu and Abodurin, 2006).

Plate 2.1: Picture of *Cyperus esculentus* seeds

Tiger nut (Plate 2.1) can be eaten raw, roasted, dried baked or be made into a refreshing beverage called tiger nut milk (Oladele and Aina, 2007). In addition, it can be used as a flavoring agent for ice cream and biscuits (Cantalejo, 1997).

The investigation (Oladele and Aina, 2007) was carried out to determine the proximate composition, vitamin concentration, elemental concentration as well as the physicochemical properties of the Nigerian tiger nut tuber variety and its oil in order to augment the available information on tiger nut research.

The globoid rhizomes of *C. esculentus* are used by the rural population of Ceará in the northeastern of Brazil as an aphrodisiac and antivenin. They are also used in Brazil for the treatment of measles and fever, but generally as a dessert for its sweet flavor (De-Abreu *et al*., 2008). Tiger nut has been reported to be high in dietary fiber content (Alegría-Torian and Farré-Rovira, 2003), which could be effective in the treatment and prevention of many diseases including colon cancer (*Adejuyitan* et *al*., 2011), coronary heart disease (Chukwuma *et al.*, 2010), obesity, diabetes, gastrointestinal disorders (Anderson *et al* ., 2009), and in losing weight (Borges *et al.*, 2008).

Tiger nut has been demonstrated to be a rich source of good-quality oil (Dubois *et al*., 2007., Yeboah *et al*., 2011) and contains a moderate amount of protein (Oladele and Aina, 2007). It is also a source of some useful minerals such as potassium, phosphorus, and calcium (Bixquert-Jiménez, 2003) as well as vitamins E and C (Belewu and Belewu, 2007).

Tiger nut “milk” has been reported to be used in the treatment of flatulence, indigestion, diarrhea, and dysentery (Bixquert-Jiménez, 2003), and its starch content presumably provides prebiotic properties for colon bacteria (Alegría-Torán and Farré-Rovira, 2003). In addition, tiger nut has been demonstrated to contain higher essential amino acids than those proposed in a protein standard by the FAO/WHO for satisfying adult needs (Bosch *et al* ., 2005).

Tiger nut milk has been found to be good for preventing arteriosclerosis, since its consumption can help prevent heart problems and thrombosis and activate blood circulation (Chukwuma *et al*., 2010), mainly because its unsaturated fatty acid content is similar to that of olive oil (Linssen, 1989) and its arginine is a precursor of nitric oxide which helps the veins to expand (Martínez-Valls, 2003). Tiger nut milk or “horchata” can be drunk by diabetics for its content in low-glycemic carbohydrates (mainly starch) and due to its arginine which liberates hormones that produce insulin (Alegría-Torán and Farré-Rovira, 2003). Tiger nut milk is also a suitable drink for celiac patients, who are not able to tolerate gluten and also for the lactose-intolerant who stay away from cow milk and many dairy foods. It could also be recommended for those who have problems with digestion, flatulence, and diarrhea because it provides some digestive enzymes like catalase, lipase, and amylase (Bixquert-Jiménez, 2003; Adejuyitan, 2011).

2.1.2 *Colocynthus vulgaris*

Taxonomy

KINGDOM	Plantae
PHYLUM	Magnoliophyta Cronquist
CLASS	Magnoliopsida
ORDER	Cucurbitales
FAMILY	Cucurbitaceae.
GENUS	Citrullus.

Plate 2.2: Picture of *Colocynthus vulgaris* seeds

Colocynthus vulgaris (Plate 2.2) a relative of watermelon, egusi is native to tropical Africa and India and highly drought tolerant is a non hardy. Annual or perennial (in wild) herbaceous vine; stems angular and rough; leaves rough, are angular 3- to 7-lobed, 5-10 cm long, middle lobe sometimes ovate, sinuses open; The flowers are yellow, long-peduncled, and solitary in the axils of the leaves. They are monecious, the stamens and pistils being borne in different flowers on the same plant. Each has a yellow campanulate, five-lobed corolla and a five-parted calyx. The female flowers are readily distinguished by a globose, hairy, inferior ovary; fruit a pepo, nearly globular, 4-10 cm in diameter with somewhat elliptical fissures, about size of small orange, green and yellow variegated becoming yellow when ripe, with hard rind, pulp light in weight, spongy, easily broken, light yellowish-orange to pale yellow; intensely bitter; seeds numerous, ovoid, compressed, smooth, dark brown to light yellowish-orange, borne on parietal placenta. It is filled with a soft, white pulp, in which are imbedded numerous seed .This pulp is the article used in medicine. The colocynth plant is a native of arid soils. It has a large, fleshy perennial root, which sends out slender, tough, angular, scabrid vine-like stems. These usually lie on the ground for want of something to climb over, but which, if opportunity present, climb over shrubs and herbs by means of axiliary branching tendrils.

Distribution

Cultivated and naturalized in North Africa and India. The colocynth plant occupies the vast area extending from the west coast of northern Africa (Senegambia, Morocco and the Cape Verde islands), eastward through the Sahara, Egypt, Arabia, Persia, Beluchistan and through India, as far as the Coromandel coast and Ceylon, touching northward the Mediterranean and Caspian seas. At the Red sea, near Kosseir, it occurs in immense quantities. It is also found here and there in southern European countries, e. g., Spain and the islands of the Grecian archipelago. Cultivation on a small scale in the island of Cyprus the raising of colocynth has been a source of revenue since the fourteenth century, and still forms an article of export at the present time.

2.1.3 *Sesamum indicum*.

Sesame (*Sesamum indicum* L.) from Pedaliaceae, is an important oil seed crop being cultivated in the tropics and the temperate zone of the world (Biabani and Pakniyat, 2008). It is one of the oldest oil crops and is widely cultivated in Asia and Africa (Ali *et al*., 2007). It was a highly prized oil crop of Babylon and Assyria at least 4000 years ago (Ross, 2005). Sesame oil, otherwise also referred to as gingelly oil, is one of the major sources of edible oil in India and is culturally associated from the Vedic period. The Sanskrit word for oil, taila is derived from the Sanskrit word for sesame tila (Shanthasheela *et al*., 2007). It is called "sesame" internationally, while it is called "benniseed" in West Africa; "simsim" in East Africa and "Till" in India. Within Nigeria it is called different names in different localities.

Plate 2.3: Picture of *Sesamum indicum* seeds

Sesamum indicum L. (Plate 2.3) is generally called "ridi" in the Northern States. The Igalas, Idomas and Tivs of Benue State call it Igogo, Ocha and Ishwa respectively. The Ibos call it "isasa" and Yorubas call it "Ekuku" or "Eeku" in parts of Ogun, Ondo and Oyo states and Ilorin in Kwara State (Aboje, 2011). Natural sesame oil derived from good quality seed has a very pleasant flavour and can be consumed without further purification. The natural oil has excellent stability due to the presence of high levels of natural antioxidants (Lyon, 1972). The oil is used widely in the some injectable drug formulations. The lignans such as sesamin, episesamin, sesaminol and sesamolin are major constituents of sesame oil and all have chemically methylenedioxyphenyl group (Gokbulut, 2010). It ranks ninth among the top thirteen oilseed crops which make up 90% of the world production of edible oil (Adeola *et al*., 2010).

The oil is also useful in the industrial preparation of perfumery, cosmetics (skin conditioning agents and moisturizers, hair preparations, bath oils, hand products and make-up), pharmaceuticals (vehicle for drug delivery), insecticides and paints and varnishes (Chemonics International Inc., 2002). Sesame seed has higher oil content(around 50%) than most of the known oil seeds (Hwang, 2005). The seed has 40-60 per cent of oil with almost equal levels of oleic (range 33-50%, typically 41%) and linoleic acids (range 33-50%, typically 43%) and some palmitic acid (range 7-12%, typically 9%) and stearic acid (range 3-6%, typically 6%) (Gunstone, 2004). *Sesamum indicum* L. oil can be classified in the oleic- linoleic acid group. The dominant saturated acids were palmitic (up to 8.58%) and stearic (up to 5.44%) (Nzikou *et al*., 2009).

2.2 Sources of Raw Material for Biodiesel Production

The choice of the kind of fat or oil used for the production of biodiesel is both a process chemistry decision and an economic decision. The former depends on the amount of free fatty acids that are associated with triglycerides, which varies among the choices of fats and oils. Also, the contaminants present in the different feedstocks can influence the extent of preparation necessary to carry out a particular chemical reaction (Alumudena, 2007).

2.3 Important Raw Materials For Biodiesel Production

2.3.1 Vegetable oils: Vegetable oils also known as triglycerides are predominantly made up of triacylglycerols with a small amount of minor compounds (2-5%) (Cert *et al*., 2000).

Triacylglycerols are made up of one glycerol molecule joined to three molecules of fatty acids by an ester link and contain substantial amounts of oxygen in their structure.

Among the vegetable oil sources are rapeseed oil, palm oil, sunflower oil, coconut oil, soybean oil, etc. Besides being the raw material for biodiesel production, those vegetable oils are mainly utilized for production of cooking oil and food purpose.

The type and concentration of fatty acid varies considerably from one vegetable oil to another. Hence, it is important to be aware of the composition of the vegetable oil used for the choice of the catalyst, as it will determine the type of reactions that are probable. The four major vegetable oils produced today are palm oil, soybean oil, sunflower oil and rapeseed oil. The production of palm oil has increased at a great rate over the past 5 years. This has led to a decrease in prices with the Malaysian average palm oil prices in 1999-2000 falling to $314 per metric tonne a decrease of around 35% from 1998-1999 (Guzman, 2001). This reduction in price and high availability makes it ideal as a fuel source. It produces two types of oil, one from the flesh (palm oil) and another from the kernel (palm kernel oil) of the fruit. The main use of soybean is the protein rich meal obtained after extraction of the oil, because of qualities such as relatively homogeneous composition, high degree of refinement, freedom from contaminants and also biodegradability. This is evidenced by the relatively large number of studies that have used canola oil, a modified rapeseed oil, to investigate cracking reactions.

Unmodified rapeseed oil is high in erucic, oleic and linoleic acid. The composition varies greatly among plant variety with some oil products being high in the saturated lauric acid. It is mainly produced in northern Europe, China, India and Canada.

Australia has recently increased its production with estimates of about 300,000 tonne now achieved annually (Department of Natural Resources and Environment, 2001).

Different types of vegetable oils have different types of fatty acids and they also differ in their acid values as summarized in Table 2.1 and Table 2.2.

Table 2.1: Composition of fatty acids in vegetable oils (%).

Fatty acid	Soyabean	Cotton seed	Palm	Coconut
Lauric	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	19.2
Palmitic	10.2	20.1	42.8	9.8
Stearic	3.7	2.6	4.5	3.0
Oleic	22.8	19.2	40.5	6.9
Linoleic	53.7	55.2	10.1	2.2
Linolenic	8.6	0.6	0.2	0.0

Source: Ampaitepin *et al*., 2006.

Table 2.2 Acid value of variety of oils (mg/g)

Vegetable oil	**Acid Value**
Corn	0.11
Cottonseed	0.07
Crambe	0.36
Peanut	0.20
Rapeseed	1.14
Soybean	0.20
Sunflower	0.15

Source: Ampaitepin *et al.*, 2006.

2.4 Animal fats

Animal Fats are by-product of the animal rendering process; it is one of the least expensive feedstock available for biodiesel production. They include beef tallow, lard, poultry fat, and fish oils. Animal fats are specially suited for the production of biodiesel in warm climate since the resulting product has poor cold-weather properties. Biodiesel from animal fats also has lower tailpipe NOx emissions than other biodiesel and is an attractive economic alternative for parts of animals that have been banned for human consumption, Nitrogen oxide (NOx) emission tests conducted with the animal fat-derived esters and compared with soybean oil biodiesel as 20 vol% blends (B20) in petroleum diesel. The data indicated that the three animal fat-based B20 fuels had lower NOx emission levels (3.2–6.2%) than did the soy-based B20 fuel (Wyatta *et al.*, 2005).

2.5 Used Cooking Oil or Waste Oil

Used cooking oil or waste oil collected from the household or restaurants is another raw material which is an effective way to reduce the raw material cost for biodiesel production. Since the major hindrance in terms of commercial use of biodiesel from vegetable oil is caused by the price of vegetable oil. It is reported that approximately 70-95% of total biodiesel production cost arises from the cost of raw material; that is, vegetable oil or animal fats. Used cooking oil as a raw material for biofuel production reduces the cost of raw material to about half the price of vegetable oil. Furthermore, it could also solve the problem of waste oil disposal.

In Japan, the amount of vegetable oil consumed in 1999 is estimated about 3 million-tonnes. 400 thousand-tonnes of oil have been discarded as waste. The half of this waste has been reused for fodder and paint etc., however, another 200 thousand-tonnes which did not appear in the statistic, may be burned with other waste or discard to nature. In year 2001, Japan for sustainable organization has reported the total amount of vegetable oil consumed in Japan was about 2.5 million-tonnes. Approximately 20 percent or 500 thousand-tonnes represents vegetable oil used in household, indicating that the annual per capita home consumption was about 4kilograms.

Additionally, around 0.45 million-tonnes of waste oil are generated from the 2.5 million-tonnes of vegetable oil consumed per year domestically or annual per capita output of waste vegetable oil is about 1.5 kilograms (Ampaitepin *et al*., 2006).

2.6 Algae

Algae are the most efficient biological producer of oil on the planet and a versatile biomass source and may soon be one of the Earth’s most important renewable fuel crops. (Chisti, 2007).

This is due to their higher photosynthetic efficiency, higher biomass productivities, a faster growth rate than higher plants. They equally have the highest CO_2 fixation and O_2 production, growing in liquid medium which can be handled easily, can be grown in variable climates and non-arable land including marginal areas unsuitable for agricultural purposes (e.g. desert and seashore lands), in non-potable water or even as a waste treatment purpose. Algae use far less water than traditional crops and do not displace food crop cultures. Their production is not seasonal and can be harvested daily. As a matter of fact, average biodiesel production yield from microalgae can be 10 to 20 times higher than the yield obtained from oleaginous seeds and/or vegetable oils (Chisti, 2007).

2.7 Methods of Biodiesel Production

Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of hydrocarbons-based diesel fuels. The problem with substituting triglycerides for diesel fuel is mostly associated with high viscosity, low volatility and polyunsaturated characters. These can be changed in at least four ways: dilution, pyrolysis, microemulsion, and transesterification (Singh and Singh, 2010).

2.7.1 Direct use and blending (dilution)

Beginning in 1980, there was considerable discussion regarding use of straight vegetable oil as a fuel. Caterpillar Brazil used pre – combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustment to the engine. At that point, it was not practical to substitute 100% vegetable oil but 80% diesel fuel was successful. Some short-term experiment used up to a 50/50 ratio (Gilbert and Perl, 2005).

Direct use of vegetable oil and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid contents as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems (Fanguri and Milford, 1999).

2.7.2 Thermal cracking (pyrolysis)

Pyrolysis, strictly defined, is the conversion of one substance into another by means of heat with the aid of a catalyst. It involves heat with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum (Fanguri and Milford, 1999).

The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Since World War 1, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. The mechanisms for the thermal decomposition of triglycerides are given in Fig. 2.1. The chemical compositions (heavy hydrocarbons) of the diesel fractions were similar to fossil fuels. The process was simple and effective compared with other cracking processes. There was no waste water or air pollution (Fanguri and Milford, 1999).

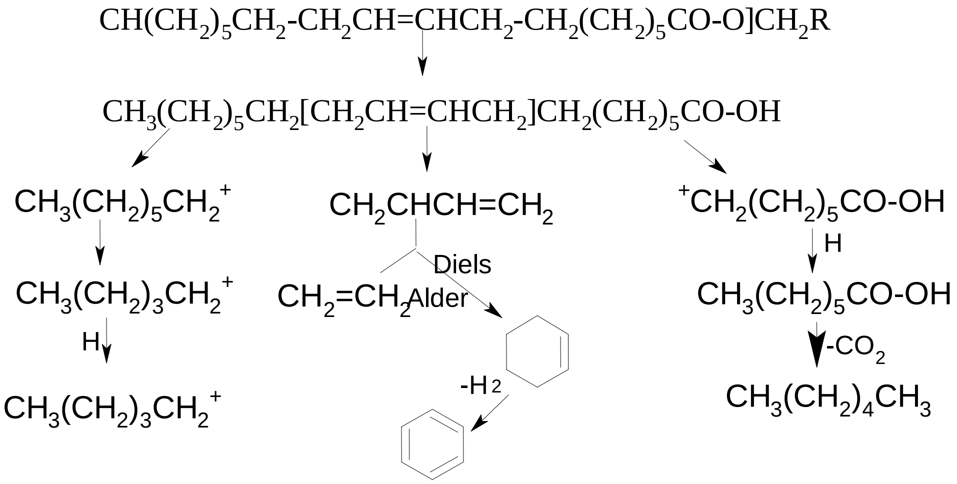


Fig 2.1: Mechanism of thermal decomposition of trigycerides

2.7.3. Micro-emulsion process

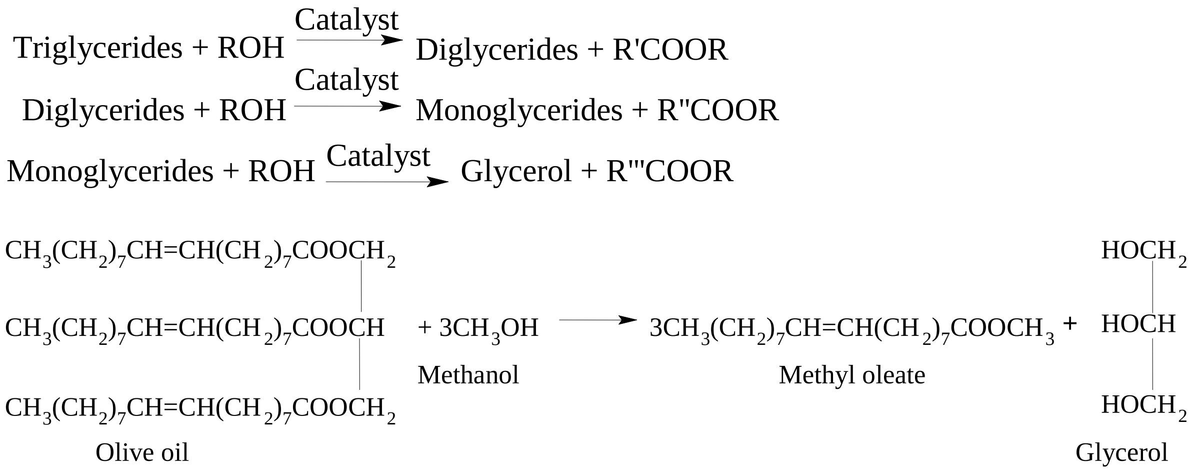
A micro emulsion is define as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally into 1–150 range formed spontaneously from two normally immiscible liquids and one or more ionic or non ionic amphiphiles. They can improve spray characteristics by explosive vaporization of the low boiling constituents in micelles. The engine performances were the same for a microemulsion of 53% sunflower oil and the 25% blend of sunflower oil in diesel. A microemulsion prepared by blending soyabean oil, methanol, and 2-octanol and cetane improver in ratio of 52.7:13.3:33.3:1.0 also passed the 200-h (Engine Manufacturers Association) (EMA) test (Singh and Singh, 2010).

2.7.4 Transesterification

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Excess alcohol is used to shift the equilibrium toward the product because of reversible nature of reaction.

For this purpose primary and secondary monohybrid aliphatic alcohols having 1-8 carbon atoms are used.

(a) Transesterification process*:* Transesterification consists of a number of consecutive, reversible reactions. The triglycerides are converted step wise to diglycerides, monoglyceride and finally glycerol (Singh and Singh, 2010). The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides, diglyceride is obtained, from diglyceride, monoglyceride is produced and in the last step, from monoglycerides, glycerin is obtained. In all these reactions esters are produced (Marchetti *et al*., 2007). In other words, a mole of ester is librated at each step. The stiochometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product (**Fig.2.2**).



$$\text{Triglycerides} + \text{ROH} \xrightarrow{\text{Catalyst}} \text{Diglycerides} + \text{R'COOR}$$

$$\text{Diglycerides} + \text{ROH} \xrightarrow{\text{Catalyst}} \text{Monoglycerides} + \text{R''COOR}$$

$$\text{Monoglycerides} + \text{ROH} \xrightarrow{\text{Catalyst}} \text{Glycerol} + \text{R'''COOR}$$

$$\begin{array}{lllll} CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_2 & & & & HOCH_2 \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH & + 3CH_3OH & \longrightarrow & 3CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 + & HOCH \\ & \text{Methanol} & & \text{Methyl oleate} & \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_2 & & & & HOCH_2 \\ \text{Olive oil} & & & & \text{Glycerol} \end{array}$$

Fig. 2.2. Transestrification reaction.

(b) Catalyst used in biodiesel production

A wide range of catalysts may be used for biodiesel production, such as homogenous and heterogeneous acids and bases, sugars, lipases, ion exchange resins, zeolites, and other heterogeneous materials. The homogenous base-catalyzed transesterification reaction is about 4,000 times faster than the corresponding acid-catalyzed process. Base-catalyzed reactions are performed at generally lower temperatures, pressures, and reaction times and are less corrosive to industrial equipment than acid-catalyzed methods. Therefore, fewer capital and operating costs are incurred by biodiesel production facilities in the case of the base-catalyzed transesterification methods (Moser, 2009).

In general, acids are more appropriate for feedstocks high in FFA content. Homogenously catalyzed reactions generally require less alcohol, shorter reaction times, and more complicated purification procedures than heterogeneously catalyzed transesterification reactions. Heterogeneous lipases are generally not tolerant of methanol, so production of ethyl or higher esters is more common with enzymatic methods (Moser, 2009).

Furthermore, non catalytic transesterification of biodiesel may be accomplished in supercritical fluids such as methanol, but a very high pressure (45–65 bar), temperature (350°C), and amount of alcohol (42:1 molar ratio) are required. Advantages of supercritical transesterification versus various catalytic methods are that only very short reaction times (4 min, for instance) are needed, and product purification is simplified because there is no need to remove a catalyst. Disadvantages of this approach include limitation to a batch-wise process, elevated energy and alcohol requirements during production, and increased capital expenses and maintenance associated with pressurized reaction vessels (Moser, 2009).

(i) Base or Alkali catalyzed transesterification: The reaction mechanism for alkali catalyzed transesterification was formulated in three steps as explained in Fig.2.3. The first step is an attack on the carbonyl carbon atom of the triglycerides molecule by the anion of the alcohol (Methoxide ion) to form a tetrahedral intermediate. In the last step, rearrangement of tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. When NaOH, KOH, K_2CO_3 or other similar catalysts were mixed with alcohol, the actual catalysts, alkoxide group is formed. Processes have been developed for the production of Biodiesel from vegetable oils using heterogeneous catalyst $Na/NaOH/Al_2O_3$. These catalysts showed almost the same activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst. For an alkali catalyzed transesterification, the glyceride and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap (Hak-Joo *et al*., 2004).

A number of researchers have worked with feed stocks that have elevated FFA (free fatty acid) levels. However, in most cases, alkaline catalysts have been used and the FFAs (Free fatty acids) were removed from the process stream as soap and considered waste. Waste greases typically contain from 10 to 25%FFAs. This is far beyond the level that can be converted to Biodiesel using an alkaline catalyst (Canakci and Gerpen, 2001).

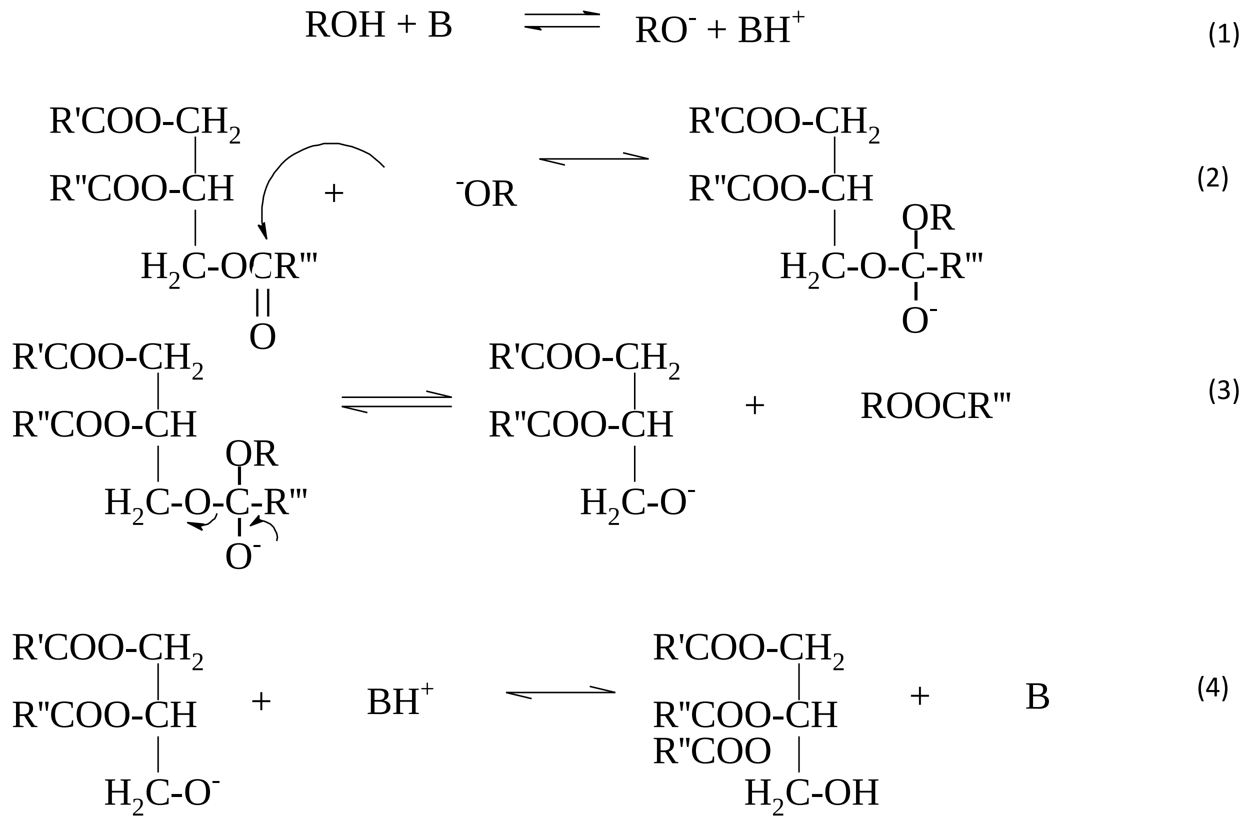


Fig. 2.3 Mechanism of the alkali-catalyzed transesterification of vegetable oils.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown above. The first step (step 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (step2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (step3). The latter deprotonates the catalyst, thus regenerating the active species (step 4), 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.

(ii) Acid catalyst transesterification:

An alternative process is to use acid catalyst that some researchers have claimed are more tolerant of free fatty acid. The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Fig.2.4. However, it can be extended to di- and triglycerides. The protonation of carbonyl group of the ester leads to the carbonation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst. We can use acid alkali and biocatalyst in transesterification method. If more water and free fatty acids are in triglycerides, acid catalyst can be used. Transmethylation occur approximately 4000 times faster in the presence of an alkali catalyst than those catalyzed by the same amount of acidic catalyst (Sing and Singh, 2010).

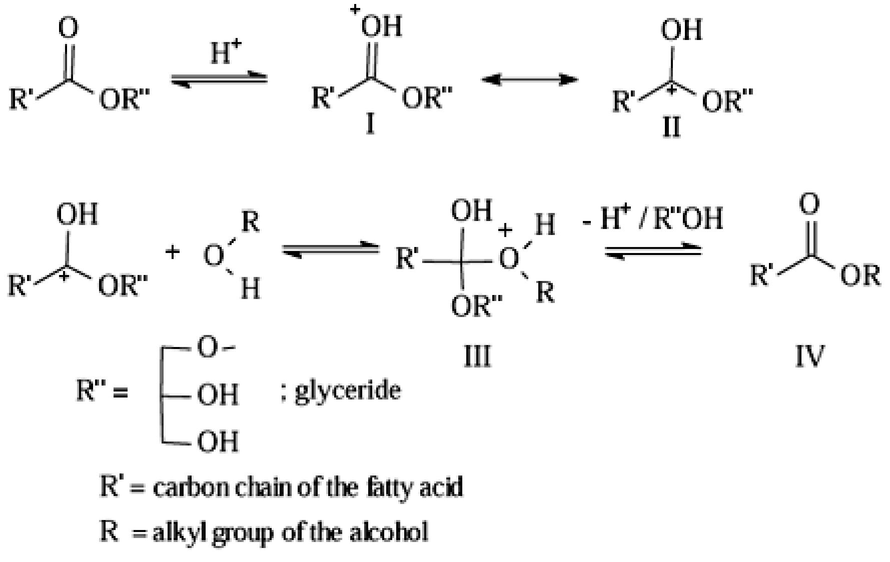


Fig 2.4: Mechanism of acid catalysed transesterification

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 transesterification 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.

(iii) Enzyme- catalyzed transesterification: Biodiesel can be obtained from enzyme or biocatalytic transesterification methods.

Transesterification can be carried out chemically or enzymatically (Ayhan, 2009). Lipases are enzymes used to catalyze some reaction such as hydrolysis of glycerol, alcoholysis and acidolysis, but it has been discovered that they can be used as catalyst for transesterification and esterification reactions too.Biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure are the desired properties in agricultural and medical applications. The extra cellular and the intracellular lipases are also able to catalyze the transesterification of triglycerides effectively (Marchetti *et al.*, 2007).

The process is explained in Fig. 2.5. Lipases are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones. Thus, in general, the efficiency of the transesterification of triglycerides with methanol (methanolysis) is likely to be very low compared to that with ethanol in systems with or without a solvent (Singh and Singh, 2010).

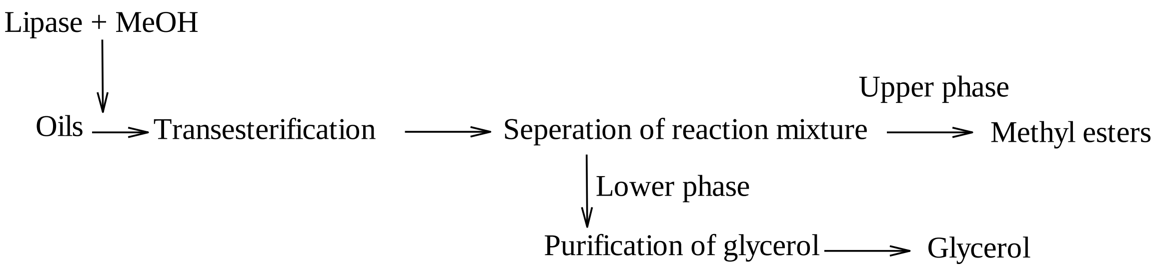


Fig. 2.5: Biodiesel production using lipase-catalysis

(iv) Catalytic supercritical methanol transesterification

Although this is a new relevant topic, there is an uncertainty regarding whether tranesterification or alkyl esterification is a better way of production and which one has a faster reaction rate. In the case where supercritical alcohol was used, it was demonstrated that one gets a higher reaction rate for esterification than for transesterification. Another advantage of this process is that the free fatty acid will be changed completely into esters (Marchetti *et al.*, 2007).

Catalytic supercritical methanol transesterification is carried out in an autoclave in the presence of 1–5% NaOH, CaO, and MgO as catalyst at 520K. In the catalytic supercritical methanol transesterification method, the yield of conversion rises to 60–90% for the first minute (Ayhan, 2009). A summary of the different technologies to produce biodiesel is outlined in Table 2.3.

Table 2.3: Comparison of the different technologies to produce biodiesel

Variable	Alkali catalysis	Lipase catalysis	Supercritical alcohol	Acid catalysis
Reaction temperature(°C)	60-70	30-40	239-385	55-80
Free fatty acid in Raw materials	Saponified products	Methyl esters	Esters	Esters
Water in raw materials No	Interference with reaction	No influence	-	Interference with reaction
Yield of methyl esters	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Easy	-	Difficult
Purification of methyl esters	Repeated washing	None	-	Repeated washing
Production cost of catalyst	Cheap	Relatively expensive	Medium	Cheap

Source: Marchetti *et al.*, (2007).

(c) Alcohols used in the production of biodiesel

As previously mentioned, methanol is the most common alcohol used in the production of biodiesel. Other alcohols may also be used in the preparation of biodiesel, such as ethanol, propanol, iso-propanol, and butanol. Ethanol is of particular interest primarily because it is less expensive than methanol in some regions of the world, and biodiesel prepared from bio-ethanol is completely bio-based. Butanol may also be obtained from biological materials, thus yielding completely bio-based biodiesel as well. Methanol, propanol, and iso-propanol are normally produced from petrochemical materials such as methane obtained from natural gas in the case of methanol (Moser, 2009).

(d) Biodiesel separation from glycerol

A brief review for the biodiesel separation techniques is presented here. Most of the researchers reported that high quality biodiesel that is economically viable can be achieved when suitable biodiesel separation process is employed. After transesterification, separation of biodiesel and by-product glycerol is usually first carried out. This process of biodiesel separation is based on the facts that the biodiesel and glycerol produced are typically sparingly mutually soluble, and that there is palpable difference in density between biodiesel (880 kg/m^3) and glycerol (1050 kg/m^3, or more) phases respectively. More so, this difference in density is sufficiently enough for the application of simple techniques such as gravitational settling or centrifugation for the separation of biodiesel and glycerol phases (Atadashi *et al.*, 2011).

(e) Biodiesel washing

A critical step in the production of Biodiesel, particularly when the feed vegetable oil contains free fatty acids, is the removal of the soap that is formed as part of the transesterification reaction and is dissolved in the biodiesel. Soap is the salt of fatty acids; and during the biodiesel esterification reaction, the free fatty acids in the oils react with the sodium (or potassium) ions of the methoxide or ethoxide to form the soap. Two approaches have been advanced for performing this chemical process separation task: extraction of the soap with water, and extraction of the soap with absorbents. The former extraction task is often described, in local biodiesel production operations, as washing the biodiesel fuel. However, the two approaches are based on the same chemical science; and the washing science application is better reflected through the extraction with water; besides, for large scale biodiesel production operation, the extraction with water supports more stable operation (Analysis Biodiesel Techs water wash biodiesel).

Water is generally known to be immiscible with biodiesel and is also heavier than oil. However, it is the latter characteristics that define the design rationale for the biodiesel washing.

The essential science to appreciate though is that as salts of fatty acids, the sodium or potassium end of the soap molecule has an attraction to, also termed affinity for, ionic substances of opposite ionic charge, while the other end which is mostly pure hydrocarbon has repulsion for such substances. The ionic end of the soap molecule is termed hydrophilic while the other end is hydrophobic or lipophilic and the molecule itself is described as amphiphilic, and called amphiphile. Water, of course, is slightly polar at the hydrogen location, and as such the hydrophilic group of the soap molecule is attracted to the water molecules when exposed to water molecules. This affinity for water then is the basis of separation of the soap from the biodiesel. When water comes into contact with the biodiesel after the transesterification reaction, the hydrophilic group of the soap gets attached with the water molecules while the hydrophobic group remains in the biodiesel.

However, the impact of the variation of length of soap molecules is relatively more intrinsic in the case of biodiesel washing than the other factors. The intrinsic feature of the biodiesel transesterification reaction is that the soap molecules are of varying carbon chain lengths: a vegetable oil is generally a mixture of oils of different carbon chain lengths; hence the free fatty acids produced from such oils also have different carbon chain lengths and consequentially result in soap of varying carbon chain lengths as well.

So first an understanding of the formation of structures as a function of carbon chain length: essentially, when several molecules of soap are added to water, the hydrophilic groups of the molecules attach themselves to water molecules and forces an isolation of the hydrophobic end from association with any water molecule; as a result a small structure of the form of a ball is formed in which the surface of the ball consists of the hydrophilic groups of the soap molecules but with the hydrophobic ends being encased or encapsulated within the sphere. This structure is commonly called a micelle.

Effectively then, if a droplet of biodiesel with soap molecules were bubbling up through water medium, then the soap molecules will reoriented themselves by jotting the hydrophilic ends into the water while keep the hydrophobic ends in the biodiesel droplet. Conceptually, the biodiesel droplet should appear to be occluded by the soap molecules as the droplet bubbles up to the top of the water medium. Inferentially then, in this case the structure that gets to be formed is of the form of micelles (Analysis Biodiesel Techs water wash biodiesel.).

However, this relation between the water and the biodiesel droplet is not preserved. The soap molecules will ultimately get pulled out of the biodiesel droplet into the water medium because of the strength of electrostatic attraction between the ionic charges of the water and soap molecules; and effectively there comes about a separation of the soap molecules and biodiesel (Analysis Biodiesel Techs water wash biodiesel.).

2.8 Factors Affecting Biodiesel Production

The transesterification reaction is strongly influenced by several factors including molar ratio of alcohol, catalyst, presence of water, free fatty acid in oil samples, reaction temperature, reaction time and agitation speed (Mathiyazhagan and Ganapathic, 2011).

2.8.1 Effect of molar ratio of alcohol

Molar ratio of alcohol plays a vital role in biodiesel yield. Normally the transesterification reaction requires 3 moles of alcohol for one mole of triglycerides to form three mol of fatty acid ester and one mole of glycerol. Excess amount of alcohol increases conversion of fats into esters within a short time. So the yield of biodiesel increases with increase in the concentration of alcohol up to certain concentration. However further increase of alcohol content does not increase the yield of biodiesel but it also increases the cost of alcohol recovery. In addition to this the ratio of alcohol content may vary with catalyst used , i.e. when we use alkali catalyst the reaction requires 6:1 ratio of alcohol to catalyze the transesterification of oils or fats. In case the oil samples contain high free fatty acid (FFA) such reaction does not respond to alkali catalyst. In that situation acid catalyst will be effective to catalyze the reaction and the reaction requires higher amount of alcohol than alkali catalyst. This is due to the fact that acid catalyst tolerates the FFA content and water content present in the oil samples (Mathiyazhagan and Ganapathic; 2011, Leung and Guo, 2006; Zhang *et al.,* 2003).

2.8.2 Effect of water and FFA contents

The water and free fatty acid (FFA) contents are critical factors for transesterification reaction. Base-catalyzed transesterification reaction requires water free and low acid value (< 1) raw materials for biodiesel production. If the oil samples have high FFA content (more than 1%) then the reaction requires more alkali catalyst to neutralize the FFA. Presence of water gives greater negative effect than that of FFAs because water can cause soap formation and frothing which can cause increase in viscosity. In addition formation of gels and foams hinders the separation of glycerol from biodiesel. Free fatty acid and water always produce negative result during transesterification and cause soap formation and consumes the catalyst which leads to reduction of catalyst effect. Water and FFA also leads to the reduction of methyl ester. To overcome this problem, supercritical methanol method (623 K, 43MPa, 4 min of treatment with a methanol to oil molar ratio of 42:1) was proposed and this was compared to alkaline and acid-catalyzed method. It may be noted that water has less influence in supercritical methanol method (Mathiyazhagan and Ganapathic, 2011).

2.8.3 Reaction time

Fatty acid esters conversion increase with reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol and oil. After that the reaction proceeds very fast. However the maximum ester conversion is achieved within < 90 min Further increase in reaction time does not increase the yield of the product i.e. biodiesel/mono alkyl ester. Besides, longer reaction time leads to the reduction of end product (biodiesel) due to the reversible reaction of transesterification resulting in loss of esters as well as soap formation (Mathiyazhagan and Ganapathic, 2011; Leung and Guo, 2006; Zhang *et al.*, 2003).

2.8.4 Reaction temperature

Reaction temperature is another important factor that will affect the yield of biodiesel. For example higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. However, it was found that increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides. Usually the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of optimal reaction temperature may vary from 50°C to 60°C depending on the oils or fats used (Mathiyazhagan and Ganapathic, 2011; Leung and Guo, 2006; Zhang *et al.*, 2003).

2.8.5 Catalyst concentration: Biodiesel formation is also affected by the concentration of catalyst. Most commonly used catalyst for biodiesel production is sodium hydroxide (NaOH), potassium hydroxide (KOH), H_2SO_4 etc. However, sodium methoxide would be more effective because mixing of sodium hydroxide with methanol produce little amount of water which inhibit the formation of end product (Biodiesel) due to the hydrolysis reaction. This is one of the reason for mixing of catalyst with methanol first and then added to the oil or fats. In addition to this when the concentration of catalyst increases with oil samples, the conversion of triglycerides into biodiesel also increases. On the other hand insufficient amount of catalyst leads to the incomplete conversion of triglycerides into fatty acid esters. However, optimal product yield (biodiesel) is achieved when the concentration of NaOH reaches 1.5 wt. % at the same time further increase of catalyst concentration proved to have negative impact on end product yield. (Mathiyazhagan and Ganapathic, 2011; Leung and Guo, 2006; Zhang *et al.*, 2003).

2.8.6 Agitation speed

Agitation speed plays an important role in the formation of end product (mono alkyl ester or biodiesel), because agitation of oil and catalyst mixture enhances the reaction. On the other hand higher stirring speed favours formation of soap. This is due to the reverse behaviour of transesterification reaction (Mathiyazhagan and Ganapathic, 2011; Leung and Guo, 2006; Zhang *et al.*, 2003).

2.9 Biodiesel fuel properties

2.9.1 Viscosity of biodiesel

The viscosity of liquid fuels is their property to resist the relative movement tendency of their composing layers due to intermolecular attraction forces (viscosity is the reverse of fluidity). Viscosity is one of the most important properties of biodiesel. Viscosity influences the ease of starting the engine, the spray quality, the size of the particles (drops), the penetration of the injected jet and the quality of the fuel-air mixture combustion (Alptekin and Canakci, 2009). Fuel viscosity has both an upper and a lower limit. The fuel with a too low viscosity provides a very fine spray, the drops having a very low mass and speed. This leads to insufficient penetration and the formation of *black smoke* specific to combustion in the absence of oxygen (near the injector) (Băţaga *et al*., 2003).

A too viscous biodiesel leads to the formation of too big drops, which will penetrate to the wall opposite to the injector. The cylinder surface being cold, it will interrupt the combustion reaction and *blue smoke* will form (intermediate combustion product consisting of aldehydes and acids with pungent odour) (Băţaga *et al*., 2003). Incomplete combustion results in lower engine power.

Too high viscosity leads to the increase of combustion chamber deposits and the increase of the needed fuel pumping energy, as well as the increased wear of the pump and the injector elements due to higher mechanical effort. Too high viscosity also causes operational problems at low temperatures because the viscosity increases with decreasing temperature (for temperatures at or below -20 °C viscosity should be at or below 48 mm^2/s). Viscosity also influences the lubricity of the fuel as some elements of the fuel system can only be lubricated by the fuel (pumps and injectors). Due to the presence of the electronegative oxygen, biodiesel is more polar than diesel fuel; as a result, the viscosity of biodiesel is higher than that of diesel fuel (Padmarag and Kavita, 2012).

2.9.2 Cetane number

Cetane number (CN) is a dimensionless indicator that characterizes ignition quality of fuels for compression ignition engines (CIE). Since in the CIE burning of the fuel-air mixture is initiated by compression ignition of the fuel, the cetane number is a primary indicator of fuel quality as it describes the ease of its self-ignition.

Theoretically, the cetane number is defined in the range of 15-100; the limits are given by the two reference fuels used in the experimental determination of the cetane number: a linear-chain hydrocarbon, hexadecane ($C_{16}H_{34}$, also called n-cetane), very sensitive to ignition, having a cetane number of 100, and a strongly branched-chain hydrocarbon, 2,2,4,4,6,8,8-heptamethylnonane (HMN, also called isocetane), having the same chemical formula $C_{16}H_{34}$, with high resistance to ignition, having a cetane number of 15. The cetane number is the percentage by volume of normal cetane in a mixture of normal cetane and HMN, which has the same ignition characteristics as the test fuel. Thus the cetane number is given by the formula: CN = n-cetane [%, v/v] + 0.15*HMN [%, v/v]. Determination of the cetane number on the monocylinder engine specially designed for this purpose (EN ISO 5165, ASTM D613) is an expensive and lengthy operation. A cheaper and faster alternative is to determine the derived cetane number through ignition delay in a constant-volume combustion chamber (ignition quality tester – IQT), a widely accepted method described in ASTM D6890 and ASTM D7170, accepted by the biodiesel quality standard ASTM D6751.

The cetane number indicates ignition delay, i.e. the time elapsed since the injection of fuel into the combustion chamber and self-ignition of the fuel-air mixture. Thus, ignition time lag means a low cetane number and vice versa. The upper and lower limits of the cetane number ensure the proper functioning of the engine. If the cetane number is too low, starting the engine will be difficult, especially at low temperatures and the engine will function unevenly and noisily, with cycles without combustion, it will warm more slowly, combustion will be incomplete and engine pollution will increase, especially hydrocarbon emissions. In case of a fuel with a very high cetane number, ignition will be carried out before a proper mix with air, resulting in incomplete combustion and the increase of the amount of exhaust smoke. Also, if the cetane number is too high the fuel will ignite close to the injector causing it to overheat, and unburned fuel particles can plug the injector nozzles (Barabás and Todoruţ, 2010).

The optimal range of the CN is between 41 and 56, but must not be higher than 65 (Băţaga *et al*. 2003). The minimum cetane number of biodiesel is 51 in the European Union, 47 in the United States and 45 in Brazil. The minimum CN for diesel oil is 40 in the USA (ASTM D 975) and 51 in Europe (EN 590). The cetane number of a substance depends on its molecular structure. The cetane number decreases with the number of double bonds in fatty acid ester molecules (degree of unsaturation, characterized by the iodine number) and increases with the number of carbon atoms. Generally, the cetane number of ethyl esters is higher than that of methyl esters (Băţaga *et al*., 2003).

The cetane number of biodiesels is higher than that of the vegetable oils from which they are produced ($34.6 < CN < 42$), and is between 39 and 67 (Anastopoulos *et al*., 2009, Barabás and Todoruţ, 2010, Chuepeng and Komintarachat, 2010, Shannon *et al*., 2009 and Fan *et al*., 2009).

Cetane number calculated by following equation.

$$\text{Cetane number} = 46.3 + 5458/SV - 0.225 \times IV \qquad (2.1)$$

where, SV = Saponification value of sample. IV = Iodine value of sample.

2.9.3 Density of biodiesel

Fuel density (ρ) is the mass of unit volume, measured in a vacuum. Since density is strongly influenced by temperature, the quality standards state the determination of density at 15 °C.

Fuel density directly affects fuel performance, as some of the engine properties, such as cetane number, heating value and viscosity are strongly connected to density. The density of the fuel also affects the quality of atomization and combustion. As diesel engine fuel systems (the pump and the injectors) meter the fuel by volume, modification of the density affects the fuel mass that reaches the combustion chamber, and thus the energy content of the fuel dose, altering the fuel/air ratio and the engine’s power (Barabás and Todoruţ, 2010).

Knowing the density is also necessary in the manufacturing, storage, transportation and distribution process of biodiesel as it is an important parameter to be taken into account in the design of these processes. The density of esters depends on the molar mass, the free fatty acid content, the water content and the temperature. The density of biodiesel is typically higher than that of diesel fuel and is dependent on fatty acid composition and purity. As biodiesel is made up of a small number of methyl or ethyl esters that have very similar densities, the density of biodiesel varies between tight limits. Contamination of the biodiesel significantly affects its density; therefore density can also be an indicator of contamination (Barabás and Todorut, 2010; Fan *et al*., 2009).

2.9.4 Flash point (FP)

The flash point is the minimum temperature calculated to a barometric pressure of 101.3 kPa at which the fuel will ignite (flash) on application of an ignition source under specified conditions. It is used to classify fuels for transport, storage and distribution according to hazard level. The flash point does not affect the combustion directly; higher values make fuels safer with regard to storage, fuel handling and transportation. FP varies inversely with the fuel's volatility. For biodiesel the minimum flash point is 93 °C in the United States, 100 °C in Brazil and 120 °C in Europe. Biodiesel's flash point decreases rapidly as the amount of residual (un-reacted) alcohol increases (methanol's flash point is 11–12 °C, and ethanol's is 13–14 °C).

Thus, measuring the biodiesel flash point helps indicate the presence of methanol or ethanol. For example, the presence of 0.5% methanol in biodiesel reduces biodiesel flash point from 170°C to 50 °C. If flash point is used to determine the methanol content, the ASTM standard imposes for it a minimum value of 130 °C. This limit may be considered too severe, because at the maximum permissible concentration of methanol of 0.2% w/w biodiesel flash point drops below 130 °C (Anastopoulos *et al*., 2009; Barabás and Todorut, 2010; Chuepeng and Komintarachat, 2010; Shannon *et al*., 2009; Fan *et al*., 2009).

2.9.5 Pour point (PP)

The pour point is the temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow. This occurs if the temperature of the biodiesel drops below Cloud points, when the microcrystals merge and form large clusters, which may disrupt the flow of the biodiesel through the pipes of the engine's fuel system. Although CP and PP are relatively easily determined, they only provide indicative values for the minimum temperature at which the fuel can be used. At cloud point the fuel can still be used in acceptable conditions whereas at pour point this is no longer possible. In other words, cloud point overestimates minimum operating temperature and pour point underestimates it (Barabás and Todorut, 2010; Fan *et al*., 2009).

2.9.6 Cloud point (CP)

The cloud point (CP) is the temperature at which crystals first start to form in the fuel. The cloud point is reached when the temperature of the biodiesel is low enough to cause wax crystals to precipitate. Initially, cooling temperatures cause the formation of the solid wax crystal nuclei that are submicron in scale and invisible to the human eye. Further decrease of temperature causes these crystals to grow. The temperature at which crystals become visible (the crystal's diameter 0.5 m) is defined as the cloud point because the crystals form a cloudy suspension. Below the Cloud Point these crystals might plug filters or drop to the bottom of a storage tank. The Cloud

Point is the most commonly used measure of low-temperature operability of the fuel. The biodiesel cloud point is typically higher than the cloud point of conventional diesel. The cloud point of biodiesel depends on the nature of the feedstock it was obtained from (Barabás & Todorut, 2010; Fan *et al.*, 2009).

2.9.7 Acid value (AV)

The acid value also called neutralization number or acid number is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize the acidic constituents in one gram of sample. The acid value determination is used to quantify the presence of acid moieties in a biodiesel sample. In a typical procedure, a known amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a colour indicator. The acidic compounds that could possibly be found in biodiesel are: (1) residual mineral acids from the production process, (2) residual free fatty acid from the hydrolysis process or the post- hydrolysis process of the esters and (3) oxidation byproducts in the form of other organic acids (Berthiaume and Tremblay, 2006). A too high amount of free glycerin can cause functioning problems at reduced temperatures and fuel filter clogging. This parameter can also be used to measure the freshness of the biodiesel. Fuel that has oxidized after long-term storage will probably have a higher acid value. The higher the acid values of oil, the higher the KOH to be used in the reaction. Consequently it can be assumed that the higher acid value oil consumes more chemical substance. (Ampaitepin *et al.*, 2006).

2.9.8 Iodine value (IV)

The iodine value (IV) or iodine number was introduced in biodiesel quality standards for evaluating their stability to oxidation. The Iodine Value is a measurement of total unsaturation of fatty acids measured in g iodine/100g of biodiesel sample, when formally adding iodine to the double bonds. Biodiesel with high Iodine Value is easily oxidized in contact with air. The iodine value highly depends on the nature and ester composition of the feedstocks used in biodiesel production. Therefore the Iodine Value is limited in various regions of the world depending on the specific conditions: 120 in Europe and Japan, 130 in Europe for biodiesel as heating oil, 140 in South Africa, in Brazil it is not limited and in the U.S., Australia and India it is not included in the quality standard. Biodiesel with high Iodine Values tends to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves. The tendency of polymerization increases with the degree of unsaturation of the fatty acids (István and Ioan-Adrian, 2011).

2.10 Benefits of using biodiesel

2.10.1 Environmental benefits

B100 contains no sulphur or aromatics, and the use of biodiesel in a conventional diesel engine results in a substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter. To address the slight increase in NOx emissions (Table 2.4), the biodiesel industry is developing an additive that reduces NOx emissions. For B5 or lower blends, the NOx increase is negligible.

2.10.2 Energy security

Life-cycle analyses show that biodiesel contains 2.5 to 3.5 units of energy for every unit of fossil energy input in its production, and because very little petroleum is used in its production, its use displaces petroleum at nearly a 1-to-1 ratio on a life-cycle basis. This value includes energy used in diesel farm equipment and transportation equipment (trucks, locomotives); fossil fuels used to produce fertilizers, pesticides, steam, and electricity; and methanol used in the manufacturing process. Because biodiesel is an energy efficient fuel, it can extend petroleum supplies. (Biodiesel Handling and Use Guide, 2008).

2.10.3 Economic benefits

Using biofuels can result in significant microeconomic benefits to both the urban and rural sectors and the balance of trade. In 2001, a USDA study indicated that an average annual increase of 200 million gallons of soy-based biodiesel demand would boost total crop cash receipts by $5.2 billion by 2010, resulting in an increase in average net farm income of $300 million per year. The price for a bushel of soybeans would increase by an average of 17 cents annually during the ten-year period (Zhiyou *et al.*, 2006). Table 2.4 shows B100 (biodiesel) emission in comparison with B20 (biodiesel 20:80 diesel).

Table 2.4: Average Biodiesel Emissions Compared to no 1 or no 2 Diesel.

Emission Type	B100	B20
Unburned Hydrocarbons	-67%	-20%
Carbon Monoxide	-48%	-12%
Particulate matter	-47%	-12%
Sulfates	-100%	-20%
PAH (Polycyclic Aromatic	-80%	-13%

Hydrocarbons)		
nPAH (nitrated PAHs)	-90%	-50%
Ozone potential of speciated HC	-50%	-10%
NOx	+10%	+2%

Source: National Biodiesel Board, Biodiesel Fact Sheets, Emissions

2.10.4 EPAct benefits

In January 2001, federal, state, and certain fuel provider fleets became eligible for EPAct (Energy Policy Act) credit for using biodiesel blends of at least 20 percent. This rule gives one credit for every 450 gallons of pure biodiesel used in biodiesel blends. The Congressional Budget Office and the United States Department of Agriculture (USDA) have confirmed that the biodiesel option is the least-cost alternative fuel option for meeting the federal government's EPAct compliance requirements. Because biodiesel works with existing diesel engines, biodiesel offers an immediate and seamless way to transition existing diesel vehicles into a cleaner burning fleet (National Biodiesel Board).

2.11 Biodiesel environmental & safety information

2.11.1 Acute Oral Toxicity/Rates

Biodiesel is nontoxic. The acute oral LD50 (lethal dose) is greater than 17.4 g/kg body weight. By comparison, table salt (NaCl) is nearly 10 times more toxic (National Biodiesel Board).

2.11.2 Skin Irritation – Humans

A 24-hr. human patch test indicated that undiluted biodiesel produced very mild irritation. The irritation was less than the result produced by a 4 percent soap and water solution (National Biodiesel Board).

2.11.3 Aquatic Toxicity

A 96-hr. lethal concentration for bluegill of biodiesel grade methyl esters was greater than 1000 mg/l. Lethal concentrations at these levels are generally deemed “insignificant” according to NIOSH (National Institute for Occupational Safety and Health) guidelines in its *Registry of the Toxic Effects of Chemical Substance* (National Biodiesel Board).

2.11.4 Biodegradability

Biodiesel degrades about four times faster than petroleum diesel. Within 28 days, pure biodiesel degrades 85 to 88 percent in water. Dextrose (a test sugar used as the positive control when testing biodegradability) degraded at the same rate. Blending biodiesel with diesel fuel accelerates its biodegradability. For example, blends of 20 percent biodiesel and 80 percent diesel fuel degrade twice as fast as number 2 diesels alone (National Biodiesel Board).

Survey of related literature on biofuel production

Ezekwe and Ajiwe 2014, carried out work on biofuel properties of oils, methyl and ethyl esters of *thevetia peruviana, lagenaria siceraria* and *cucumis melo,* they reported that the biofuels were more environmentally friendly than fossil diesel in terms of the acidity of the emitted effluents, the differences between the esters of the three oils depended upon their fatty acid profile and their saturation levels, blending esters with diesel improved the efficiency of the fuels, the fuels were stable at high temperatures (250^{o}C max) ,both methylation and ethylation of the three oils were likely to be second order reaction with similar activation energy.

Onyiah *et al*., (2015) reported the kinetic study of base catalyzed transesterification of soybean oil carried out at an optimum temperature of 338K, methanol to oil ratio of 6:1 and catalyst concentration 1% (w/w) for KOH. The yield of methyl ester (FAME) has been used to study the effect of different parameters which resulted in a maximum yield of 87.9%. The kinetic model of the transesterification reaction was analyzed using zero order, first order and second order kinetic models. The kinetic data informed to second order kinetic model. Activation energy obtained from this study was – 10076.568KJ/kmol and a preexponential factor of 1.1195x10-5min^{-1}.

Nwadike *et al*., (2014) reported the FTIR analysis cow tallow for biodiesel production in a pilot plant. Using methanol as the solvent and potassium hydroxide as catalysts. The biodiesel quality was determined by FTIR method. The method showed that the final product had ester compositions which can be used as a biodiesel fuel in diesel engine. It was shown that other blends of biodiesel/diesel with higher levels of cow tallow biodiesel (B5, B10, B20, and B30) have similar or better fuel properties than diesel, indicating that this is a good way to improve certain properties of diesel without the loss of efficiency or increase in consumption. Furthermore the transesterification of cow tallow with methanol decreases the fat viscosity and produces a biodiesel with high quality.

The effect of compound structures on the properties of biodiesel (methylesters) from some Nigerian oil crops (*cucurbita pepo L, afzelia africana* and *hura crepitans*) was studied by Ogbu and Ajiwe, (2013). In their report they found out that the three samples were good feedstocks for biofuel production and their fuel properties correlated very well with the fatty acid compositions.

Cucurbita pepo L, *afzelia africana* and *hura crepitans* were rich in saturated fatty acids (62.43%) and monounsaturated fatty acids (54.33%) indicating high cetane number, calorific value and oxidative stability. *Hura crepitans* had the best flash point and cold flow properties among the three feedstocks.

Umer *et al.*, (2011) studied Methanolysis of a related species of *colocynthus vulgaris* Muskmelon (*Cucumis melo*) seed oil) and found that *Cucumis melo* gave yield 89.5% of the methyl esters at the following reaction conditions; 5.8:1 methanol-to-oil ratio, 0.79% catalyst concentration, 55 °C reaction temperature and 72.5-min reaction time. The biodiesel was analyzed using GC-MS (gas chromatographic-mass spectrometry) which indicated four FAMEs (fatty acid methyl esters) (linoleic-, oleic-, palmitic- and stearic acids) as its major components. In this current study the fatty acid present in *colocynthus vulgaris* were (palmitic acid, linoleic acid, stearic acid) in the methyl ester and (linoleic acid and stearic acid) in the ethyl esters, they optimum catalyst concentration was 10ml for both methyl and ethyl esters, 40^{o}C and 70^{o}C reaction temperature respectively for methyl and ethyl esters and 40 and 60 min reaction time respectively for its ethyl and methyl esers.

Leung and Guo (2006),compared and optimized the parameters which affect the yield of biodiesel using neat canola oil and used frying oil. They reported that conversion efficiency for neat canola oil was 90.4%, when it was transesterified using methanol/oil molar ratio of 7 and 1% NaOH, maintaining the reaction temperature at 70^{o}C, and reaction time was 20 min. They also revealed that optimum parameters for used frying oil were: methanol/oil molar ratio 7; 1.1% NaOH; reaction temperature 60◦C; and reaction time 60minutes. The maximum yield was 88.8%.

Okullo *et al*., (2011) studied the transesterification of jatropha oil with methanol was carried out in a well mixed reactor at different agitation speeds (600-900 rpm) and temperatures (35-65 ^{o}C) using sodium hydroxide as a catalyst. The methanol to oil molar ratio of 6:1 was used and catalyst loading was 0.5% weight of oil. Mass transfer controlled state was assumed to be minimal using the above agitation speeds. A second order kinetic model was used to determine the reaction rate constants. The goodness of fit predicting the moles of methyl ester in the reaction products was determined by correlation coefficient (R^2) and least square curve fit. The forward reactions were the most important as revealed by the rate constants.

Transesterification of waste groundnut oil (WGO), waste soybean oil (WSO) and waste palm kernel Oil (WPKO) catalyzed with potassium hydroxide (KOH) was studied by Ayodele *et al*., (2017) they found that Waste cooking oils constitute ready feedstock for high volume, good quality and sustainable production of biodiesel as well as a realistic means of eliminating the pollution resulting from the indiscriminate disposal of waste oils common to both household and industrial users. The optimal conditions for biodiesel yielded are 10.67 methanol per oil mole ratio, 0.86 w/w oil catalyst concentration, 60°C reaction temperature and 71 min reaction time for WGO, 9.76 methanol per oil mole ratio, 1.04 w/w oil catalyst concentration, 60°C reaction temperature and 70 min reaction time for WSO and 9.51 methanol per oil mole ratio, 1.24 w/w oil catalyst concentration, 62°C reaction temperature and 80 min reaction time for WPKO.

Umer et al., (2014) in a work carried out to optimize transesterification for biodiesel production using *Thespesia Populnea* seed oil reported operational variables such as methanol/oil molar ratio (3:1–9:1), catalyst concentration (0.50%–1.30%, in relation to oil mass), temperature (45°C to 70°C), and mixing intensity (350–800 rpm) at fixed reaction time (120 min). The biodiesel was synthesized by transesterification of *Thespesia populnea* seed oil with methanol, using sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide as catalysts. The optimum set of transesterifications reaction conditions: 7:1 molar ratio of methanol/oil, 65°C temperature, 0.90% (oil weight basis) $NaOCH_3$ catalyst, and 650 rpm yielded 98.1% *Thespesia populnea* oil methyl esters (TPOMEs)/biodiesel. They concluded that *Thespesia populnea* oil can be transformed into biodiesel with high yield (98.1%) under an optimized set of transesterification conditions.

Dominic et *al.,* (2017) provided information on Optimization of biodiesel production from refined cotton seed oil and its characterization with methanol and potassium hydroxide (KOH) as a catalyst using batch mode, an optimum yield of 96% was achieved with optimal conditions of methanol/oil molar ratio, 6:1; temperature, 55 °C; time, 60 min; and catalyst concentration, 0.6%.

Foluso and Tolulope, (2014) provided information on *Carica papaya* Seed Oil CPSO as a potential for biodiesel production in their study, The CPSO oil was transesterified by two-stage catalysis with oil to methanol mole ratio of 1 : 9. The biodiesel produced was subjected to standard fuel tests. The seed has an oil yield of 31.2% which is commercially viable. The kinematic viscosity of the oil at 313 K was 27.4 mm2s−1 while that of Carica papaya oil methylester (CPOME) was reduced to 3.57 mm2s−1 and the specific gravity was 0.84 comparable with other seed-oil biodiesels and number 2 diesel. Other oil properties were compared favourably with seed oils already documented for biodiesel synthesis. CPOME's cloud and pour points were 275 K and 274 K, respectively, and relatively higher than other biodiesels and number 2 diesel. CPOME exhibits moderate corrosion of copper strip. The methanolysis improved the fuel properties of the CPOME similar to other biodiesels.

Panagiotis et *al*., (2014) introduced a novel biodiesel production method that features direct base-catalyzed methanolysis of the cellular biomass of oleaginous yeast Rhodosporidium toruloides Y4. NaOH was used as catalyst for transesterification reactions and the variables affecting the esterification level including catalyst concentration, reaction temperature, reaction time, solvent loading (methanol) and moisture content were investigated using the oleaginous yeast biomass. The most suitable pretreatment condition was found to be 4 g L−1 NaOH and 1:20 (w/v) dried biomass to methanol ratio for 10 h at 50 °C and under ambient pressure. Under these conditions, the fatty acid methyl ester (FAME) yield was 97.7%. Therefore, the novel method of direct base-catalyzed methanolysis of R. toruloides is a much simpler, less tedious and time-consuming, process than the conventional processes with higher FAME (biodiesel) conversion yield.

Ofoefule et *al*.,(2013), evaluated transesterification of *Cyperus esculentus* oil using potassium methoxide as a catalyst at the temperature of 60^oC for 60 min at a catalyst concentration of 0.65% and under a constant stirring speed. Physicochemical parameters were carried out on the oil, biodiesel and various blends of B10, B20, B30 and B40, their results showed that the oil yield from the feedstock was 16%, while the biodiesel yield was 82%. The high and moderate flash points of the biodiesel and blends ranged between $90\text{-}178^oC$.

Biodiesel production from *Sesamum indicum* L. seed oil was carried by Dawodu *et al*., (2014) with methanol in the presence of sodium methoxide at an optimum condition of 1:6 oil/methanol molar ratio, catalyst concentration of 0.75% and reaction time of 30 min, biodiesel yield of 87.80% was achieved.

Abdurrahman *et al*., 2008 evaluated the methylesters of sesame (*Sesamum indicum* L.) seed oil as a biodiesel fuel, he reported that transesterification of the oils showed improvement in fuel properties of sesame seed oil. This study supports the production of biodiesel from sesame seed oil as a viable alternative to the diesel fuel.

Gaps in literature

Although previous works have been carried out on *sesame indicum* methylesters by Abdurrahman *et al*., (2008) and Dawodu *et al*., (2014) , also on *Cyperus esculentus* methyl esters by Sendžikienė *et al*. (2011) and Ofoefule et *al*.,(2013), this current study provided a detailed research which included methyl and ethylesters of the oils, blending of the fossil fuel with diesel (B10-B100), kinetics study and rate of reactions for the transesterification reaction, FTIR studies on bond stability of the biofuel and its blends at high temperature , the metallic composition of the biofuels and engine test and concentration of acidic emission from engine test which were not done in the previous works by the other researchers.

CHAPTER THREE

MATERIAL AND METHODS

3.1 Collection and preparation of samples

Colocynthus vulgaris, cyperus esculentus L., and *sesamum indicum L.* seeds were identified by P.C Ugwuozor a Herbarium Curator of the Department of Botany, Nnamdi Azikiwe University, Awka Nigeria. Samples of *Cyperus esculentus L., Colocynthus vulgaris and Sesamum indicum L.* seeds were bought from Ochanja market Onitsha, Anambra State and air-dried to remove moisture for 4 days. The seeds were ground to powder, and stored in screw-cap plastic containers before extraction of their oils. The diesel (AGO) was purchased from NNPC mega fuel station at Awka, Anambra State, Nigeria.

3.2 Materials and reagents

The material and reagent used in this study are as listed.

3.2.1 Materials

Beaker, stirrer, conical flask, , Flash point cup, Fume cupboard, Magnetic stirrer, Pensky Martens flash point tester, Pour point tester, Powdered seeds, Samples (oil, esters, ester/diesel blends and diesel), Separatory funnel, Soxhlet extractor, TECHNO R175A diesel engine, Viscosity bath and Viscometer, Digital densitymeter model AP PAAR DMA 35
`Atomic absorption spectrophotometer model Buck Scientific 210
Flame Atomic Absorption and visible spectroscopy model Corning 400
GC-MS QP2010 Plus Shimadzu Japan,

3.2.2 Reagents

N.B: All the reagents used were of analytical grade.

Potassium Hydroxide (BDH), Hydrochloric Acid (Sigma-Aldrich), Chloroform (BDH), Concentrated sulphuric acid (Sigma-Aldlrich), Distilled Water, Ethanol, Glacial Acetic Acid (BDH), Iodine Monochloride, Methanol (BDH), Petroleum Ether (BDH), Phenolphthalein Indicator, Potassium Iodide, Sodium Hydroxide, Sodium Thiosulphate, Sodium Chloride.

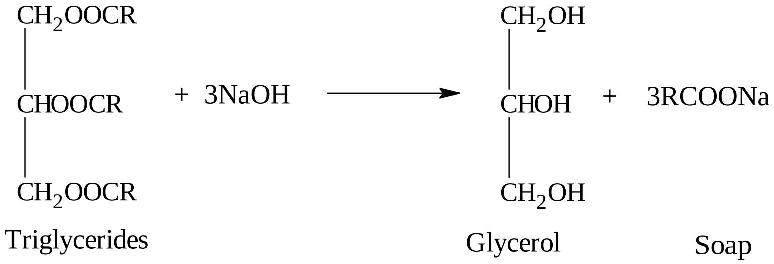
3.3 Extraction of oils from the powdered seed samples

Procedure: Each ground sample (10g) was exhaustively extracted with petroleum ether (60-80°C) by the use of soxhlet apparatus. The solvent was later recovered by distillation under reduced pressure by the use of the rotatory evaporator.

3.3 Preparation of methyl and ethyl esters.

7.92M Sodium hydroxide solution was prepared by dissolving 47.5g of sodium hydroxide pellets in 150cm^3 of distilled water. The sodium hydroxide solution was poured into a 1000cm^3 beaker containing 300cm^3 of oil sample with vigorous stirring till soap was formed.

Equation for soap making



$$\begin{array}{l} CH_2OOCR \\ | \\ CHOOCR \\ | \\ CH_2OOCR \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOONa$$

The soap produced was redissolved in water. Super saturated sodium chloride solution was added while heating with vigorous stirring at 200 rpm. A pure soap precipitated on the upper layer of the solution while the spent lye (water, glycerol and salt) was left at the bottom. This was separated with the help of filter paper followed by addition of excess brine on the precipitate to salt out the remaining glycerol and dirt, making the colour of the soap whiter and dried.

The precipitated soap was redissolved in 1000cm^3 beaker containing 250m^3 of distilled water and heated until a homogenous solution was formed. The solution was confirmed to be alkaline by testing with litmus paper. Concentrated sulphuric acid was made dilute with water in the ratio of 1:3(conc sulphuric acid: water). The dilute sulphuric acid was then used to bring the solution to neutral point of the indicator. The top oily layer was separated from the aqueous layer using separatory funnel. This oily layer contained the mixture of fatty acids.

The filtrate (the top oily layer) was measured into a beaker containing six times the volume of the sample of methanol or ethanol (as the case may be). Conc. H_2SO_4 was diluted with water in the ratio of 1:2(conc sulphuric acid: water). This dilute sulphuric acid (10cm^3) was added as a catalyst. The mixture was heated to 150^{o}C and stirred for 20 minutes to enable reaction to reach completion. Three layer were formed, the methyl or ethyl ester layer as the case may be, the aqueous acid layer and the foot. The ester layer was separated from the other two layers using a separatory funnel.

3.4 Verification of the effect of catalyst, time and temperature on transesterification reaction.

The kinetics of the transesterification reaction was determined from effect of catalyst, time and temperature as described below.

3.4.1 Optimum catalyst determination

A volume of 100ml of oil was measured into a conical flask. Sodium hydroxide solution was made by dissolving 15.83g of NaOH pellets in 50ml of distilled water. The NaOH solution was then used to saponify the oil followed by salting out and separation with a separatory funnel. The upper layer was collected and acidified with 1:3 (conc sulphuric acid: water) sulphuric acid until neutral. Two layers were formed; the solution was heated and stirred to dissolve lumps for clear separation of the two layers. The upper oily layer was collected into a 200ml beaker. 5 ml of the oil layer was taken into a clean beaker; 30ml of methanol was added to it. 5ml of the catalyst (1:2 H_2SO_4, conc sulphuric acid: water) was added to the solution. The solution was heated at 70^oC for 30 minutes. The biodiesel (upper layer) and glycerol (lower layer) formed was separated using a separatory funnel. The yield of the biodiesel was recorded. The process was repeated three times with 10ml, 15ml and 20ml of H_2SO_4 catalyst as there was no conversion with 1-4ml of the catalysts. The optimum catalyst was noted for each sample. The heating time and temperature were kept constant throughout this experiment.

3.4.2 Optimum time of reaction determination

A volume of 100ml of oil was measured in a conical flask sodium hydroxide solution was made by dissolving 15.83g of NaOH pellets in 50ml of distilled water. The NaOH solution was used to saponify the oil followed by salting out and separation with separatory funnel. The upper layer was collected and acidified with 1:3 (conc sulphuric acid: water) sulphuric acid until neutral.

Two layers were formed. The solution was then heated and stirred to dissolve lumps and form clear separation of the two layers. The upper oily layer was collected in a 200ml beaker. 5ml of the oily layer was taken into another 200ml beaker and 30ml 0f methanol was added to it. Optimum catalyst for each sample was added to the solution. The solution was heated at 70^{o}C for 30minutes. The biodiesel produced was recorded. The process was repeated for varying times of 40, 50 and 60 minutes. The temperature and catalyst volume were kept constant.

3.4.3 Optimum temperature determination

A volume of 100ml of oil was weighed in a conical flask. Sodium hydroxide solution was made by dissolving 15.83g of NaOH pellets in 50ml of distilled water. The NaOH solution was used to saponify the oil followed by salting out and separation with separatory funnel. The upper layer was collected and acidified with 1:3 (conc sulphuric acid: water) sulphuric acid until neutral. Two layers were formed. The solution was then heated and stirred to dissolve lumps and form clear separation of the two layers. The upper oily layer was collected in a 200ml beaker. 5ml of the oily layer was taken into another 200ml beaker and 30ml 0f methanol was added to it. Optimum catalyst for each sample was added to the solution. The solution was heated at 40^{o}C for 30minutes. The biodiesel yield was recorded. The process was repeated with the solution being heated at 50^{o}C, 60 ^{o}C, 70 ^{o}C and 80 ^{o}C for methyl ester and ethyl ester samples respectively. The catalyst volume and time were kept constant.

3.4.4 Verification of Rate Constant and Order of Reaction

The kinetics of the transesterification reaction was tested with pseudo zero order, first order and second order kinetic model as shown in equations 4.1, 4.2 and 4.3 respectively (Onyiah *et al.*, 2015).

$1\text{-}X_A = Kt$ (4.1)

$\text{In } (1\text{-} X_A) = Kt + C$ (4.2)

$1/(1\text{-}X_A) = KC_{Ao}t + C$ (4.3)

The conformity of the reaction with the first order kinetics and second order kinetics models were tested by plotting $Y(t) = -\ln(1\text{-}X_A)$ against t and $Y(t) = 1 / (1\text{-}X_A)$ against t respectively. This was done to verify the possible order of reaction which the experiment obeyed.

3.4.5 Activation energy

Arrhenius Parameters

The Arrhenius equation, equation 4.4 was used to determine the activation energy.

$\text{In } K = \text{In } A - (E_a/RT)$ 4.4

Where K is reaction rate constant, A is pre-exponential factor (min-1), E_a the activation energy in kJ/mol, T is the absolute temperature (K) and R is the universal gas constant. Since the activation energy is dependent on temperature and therefore, the rate constants at any temperature within the validity of the Arrhenius equation can be computed using equation 4.4.

3.5 Blending of the esters

The corresponding volumes of each ester and diesel were measured with the measuring cylinders and mixed in the ratios of 10:90, 20:80, 30:70, 40:60, 50:50, and 60:40, 70:30, 80:20, 90:10 esters to diesel respectively.

Analysis of each of the samples

Each seed oil sample, its methyl and ethyl ester, ester/diesel blends and diesel oil (AGO) were comparatively analysed for their fuel properties-relative densities, acid values, calorific values, viscosities at different temperatures, flash points, pour points, moisture contents and ash contents.

3.6 Characterization of the oil samples

The oils were characterized using American Oil Chemical Society (A.O.C.S) methods.

3.61 Determination of relative density

The oil was aspirated into a densitometer bulb using a 2ml syringe and the readings were displayed on the densitometer screen.

3.6.2 Total acid number

Each sample (1.0g) was accurately weighed on an analytical balance into a clean dry conical flask. 10cm^3 of chloroform were added to the oil and was properly shaken to dissolve the oil. Two drops of phenolphthalein indicator were added into the mixture. 0.05M alcoholic potassium hydroxide was poured into a burette and was used to titrate the oil in the conical flask. The end point was reached when the indicator changed from colourless to pink colour. The acid value is calculated using equations 3.1

$$\text{Acid value} = \frac{\text{ml of KOH x Molarity of KOH x Molar mass of KOH}}{\text{Mass of sample}} \qquad (3.1)$$

3.6.3 Iodine value determination

Each sample (1.0g) was accurately weighed into a reagent bottle and dissolved with 5ml of chloroform after which the solution became clear. Some quantity of glacial acetic acid was added to the clear solution in the reagent bottle with stopper. Then 100ml of iodine monochloride was added to the solution and was kept in a dark cupboard for 2 hours with occasional shaking at interval of 30 minutes. This was followed by addition of potassium iodide to convert the unused reagent to iodine. The liberated iodine was titrated with a standard solution of 0.1M sodium thiosulphate to a colourless end point. The iodine value was calculated using equation 3.2.

$$\text{Iodine value} = \frac{(a-b) \text{ x } M \text{ x Molarity of Iodine x Molar mass of Iodine}}{c} \qquad (3.2)$$

Where a= ml of iodine monochloride added

b = ml of thiosulphate consumed

c = mass of sample

M = molarity of thiosulphate

3.6.4 Saponification value determination

Each Sample (1.0g) was accurately weighed on an analytical balance in a suitable round bottom flask. 50ml of 1M alcoholic potassium hydroxide and anti-bumping chips were added to each weighed sample. This was followed by addition of two drops of phenolphthalein indicator. With the condenser vertically positioned on the round bottom flask, the flask was heated under reflux for 45 minutes.

The solution was titrated hot against 1M hydrochloric acid to a colourless end point. The saponififcation value was calculated using equation 3.3.

$$\text{Saponification value} = \frac{(a-b) \times M \times \text{Molar mass of KOH}}{c} \qquad (3.3)$$

Where a = volume of KOH used in titration

b = volume of HCl used for titration

M = molarity of HCl

c = mass of sample

3.6.5 Mean molecular mass determination

Mean molecular mass was calculated from iodine value using equation 3.4.

$$\text{Mean molecular mass} = \frac{1000 \times 56.1}{\text{Saponification value}} \qquad (3.4)$$

3.6.6 Determination of calorific value

The calorific value of the oil, esters, ester/diesel blends and diesel were determined using the API Table (Appendix 1) which relates the relative density and gross calorific value.

3.7 Determination of the fuel properties

The fuel properties were determined using American Society for Testing and Materials (ASTM) method (Annual book of ASTM standards, 2003).

3.7.1 Determination of kinematic viscosity

The kinematic viscosities of the samples were determined at 40^{o}C, 70^{o}C and 100^{o}C.

Each sample was aspirated into the viscometer tube using a vacuum pump to the upper mark and allowed to settle to attain the corresponding viscosity bath temperature (40^{o}C/70^{o}C/100^{o}C), the sample was then again aspirated to an upper mark of the viscometer tube, the stop watch was switched on and stopped when the sample got to the lower mark of the viscometer tube. The stop watch gave the exact flow rate of the oil sample. The experiment procedure was repeated. The average rate of flow was calculated.

The viscosity in centistokes was recorded as the time taken to flow from the upper mark to the lower mark multiplied by the viscometer tube constant.

3.7.2 Flash point test

Procedure: Each sample was shaken and poured into the flash point cup to a level inscribed on the cup. The cup was placed in the Pensky Martens tester, the power was switched on to heat and stir. The pilot flame was then ignited and with the aid of the shutter operating knob, the cup was lowered at intervals to check when it had finished. The flash point was noted at the temperature when the flame flashed inside the cup.

3.7.3 Determination of pour point

Each sample was shaken and poured into the test jar to the mark. The test jar was closed with the cork carrying the high pour thermometer to fit tightly. The test jar was immersed in the test bath jacket. The oil was allowed to cool to allow formation of wax and when the oil does not move when held in a horizontal position. The pour point result was recorded at this point from the thermometer.

3.8 Determination of heavy metals using Atomic Absorption Spectrophotometer Model Buck Scientific 210 and Flame absorption and visible spectroscopy model Corning 400

Preparation of sample

Procedure: the sample was weighed (0.5g) into a conical flask. 10cm^3 of concentrated nitric acid was added and heated until black and brown fumes reduced. Concentrated sulphuric acid (10cm^3) was added and heated for 20minutes until the liquid turned colourless. For some liquids that did not turn colourless after 20 minutes, more 5cm^3 of concentrated nitric acid was added and heated for 5 minutes followed by addition of more 5cm^3 of concentrated sulphuric acid. The liquid was heated until colourless condition was achieved. Then 5cm^3 of saturated solution of ammonium oxalate was added to facilitate the removal of coloured nitro compounds. The liquid was heated till no brown fumes were observed (Usoro *et al.,* 1982). The clear solution was made up to a standard solution in a 100ml volumetric flask. Each sample was stored in a 100ml sample bottle.

Instrument operation

The hollow cathode lamp of the desired metal was installed in the instrument. The lamp was then aligned in accordance with the manufacturer's instruction. The slit width was set according to the manufacturer's suggested setting of the element being measured. The instrument was turned on and the amount of current according to manufacturer's instruction was applied to the hollow cathode lamp. The instrument was allowed to warm up and stabilize for 10-20 minutes and the current was readjusted as necessary after warming. The burner heads were then installed. The air (compressor) was turned on, the flow rate was adjusted to suit the specified maximum sensitivity for the metal being measured.

In order to analyze a sample for its constituents, it was atomized. The sample was illuminated by its emission lines. The light transmitted was finally measured by a detector.

Standardization: At least, five concentration of each metal solution was standardized with 0.1M HCl so as to bracket the expected metal concentration of the sample. Each standard was aspirated in turn into the flame and their respective absorbances were recorded.

Analysis of Samples: The atomizer was rinsed by aspirating the de-ionised distilled water into the flame and the instrument was adjusted to read zero absorbance. Each sample solution was atomized and the absorbance of each was taken. Five readings were taken for each sample and average absorbance reading recorded.

Calculation: The concentration of each metal was calculated by referring to the appropriate calibration curve drawn by the in-built computer interface. The concentrations were equally read out from the print out from the computer.

3.9 Fourier Transform Infrared (FTIR) structure/stability relationship determination

Each sample was mixed with a little nujol and placed in between two sodium chloride plates with groove. The chloride plate was then attached to a Fourier Transform Infrared Spectrometer coupled to a computer with a print out system. The sample in the plate was irradiated by infrared lamp source at one end of the spectrometer and each sample was excited to different energy frequencies (cm^{-1}) Che-Man *et al*., (2010).

3.10 Gas Chromatographic - Mass Spectroscopy (GC-MS) analysis of the extracted oils using –GC-MS model QP2010 Plus Shimadzu Japan.

GCMS-QP2010 PLUS SHIMADZU JAPAN auto sampler and auto analyser model was fused with HP-Innowax fused capillary column (60 x 0.25mm i.d) and helium as the carrier gas (flow rate : 1.61 ml/min). The injection temperature was 250^{o}C and oven temperature kept at 60^{o}C for 5 minutes, then kept constant at 140^{o}C for another 5minutes and then programmed to 280 ^{o}C at a rate of 20^{o}C/min and then kept at 280^{o}C for 15 minutes. The end of the capillary column was inserted directly into the ion source of MS and interface temperature was maintained at 250^{o}C. The mass spectrometric data were acquired and processed with SHIDMAZU MAT 330 data system. The run button was pressed and later the peaks started appearing on the computer screen at different times.

The instrument has an accompanying library embedded in the computer soft ware attached to the equipment. The fatty acids and their methyl/ethyl esters were identified from, the mass spectral library based on their similarity index.

3.11 Engine performance/emission test

Each sample was tested for its diesel engine fuel consumption rate, emission level, powering capability and performance in comparison to diesel engine using a TECHNO R175A diesel engine. The emission test was also carried out by passing the fumes generated by each sample during the engine performance test in a conical flask containing 25ml of 1M solution of sodium hydroxide. This solution was then titrated against 1M hydrochloric acid solution to determine the acidity of the fumes. The rate of consumption was tested by passing 50ml of each sample at a time interval. The acidity of the fumes was then calculated as:

$$\text{Acidity of fumes} = (a-b) \times (\text{Molar mass of NaOH}) \times (\text{Molarity of NaOH}) \qquad (3.5)$$

Where

a = Volume of NaOH used in titration

b = Volume of HCl used in titration

Rate of fuel consumption was calculated thus:

$$\text{Rate of fuel consumption} = \frac{\text{Volume of fuel consumed}}{\text{Time taken}} \qquad (3.6)$$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1: Physicochemical Properties of the extracted oils

The results of the physicochemical properties of the samples are shown in Table 4.1 and Fig 4.1

Table 4.1: Physicochemical properties of *Cyperus esculentus, Sesamum indicum and Colocynthus vulgaris* oils.

Parameters	***Cyperus esculentus****	***Sesamum indicum****	***Colocynthus vulgaris****	***Diesel****
Appearance	Golden yellow	Brown	Bright yellow	Brown
% Oil	26.2	51.3	53.6	ND
Saponification value(mgKOH/g)	126.23	74.05	81.35	ND
Iodine value (g/100g oil)	121.83	122.46	123.01	ND
Acid value(mgKOH/g)	0.45	0.65	0.15	0.14
Density @28^{0}C (kg/m^3)	0.887	0.890	0.899	0.851
Mean molecular mass(g/mgKOH)	448.43	756.6	689.61	ND

ND = Not Determined, *average value of 3 replicate experiments.

The saponification values of the oils indicated that they are normal triglycerides that would be useful in production of shampoo and soaps.

Colocynthus vulgaris with iodine value 123.01g/100g had the highest iodine value followed by that of *sesamum indicum* with 122.46g/100g while *cyperus esculentus* iodine value was 121.83g/100g. These values placed the oils into semi-drying oils group. This means that *Colocynthus vulgaris* is likely to polymerise and oxidize at higher temperature more than *sesamum indicum* and *cyperus esculentus* since iodine value is used to determine the level of unsaturation in fatty acids. The higher the iodine value, the more unsaturated, the faster the oil will oxidize and the more it will polymerise (Thomas, 2000). The greater the degree of unsaturation in fatty acids, the more vulnerable the fatty acid is to lipid peroxidation (rancidity), but antioxidants can protect fats from lipid peroxidation.

High iodine values are reportedly associated with polymerisation and subsequent engine damage not just when using straight vegetable oil but in biodiesel made from the oils as well. While some oils with low iodine are suitable for use as fuel without further processing other than extracting and filtering, the majority of vegetable and animal oils have an iodine value which may cause problem if used as neat fuel. Iodine values are very important because many fuel standards specify iodine value limit for fuels that meet specification. For example the Euro standard for iodine value for biodiesel EN 14214 is 120 while German standard is 115 for DIN 5160 (Philip and TClark, 2004). The iodine value highly depends on the nature and ester composition of the feedstocks used in biodiesel production.

Biodiesel with high iodine value tends to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves. The tendency of polymerization increases with the degree of unsaturation of the fatty acids (István and Ioan-Adrain, 2011). This implies that biodiesel with high iodine value will be less stable at higher temperature.

The result of the density of *Colocynthus vulgaris, Cyperus esculentus* and *Sesamum indicum* ethyl esters are as shown in Table 4.1. *Colocynthus vulgaris* ethyl esters had the highest density followed by *Sesamum indicum* then *Cyperus esculentus* ethyl esters. The densities of the oils were higher than that of the petrodiesel. This is as a result of the fatty acid composition and molecular weight of the oils (Ezekwe and Ajiwe, 2011). Density directly affects the fuel performance like the quality of atomisation and combustion. The density of these oils fell within the range of ASTM (0.8-0.9).

The acid value (AV), also called neutralization number or acid number is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize the acidic constituents in one gram of sample. From Table 4.1, *Cyperus esculentus, Sesamum indicum and Colocynthus vulgaris* had acid values of 0.45, 0.65 and 0.15mg/g respectively. *Colocynthus vulgaris* oil had the low acid value while *Cyperus esculentus and Sesamum indicum* had high acid value. This could be as a result of the fatty acid contents of the oils unlike that of fossil diesel which is as a result of its sulphur content. The acidic compounds that are possibly found in biodiesel are from residual mineral acids from the production process, residual free fatty acids from hydrolysis process or post hydrolysis process of the esters and finally from oxidation bye products in form of other organic acids (Berthiaume, *et al*., 2006).

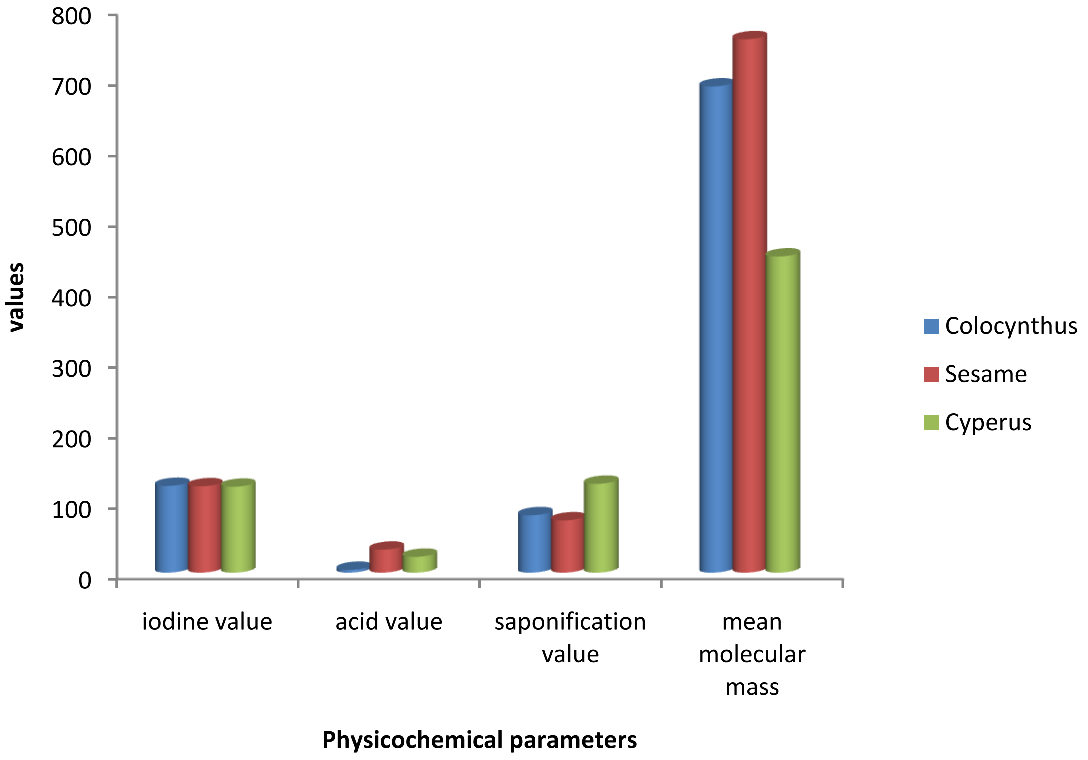


Fig 4.1: Iodine value, acid value, saponification values of the ethyl esters/diesel blends

From Fig 4.1, it was observed that the iodine values of the oil samples were very much similar to each other while *sesamum indicum* oil had highest acid value and mean molecular mass; *cyperus esculentus* oil also had the highest saponification value.

4.2: The Biodiesel Properties of oils, ethyl ester/diesel blends and diesel.

The Biodiesel Properties of oils, ethyl ester/diesel blends with diesel are shown on Tables 4.2-4.4

Table 4.2 Comparative analysis on the fuel properties of *Cyperus esculentus* oil, its ethylester and ethylester/diesel blends.

Sample	**Relative Density**	**Viscosity at 100^{o}C mm^2/s**	**Viscosity at 70^{o}C mm^2/s**	**Viscosity at 40^{o}C mm^2/s**	**Flash Point (^{o}C)**	**Pour Point (^{o}C)**	**Calorific Value (kJ/kg)**
Diesel	0.85	1.28	1.59	2.57	70	-9	45334
Cyperus Oil	0.88	5.49	10.02	25.14	94	-3	44752
B10	0.85	2.19	3.52	6.28	110	-16	45334
B20	0.85	2.2	2.89	6.25	116	-14	45334
B30	0.85	2.57	4.58	7.65	130	-14	45334
B40	0.85	2.88	4.45	8.39	128	-13	45334
B50	0.86	3.06	5.03	9.66	120	-12	45124
B60	0.86	3.24	5.44	9.87	110	-14	45124
B70	0.86	3.57	5.22	10.23	98	-13	45124
B80	0.86	3.42	5.99	10.51	110	-11	45124
B90	0.86	3.17	6.17	10.92	86	-9	45124
B100	0.86	4.43	8.54	15.32	94	-10	45124

Table 4.3 Comparative analysis on the fuel properties of *Colocynthus vulgaris* oil, its ethylester and ethylester/diesel blends.

Sample	**Relative Density**	**Viscosity at 100^{o}C mm^2/s**	**Viscosity at 70^{o}C mm^2/s**	**Viscosity at 40^{o}C mm^2/s**	**Flash Point (^{o}C)**	**Pour Point (^{o}C)**	**Calorific Value kJ/kg**
Diesel	0.85	1.28	1.59	2.57	70	-9	45334
Oil	0.89	5.73	11.16	26.63	120	-1	44543
B10	0.86	2.54	3.91	6.9	118	-11	45124
B20	0.86	2.62	4.52	7.67	108	-13	45124
B30	0.87	3.23	9.83	10.12	112	-12	44938
B40	0.87	3.5	6.4	11.44	126	-14	44938
B50	0.88	3.83	6.73	13.04	128	-12	44752
B60	0.88	4.03	6.82	14.34	130	-10	44752
B70	0.89	5.15	9.32	17.81	122	-12	44543
B80	0.89	5.65	10.46	20.63	118	-9	44543
B90	0.89	8.03	22.69	37.07	118	-8	44543
B100	0.89	9.59	22.56	47.61	130	-12	44543

Table 4.4 Comparative analysis on the fuel properties of *Sesamum indicum* oil, its ethylester and ethylester/diesel blends.

Sample	**Relative Density**	**Viscosity at 100^{o}C mm^2/s**	**Viscosity at 70^{o}C mm^2/s**	**Viscosity at 40^{o}C mm^2/s**	**Flash Point (^{o}C)**	**Pour Point (^{o}C)**	**Calorific Value kJ/kg**
Diesel	0.85	1.28	1.59	2.57	70	-9	45334
Oil	0.89	5.02	10.38	24.29	94	-1	44543
B10	0.85	2.45	3.39	6.77	114	-14	45334
B20	0.85	2.59	4.05	6.64	126	-12	45334
B30	0.86	2.75	4.31	7.59	112	-15	45124
B40	0.86	2.98	5.48	9.2	118	-9	45124
B50	0.86	3.39	5.28	9.67	120	-16	45124
B60	0.87	2.89	5.68	9.67	118	-12	45938
B70	0.87	3.82	7.17	14.27	110	-11	45938
B80	0.87	4.07	9.76	15.62	134	-7	45938
B90	0.87	4.12	10.67	18.33	136	-8	45938
B100	0.87	5.77	11.1	25.67	142	-8	45938

Tables 4.2-4.4 showed the variation of viscosity of the ethyl esters and their corresponding diesel blends. The viscosity of pure ethyl esters were *Cyperus esculentus* (15.32 mm^2/s), *Sesamum indicum* (25.67 mm^2/s) and *Colocynthus vulgaris* (47.61 mm^2/s) at 40°C. *Colocynthus vulgaris* ethyl esters and its diesel blends had the highest viscosity when compared to the other ethyl esters at 40°C, followed by *Sesamum indicum* ethyl esters, then *Cyperus esculentus* ethyl esters.

There was a progressive decrease in viscosity of the ethyl esters blends (B10-B100). This showed that blending petrodiesel with biodiesel improves the viscosity of the blend thereby ensuring their compatibility with modern diesel engines which have fuel injection systems and are sensitive to viscosity change (Jaichander and Annamaiia, 2011). Viscosity affects fuel injection into engine combustion chamber. The higher the viscosity of a fuel, the greater its tendency to cause problems (Knothe and Steidley, 2005).

The viscosities of the ethyl esters were lower than that of the oils because of the fatty acids present in the oils which were reduced in the esters during saponification and esterification (Ajiwe, 2004). This decrease in the viscosities of the esters also indicated complete ester formation. For all fatty acids and aliphatic hydrocarbons, the kinematic viscosity increases with chain length (i.e. the number of carbon atoms). Generally, the aliphatic and aromatic hydrocarbons which are the major components of petrodiesel have lower viscosity than biodiesel due to lack of oxygen and other heteroatoms. Hence for the same number of carbon atom, fatty acids have greater viscosity than their hydrocarbon counterparts. Example pentadecane (2.49) has a lower kinematic viscosity at 40°C than propyl laurate (3.04) and methyl myristate (3.30) which have the same number of carbon atoms (Knothe and Steidley, 2005).

Double bonds reduce kinematic viscosity in both fatty acid compounds and aliphatic hydrocarbons. The influence of the double bonds was investigated and found that the decrease in viscosity was caused by the second double bond (Kaufmann *et al*., 1938). This was also observed in the viscosity results. *Colocynthus vulgaris* ethylester had the highest viscosity and this could be attributed to the fact that it contained longer chain lengths (Table 4.3). The chain length ranged from C16-C20 while that of *sesamum indicum* ranged from C16-C19. The high level of unsaturation of *Colocynthus vulgaris* ethylester as shown in Table 4.3 was expected to be an advantage to lower its viscosity since viscosity decreases with unsaturation (Keith, 2001).

Tables 4.2-4.4 showed the results of flash point which is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions. It is used to classify fuels for transport, storage and distribution according to hazard level. *Colocynthus vulgaris* (120^{o}C) had the highest value of flash points, followed by *Sesamum indicum* (114^{o}C) and then *Cyperus esculentus* (94^{o}C). The high flash point value of *Colocynthus vulgaris* made it safe as regards to storage, fuel handling and transportation. A flash point varies with fuels volatility meaning that these biodiesels contained low volatile components compared to other feedstocks. For biodiesel the minimum flash point is 93 °C in the United States, 100 °C in Brazil and 120 °C in Europe. Biodiesel’s flash point decreases rapidly as the amount of residual (un-reacted) alcohol increases (methanol’s flash point is 11–12 °C, and ethanol’s is 13–14 °C). The flash points of the ethylesters confirmed that there was no residual ethanol in the samples. Thus, measuring the biodiesel flash point helps indicate the presence of methanol or ethanol (Barabás and Todoruţ, 2010; Pinyaphong *et al*., 2011).

Table 4.2-4.4 showed the results of pour point of the ethyl esters which is the temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow. This occurs if the temperature of the biodiesel drops below cloud point, when the microcrystals merge and form large clusters, which may disrupt the flow of the biodiesel through the pipes of the engine's fuel system. Similarly to the cloud point, the pour point values also depend on the feedstock the biodiesel was produced from. Pour point provides indicative values for the minimum temperature at which the fuel can be used. *Cyperus esculentus* ethyl ester had the poorest pour point; this result could be explained further from the result obtained in Table 4.11 which showed that *Cyperus esculentus* ethylester contained high amount of saturated fatty acids (57.14%). Cold flow properties could worsen with increase in degree of saturation of fatty acids (Knothe, 2007; Shrestha *et al*., 2008). For countries like Nigeria with high temperatures the pour points of these biofuels will not affect their use as afeedstock for biofuel production.

The results of the calorific value of *Colocynthus vulgaris, Cyperus esculentus* and *Sesamum indicum* ethyl esters are as shown in Tables 4.2-4.4. *Sesamum indicum* had the highest calorific value followed by *Cyperus esculentus* then *Colocynthus vulgaris* ethyl esters. This is because *Sesamum indicum* contained the highest number of saturated fatty acids. It was also observed that the calorific value of the samples decreased as the concentration of the ethyl esters in the blends increased. Petrodiesel had higher calorific value than the esters because of presence of chemically bond oxygen present in biodiesel and this in turn lowered the heating values (Kaplan *et al.,* 2006).

Figures 4.2-4.4 showed the line graph of viscosities of ethyl esters of the three seed oil samples.

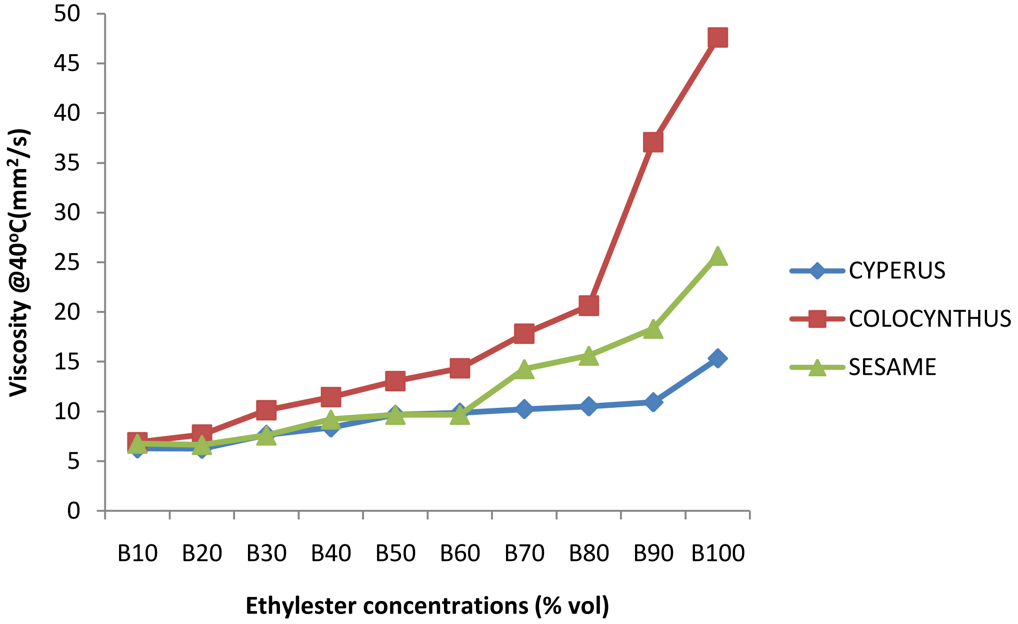


Fig 4.2: Viscosity at 40°C versus ethyl esters concentration in ethyl esters/diesel blends

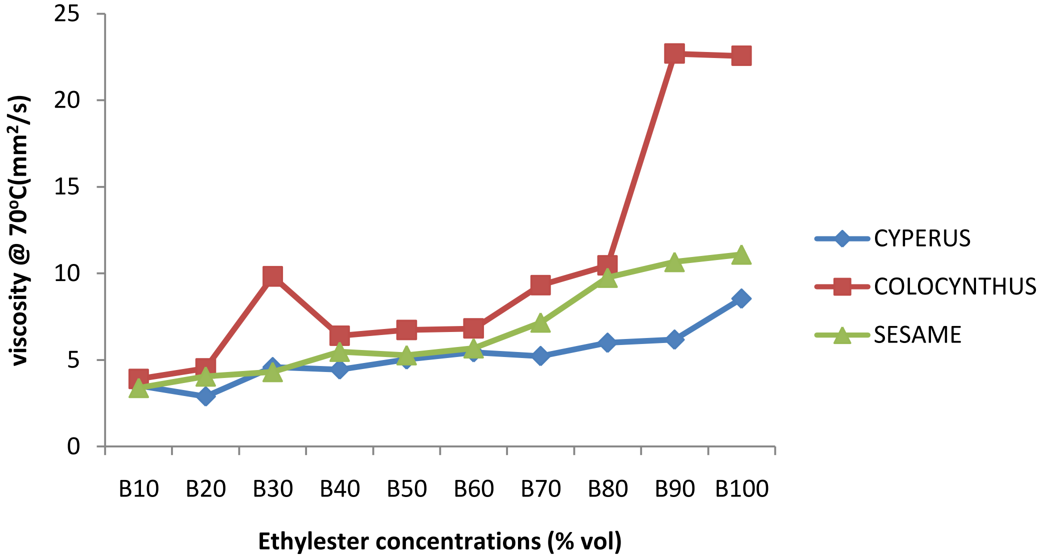


Fig 4.3: Viscosity at 70°C versus ethyl esters concentration in ethyl esters/diesel blends

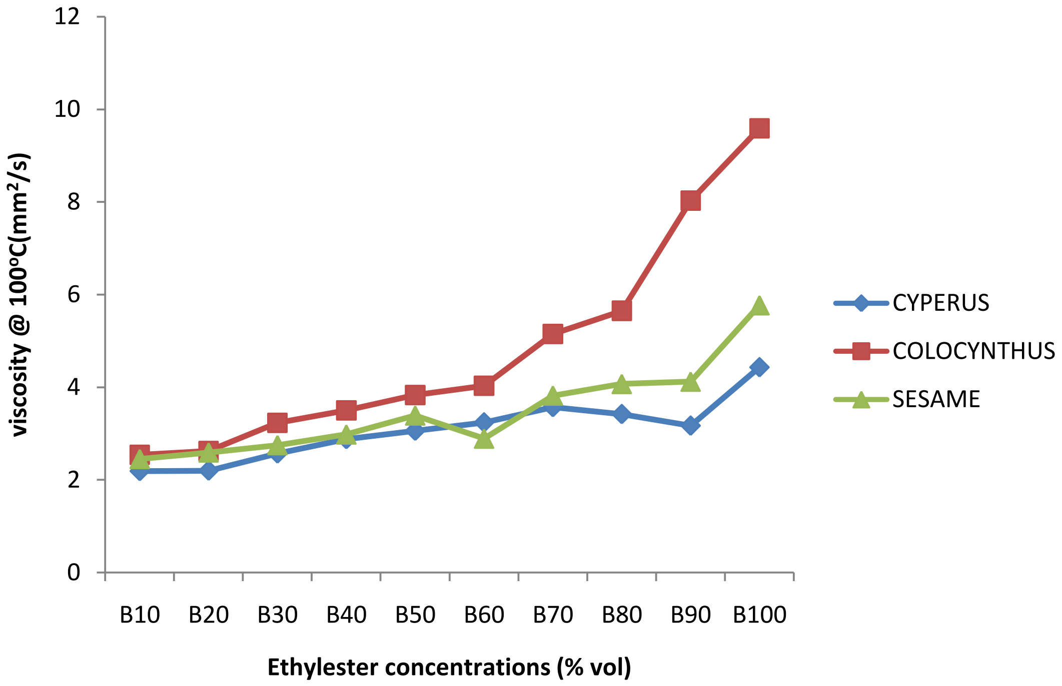


Fig 4.4: Viscosity at 100°C versus ethyl esters concentration in ethyl esters/diesel blends

From the plot, *Colocynthus vulgaris* ethylester had the highest viscosity on dilution with diesel while the *Cyperus esculentus* had the least viscosity on dilution showing the interaction between diesel and these esters were the same and that the diesel had little or no interaction with the esters.

The line graph of viscosity at different temperatures as in Fig 4.4 showed that the viscosity of oils and esters at different dilutions decreased with increase in temperature. This might be as a result of weakening (deformation) of bonds or breaking of bonds at higher temperatures. This is confirmed from FTIR results in Tables 4.41 – 4.44.

Figs 4.5- 4.8 showed the line graph plot of flash point, pour point, relative density and calorific values respectively

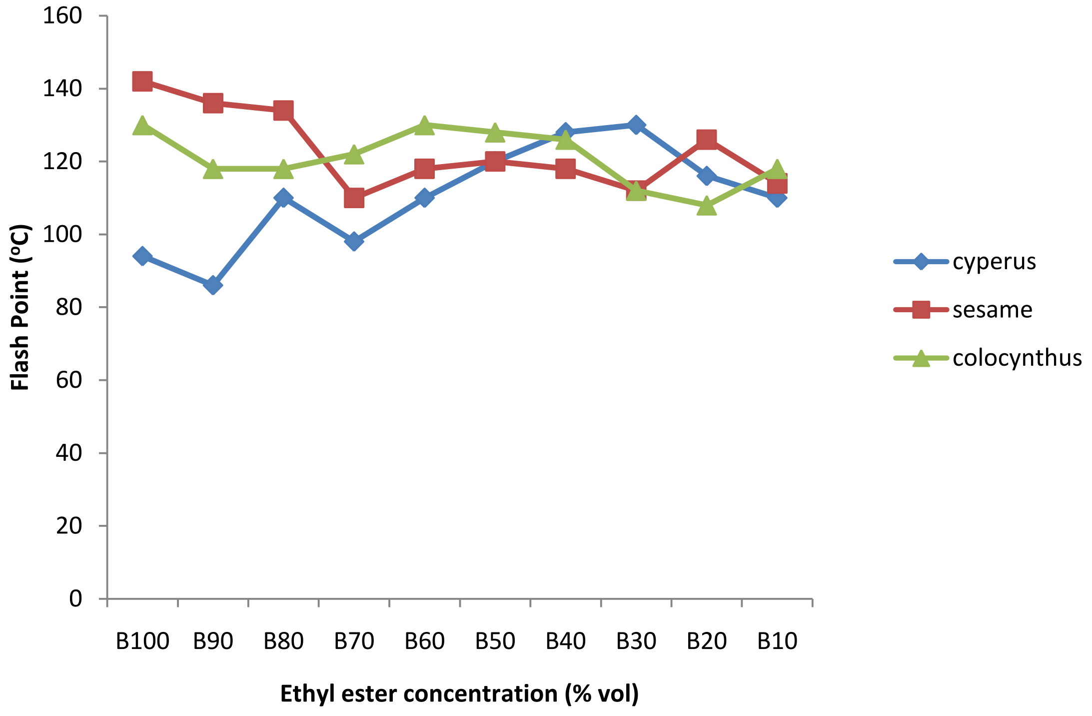


Fig: 4.5: Flash point versus ethylester concentrations in ethyl esters/diesel blends.

Fig 4.5 showed the variation of flash points of *Colocynthus vulgaris*, *Cyperus esculentus* and *Sesamum indicum* ethyl esters and their corresponding diesel blends. From the plot it was observed that *Colocynthus vulgaris* ethyl esters and its diesel blends had the highest value of flash points, followed by *Sesamum indicum* then *Cyperus esculentus.* The high flash point value of *Colocynthus vulgaris* ethyl esters indicated that the samples contained relatively low volatile components when compared to *Cyperus esculentus* and *Sesamum indicum*. From the plot, it was also observed that the flash point increased with increase in concentration of the esters in the biodiesel blends.

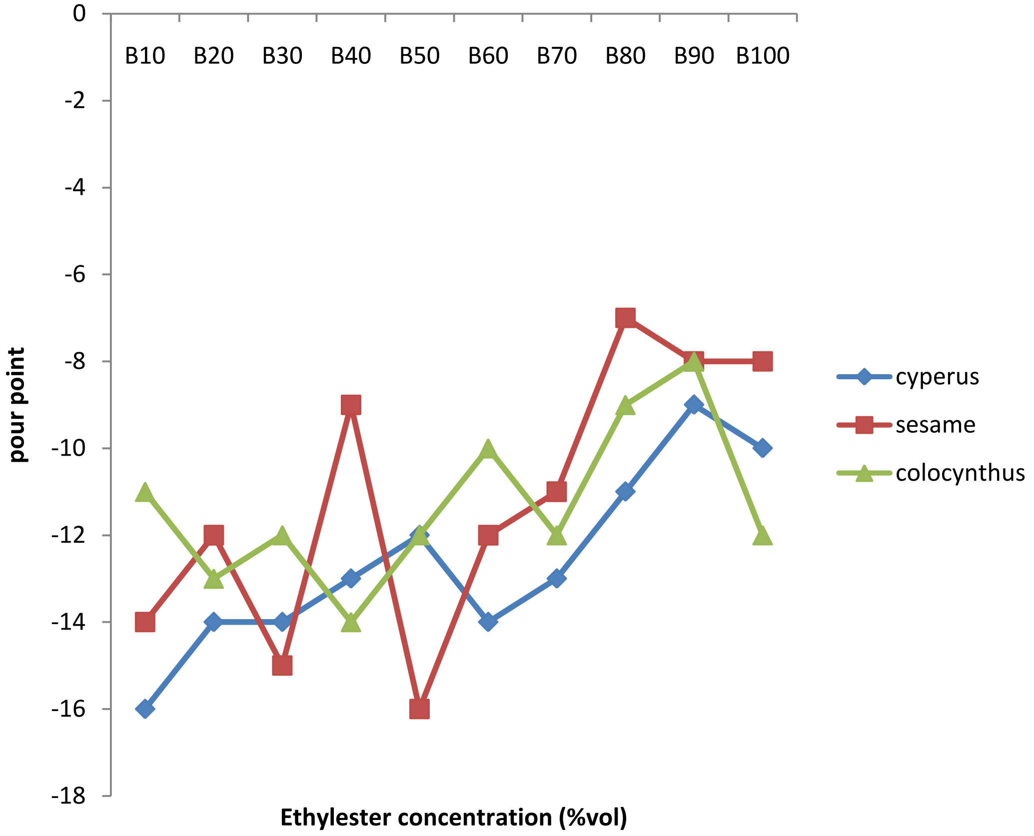


Fig 4.6: Pour point versus ethylester concentrations in ethyl esters/diesel blends.

Dilution of the ethyl esters decreased the pour point of the biodiesels as shown in Fig 4.6. The ethyl esters and their diesel blends were liquid at room temperature (27^{o}C) and would have no cold flow problems in countries like Nigeria where room temperature is always above 10^{o}C. *Colocynthus vulgaris* ethyl ester showed better cold flow properties than *Cyperus esculentus* and *Sesamum indicum*.

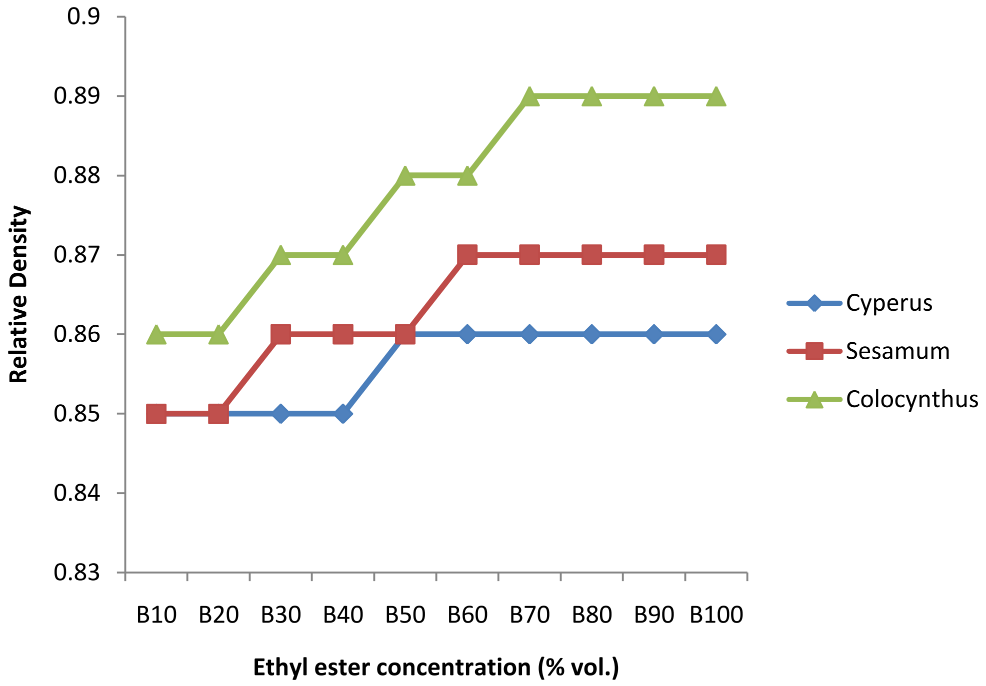


Fig 4.7: Relative density versus Ethylester concentrations in ethyl esters/diesel blends.

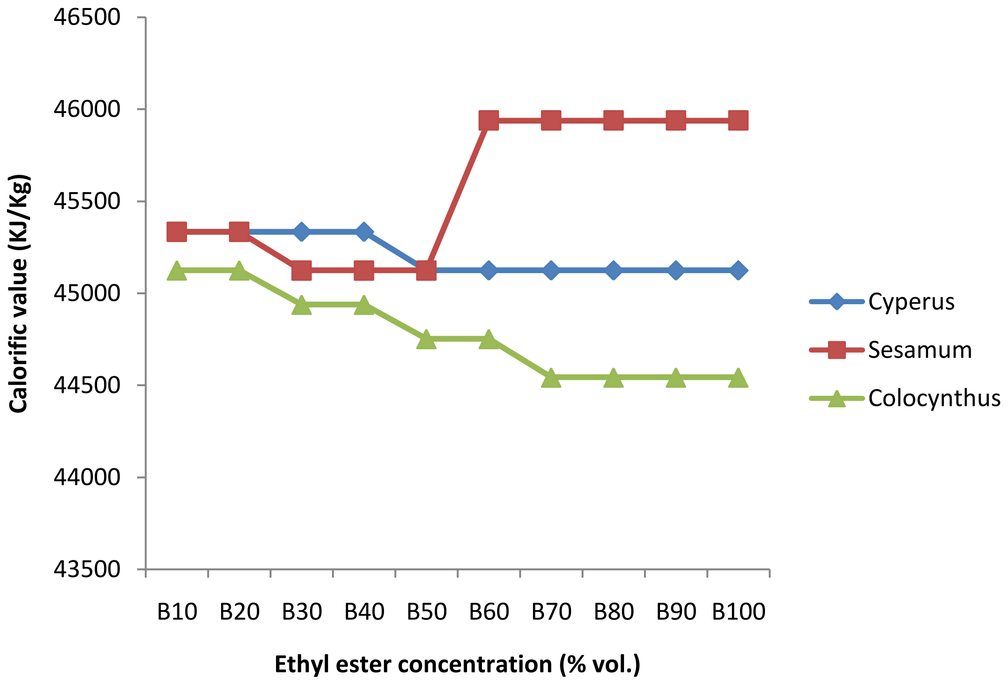


Fig 4.8: Calorific value versus ethylester concentrations in ethyl esters/diesel blends.

Fig 4.7 and 4.8 showed the variation of relative density and calorific values of *Colocynthus vulgaris*, *Cyperus esculentus* and *Sesamum indicum* ethyl esters and their corresponding diesel blends. From the plots, it was observed that *Colocynthus vulgaris* had the highest value for relative density followed by *Sesamum indicum*, then *Cyperus esculentus*. These variations of the relative density can be attributed to the degree of unsaturation in the esters. It has been reported that increase in density also increases with of degree of unsaturation (Giakoumis, 2013)

From Fig 4.8 *Sesamum indicum* ester had highest calorific values followed by *Cyperus esculentus* ester then *Colocynthus vulgaris* ester. In *Sesamum indicum* and *Colocynthus vulgaris* ester, the calorific values increased as the concentration of the ethyl esters in the samples increased in all the blends except for *Cyperus esculentus* ester the calorific values decreased as the concentration of the ethyl esters in the samples increased.

4.3: The heavy metal composition of oils and ethyl ester samples

The heavy metal composition of oils and ethyl esters of oils are shown in Table 4.5

Table 4.5 Heavy metal composition of *Colocynthus vulgaris*, *Cyperus esculentus* and *Sesamum indicum* oil and its ethyl esters

ELEMENT	Diesel (mg/l)	*Cyperus oil*(mg/l)	*Cyperus* ethylester (mg/l)	*Colocynthus oil*(mg/l)	*Colocynthus* ethylester(mg/l)	*Sesamum oil*(mg/l)	*Sesamum* ethylester (mg/l)
Calcium	4.25	0.0073	0.0141	0.0134	0.0175	0.0213	0.021
Cadmium	1.35	0.0038	0.002	0.0052	0.003	0.0002	0.0035
Copper	0.45	0.0041	0.0029	0.0019	0.0011	0.0017	0.0005
Iron	4.50	0.0139	0.0027	0.0176	0.0111	0.0155	0.0149
Manganese	1.40	0.0056	0.0055	0.0045	0.0025	0.0029	0.0012
Sodium	1.42	0.0002	0.001	0.0006	0.0018	0.0172	0.0009
Nickel	3.52	0.0176	0.0093	0.0024	0.0061	0.017	0.0112
Zinc	1.58	0.0043	0.0033	0.0009	0.001	0.0048	0.0019
Potassium	1.12	0.0232	0.0011	0.0373	0.0006	0.0059	0.0189
Magnesium	3.30	0.0008	0.0003	0.0118	0.0030	0.0004	0.0006
Arsenic	2.14	0.0000	0.0000	2.6400	2.5000	2.1100	0.0000
Lead	0.52	0.8100	0.5000	2.4300	5.4200	1.1200	0.5100

The heavy metal compositions of the oil and their esters are shown in Table 4.5. The compositions of the esters were lower than that of the corresponding oils which showed that the esters were purified during the esterification process. The result showed that all the elements were in trace amount except for *Colocynthus vulgaris*, *Colocynthus vulgaris* ethyl ester, *Sesamum indicum* ester which had high concentration of arsenic. This showed that most of the samples would not constitute a corrosion inhibition in the injector and piston chambers of diesel engines.

4.4: Grading of the oils, ethyl esters and its diesel blends

The grading of the oils, ethyl esters and its diesel blends is as shown in Table 4.6

Table 4.6 Grading of the oils, ethyl esters and its diesel blends based on their viscosities according to ASTM standards.

Ethyl esters	**1D**	**2D**	**4D**
at 40°C			
Colocynthus	-	-	B10-B80
Sesamum	-	-	B10-B90
Cyperus	-	-	B10-B100
at70°C			
Colocynthus	-	B10-B20	B30-B100
Sesamum	-	B10-B30	B40-B100
Cyperus	-	B10-B40	B50-B100
at100°C			
Colocynthus	-	B10-B60	B70-B100
Sesamum	-	B10-B90	B100
Cyperus	-	B10-B100	-

From Table 4.6, it was observed that *Colocynthus vulgaris* ethyl esters B90-B100, *Sesamum indicum* B100 at 40^{o}C did not fall into any grade because of its high viscosity while others fell into grade 4D diesel class (heavy diesel grades) showing that they are more likely to be used as diesel fuels after heating and cooling while at70^{o}C and 100^{o}C some fell into group 2D.

Based on their viscosities, the oils and ester blends fell within group 2D (2.0-4.9mm^{2}/s) or 4D (5.0-24.0mm^{2}/s) diesel grades at 40^{o}C, 70^{o}C and 100^{o}C (Ezekwe and Ajiwe, 2011).

4.5: Fatty acid profile of the ethyl esters, the average chain lengths and Saturation levels of fatty acids components of the ethyl esters.

Tables 4.7- 4.9 showed the fatty acid profile of the ethyl esters respectively while Table 4.10 showed the average chain lengths of the fatty acid components of the ethyl esters.

Table 4.7: Fatty acid profile of *Cyperus esculentus* ethyl ester seed oil

S/no	**Common name**	**Systematic name**	**Shorthand name**	**R.A (%)**
1	Myristic acid	Tetradecanoic acid	14:0	0.75
2	-	9-hexadecenoic acid		1.12
3	Palmitic acid	Hexadecanoic acid	16:0	24.15
4	Linoleic acid	9,12-octadecadienoic acid	18:2	18.04
5	Oleic acid	9-octadecenoic acid	18:1	36.31
6	Stearic acid	Octadecanoic acid	18:0	17.02
7	-	Heptadecanoic acid	18:1	2.61

Table 4.7 showed that the major fatty acids present in *Cyperus esculentus* ethyl esters were myristic acid (0.75%), palmitic acid (24.15%), stearic acid (17.02%) and heptadecanoic acid (2.61%) as the saturated fatty acids while 9-hexadecenoic acid (1.12%) and oleic acid (36.31%) were the monounsaturated fatty acids, linoleic acid (18.04%) was the only polyunsaturated fatty acid.

The presence of four saturated fatty acid , 2 monounsaturated fatty acids and one polyunsaturated indicated that *Cyperus esculentus* ethylester could have good oxidation stability without the aid of additives to improve oxidation stability since the palmitic acid present in it is a natural anti oxidant.

Table 4.8: Fatty acid profile of *Colocynthus vulgaris* ethyl ester seed oil

S/no	**Common name**	**Systematic name**	**Shorthand name**	**R.A (%)**
1	-	Pentadecanoic acid		22.42
2	Linoleic acid	9,12-octadecadienoic acid	16:0	54.86
3	Stearic acid	Octadecanoic acid	18:0	22.73

Table 4.8 showed the major fatty acids present in *colocynthus vulgaris* ethyl esters as pentadecanoic (22.42%) and stearic acid (22.73%) as the only saturated fatty acids while linoleic acid (54.86%) was the only polyunsaturated fatty acid. There were no monounsaturated fatty acids. The presence of polyunsaturated fatty acids indicated that that it might have a poor oxidative stability and the possibility of polymerising at high temperature. It would therefore require an anti oxidant to prevent lipid peroxidation (Razon, 2009).

Table 4.9: Fatty acid profile of *Sesamum indicum* ethyl ester seed oil

S/no	**Common name**	**Systematic name**	**Shorthand name**	**R.A (%)**
1	Palmitic acid	Hexadecanoic acid	16:0	2.76
2	-	Hexadecanoic acid	-	27.76
3	Cis vaccenic acid	11-octadecadienoic acid	18:1	9.26
4	Oleic acid	9-octadecenoic acid	18:1	41.09
5	-	Pentadecenoic acid	-	16.10
6	-	Heptadecanoic acid	-	3.03

Table 4.9 showed the major fatty acids present in *Sesamum indicum* ethyl esters as palmitic acid (22.76%), pentadecenoic acid (16.1%) and heptadecanoic acid (3.03%)as saturated fatty acids, while cis vaccenic acid (9.26%) and oleic acid (41.09%) were the monounsaturated fatty acid. The sample had no polyunsaturated fatty acid.

The absence of polyunsaturated fatty acid and the presence of palmitic acid (a natural antioxidant) showed that it had a good oxidation stability and low possibility of polymerising at high temperatures. This means that it would form a perfect feedstock for biodiesel production.

Table: 4.10 Average chain lengths of the fatty acid components of the ethyl esters

Chain length	***Cyperus esculentus***	***Colocynthus vulgaris***	***Sesamum indicum***
%C16	100	-	-
%C17	-	33.33	66.67
%C18	66.67	-	33.33
%C19	33.33	-	66.67

Table 4.10 showed average chain length by composition of ethyl esters. The predominant chain lengths were C16, C18 and C20. The chain length by composition of *Sesamum indicum* ethyl esters were C_{17} (2), C_{18} (1), C_{19} (2), C_{20} (1) while the chain length by composition of *Colocynthus vulgaris* ethyl esters were C_{17} (1) and C_{20} (2). The chain length by composition and the predominant chain lengths present in *Cyperus esculentus* ethyl esters were C_{16} (1), C_{18} (2), C_{19} (1), C_{20} (3). Viscosity, calorific value, cetane number and oxidative stability increases with increase in number of chain lengths (Razon, 2009), this was observed in *Sesamum indicum* ethylesters which had highest chain length also had very high calorific value (45938kJ/kg) and high viscosity (25.67mm^2/s at 40^{o}C)

Table 4.11 outlined the saturation levels of fatty acids found in the ethyl esters of the oils.

Table 4.11: Saturation levels of fatty acids components of the ethyl esters

Sample	**%SFA**	**%MUSFA**	**%PUSFA**
Sesamum indicum	66.67	33.33	-
Cyperus esculentus	57.14	28.57	-
Colocynthus vulgaris	66.67	-	33.33

Sesamum indicum and *Colocynthus vulgaris* ethyl esters had greater percentage of saturated fatty acids than *Cyperus esculentus* ethyl esters (Table 4.11), this means that they have good oxidative stability. *Sesamum indicum and Cyperus esculentus* ethyl esters contained no polyunsaturated fatty acid. The absence of PUSFA means it has a good oxidative stability and wll not require an oxidant thereby making them very good source for biodiesel production. *Colocynthus vulgaris* ethyl esters contained no monounsaturated fatty acid, it had the highest % of polyunsaturated fatty acids (PUSFA), and hence it is more susceptible poor oxidation stability than others. High PUSFA favours lubricity and cold flow properties (pour point) (Razon, 2009).

4.6: The acidity concentration of fumes emitted from combustion of the ethyl ester and diesel samples.

The acidity concentration of fumes emitted from combustion of the biodiesel and diesel samples during combustion results are shown on Table 4.12

Table 4.12 Concentration of acidic emissions of the samples (ethyl esters) from the engine performance tests

	Cyperus esculentus **g/dm^3**	***Sesamum indicum*** **g/dm^3**	***Colocynthus vulgaris*** **g/dm^3**
Diesel	0.0045	0.0045	0.0045
B100	0.0015	0.0013	0.0031
B90	0.0028	0.0026	0.0029
B80	0.0017	0.0026	0.0023
B70	0.0028	0.0018	0.0025
B60	0.0016	0.0025	0.003
B50	0.0026	0.0029	0.0023
B40	0.0015	0.0023	0.0027
B30	0.0027	0.0025	0.0029
B20	0.0025	0.0024	0.0026
B10	0.0026	0.0019	0.0029

The powering capability test carried out on a Techno R175A diesel engine showed that all the samples were able to power the diesel engine at the same interval and almost the same volume. The biodiesel and diesel-blend samples had the similar volume consumption. The samples showed lighter emissions with less irritating smell than the diesel which had darker emission. The use of biofuel as alternative fuel reduces air quality detoriation caused by fossil fuel combustion (EPA, 2002). From the results it was confirmed that the acid concentrations in the exhaust gas from the samples were lower than that of hydrocarbon diesel. Also the acid concentrations in the exhaust smokes increased as the amount of diesel blended into the biodiesel increased. B100 provided the least emission reduction. This may be as a result of the biodiesel's oxygen content which allowed the fuel to burn completely thereby reducing hydrocarbon and monoxide emissions. Hence, Engine performance of diesels could be improved by more dilution with esterified vegetable oils. These results are in line with the works of (Ajiwe *et al.*, 2006, 2001, Ezekwe and Ajiwe, 2013).

4.7 Kinetics of Transesterification Reactions

Tables 4.13-4.15 showed the effects of catalyst, time and temperature on %conversion of biodiesel respectively.

Table 4.13 Effect of catalyst on percentage conversion of oil to biodiesel

Volume of catalyst (ml)	**Volume of CM ester %**	**Volume of CE ester %**	**Volume of SE ester %**	**Volume of SM ester %**	**Volume of CoM ester %**	**Volume of CoE ester %**
2	-	64	-	-	-	-
4	-	68	50	60	-	-
6	70	70	70	60	80	80
8	74	76	80	80	90	90
10	78	80	80	60	100	100
12	68	68	70	50	90	90

CM= *Cyperus esculentus* methylester, CE = *Cyperus esculentus* ethylester
SE =*Sesamum indicum* ethylester, SM =*Sesamum indicum m*ethylester
CoM=*Colocynthusvulgaris* methylester, CoE=*Colocynthus vulgaris* ethyl ester

Table 4.13 showed variation of amount of catalyst with biodiesel yield. The result showed that the amount of catalyst added at constant volume of oil, temperature and time for all the samples increased and decreased at different catalyst concentrations. The density of the oil was used to monitor the conversion of theoils into esters. The optimum catalyst (1:2 H_2SO_4:Water) needed for biodiesel production of *Colocynthus vulgaris* ethyl and methyl ester, *Cyperus esculentus* ethyl and methyl ester and *Sesamum indicum* ethyl ester was 10ml, while *Sesamum indicum* methyl ester was 8ml.

Table 4.14 Effect of time on percentage conversion of oil to biodiesel

Time (mins)	**Volume of CE ester %**	**Volume of CM ester %**	**Volume of SE ester %**	**Volume of SM ester %**	**Volume of CoE ester %**	**Volume of CoM ester %**
30	80	68	80	60	90	78
40	86	64	70	60	100	80
50	88	64	60	80	90	80
60	88	64	80	75	100	90
70	90	64	70	75	100	80
80	84	-	-	-	-	-

CM= *Cyperus esculentus* methylester, CE = *Cyperus esculentus* ethylester
SE =*Sesamum indicum* ethylester, SM =*Sesamum indicum m*ethylester
CoM=*Colocynthusvulgaris* methylester, CoE=*Colocynthus vulgaris* ethyl ester

Table 4.14 showed the effects of reaction time on biodiesel production. It could be seen from the Table that the rate of conversion to biodiesel increased with increase in the reaction time. The effect of reaction time was studied from time interval of 30 to 80 minutes. The result showed that each sample had different reaction time ranging from 40 minutes to 70 minutes for each of the samples. Beyond these times the ester yield decreased and remained constant in some of these samples. The rate of methylation was faster than those of the ethylation reactions as observed that most methylation took place within 40-50 minutes while the ethylation reached 70 minutes. (Alipio *et al*., 2009) reported that bigger alcohols have higher activation energy and tend to react more slowly than smaller alcohols. This variation in the rate of methylation and ethylation can be seen in the differences in their activation energy as the ethyl esters had higher activation energy than the methyl esters.

Table 4.15 Effect of temperature on percentage conversion of biodiesel

Temperature (^oC)	**Volume of CE ester %**	**Volume of CM ester %**	**Volume of SE ester %**	**Volume of SM ester %**	**Volume of CoE ester %**	**Volume of CoM ester %**
40	92	80	96	90	80	100
50	84	80	84	80	90	90
60	64	80	80	80	90	90
70	64	100	80	80	100	80

CM= *Cyperus esculentus* methylester, CE = *Cyperus esculentus* ethylester
SE =*Sesamum indicum* ethylester, SM =*Sesamum indicum m*ethylester
CoM=*Colocynthusvulgaris* methylester, CoE=*Colocynthus vulgaris* ethyl ester

Table 4.15 showed the effect of reaction temperature on yield of biodiesel. Entropy increases with increasing temperature thus causing reacting species to collide faster with sufficient energy and this shifts the equilibrium position towards a favoured direction. In this study, the reaction temperature was varied at 40^{o}C, 50^{o}C, 60^{o}C and 70^{o}C respectively. The optimum temperature for all the samples was 40^{o}C except for *Cyperus esculentus* methyl ester and *Colocynthus vulgaris* ethyl ester that was 70^{o}C. (Mittelbach and Trathnigg, 1990) reported that the rate of transesterification is temperature dependent, but the percentage conversion is not a strong function of temperature provided that the reaction proceeds at least ten minutes.

Verification of Rate Constant and Order of Reaction

The results obtained for testing of conformity of reaction with zero order, ist order and second order of reactions are presented in Table 4.16. The Tables, graphs, slope, intercept and R^2 values of the trend lines are shown as figures in appendix 2a-25b.

The rate constants and correlation coefficients of ethylesters and methylesters are shown in Tables 4.16 and 4.17 respectively.

Table 4.16 Rate constants and Correlation coefficients (R^2) values of ethylesters at different temperatures for the first order and second order kinetic models

Sample	**Temp (^{o}C)**	**Zero order K_o**	**R^2**	**1storder K_1 (min^{-1})**	**R^2**	**2nd order K_2 ml/mol,min^{-1})**	**R^2**
Colocynthus	30	0.013	0.798	0.199	0.849	3.294	0.905
	50	0.01	0.925	0.172	0.939	3.071	0.939
	70	0.011	0.857	0.164	0.901	2.390	0.933
Cyperus	30	0.022	0.817	0.151	0.849	1.118	0.915
	50	0.013	0.880	0.091	0.907	0.603	0.907
	70	0.015	0.892	0.121	0.898	1.000	0.900
Sesamum	30	0.010	0.035	0.040	0.046	0.166	0.055
	50	0.004	0.750	0.028	0.760	0.178	0.771
	70	0.013	0.897	0.095	0.899	0.681	0.899

Table 4.17 Rate constants and Correlation coefficients (R^2) values of methyl esters at different temperatures for the first order and second order kinetic models

Sample	**Temp (°C)**	**Zero order K_o**	**R^2**	**1st order K_1 (min^{-1})**	**R^2**	**2nd order K_2 ($ml/mol,min^{-1}$)**	**R^2**
Colocynthus	30	0.017	0.938	0.093	0.943	0.152	0.948
	50	0.05	0.925	0.027	0.928	0.154	0.931
	70	0.011	0.864	0.076	0.834	0.531	0.802
Cyperus	30	0.007	0.322	0.020	0.322	0.061	0.344
	50	0.007	0.720	0.024	0.726	0.087	0.731
	70	0.005	0.781	0.018	0.783	0.069	0.785
Sesamum	30	0.036	0.880	0.107	0.888	0.321	0.895
	50	0.027	0.880	0.086	0.887	0.277	0.892
	70	0.016	0.886	0.050	0.890	0.154	0.893

The values of correlation coefficients R^2 of the trend line presented in Table 4.16 and 4.17 gave the confidence levels of the reaction conformity with the corresponding kinetic model (Shahal *et al*., 2012). The values of R^2 in the second order were higher than those of the first order and this showed that the methylation and ethylation of these esters gave confidence level in conformity with the pseudo second order reaction. The experimental data in this study fitted well with the pseudo second order kinetic model.

The order of reaction x-rays the functional relationship between concentration and rate of reaction. It determines how the amount of a compound (concentration of a reactant) speeds up or retards a reaction (Laude, 2002).

The activation energies of both ethyl and methyl esters are shown in Table 4.18

Table 4.18 Activation energies E_a of ethyl esters and methyl esters and their R^2 values

Ethyl esters	**E_a (kJ/mol)**	**R^2**
Colocynthus	6651.2	0.884
Cyperus	2286.35	0.028
Sesamum	28891.5	0.782
Methyl esters		
Colocynthus	831.4	0.001
Cyperus	45311.3	0.521
Sesamum	16796.6	0.882

The activation energies of the ethyl esters were generally higher than that of the methylester in all the samples. The activation energies of *Sesamum indicum* ethyl and methyl esters were the highest 28891.5 kJ/mol and 16796.6 kJ/mol respectively followed by *Cyperus esculentus* ethyl and methyl esters 2286.35 kJ/mol and 45311.3 kJ/mol while Colocynthus vulgaris ethyl and methyl esters were 6651.2kJ/mol and 831.4 kJ/mol. The graphs are shown in the appendix 2a-25b.

4.8: The Biodiesel Properties of methyl ester Samples

Tables 4.19, 4.20 and 4.21 showed the Comparative Analysis Of the fuel Properties of *Cyperus esculentus, Colocynthus vulgaris and Sesamum indicum* oils, methyl esters and methylester/Diesel blends respectively.

Table 4.19 Comparative analyses on the fuel properties of *Cyperus esculentus* oil, its methyl ester and methyl ester/diesel blends.

Sample	**Relative Density**	**Viscosity at 100^{o}C mm^2/s**	**Viscosity at 70^{o}C mm^2/s**	**Viscosity at 40^{o}C mm^2/s**	**Flash Point (^{o}C)**	**Pour Point (^{o}C)**	**Calorific Value kJ/kg**
Diesel	0.85	1.28	1.59	2.57	70	-9	45334
Oil	0.88	5.49	10.02	25.14	94	-3	44752
B10	0.85	2.11	3.84	6.50	114	-13	45334
B20	0.85	2.71	4.47	8.34	122	-14	45334
B30	0.86	3.21	4.42	9.05	114	-15	45124
B40	0.86	3.36	5.18	12.28	116	-11	45124
B50	0.86	3.70	5.93	12.2	128	-16	45124
B60	0.86	4.20	6.97	14.05	118	-14	45124
B70	0.87	4.75	7.59	15.84	114	-8	44938
B80	0.87	4.77	8.14	17.61	134	-10	44938
B90	0.87	5.39	9.83	21.12	124	-8	44938
B100	0.88	6.19	10.77	26.11	124	-7	44752

Table 4.20 Comparative analyses on the fuel properties of *Colocynthus vulgaris* oil, its methyl ester and methyl ester/diesel blends.

Sample	**Relative Density**	**Viscosity at 100°C mm^2/s**	**Viscosity at 70°C mm^2/s**	**Viscosity at 40°C mm^2/s**	**Flash Point (°C)**	**Pour Point (°C)**	**Calorific Value kJ/kg**
Diesel	0.85	1.28	1.59	2.57	70	-9	45334
Oil	o.89	5.73	11.16	26.63	120	-1	44543
B10	0.86	2.56	3.89	7.17	120	-9	45124
B20	0.86	2.75	4.25	7.9	122	-12	45124
B30	0.87	3.17	4.97	9.68	110	-15	44938
B40	0.88	3.37	6.06	11.57	118	-8	44752
B50	0.88	3.72	6.48	11.63	116	-10	44752
B60	0.88	4.15	7.35	14.5	118	-8	44752
B70	0.88	4.68	9.22	17.25	122	-13	44752
B80	0.89	5.64	11.16	21.29	126	-6	44543
B90	0.9	6.24	12.68	23.46	128	-8	44357
B100	0.9	7.25	13.12	28.25	138	-4	44357

Table 4.21 Comparative analysis on the fuel properties of *Sesamum indicum* oil, its methylester and methylester/diesel blends.

Sample	**Relative Density**	**Viscosity at 100^oC mm^2/s**	**Viscosity at 70^oC mm^2/s**	**Viscosity at 40^oC mm^2/s**	**Flash Point (^oC)**	**Pour Point (^oC)**	**Calorific Value kJ/kg**
Diesel	0.85	1.28	1.59	2.57	70	-9	45334
Oil	0.89	5.02	10.38	24.29	94	-1	44543
B10	0.85	2.38	3.73	6.55	112	-15	45334
B20	0.86	2.38	4.24	8.58	108	-13	45124
B30	0.86	2.61	4.13	7.88	104	-14	45124
B40	0.86	3.09	5.13	8.65	100	-14	45124
B50	0.87	3.28	5.49	9.45	116	-17	44938
B60	0.87	3.32	6.39	9.87	136	-16	44938
B70	0.87	3.43	6.52	11.34	110	-12	44938
B80	0.87	3.65	7.05	12.09	116	-10	44938
B90	0.88	4.18	7.34	13.82	114	-10	45752
B100	0.88	4.99	8.59	16.68	112	-9	45752

There was a progressive increase in viscosity of the methyl esters blends (B10-B100), this showed that blending petrodiesel with biodiesel improved the viscosity of the blend thereby ensuring their compatibility with modern diesel engines which have fuel injection systems and are sensitive to viscosity change (Jaichander and Annamaiia, 2011).

The viscosities of the methyl esters were as well lower than that of the oils because of the fatty acids present in the oils which were reduced in the esters during saponification and esterification. This decrease in the viscosities of the esters also indicated complete ester formation. For all fatty acids and aliphatic hydrocarbons, the kinematic viscosity increased with chain length (ie the number of carbon atoms).Generally, the aliphatic and aromatic hydrocarbons which are the major components of petrodiesel have lower viscosity than biodiesel due to lack of oxygen and other heteroatoms. Hence for the same number of carbon atom, fatty acids have greater viscosity than their hydrocarbon counterparts. Example pentadecane (2.49 mm^2/s) has a lower kinematic viscosity at 40^oC than propyl laurate (3.04 mm^2/s) and methyl myristate (3.30 mm^2/s) which have the same number of carbon atoms (Knothe and Steidley, 2005).

Double bonds reduce kinematic viscosity in both fatty acid compounds and aliphatic hydrocarbons. The influence of the double bonds was investigated by some workers who found that the decrease in viscosity was caused by the second double bond (Kaufmann *et al*., 1938).

Colocynthus vulgaris methylester had the highest viscosity and this could be attributed to the fact that it contained longer chain lengths (Table 4.27). The chain length ranged from C16-C19, *sesamum indicum* ranged from C16-C21

Generally speaking, *Colocynthus vulgaris* and *Cyperus esculentus* had higher viscosity for their ethyl esters than their methyl esters while only *Sesamum indicum* had lower values of viscosity in its methyl esters at all temperatures.

Tables 4.19-4.21 showed the results of flash point which is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions. Flash point is used to classify fuels for transport, storage and distribution according to hazard level. *Colocynthus vulgaris* methyl esters (120^{o}C) had the highest value of flash points, followed by *Cyperus esculentus* (94^{o}C) and then *Sesamum indicum* (84^{o}C). The high flash point value of *Colocynthus vulgaris* made it safe with regards to storage, fuel handling and transportation. Flash points vary with fuels volatility meaning that these biodiesels contained low volatile components compared to other feedstocks; this means that they would form a good feedstock for biodiesel production. For biodiesel the minimum flash point is 93 °C in the United States, 100 °C in Brazil and 120 °C in Europe. Biodiesel's flash point decreases rapidly as the amount of residual (un-reacted) alcohol increases (methanol's flash point is 11–12 °C, and ethanol's is 13–14 °C).

Thus, measuring the biodiesel flash point helps to indicate the presence of methanol or ethanol. In this work, the flash points confirmed absence of residual methanol or ethanol.

The results of the density of *Colocynthus vulgaris, Cyperus esculentus* and *Sesamum indicum* methyl esters are shown in Tables 4.19-4.21 *Colocynthus vulgaris* ethyl esters had the highest density followed by *Sesamum indicum* then *Cyperus esculentus* methyl esters. The density of the oils and methyl biofuels were higher than that of the petrodiesel. This is as a result of the fatty acid composition and molecular weight of the methyl biofuels (Ezekwe and Ajiwe, 2011).

Tables 4.19-4.21 also showed the results of pour point which is the temperature at which the fuel contains so many agglomerated crystals (a gel) and will no longer flow. This occurs if the temperature of the biodiesel drops below Cloud Point, when the microcrystals merge and form large clusters, which may disrupt the flow of the biodiesel through the pipes of the engine's fuel system. Similarly to the cloud point, the pour point values also depend on the feedstock the biodiesel was produced from. Pour point provides indicative values for the minimum temperature at which the fuel can be used. *Sesamum indicum* methylester had the poorest pour point followed by *Cyperus esculentus* methyl ester. This result could be explained further from the result obtained from saturation levels of fatty acids in Table 4.28 which showed that *Sesamum indicum* methyl ester (66.67%), *Cyperus esculentus* methyl ester (62.5%) contained high amount of saturated fatty acids. Cold flow properties could worsen with increase in degree of saturation of fatty acids (Knothe, 2007; Keith, 2001; Shrestha *et al*., 2008). Nevertheless, poiur point of these biofuels will not affect the use of these samples as a feedstock in tropical countries like Nigeria with high temperatures.

Dilution of the methyl esters decreased the pour point of the biodiesels. The methyl esters and their diesel blends were liquid at room temperature (27^{o}C) and will have no cold flow problems in countries where room temperature is always above 10^{o}C. *Colocynthus vulgaris* methyl ester also showed better cold flow properties than *Sesamum indicum* and *Cyperus esculentus* methylesters.

The results of the calorific value of *Colocynthus vulgaris, Cyperus esculentus* and *Sesamum indicum* methyl esters is as shown in Table 4.19-4.21. *Sesamum indicum* had the highest calorific value followed by *Cyperus esculentus* then *Colocynthus vulgaris m*ethylesters. This is because *Sesamum indicum* contained the highest number of saturated fatty acids. It was as well observed that the calorific value of the samples decreased as the concentration of the methyl esters in the blends increased. Petrodiesel had higher calorific value than the esters because of presence of chemically bond oxygen present in biodiesel and this in turn lowered the heating values (Kaplan *et al.*, 2006).

Figures 4.9-4.11 showed the line plot of viscosities of the oils, methyl esters at 40, 70 and 100°C respectively.

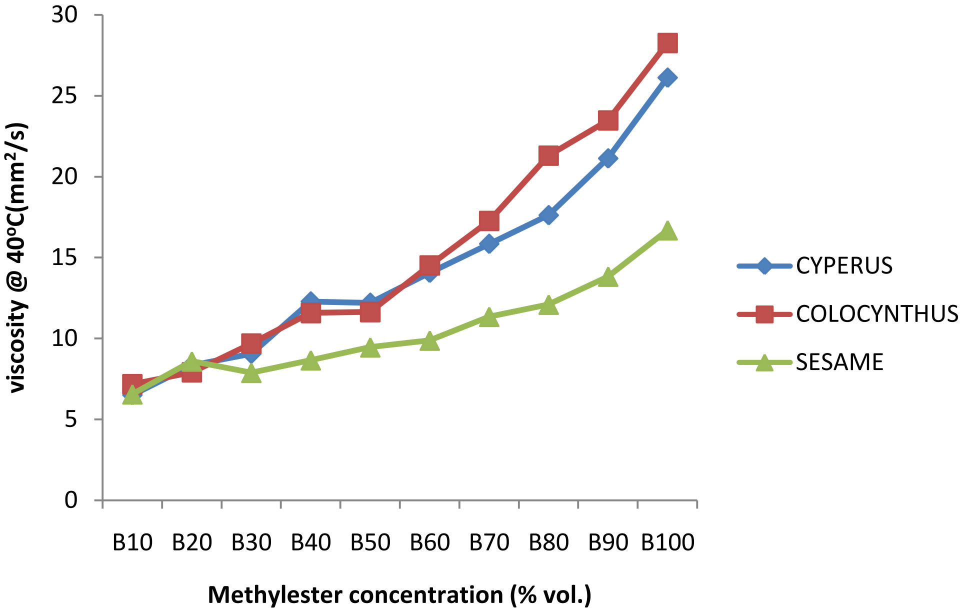


Fig 4.9: Viscosity at 40°C versus methyl esters concentration in methyl esters/diesel blends

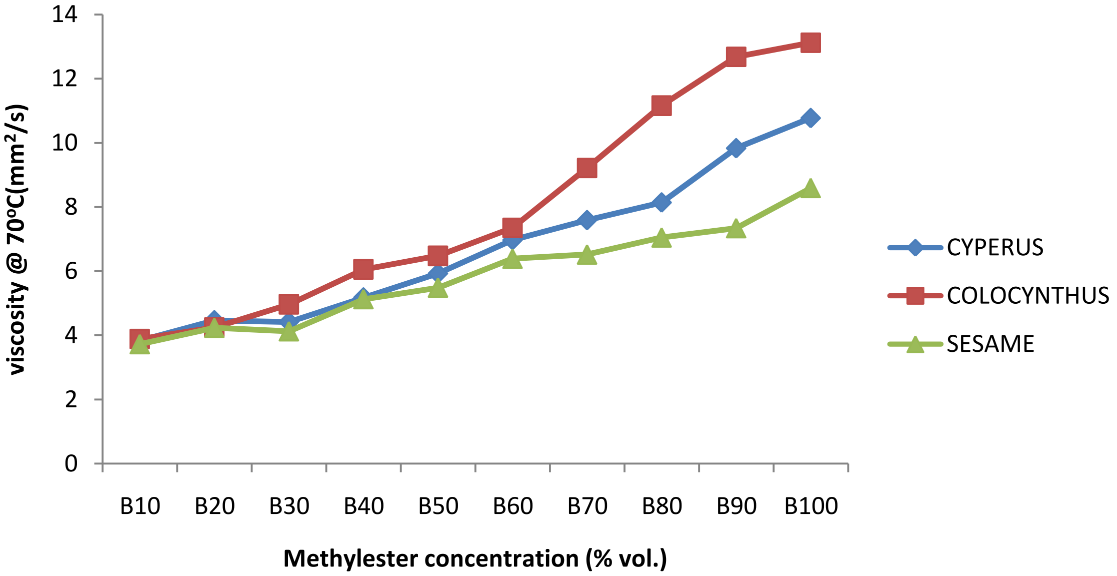


Fig 4.10: Viscosity at 70°C versus methyl esters concentration in methyl esters/diesel blends

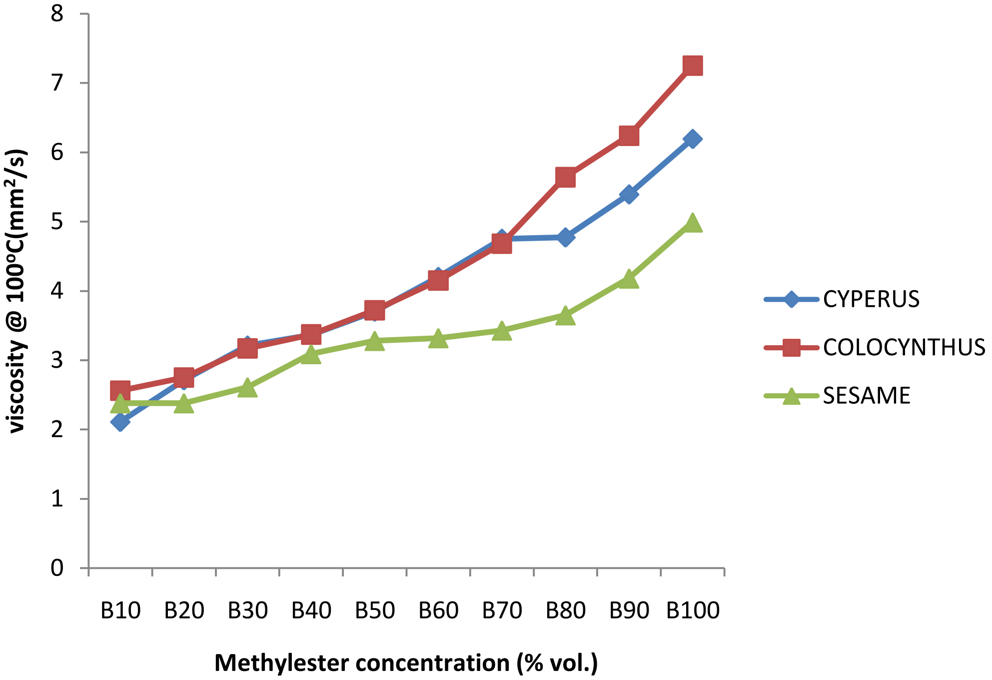


Fig 4.11: Viscosity at 100°C versus methyl esters concentration in methyl esters/diesel blends

Figure 4.9 showed the variation of viscosity of the methyl esters and their corresponding diesel blends at 40°C. The viscosity of pure methyl esters of *Colocynthus vulgaris* (28.25mm^2/s), *Cyperus esculentus* (26.11mm^2/s) and *Sesamum indicum* (16.68mm^2/s) were higher than their corresponding diesel blends this showed that blending thses esters with diesel improves their viscosities. This variation was similiar to that of the ethyl esters which had *Colocynthus vulgaris* (47.61mm^2/s*)* as the highest, followed *Sesamum indicum* (25.67mm^2/s) while *Cyperus esculentus* (15.32mm^2/s) was the least.

The line plots for flash point, pour point, relative density and calorific values versus methyl esters concentrations of samples are shown in figures 4.12-4.15 respectively.

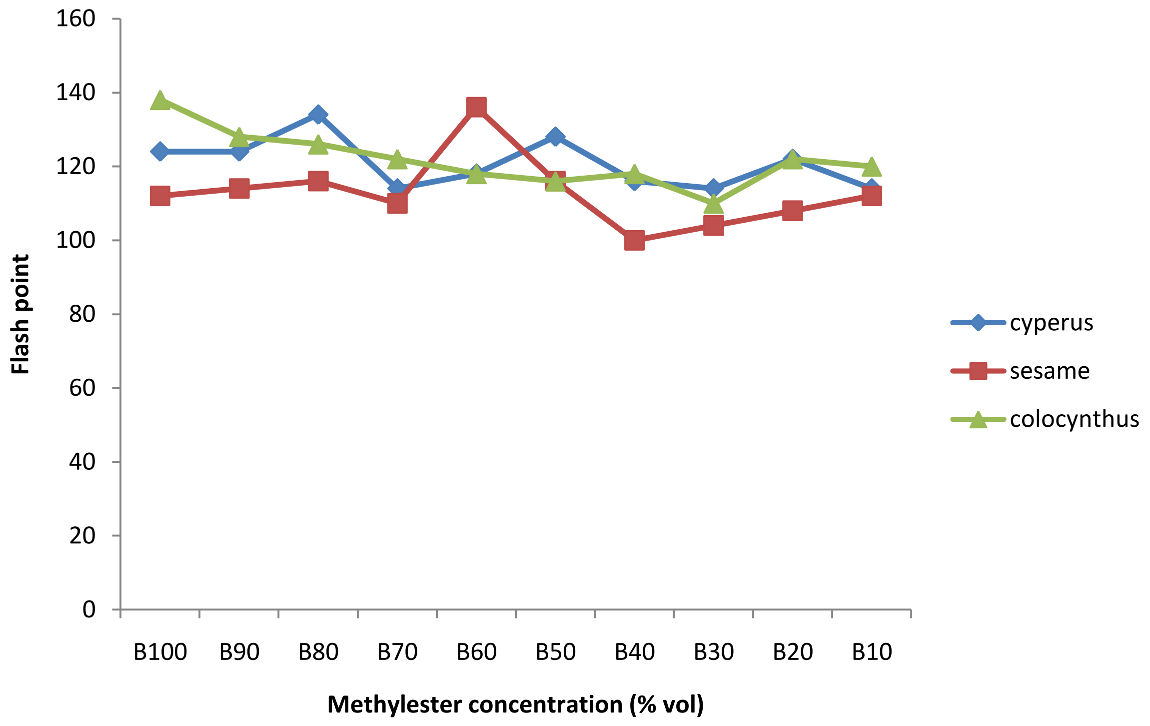


Fig 4.12: Flash point versus methylester concentrations in methyl esters/diesel blends.

Fig 4.12 showed the variation of flash points of *Colocynthus vulgaris, Cyperus esculentus* and *Sesamum indicum* methyl esters and their corresponding diesel blends. From the plot it was observed that *Colocynthus vulgaris* methyl esters and its diesel blends had the highest values of flash points, while *Sesamum indicum* and its diesel blends had the least flash point except for B50 where the value rose high above the other biodiesels. The high flash point values of *Colocynthus vulgaris* methyl esters indicated that the samples contained relatively low volatile components when compared to *Cyperus esculentus* and *Sesamum indicum*. From the plot, it was also observed that the flash point increased with increase in concentration of the esters in the biodiesel blends.

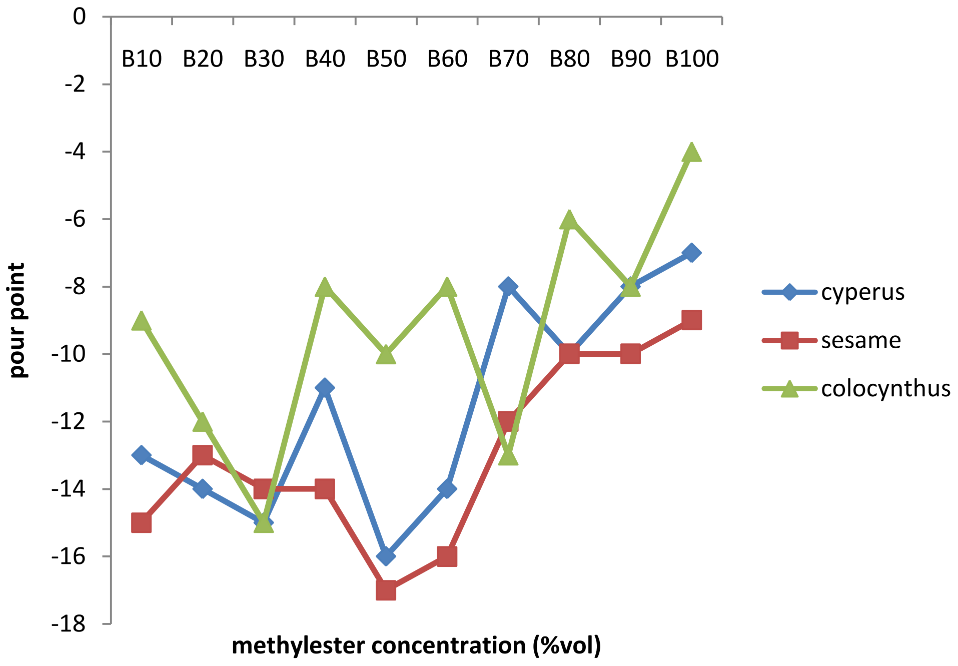


Fig 4.13: Pour point versus methylester concentrations in methyl esters/diesel blends.

The pour points of the methyl ester diesel blends were lower than their methyl esters as shown in Fig 4.13, this means that dilution of the methyl esters decreased the points of the biofuels and this makes the ethyl ester blends a better feedstock for biofuels in countries with low temperature. For countries like Nigeria with high temperatures the pour points of these biofuels will not affect their use as a feedstock for biofuel production.

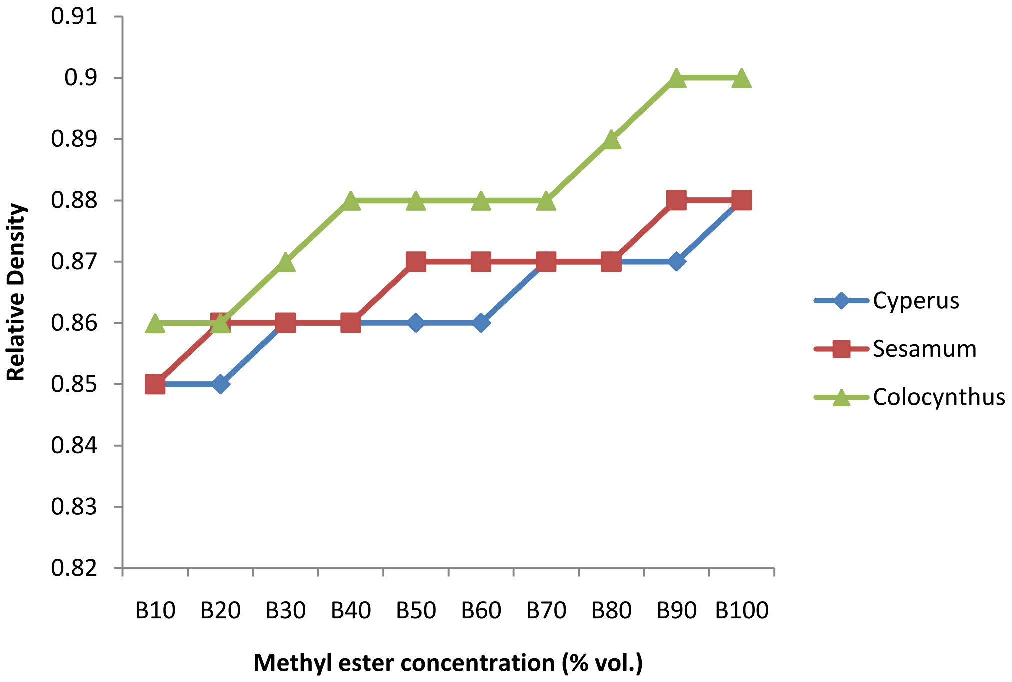


Fig 4.14: Relative density versus methylester concentrations in methyl esters/diesel blends.

Fig 4.14 showed the variation of relative density *Colocynthus vulgaris*, *Cyperus esculentus* and *Sesamum indicum* methyl esters and their corresponding diesel blends. From the plot, it was observed that *Colocynthus vulgaris* had the highest value for relative density followed by *Sesamum indicum*, then *Cyperus esculentus*. These variations were similar to that of their ethyl esters where *Colocynthus vulgaris* had the highest value for relative density followed by *Sesamum indicum*, then *Cyperus esculentus*. These variations of the relative density can be attributed to the degree of unsaturation in the esters. It has been reported that increase in density also increases with of degree of unsaturation (Giakoumis, 2013)

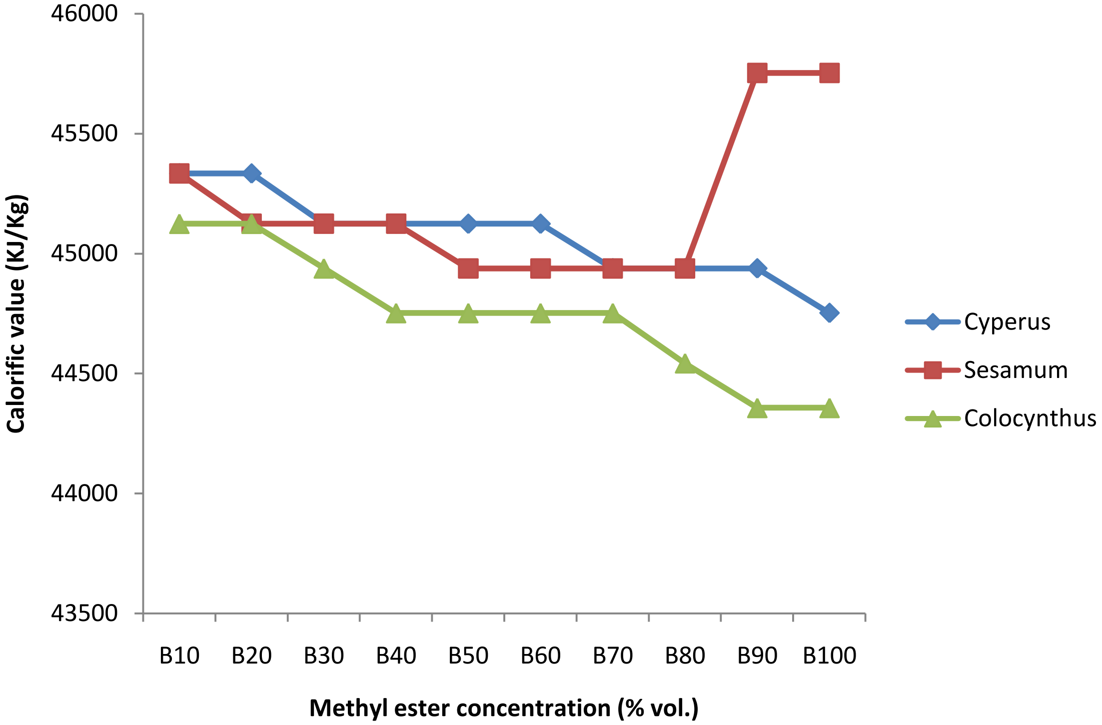


Fig 4.15: Calorific values versus methylester concentrations in methyl esters/diesel blends.

Fig 4.15 showed the variation of calorific values of *Colocynthus vulgaris*, *Cyperus esculentus* and *Sesamum indicum* methyl esters and their corresponding diesel blends. *Sesamum indicum* had highest calorific values followed by *Cyperus esculentus*, then *Colocynthus vulgaris*.

4.9: The heavy metal composition of oils and methyl ester samples

The heavy metal composition of oils and methyl esters of oils are shown in Table 4.22

Table 4.22 Heavy metal composition of *Colocynthus vulgaris*, *Cyperus esculentus* and *Sesamum indicum* oil and its methyl esters

ELEMENT	**Diesel (mg/l)**	***Cyperus oil*(mg/l)**	***Cyperus* ethylester (mg/l)**	***Colocynthus oil*(mg/l)**	***Colocynthus* ethylester(mg/l)**	***Sesamum oil*(mg/l)**	***Sesamum* ethylester (mg/l)**
Calcium	4.25	0.0073	0.0241	0.0134	0.0102	0.0213	0.0122
Cadmium	1.35	0.0038	0.0036	0.0052	0.0031	0.0002	0.0027
Copper	0.45	0.0041	0.0030	0.0019	0.0013	0.0017	0.0008
Iron	4.50	0.0139	0.0076	0.0176	0.0109	0.0155	0.0075
Manganese	1.40	0.0056	0.0008	0.0045	0.0053	0.0029	0.0007
Sodium	1.42	0.0002	0.0004	0.0006	0.0007	0.0172	0.0015
Nickel	3.52	0.0176	0.0121	0.0024	0.0102	0.0170	0.0067
Zinc	1.58	0.0043	0.0042	0.0009	0.0014	0.0048	0.0018
Potassium	1.12	0.0232	0.0041	0.0373	0.0234	0.0059	0.0521
Magnesium	3.30	0.0008	0.0002	0.0118	0.0002	0.0004	0.0024
Arsenic	2.14	0.0000	0.0000	2.6400	0.0000	2.1100	0.0000
Lead	0.52	0.8100	6.7800	2.4300	0.0000	1.1200	0.3100

The heavy metal compositions of the esters were lower than that of the corresponding oils which showed that the esters were purified during the esterification process. The concentration of lead in *Cyperus esculentus* methyl ester and *Colocynthus vulgaris* was high.

4.10: Grading of the oils, methyl esters and its diesel blends

The grading of the oils, methyl esters and its diesel blends based on their viscosities according to ASTM standards are shown on Table 4.23

Table 4.23: Grading of the oils, methyl esters and its diesel blends based on their viscosities according to ASTM standards.

Methyl esters	**1D**	**2D**	**4D**
at 40°C			
Colocynthus	-	-	B10-B90
Sesamum	-	-	B10-B100
Cyperus	-	-	B10-B100
at70°c			
Colocynthus	-	B10-B30	B40-B100
Sesamum	-	B10-B30	B40-B100
Cyperus	-	B10-B30	B40-B100
at100°C			
Colocynthus	-	B10-B70	B80-B100
Sesamum	-	B10-B100	-
Cyperus	-	B10-B80	B90-B100

From Table 4.23 above, it was observed that *Colocynthus vulgaris* methylester B100 at 40^{o}C did not fall into grade 1D and 2D but into 3D, while others fell into grade 4D diesel class (heavy diesel grades) showing that they are more likely to be used as diesel fuels after heating and cooling. They are mostly useful in heavy diesel engines. *Sesamum indicum* at 100^{o}C, (B10-B100) fell into 2D, at 70^{o}C and 100^{o}C some fell into group 2D and 4D. This was an indication of more complete combustion of the fuels at higher temperatures.

Based on their viscosities, the oils and ester blend fell within group 2D (2.0-4.9mm^2/s) or 4D (5.0-24.0mm^2/s) diesel grades at 40^{o}C, 70^{o}C and 100^{o}C. These results confirmed that most methylesters and petrodesel blends served as 2D diesel fuels once the engine warms upto 100^{o}C (Table 4.23).

4.11: Fatty acid profile, average chain lengths and Saturation levels of fatty acids components of the methyl esters.

Tables 4.24-4.26 depicted the fatty acid profiles of *Cyperus esculentus* methyl ester *Colocynthus vulgaris* and *Sesamum indicum* methyl ester oils respectively.

Table 4.24: Fatty acid profile of *Cyperus esculentus* methyl ester of seed oil

S/no	**Common name**	**Systematic name**	**Shorthand name**	**R.A (%)**
1	Myristic acid	Methyl tetradecanoate	14:0	0.60
2	Palmitoleic acid		16:1	1.03
3	Palmitic acid		16:0	19.35
4	l-(+)-Ascorbic acid	2,6-dihexadecanoate		13.36
5	Elaidic acid,	9-octadecanoic acid	18:1	13.88
6	Stearic acid	Octadecanoic acid	18:0	8.70
7	Oleic acid	9-octadecenoic acid	18:1	41.54
8	Arachidic acid	Eicosanoic acid	20:0	1.55

Table 4.24 showed that the major fatty acids of *Cyperus esculentus* methyl esters were myrisitic acid (0.60%), palmitic acid (19.35%), ascorbic acids (13.36%), stearic acid (8.70%), arachadic acid (1.55%) as the saturated fatty acid while palmitoleic acid (1.03%), eladic acid (13.88%) and oleic acid (41.54%) were the mono unsaturated fatty acids present.

Hence *Cyperus esculentus* methylester is a good feedstock for biodiesel production since it has good oxidation stability. The absence of polyunsaturated fatty acid and the presence of palmitic acid (a natural antioxidant) showed that it had a good oxidation stability and low possibility of polymerising at high temperature.

Table: 4.25 Fatty acid profile of *Colocynthus vulgaris* methyl ester of seed oil

S/no	**Common name**	**Systematic name**	**R.A (%)**
1	Palmitic acid	Hexadecanoic acid	23.49
2		n-hexadecenoic acid	2.59
3	Linoleic acid	9,12-octadecadienoic acid	37.57
4	Stearic acid	Octadecanoic acid	22.32
5	Cis, cis Linoleic acid	Cis 9,cis 12 octadecadienoic acid	14.03

Table 4.25 showed that the major fatty acids present in *Colocynthus vulgaris* methyl esters were palmitic acid (23.49%), n-palmitic acid (2.59%) and stearic acid (22.32%) as saturated fatty acids while lineoleic acid (37.57%), Cis cis linoleic acid (14.03%) were the polyunsaturated fatty acids present. There was no monounsaturated fatty acid. The presence of polyunsaturated in *Colocynthus vulgaris* methyl ester indicated that it had a poor oxidative stability and the possibility of polymerising at high temperatures. It would therefore require an anti oxidant to prevent lipid peroxidation.

Table : 4.26 Fatty acid profile of *Sesamum indicum* methyl ester of seed oil

S/no	**Common name**	**Systematic name**	**Shorthand name**	**R.A (%)**
1	Palmitic acid	Hexadecanoic acid	16:0	17.18
2	Palmitoleic acid	n-hexadecenoic acid	16:1	6.40
3	Linoleic acid	9,12-octadecadienoic acid		34.71
4	Stearic acid	Octadecanoic acid	18:0	8.64
5	Oleic acid	9-octadecenoic acid	18:1	32.04
6	Arachidic acid	Eicosanoic acid	20:0	1.02

Table 4.26 showed the major fatty acids present in *Sesamum indicum* methyl esters as palmitic acid (17.18%),n-palmitic acid (6.40%) stearic acid (8.46%)and arachidic acid (1.02%) as saturated fatty acids while cis oleic acid (32.04%) was the monounsaturated fatty acids, linoleic acid (34.7%) was the only polyunsaturated . These results slightly differed from Abdurrahaman *et al.*, (2008) report may be due to climate/geographical area of cultivation. The presence of four saturated fatty acid , one monounsaturated fatty acids and one polyunsaturated indicated that *Sesamum indicum* methylester could have good oxidation stability without the aid of additives to improve oxidation stability since the palmitic acid present in it is a natural anti oxidant. The occurance of palmitic acid and n-palmitic acid was observed in *Cyperus esculentus* methyl ester and as well in *Sesamum indicum* methylester.

Tables 4.27 and 4.28 showed the average chain lengths and saturation levels of the fatty acid components of the methyl esters respectively.

Table: 4.27 Average chain lengths of the fatty acid components of the methyl esters

Chain length	***Cyperus esculentus***	***Colocynthus vulgaris***	***Sesamum indicum***
%C15	100	-	-
%C16	-	50	50
%C17	50	25	25
%C18	33.33	33.33	33.33
%C19	33.33	33.33	33.33
%C21	50	-	50
%C38	100	-	-

Table 4.27 showed the average chain lengths of fatty acids present in the methyl esters according to percentage composition. The predominant chain lengths in all the oils seeds were C16, C17, C18, C19 and C21. *Cyperus esculentus* had C_{15} (1), C_{17} (2), C_{18} (1), C_{19} (2), C_{38} (1). The chain lengths present in *Colocynthus vulgaris* methyl esters were C_{16} (1), C_{17} (1), C_{18} (1), C_{19} (3), while the chain length by composition of *Sesamum indicum* methyl esters were C_{16} (1), C_{17} (1), C_{18} (1), C_{19} (2). Viscosity, calorific value, cetane number and oxidative stability increases with increase in number of chain lengths (Razon, 2009), this was observed in *Cyperus esculentus* methylesters which had highest chain length also had very high calorific value (44752kJ/kg) and high viscosity (26.11mm^2/s at 40^{o}C)

Table: 4.28: Saturation levels of fatty acids components of the methyl esters

Sample	**%SFA**	**%MUSFA**	**%PUSFA**
Sesamum indicum	66.67	16.67	16.67
Cyperus esculentus	62.5	37.5	Absent
Colocynthus vulgaris	60	Absent	40

The results in Table 4.28 showed that *Cyperus esculentus* methyl esters had 62.5% of saturated fatty acid and 37.5% of mono unsaturated fatty acids thus *Cyperus esculentus* methyl esters contained higher percentage of saturated fatty acid than that of mono unsaturated fatty acid and no polyunsaturated fatty acid. *Sesamum indicum* and *Cyperus esculentus* methyl esters had greater percentage of saturated fatty acids than *Colocynthus vulgaris* methyl esters, this means that they have good oxidative stability.. *Cyperus esculentus methylester* contained no polyunsaturated fatty acid and *Colocynthus vulgaris* methyl esters like the ethyl ester contained no monounsaturated fatty acid, it had the highest % of polyunsaturated fatty acids (PUSFA), and hence it is more susceptible poor to oxidation stability than others. High PUSFA favours lubricity and cold flow properties (pour point)(Razon, 2009).

4.12: The acidity concentration of fumes emitted from combustion of the methyl ester and diesel samples.

The acidity concentration of fumes emitted from combustion of the biodiesel and diesel samples during combustion results are shown on Table 4.29

Table: 4.29 concentrations of acidic emissions of the samples (methyl esters) from the engine performance tests

	Cyperus esculentus **g/dm^3**	***Sesamum indicum*** **g/dm^3**	**Colocynthus vulgaris g/dm^3**
Diesel	0.0045	0.0045	0.0045
B100	0.0028	0.0028	0.0025
B90	0.0033	0.0029	0.0035
B80	0.0025	0.0017	0.0017
B70	0.0034	0.0024	0.0026
B60	0.001	0.0019	0.0015
B50	0.0022	0.0027	0.0018
B40	0.0018	0.0026	0.0025
B30	0.0028	0.0025	0.0028
B20	0.0034	0.0015	0.0034
B10	0.0019	0.0018	0.0025

The acidity concentration of fumes emitted from combustion of the methyl ester biodiesel and diesel samples during combustion results are shown on Table 4.29. The powering capability test carried out on a Techno R175A diesel engine showed that all the methy ester samples were able to power the diesel engine at the same interval and almost the same volume similar to those of the ethyl esters. The emissions from those of the ethyl esters were slightly higher than their corresponding methyl esters in most cases. The acid concentrations in the exhaust gas from the methyl ester samples were lower than those of hydrocarbon diesel and these acid concentrations in the exhaust gas increased as the amount of diesel blended into the biodiesel increased. B100 provided the least emission reduction in both ester samples with the ethyl esters having higher acid concentration than the methyl esters..

From the emission results, it was obvious that B100-B10 of the ester diesel blends produced good environmentally friendly biofuel blends than pure fossil diesel. Engine performance of diesels could be improved by mere dilution with esterified vegetable oils.These results are in line with the works of (Ajiwe *et al*., 2000, 2001, Ezekwe and Ajiwe, 2013).

4.13: FTIR Analysis of the Bond Structures of the diesel, ethyl/methyl ester and their blends.

FTIR was used to compare the bond stability and structures of the petroleum diesel and biofuel samples at different temperatures, 28^{o}C, 50^{o}C, 100^{o}C, 150^{o}C and 200^{o}C. The bands and its corresponding functional groups for the spectra at different temperatures are shown in Appendices 26-44.

It was observed from Appendices 26-44 that the biofuels (ethyl esters and methyl esters) had similar spectra and this showed that their fuel properties were similar to each other. Absorptions of carbonyl functional group (C=O) of esters, aldehydes ketones and carboxylic acids were observed between 1730-1748cm^{-1} in the biofuels/diesel blends. From the spectra, it was observed that the band was stable up to 200^{0}C in all the samples. This peak intensity was absent in the petroleum diesel but it later appeared as the temperature approached 150^{0}C showing that there were thermal oxidation in the petroleum diesel that yielded carbonyl compounds (Alipio *et al.*, 2009).

The absorption band of 3200-3600cm^{-1} which is due to OH stretching of alcohols, carboxylic acids and hydroperoxides was absent in the petrodiesel sample. This confirmed that petrodiesel does not contain hydroxyl/carboxylic groups but only a mixture of hydrocarbons. It was also observed that this band (3200-3600cm^{-1}) later appeared at 200^{o}C as a result of thermal oxidation of the petrodiesel that yielded carboxylic acids, aldehydes and ketones as the oxidative products. Increase in hydrogen bonding was observed as the temperature increased to 150^{o}C, a progressive shift in wave number from 3476.81 to 3537.5 cm^{-1} was observed and this is as a result of increase in internally bonded OH (Alipio *et al*; 2009).

Many strong and sharp signals of asymmetric C-H stretching frequency of methyl and methylene groups around 2930 cm^{-1} and asymmetric vibrations around 2871 cm^{-1} were observed.

Absorption bands around 1442 cm^{-1} and 1362 cm^{-1} were due to C-H bond asymmetric bending , absorption bands 1162-1168cm^{-1} were due to C-O stretch for esters, carboxylic acids and ethers. Absorption bands between 711-726 cm^{-1} were due to carbon-hydrogen bending out of plane of carbon-carbon double bonds (cis RCH=CHR) (Alipio *et al*; 2009).

4.14: Effect of temperature on the intensity of the bands

Intensity of a band in a spectrum is proportional to the concentration of the respective functional group according to beer-lambert's law (Hamed *et al*., 2006; Chiniwalla *et al*., 2003). The relative changes in peak intensities and formation of multiple bands within the same range showed there was thermal oxidation in the biofuels/diesel and petrodiesel at different temperatures.

Figure 4.16-4.21 showed the effect of temperature on the peak intensities of functional groups in the methyl and ethyl ester samples. The figures on the plot were derived from ratio of peak areas of C=O (1740cm^{-1}), C-H (2929cm^{-1}) and C-H (1443cm^{-1}) to C-H (2929cm^{-1}) to obtain normalized values (Chiniwalla *et al*., 2003).

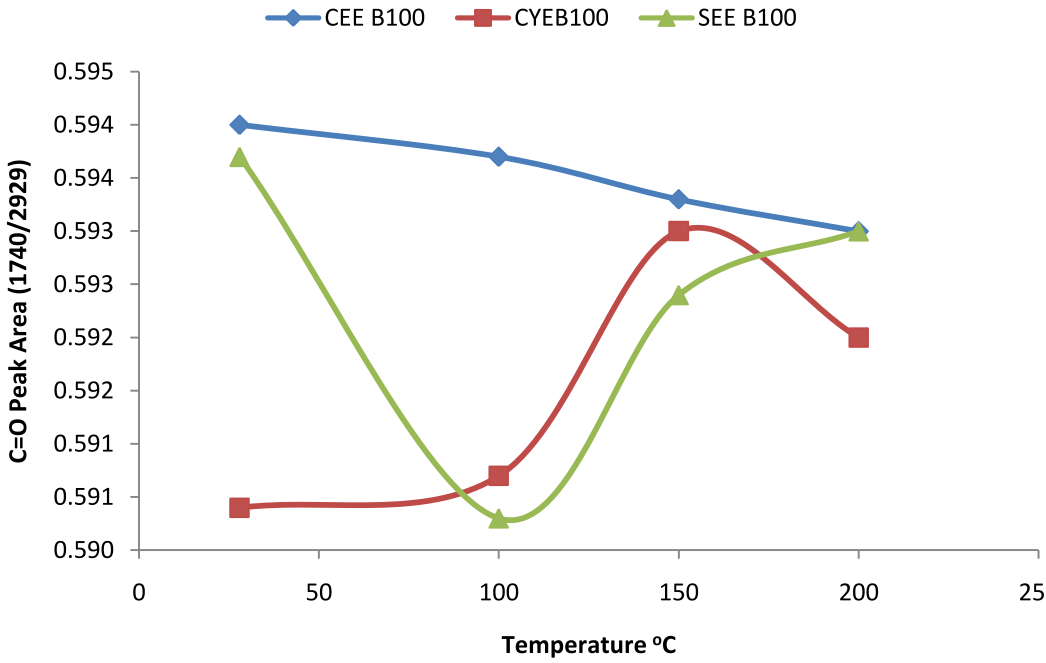


Fig 4.16: Changes in intensity of C=O (1740 cm^{-1}) of ethyl esters

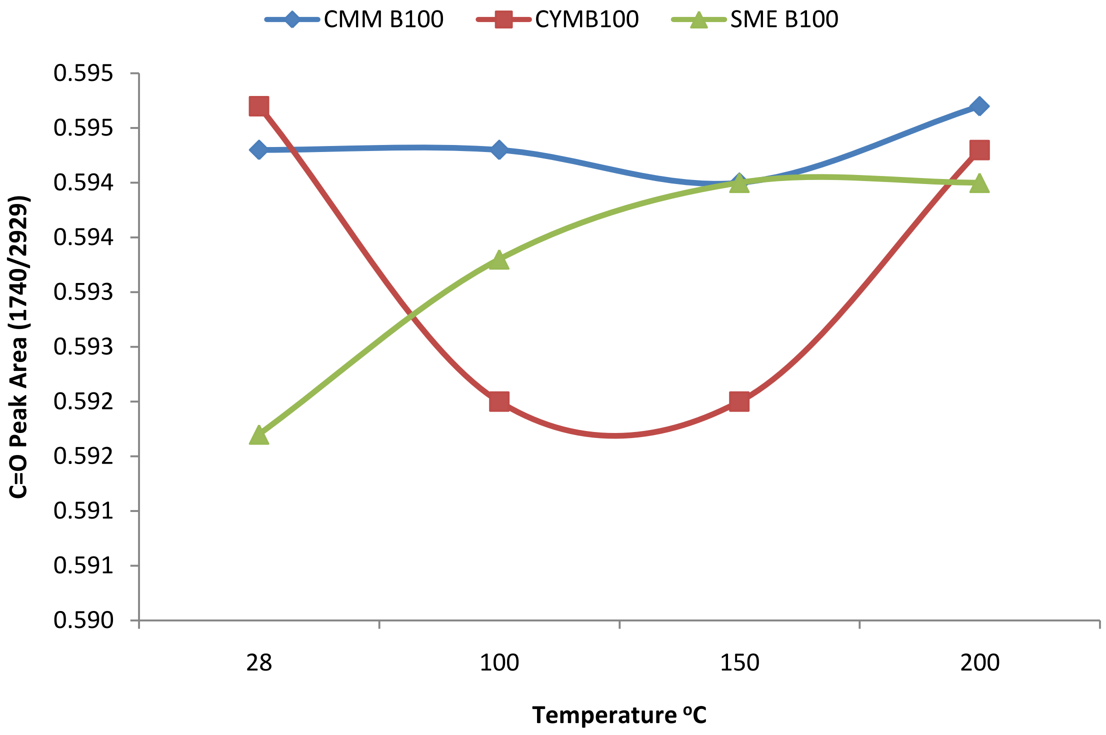


Fig 4.17: Changes in intensity of C=O (1740 cm^{-1}) of methyl esters

CYM = *Cyperus* esculentus methyl esters, CYE = *Cyperus* esculentus ethyl esters

CMM = *Colocynthus vulgaris* methyl esters, CMM = *Colocynthus vulgaris* ethyl esters

SME = *Sesamum indicum* methyl esters, SME = *Sesamum indicum* ethyl esters

Changes in peak intensities of C=O (1740cm^{-1}) in the ethyl and methyl esters are shown in figure 4.16 and 4.17 respectively. It was observed that C=O bond was stable upto 200^{0}C in the samples. *Sesamum indicum* methyl esters, *Colocynthus vulgaris* ethyl and methyl esters showed more stability as the bond intensity increased gradually till 200^{0}C while, *Cyperus* esculentus methyl and ethyl esters decreased and increased again as the temperature increased.

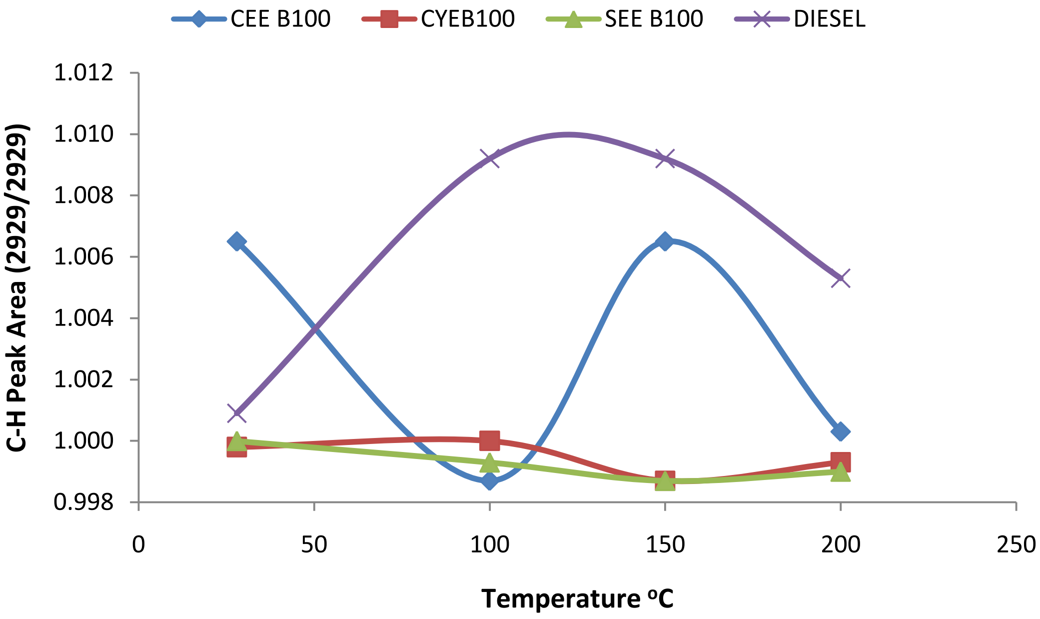


Fig 4.18: plot of changes in intensity of C-H (2929 cm^{-1}) of ethyl esters and diesel.

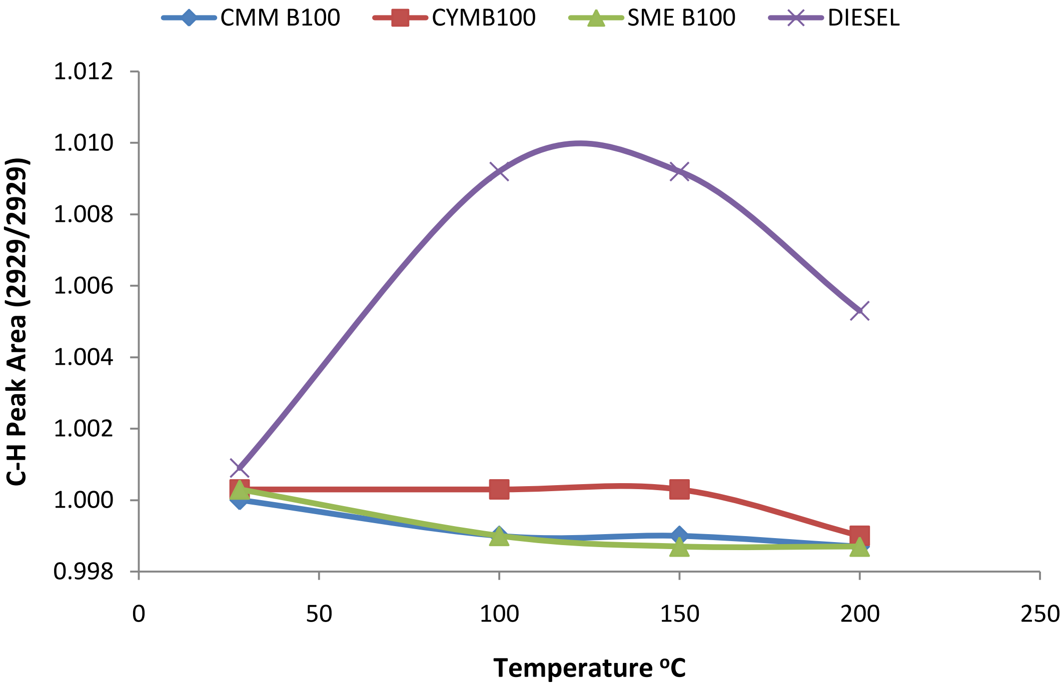


Fig 4.19: Changes in intensity of C-H (2929 cm^{-1}) of methyl esters and diesel

Changes in peak intensities of C-H (2929cm^{-1}) in the ethyl and methyl esters are shown in figure 4.18 and 4.19 respectively, it was observed that the intensity of the bond increased as the temperature increased but it later decreased at 150^{0}C in all the samples. Diesel had the highest peak intensity showing that petroleum diesel, a mixture of hydrocarbon contained more C-H bonds than the methyl and ethyl ester biofuels.

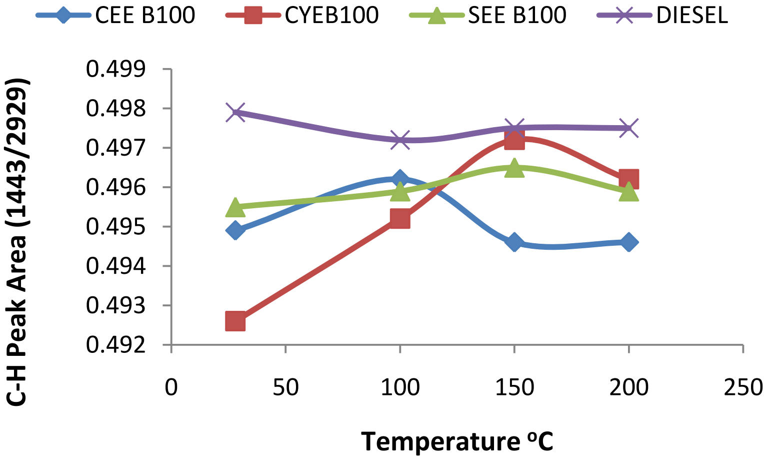


Fig 4.20: Changes in intensity of C-H (1443 cm^{-1}) of ethyl esters and diesel

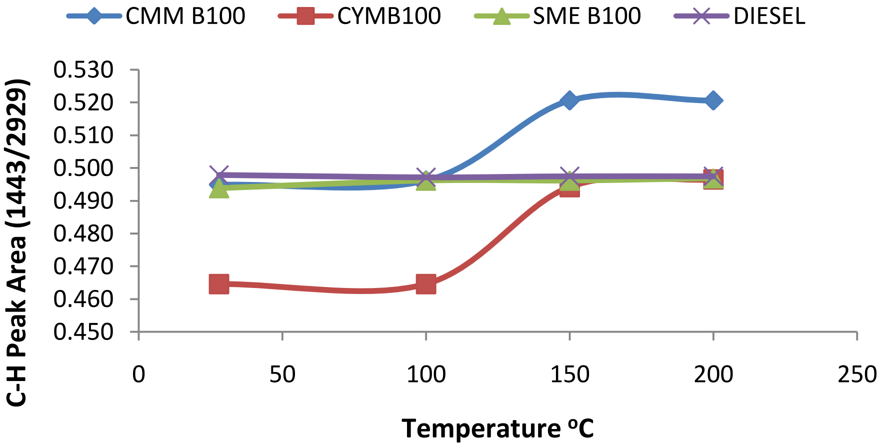


Fig 4.21: Changes in intensity of C-H (1443 cm^{-1}) of methyl esters and diesel

Changes in peak intensities of C-H (1443cm^{-1}) in the ethyl and methyl esters are shown in figure 4.20 and 4.21 respectively, it was observed that C-H bands increased as temperature increased in the methyl ester samples while in the ethyl ester samples the bands decreased from temperature of 150^0C.

Generally speaking, the effect of temperature on the bond stability was also observed in the samples from 100^oC in most of the samples and this was clearly seen by appearance of multiple bands within the same region.

Changes in peak intensities of C=O (1740cm^{-1}), C-H (2929cm^{-1}) and C-H (1443cm^{-1}) indicated that the bands were thermally stable upto 200^0C for all samples owing to the fact that these bonds did not disappear at these temperature ranges.

4.15: Correlations of the Fuel properties of the methyl and ethyl esters of *Colocynthus vulgaris, Sesamum indicum* and *Cyperus esculentus* oils

Table 4.49 Pearson correlation coefficients of the fuel properties of the methyl and ethyl esters of Colocynthus vulgaris, Sesamum indicum and Cyperus esculentus oils

	Flash Point	**Pour Point**	**Relative Density**	**Viscosity at 100**	**Viscosity at 70**	**Viscosity at 40**	**Calorific value**	**% SFA**	**% MUFAs**	**% PUFAs**
Flash Point	1									
Pour Point	0.420 (0.407)	1								
Relative Density	0.601 (0.207)	0.414 (0.414)	1							
Viscosity at 100	0.577 (0.231)	-0.169 (0.749)	0.721 (0.106)	1						
Viscosity at 70	0.447 (0.375)	-0.388 (0.448)	0.556 (0.252)	0.97 (0.001)	1					
Viscosity at 40	0.570 (0.238)	-0.287 (0.581)	0.584 (0.224)	0.98 (0.001)	0.981 (0.001)	1				
Calorific value	-0.126 (0.812)	-0.207 (0.694)	-0.638 (0.173)	-0.637 (0.174)	-0.545 (0.263)	-0.539 (0.27)	1			
% SFA	0.490 (0.324)	-0.333 (0.519)	0.198 (0.707)	0.353 (0.493)	0.371 (0.469)	0.417 (0.411)	0.431 (0.393)	1		
% MUFAs	-0.257 (0.623)	0.011 (0.984)	-0.774 (0.071)	-0.686 (0.132)	-0.655 (0.158)	-0.562 (0.246)	0.541 (0.268)	-0.102 (0.847)	1	
% PUFAs	0.383 (0.453)	0.162 (0.759)	0.885 (0.019)	0.712 (0.113)	0.631 (0.179)	0.573 (0.235)	-0.602 (0.206)	0.105 (0.843)	-0.978 (0.001)	1

The values in parenthesis are for ethyl esters. %SFAs=saturated fatty acids, %MUFAs= monounsaturated fatty acids, %PUFAs= polyunsaturated fatty acids.

The linear relationship between the biofuel properties and fatty acid variables of the biofuel samples were measured using Pearson correlation (Table 4.49). It was observed from Table 4.49 that %MUFAs had strong correlations with pour point and relative density r = 0.984 and 0.885 respectively. This implied that as the value of %MUFAs increases the values of pour point and relative density increases and as the values of %MUFAs decreases the values of pour point and relative density also decreases.

The kinematic viscosities at various temperatures had very strong correlations between each other, the viscosity at 70^0C had strong correlations with the viscosity at 100^0C (r=0.970) while the viscosity at 40^0C had strong correlations with viscosity at 100^0C and 70 r= 0.980 and 0.981 respectively. This showed that as the values of the viscosities at that temperature increases, the corresponding viscosity at the other temperature also increases and vice versa.

A strong inverse correlation was observed between %PUFAs and %MUFAs r=0.978, this implied that as the values of the %PUFAs increases, the value of %MUFAs decreases.

The Pearson correlation results also confirmed a moderate interdependence of relative density, flash point and %SFAs and also between viscosity at 100^0C and flash point, pour point and relative density; this showed that these variables tend to vary irrespective of the other.

Weak correlations were also observed between %PUFAs and pour point, %MUFAs and viscosities at different temperatures and finally between %SFAs and %PUFAs.

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATION

5.1 SUMMARY

The increasing global emphasis on biofuel results in a growing need for rapid and reliable analysis of pure biofuels and its disel blends. These biofuels are produced by transeserification reactions. Transesterification reactions are very necessary because it produces esters of oils (biofuel) with better fuel properties when compared to diesel.

In this research, the primary aim which was to determine the biofuel properties of the oils, methyl, ethyl esters and ester/diesel blends of the oils from *Cyperus esculentus L., Colocynthus vulgaris and Sesamum indicum L.* seeds were met.

The three seed crops *Colocynthus vulgaris, Sesamum indicum* and *Cyperus esculentus* oils were analysed for their biofuel properties ranging from viscosity, pour point, flash point, relative density, fatty acid profile using GC-MS, to thermal stability using FTIR. The three samples proved to be good feedstocks for biofuel production.

Colocynthus vulgaris was the best feedstock amongst the three samples as it showed better fuel properties. From the FTIR studies, the biofuels were seen to have similar chemical structures and were stable at high temperatures. Equally, the methylesters and its diesel blends proved to be better biofuels than the ethylesters based on their fuel properties like flash point, viscosity etc.

The biofuels were tested and proven to be able to power a techno R175A diesel engine and also produced emissions that were more environmentally friendly than those of petro diesel.

5.2 CONCLUSIONS

The need for biofuels sourcing cannot be overemphasized owing to its interesting benefits based on the facts that it is a renewable source of energy that is readily available within the environment. It is biodegradable and has economic importance.

The results of this research revealed that:

i. The samples had good percentage oil compositions and based on these oil compositions (yields) *Sesamum indicum* 51.3%, *Colocynthus vulgaris* 53,6% and *Cyperus esculentus* 26.2% , the research samples proved to be good major feed stocks for biofuel productions.

ii. Transeserification of these vegetable oils enhanced the fuel properties of the oils and these esterified oils can be better alternatives to fossil diesel.

iii. Blending of the methyl and ethyl esters with fossil diesel showed improved fuel efficiency of the fuels as shown from the fuel properties like the viscosities and flashpoints.

iv. The presence of polyunsaturated fatty acids in *Colocynthus vulgaris* ethylester indicated that it might have a poor oxidative stability and the possibility of polymerising at high temperature. It would therefore require an anti oxidant to prevent lipid peroxidation when it is to be used in a diesel engine. The absence of polyunsaturated fatty acid in *Sesamum indicum* ethylester and the presence of palmitic acid (a natural antioxidant) showed that it had a good oxidation stability and low possibility of polymerising at high temperature and is a preferred feedstock in terms of the fatty acid contents.

v. *Colocynthus vulgaris* ethyl and methyl esters proved to be better feedstock for biodiesel production than *Cyperus esculentus* and *Sesamum indicum* esters from the results obtained from some of their fuel properties (flash points, viscosity, density etc).

vi. Methylation and ethylation of the esters showed similar properties.

vii. The biofuels were stable at high temperatures of 50-200^{o}C from their bond structures/stability test. The effect of temperature on the bond stability were observed in the samples from 100^{o}C in most of the samples and this was clearly seen by appearance of multiple bands within the same region.

viii. Changes in peak intensities of C=O (1740cm^{-1}), C-H (2929cm^{-1}) and C-H (1443cm^{-1}) indicated that the bands were thermally stable upto 200^{0}C for all samples owing to the fact that these bonds did not disappear at these temperature ranges.

ix. The optimum temperature for the ethylation and methylation of the samples was 40^{o}C except for *Cyperus esculentus* methyl ester and *Colocynthus vulgaris* ethyl ester that had 70^{o}C as the optimum temperature.

x. The ethylation and methylation of the samples showed 100% second order reactions as shown by the R^2 values.

xi. The activation energies of the ethyl esters were generally higher than that of the methylester in all the samples.

xii. The engine performance/ emission/ consumption test showed that the biofuels could power a techno R175A diesel engine and the emissions were environmentally friendly when compared to the fossil fuels; hence the engine performance of fossil diesels could be improved by mere dilution with esterified vegetable oils.

xiii. The heavy metal compositions of the esters were lower than that of the corresponding oils which showed that the esters were purified during the esterification process.

5.3 RECOMMENDATIONS

At the end of this study, it is recommended that:

1. Other alcohols like butanol, propanol etc should be used to carry out transesterification of these oil samples to compare their performance to the ethanol and methanol esters.
2. The oxidative stability of these biofuels be tested beyond 250^{o}C.
3. More research should be carried out on other local feed stocks so as to diversify feedstocks available in our local environment for their biofuel properties and usability.
4. The biodiversity and sustainability development of these seed crops be considered vital due to their economic importance to biofuel.
5. The cultivation and protection of these seed crops should be encouraged in large scale since they are very important feed stock in biofuel production to ensure steady availability.
6. The feed stocks used for biofuel production that are edible can be replaced with genetic modified crops to reduce competition.

5.4 CONTRIBUTIONS TO KNOWLEDGE

This study has also been able to prove that the three seed oils can be used in production of biodiesel an alternative to crude oil and these biodiesel produced when used can help reduce the greenhouse gas being introduced into the atmosphere that cause climate change.

The study provided detailed information on the optimisation and fuel properties of the methyl and ethyl ester of these seed oils.

Transeserification of these vegetable oils enhanced the fuel properties of the oils and these esterified oils can be better alternatives to fossil diesel.

Blending of these esters with fossil diesel improves the fuel properties of the esters and can extend the longevity of the use of fossil diesel.

The FTIR analyses of the samples at various temperatures showed the chemistry of stability of the samples under thermal stress.

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APPENDIX I

Table 4.50: RELATIONSHIP BETWEEN CALORIFIC VALUE AND SPECIFIC GRAVITY OF FUEL (SHELL)

Approximate relation between gross calorific value and specific gravity (Shell International Ltd)

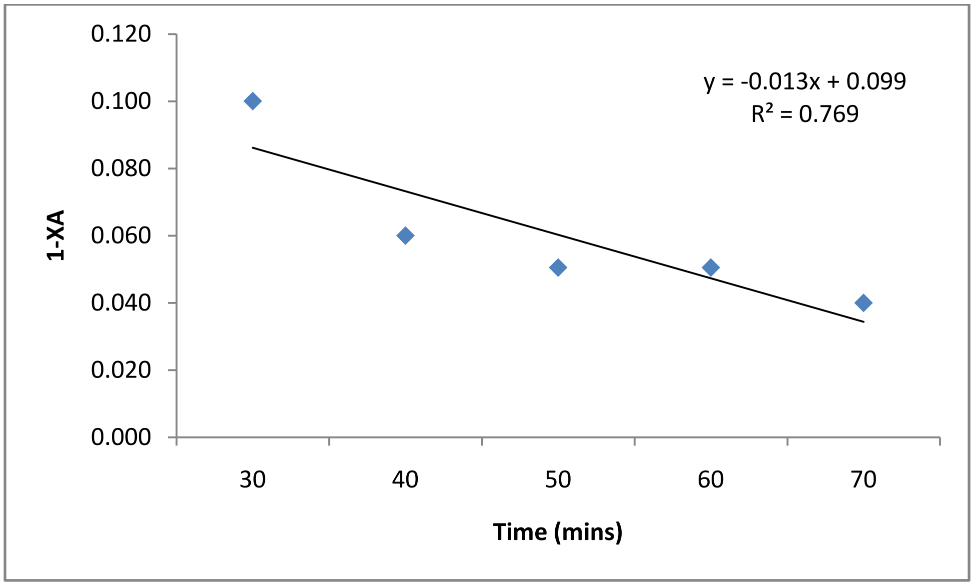
Specific gravity relation density 15%4°C	**Gross Calorific value (Specific Energy) in Cal/g, Cal/cm^3, kJ/kg**		
	Cal/g	**Cal/cm^3**	**kJ/kg**
0.80	11,050	8,840	46,287
0.81	11,010	8,920	46,101
0.82	10,970	8,990	45,915
0.83	19,920	9,060	45,729
0.84	10,870	9,130	45,520
0.85	10,830	9,200	45,334
0.86	10,780	9,270	45,124
0.87	10,730	9,340	44,938
0.88	10,690	9,410	44,752
0.89	10,640	9,470	44,543
0.90	10,590	9,540	44,357
0.91	10,540	9,590	44,147
0.92	10,400	9,660	43,938
0.93	10,440	9,710	43,729
0.94	10,390	9,770	43,519
0.95	10,340	9,830	43,310
0.96	10,290	9,880	43,101
0.97	10,240	9,940	42,891
0.98	10,190	9,990	42,682
0.99	10,140	10,040	42,475
1.00	10,090	10,090	42,263

APPENDIX 2

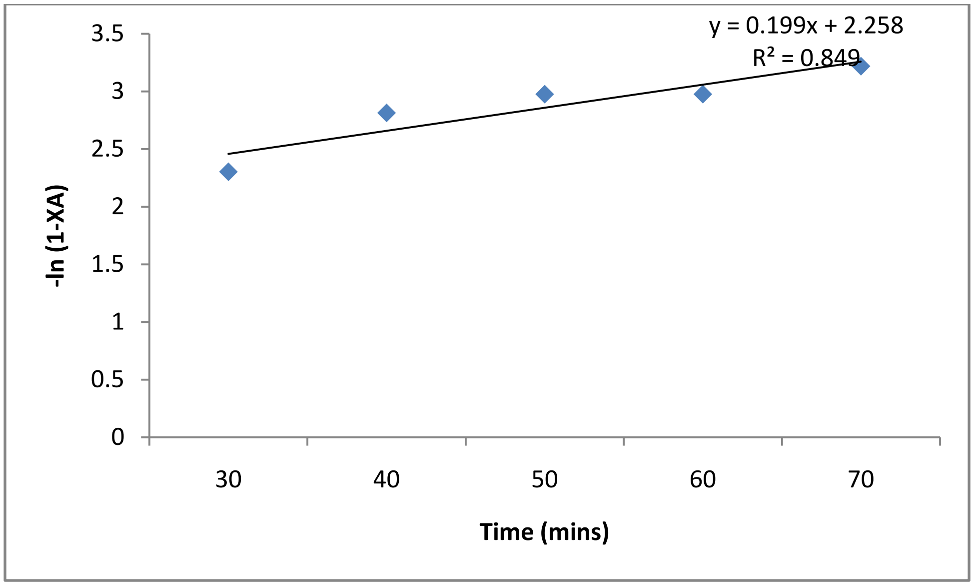
CALCULATION FOR KINETIC STUDIES

Appendix 2a: *Colocynthus vulgaris* ethyl ester @30^{o}C

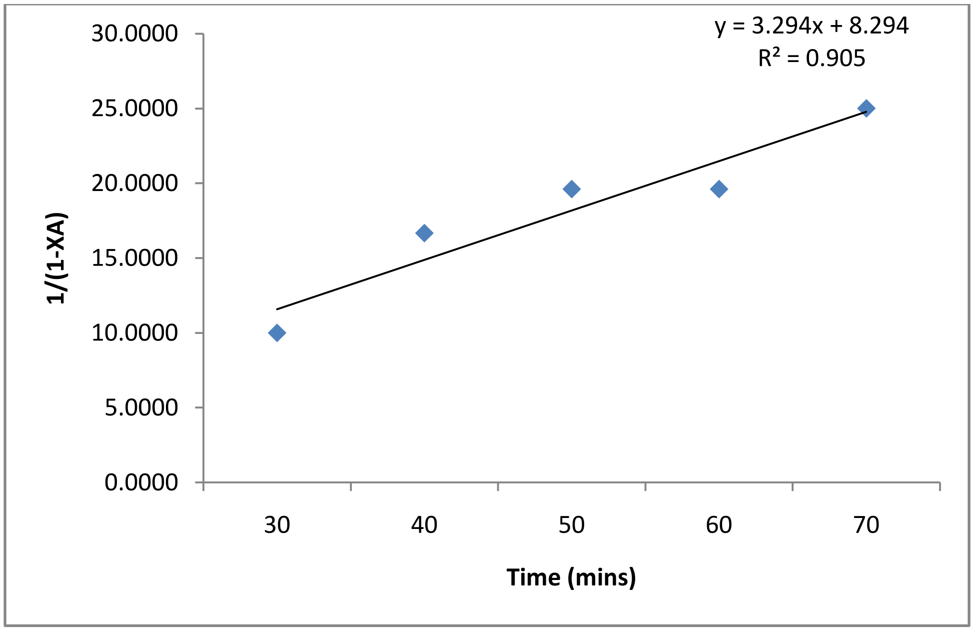
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.900	0.100	2.3026	10.0000
40	0.940	0.060	2.8134	16.6667
50	0.949	0.051	2.9759	19.6078
60	0.949	0.051	2.9759	19.6078
70	0.960	0.040	3.2188	25.0000



Appendix 2b: Verification of Zero order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 30^{o}C



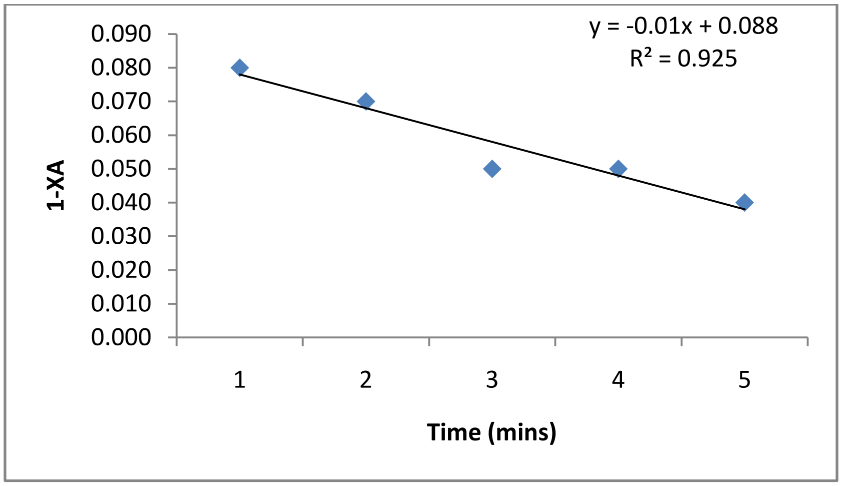
Appendix 2c : Verification of Ist order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 30^{o}C



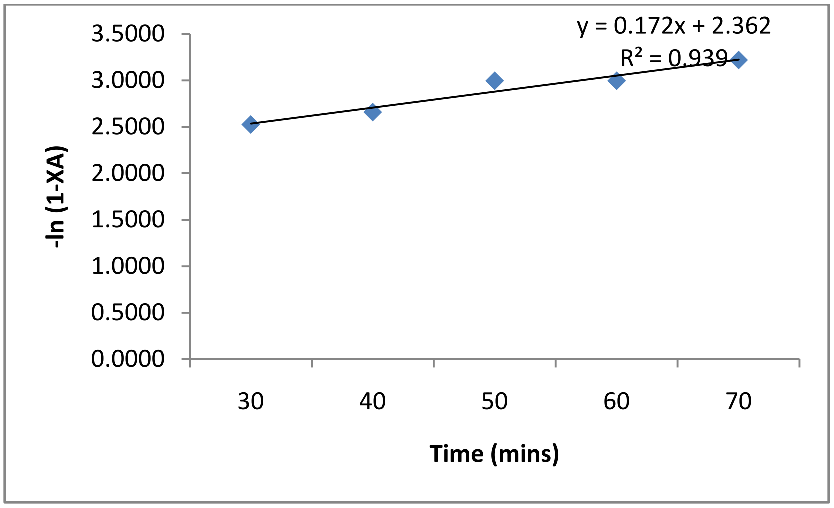
Appendix 2d: Verification of Second order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 30^{o}C

Appendix 3a: *Colocynthus vulgaris* ethyl ester @50^{o}C

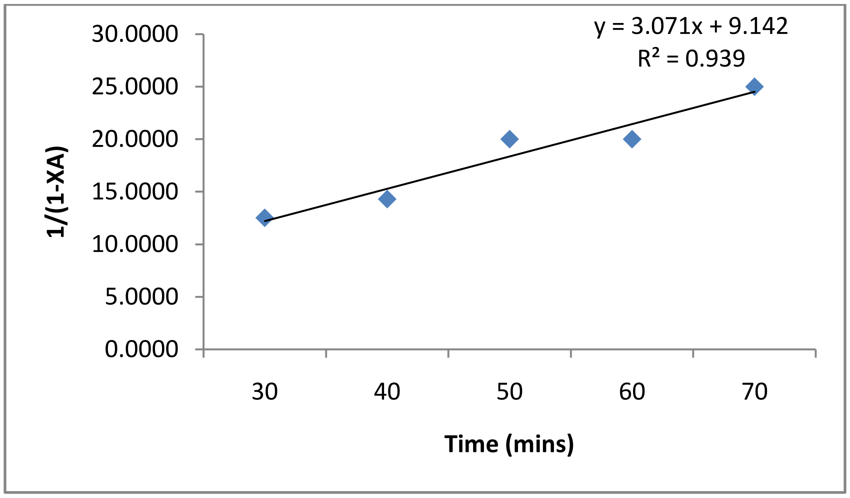
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.920	0.080	2.5257	12.5000
40	0.930	0.070	2.6592	14.2857
50	0.950	0.050	2.9957	20.0000
60	0.950	0.050	2.9957	20.0000
70	0.960	0.040	3.2189	25.0000



Appendix 3b: Verification of zero order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 50^{o}C



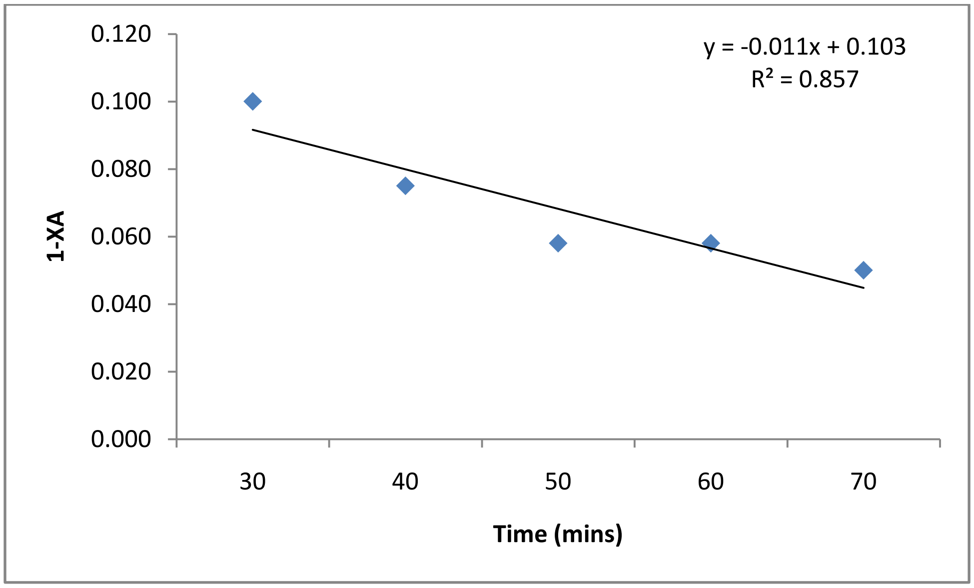
Appendix 3c: Verification of ist order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 50°C



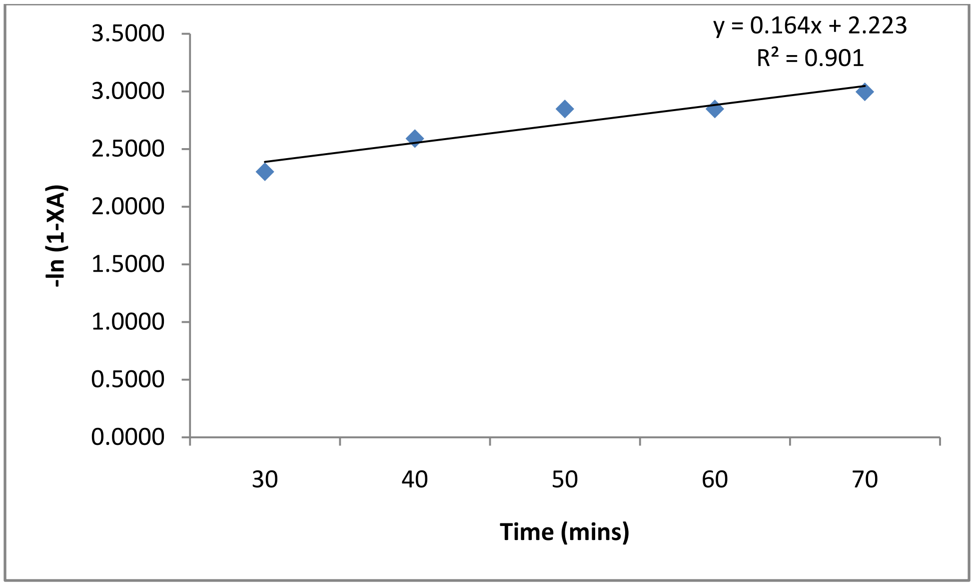
Appendix 3d: Verification of Second order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 50°C

Appendix 4a: *Colocynthus vulgaris* ethyl ester @70^{o}C

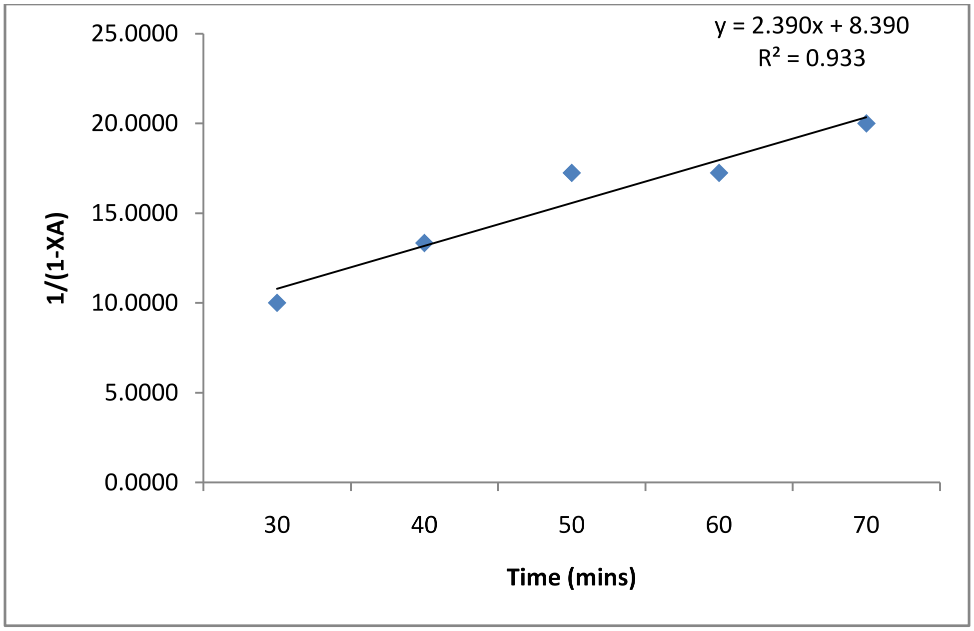
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.900	0.100	2.3026	10.0000
40	0.925	0.075	2.5903	13.3333
50	0.942	0.058	2.8473	17.2414
60	0.942	0.058	2.8473	17.2414
70	0.950	0.050	2.9957	20.0000



Appendix 4b: Verification of zero order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 70^{o}C



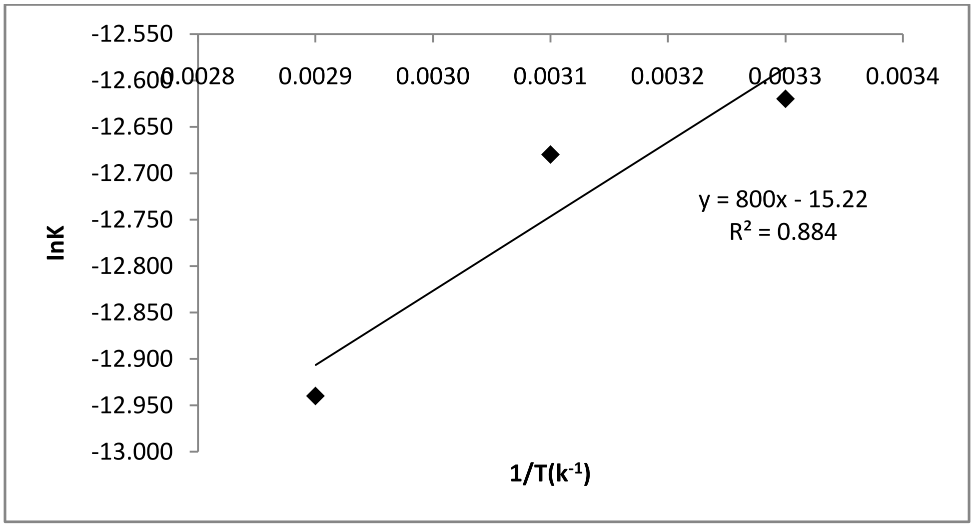
Appendix 4c: Verification of ist order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 70^{o}C



Appendix 4d: Verification of Second order behaviour for transesterification of *colocynthus vulgaris* ethyl ester at 70^{o}C

Appendix 5a: Determination of rate constants (K) for a second order reaction at different temperatures for *colocynthus vulgaris* ethyl ester

Temp ^oC	Temp k	1/T (k^{-1})	K	InK
30	303	0.0033	0.0000033	-12.620
50	323	0.0031	0.0000031	-12.680
70	343	0.0029	0.0000024	-12.940



Appendix 5b: Determination of activation energy from plot of Ink versus 1/T

Slope = $-E_a/R$

Slope = -800K

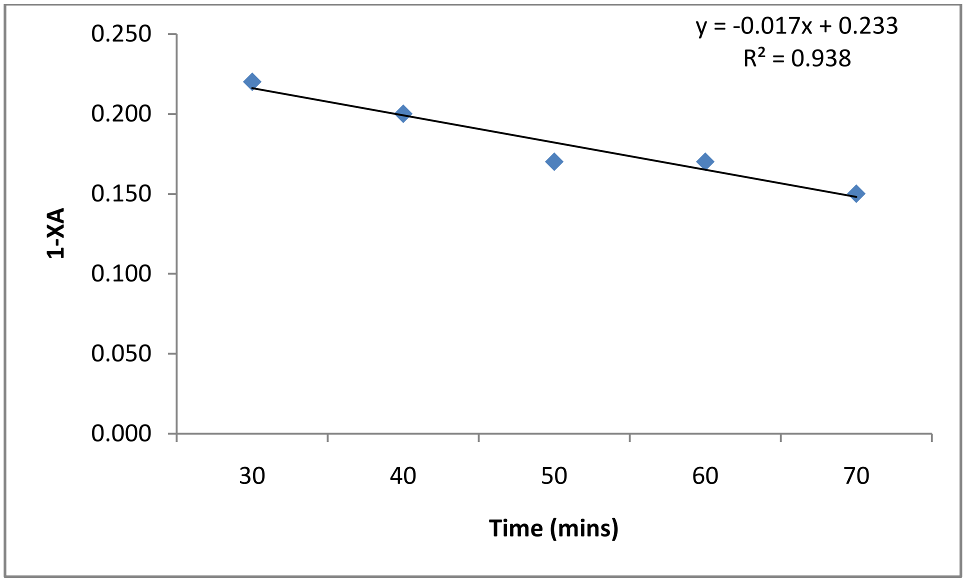
R =8.314J/K.mol

E_a = (8.314J/K.mol x 800K)

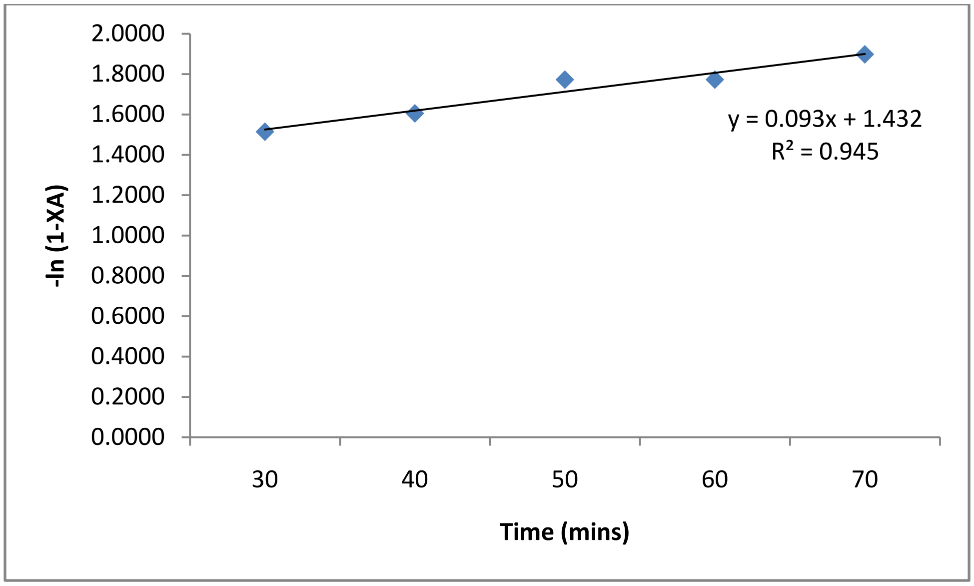
Activation energy = 6651.2 J/mol

Appendix 6a: *Colocynthus vulgaris* methyl ester @30^{o}C

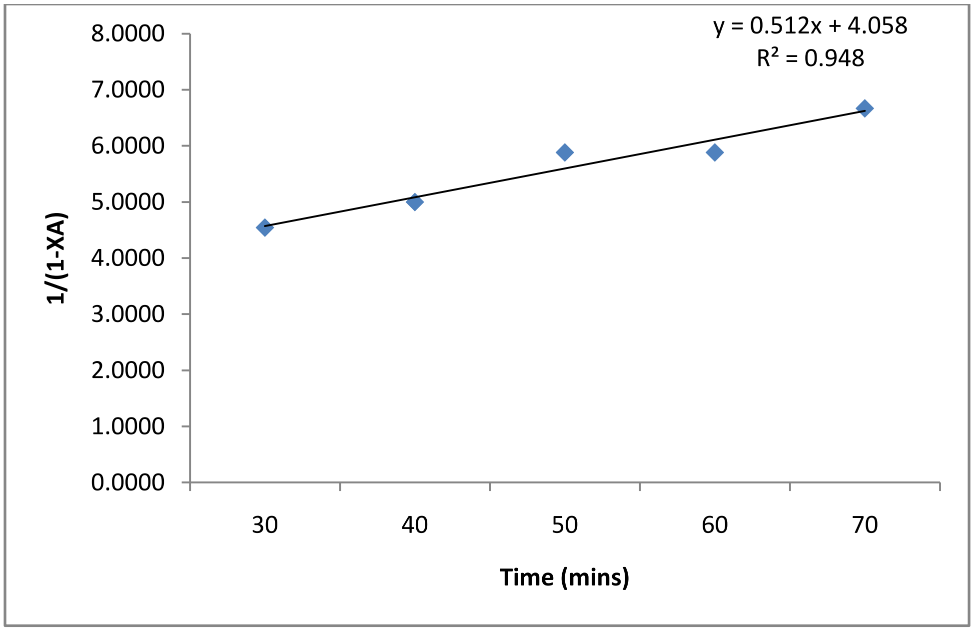
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.780	0.220	1.5141	4.5455
40	0.800	0.200	1.6049	5.0000
50	0.830	0.170	1.7720	5.8824
60	0.830	0.170	1.7720	5.8824
70	0.850	0.150	1.8971	6.6667



Appendix 6b: Verification of Zero order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 30^{o}C



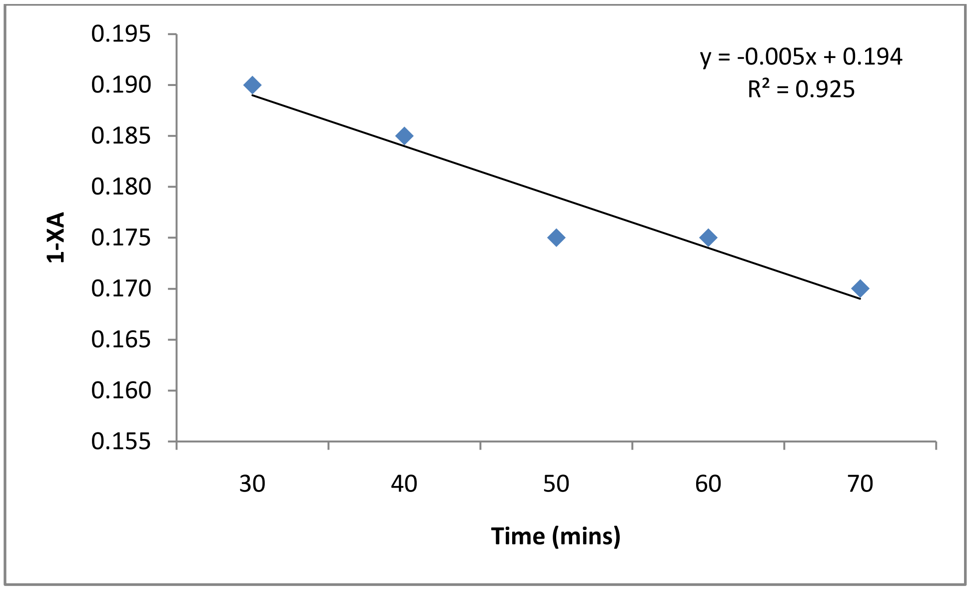
Appendix 6c: Verification of ist order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 30^{o}C



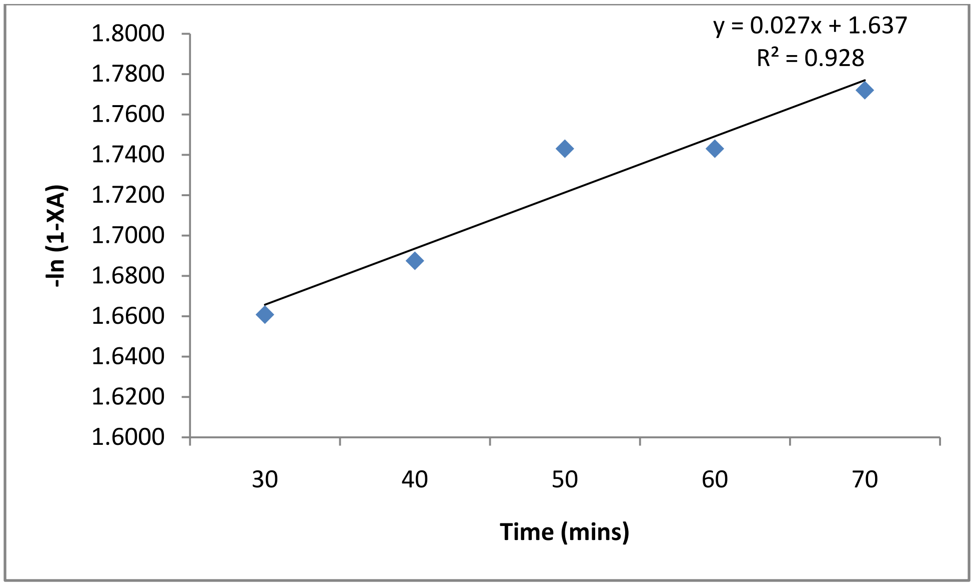
Appendix 6d: Verification of Second order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 30^{o}C

Appendix 7a: *Colocynthus vulgaris* methyl ester @50^{o}C

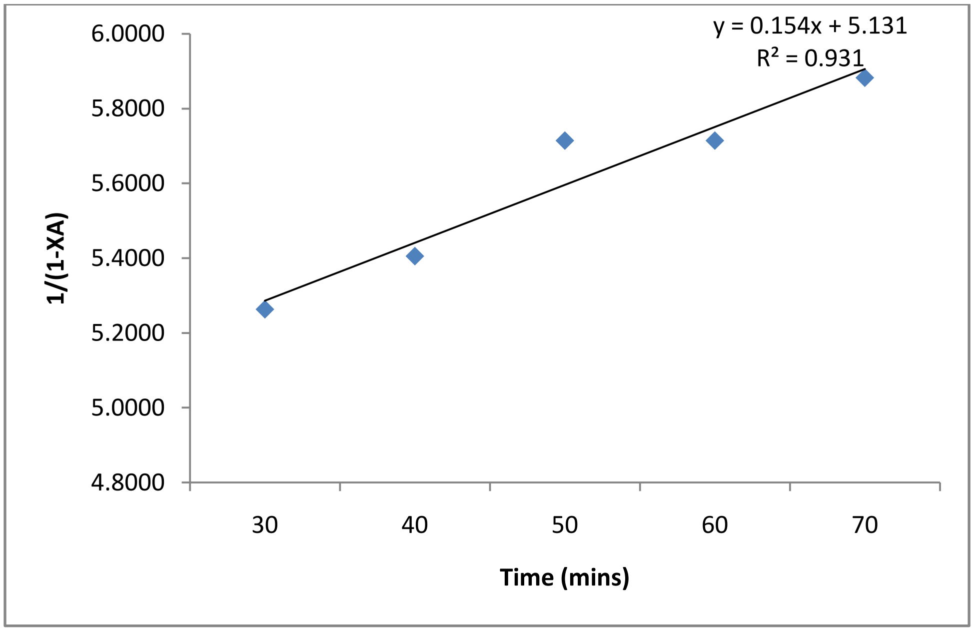
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.810	0.190	1.6607	5.2632
40	0.815	0.185	1.6874	5.4054
50	0.820	0.180	1.7148	5.5556
60	0.820	0.180	1.7148	5.5556
70	0.830	0.170	1.7720	5.8824



Appendix 7b: Verification of Zero order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 50^{o}C



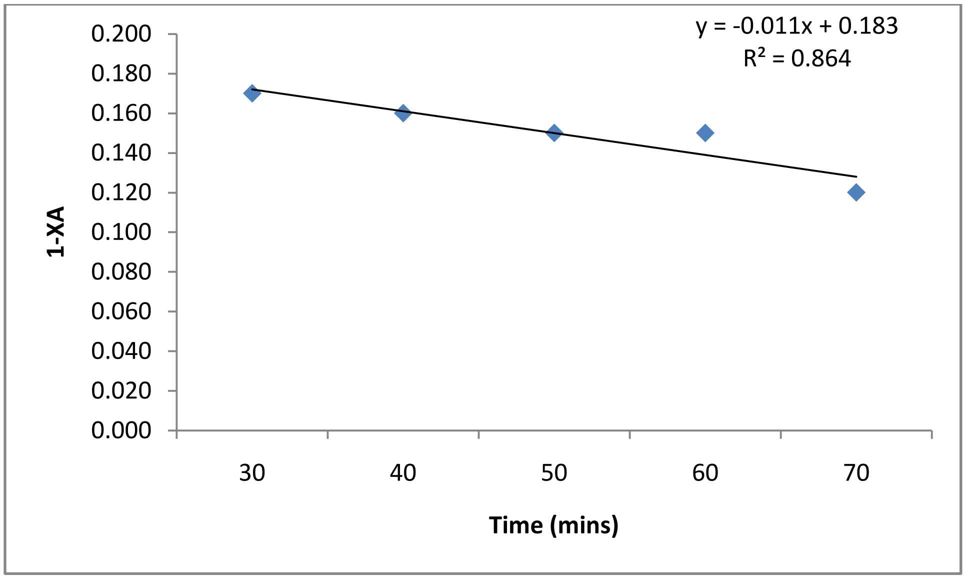
Appendix 7c: Verification of ist order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 50°C



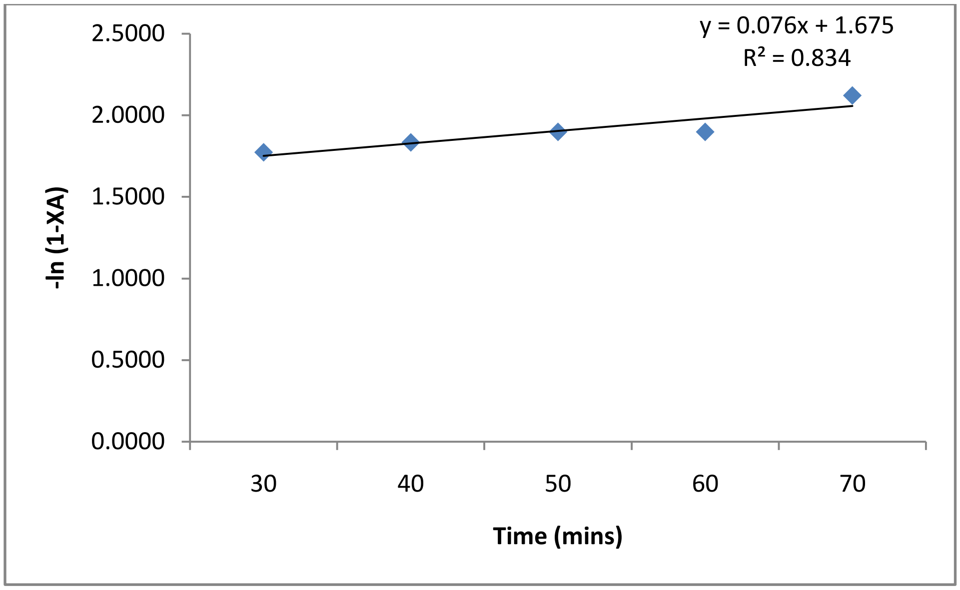
Appendix 7d: Verification of Second order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 50°C

Appendix 8a: *Colocynthus vulgaris* methyl ester @70^{o}C

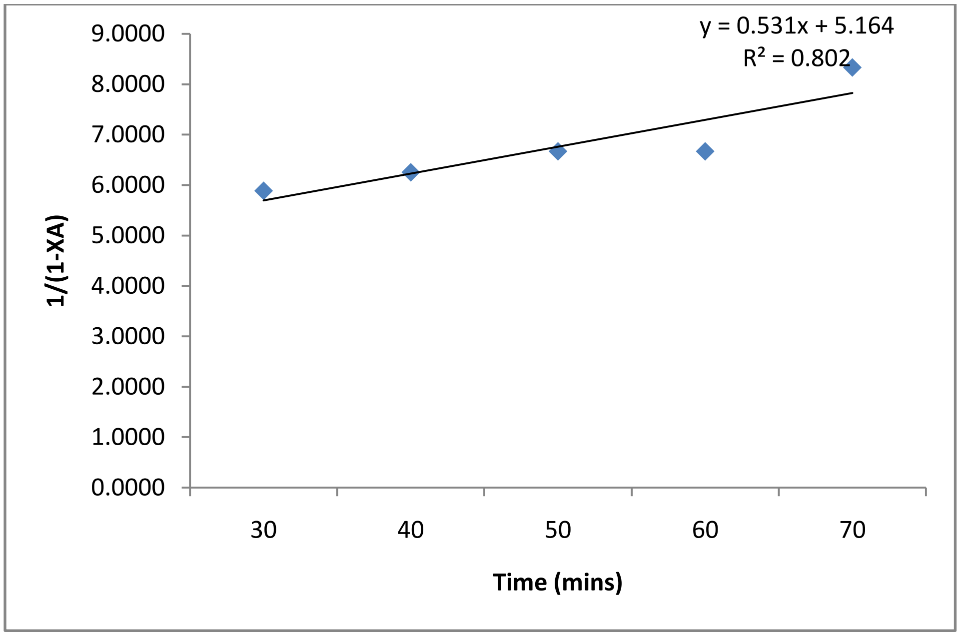
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.830	0.170	1.7720	5.8824
40	0.840	0.160	1.8326	6.2500
50	0.850	0.150	1.8971	6.6667
60	0.850	0.150	1.8971	6.6667
70	0.880	0.120	2.1203	8.3333



Appendix 8b: Verification of zero order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 70^{o}C



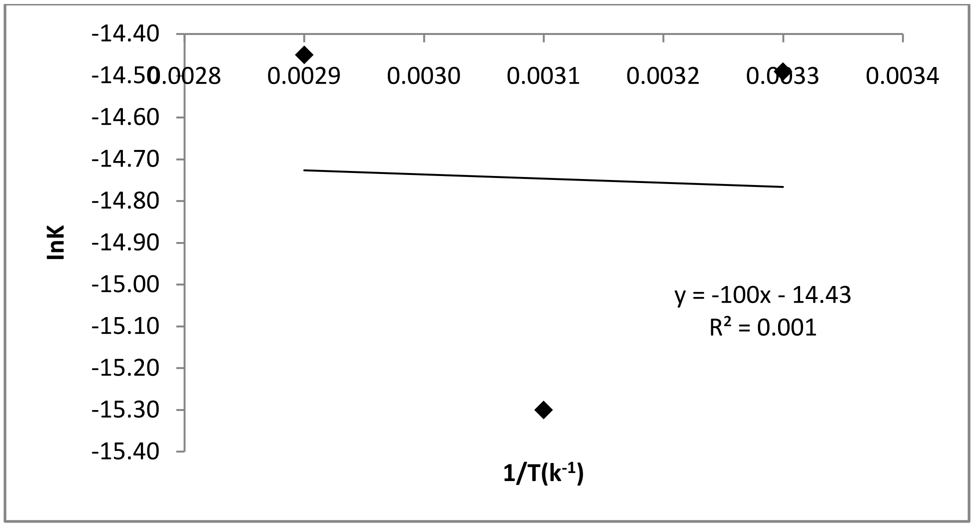
Appendix 8c: Verification of ist order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 70^{o}C



Appendix 8d: Verification of Second order behaviour for transesterification of *colocynthus vulgaris* methyl ester at 70^{o}C

Appendix 9a: Determination of rate constants (K) for a second order reaction at different temperatures for *colocynthus vulgaris* methyl ester

Temp ^oC	Temp k	1/T (k^{-1})	K	InK
30	303	0.0033	0.0000051	-14.49
50	323	0.0031	0.0000015	-15.30
70	343	0.0029	0.0000053	-14.45



Appendix 9b: Determination of activation energy from plot of Ink versus 1/T

Slope = $-E_a/R$

Slope = -100K

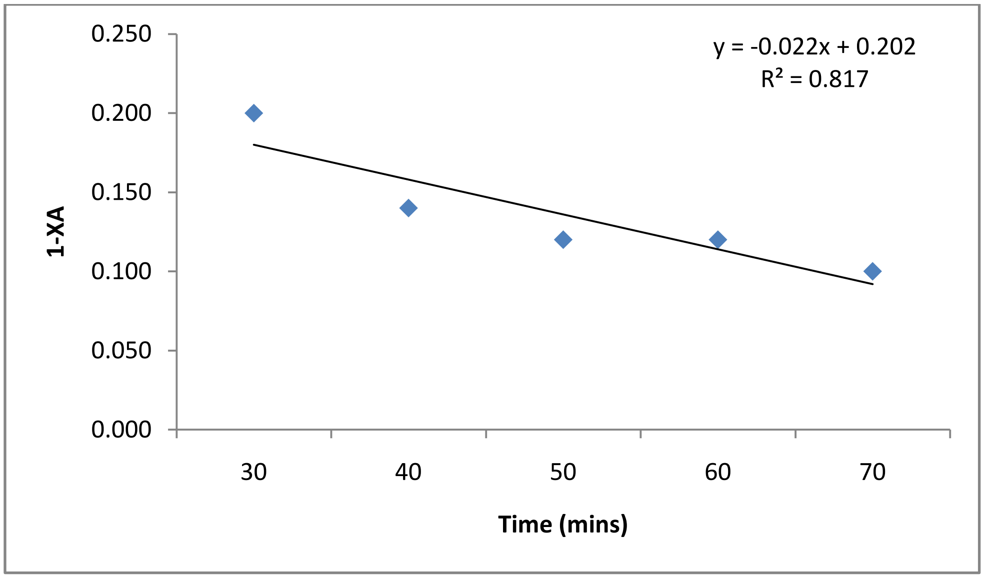
R =8.314J/K.mol

E_a = (8.314J/K.mol x 100K)

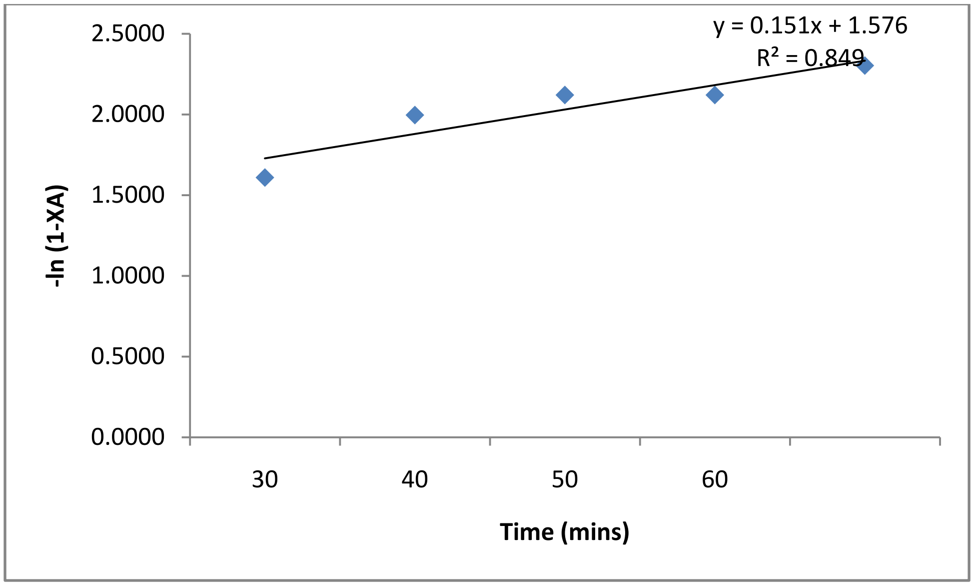
Activation energy = 8.314KJ/mol

Appendix 10a: *Cyperus esculentus* ethyl ester @30^{o}C

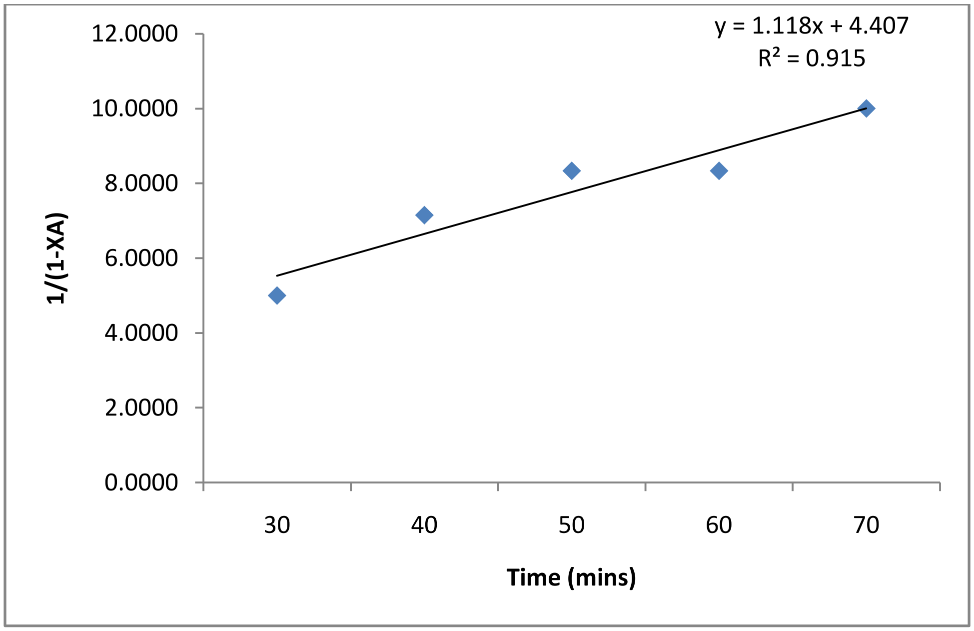
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.800	0.200	1.6094	5.0000
40	0.860	0.140	1.9961	7.1486
50	0.880	0.120	2.1203	8.3333
60	0.880	0.120	2.1203	8.3333
70	0.900	0.100	2.3026	10.0000



Appendix 10b: Verification of zero order behaviour for transesterification of *cyperus esculentus* ethyl ester at 30^{o}C



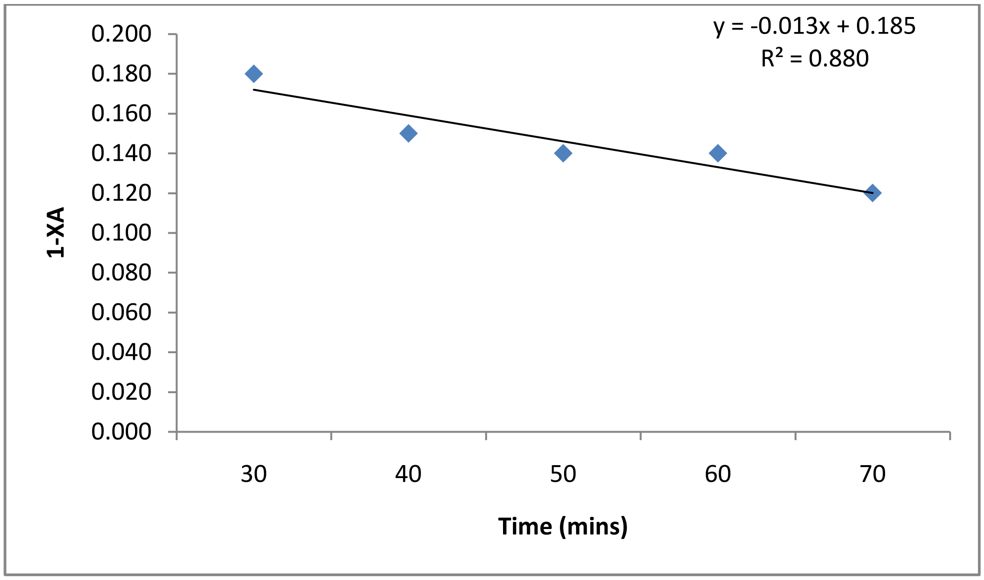
Appendix 10c: Verification of ist order behaviour for transesterification of *cyperus esculentus* ethyl ester at 30^{o}C



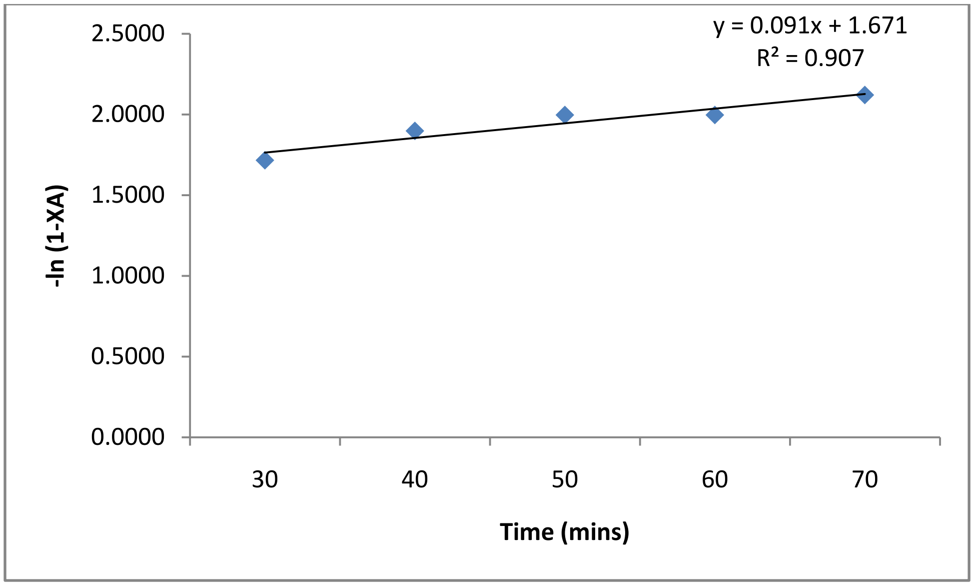
Appendix 10d: Verification of Second order behaviour for transesterification of *cyperus esculentus* ethyl ester at 30^{o}C

Appendix 11a: *Cyperus esculentus* ethyl ester @50^{o}C

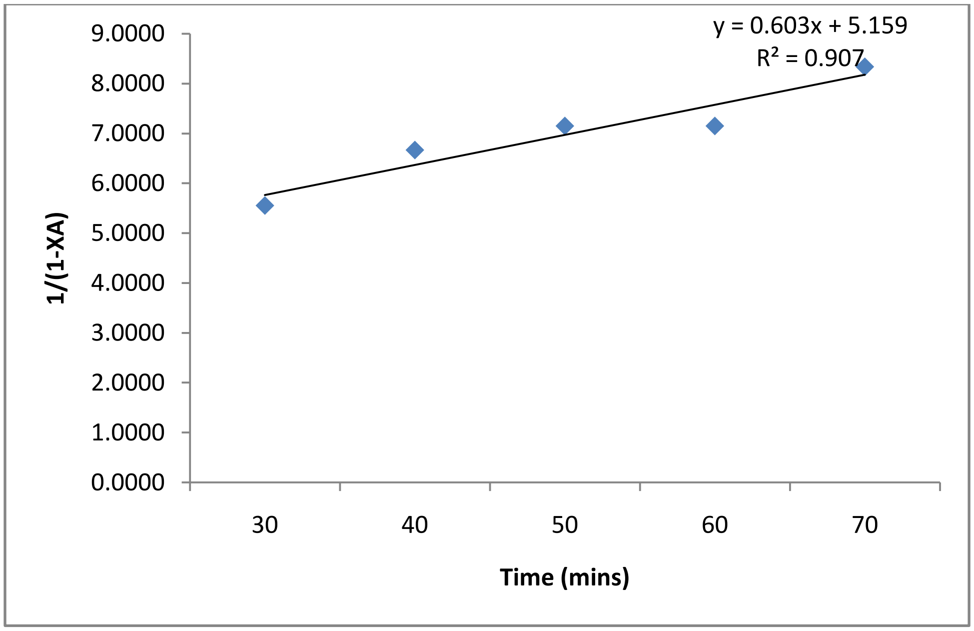
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.820	0.180	1.7148	5.5556
40	0.850	0.150	1.8971	6.6667
50	0.860	0.140	1.9961	7.1486
60	0.860	0.140	1.9961	7.1486
70	0.880	0.120	2.1203	8.3333



Appendix 11b: Verification of zero order behaviour for transesterification of *cyperus esculentus* ethyl ester at 50^{o}C



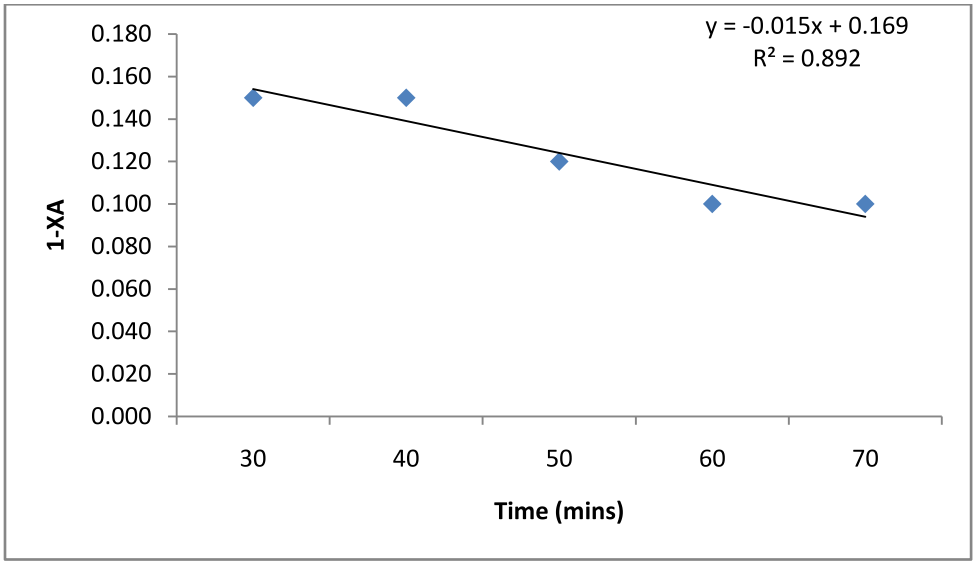
Appendix 11c: Verification of ist order behaviour for transesterification of *cyperus esculentus* ethyl ester at 50^{o}C



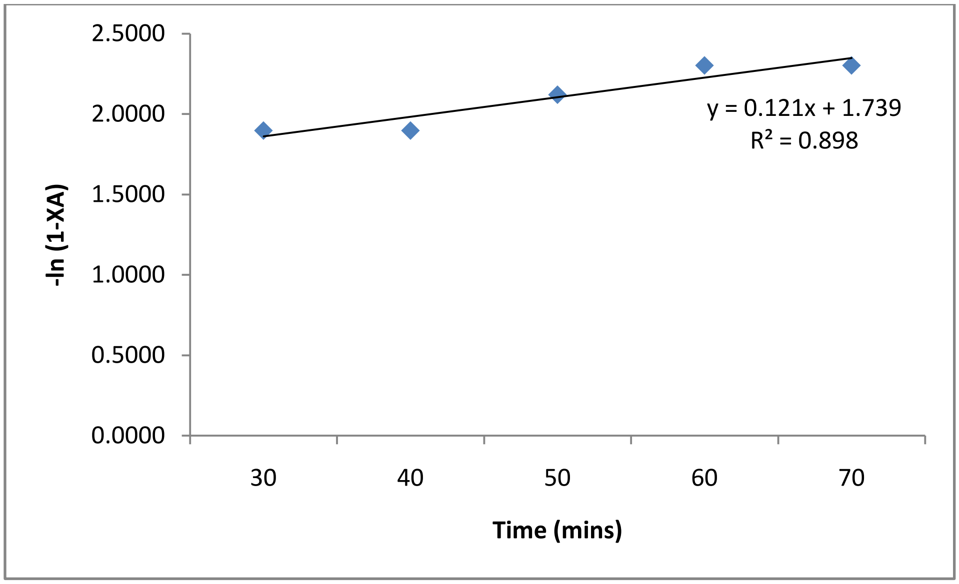
Appendix 11d: Verification of Second order behaviour for transesterification of *cyperus esculentus* ethyl ester at 50^{o}C

Appendix 12a: *Cyperus esculentus* ethyl ester @70^{o}C

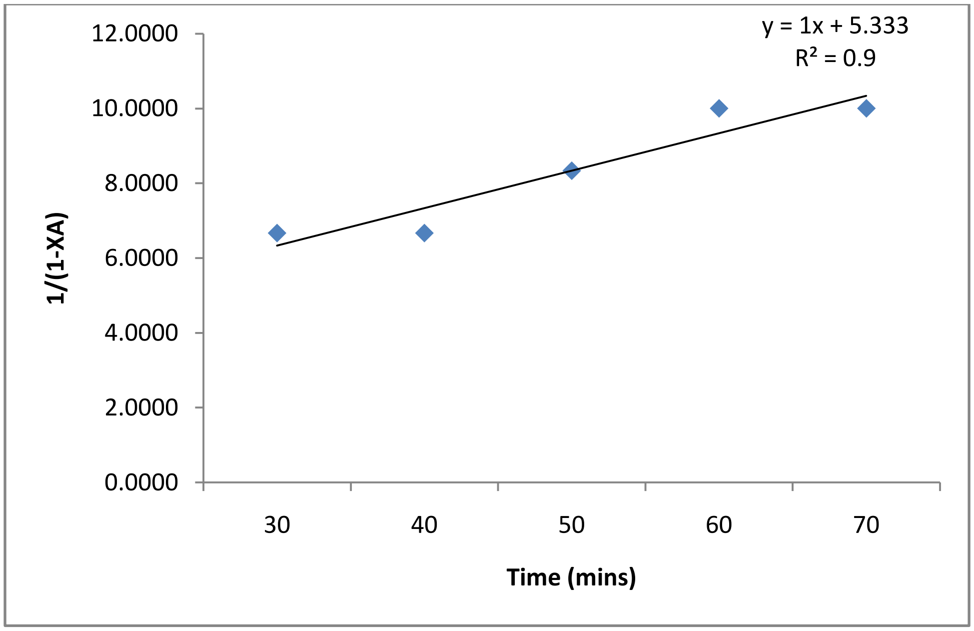
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.850	0.150	1.8971	6.6667
40	0.860	0.140	1.9961	7.1486
50	0.880	0.120	2.1203	8.3333
60	0.900	0.100	2.3026	10.0000
70	0.900	0.100	2.3026	10.0000



Appendix 12b: Verification of zero order behaviour for transesterification of *cyperus esculentus* ethyl ester at 70^{o}C



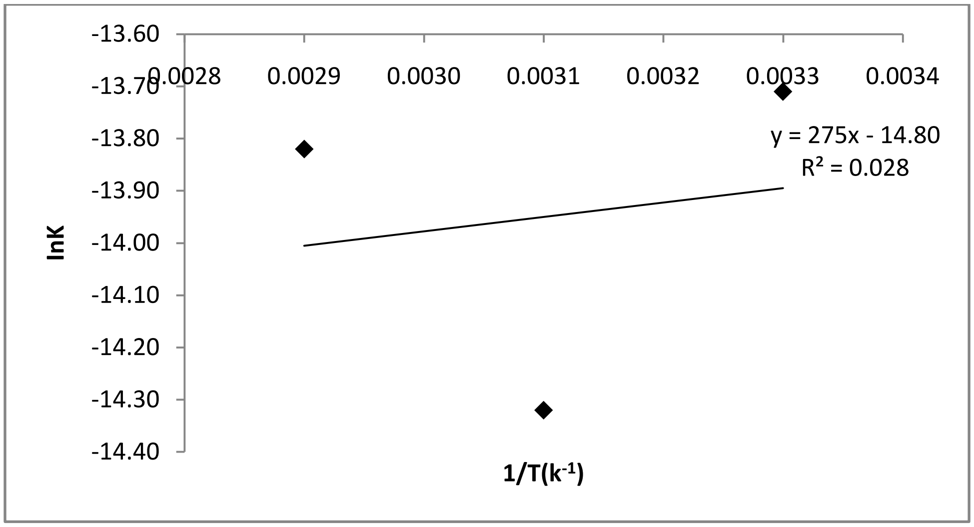
Appendix 12c: Verification of ist order behaviour for transesterification of *cyperus esculentus* ethyl ester at 70^{o}C



Appendix 12d: Verification of Second order behaviour for transesterification of *cyperus esculentus* ethyl ester at 70^{o}C

Appendix 13a: Determination of rate constants (K) for a second order reaction at different temperatures for *Cyperus esculentus* ethyl esters

Temp ^oC	Temp k	1/T (k^{-1})	K	InK
30	303	0.0033	0.0000011	-13.71
50	323	0.0031	0.0000060	-14.32
70	343	0.0029	0.000001	-13.82



Appendix 13b: Determination of activation energy from plot of Ink versus 1/T

Slope = $-E_a/R$

Slope = 275K

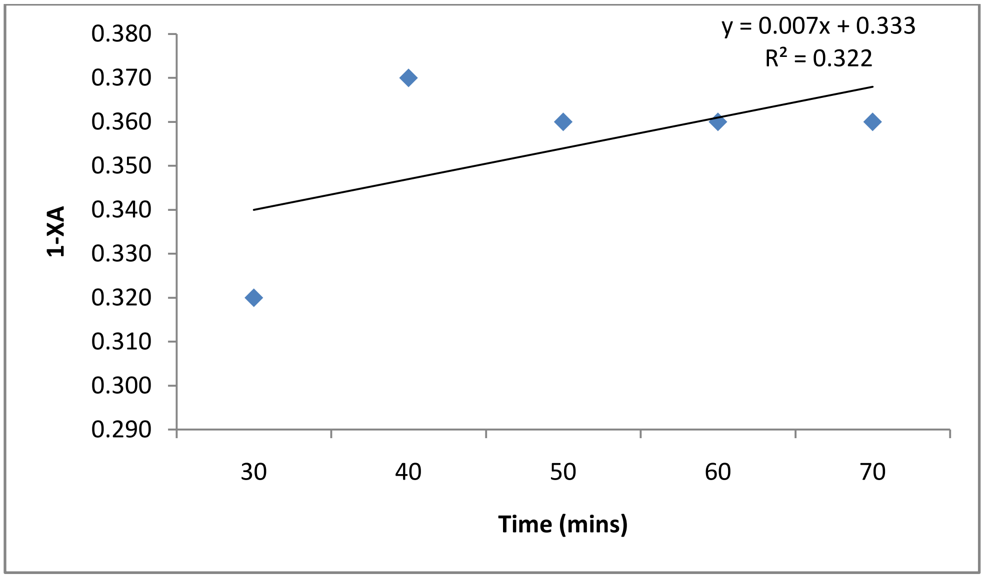
R =8.314J/K.mol

E_a = (8.314J/K.mol x 275K)

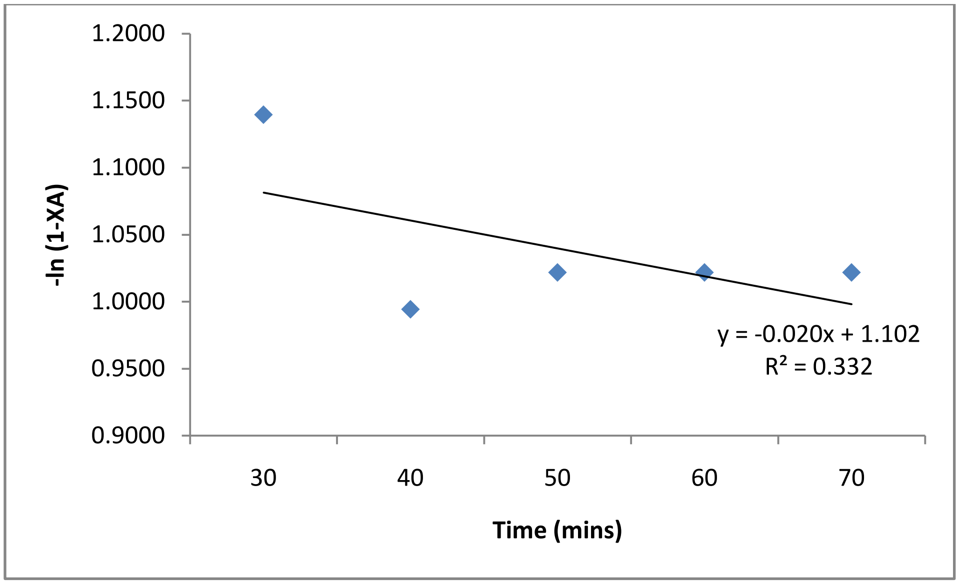
Activation energy = 2286.35KJ/mol

Appendix 14a: *Cyperus esculentus* methyl ester @30^{o}C

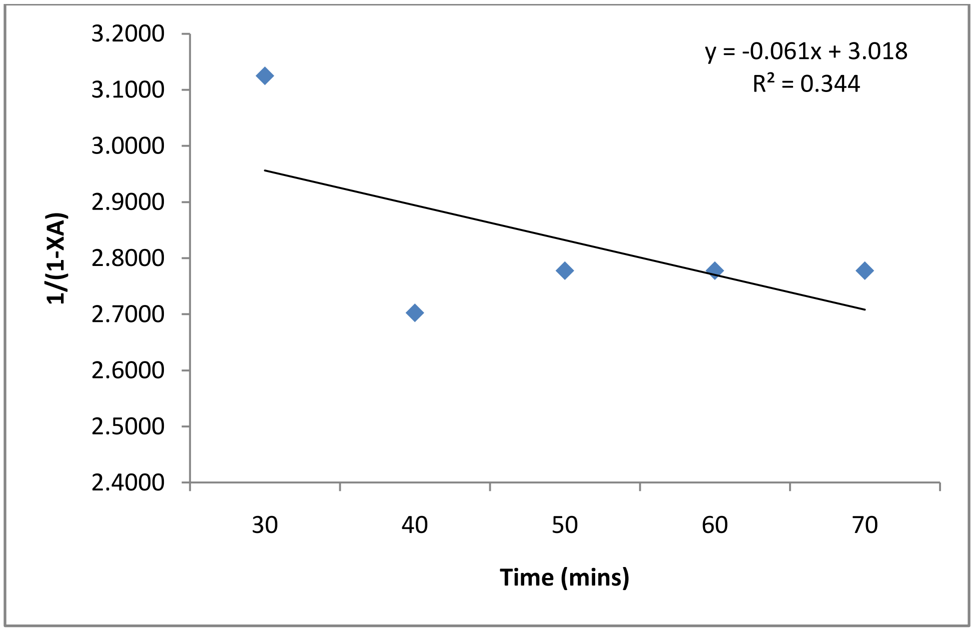
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.680	0.320	1.1394	3.1250
40	0.630	0.370	0.9942	2.7027
50	0.640	0.360	1.0217	2.7778
60	0.640	0.360	1.0217	2.7778
70	0.640	0.360	1.0217	2.7778



Appendix 14b: Verification of zero order behaviour for transesterification of *cyperus esculentus* *m*ethyl ester at 30^{o}C



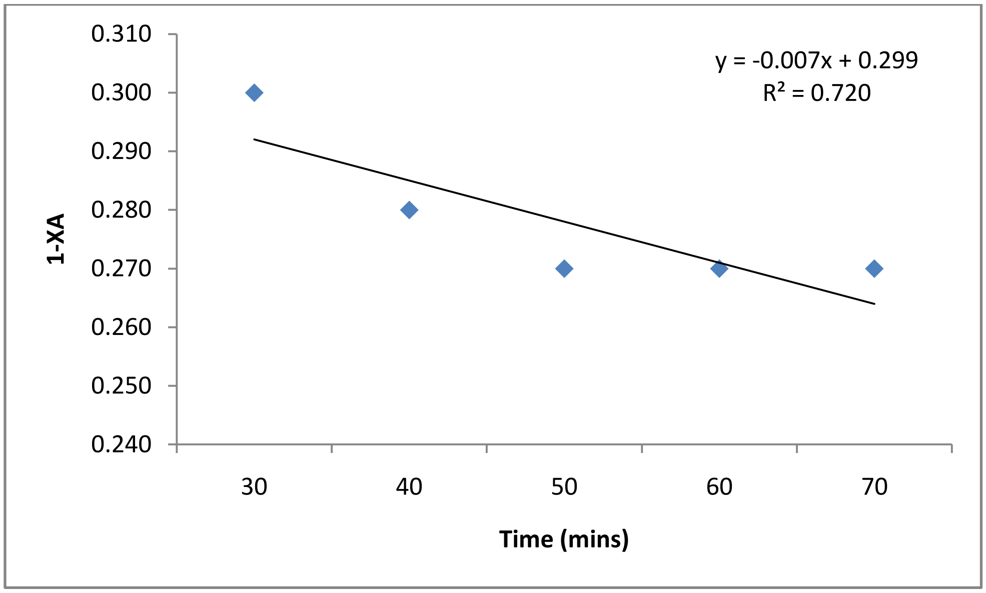
Appendix 14c: Verification of ist order behaviour for transesterification of *cyperus esculentus* methyl ester at 30^{o}C



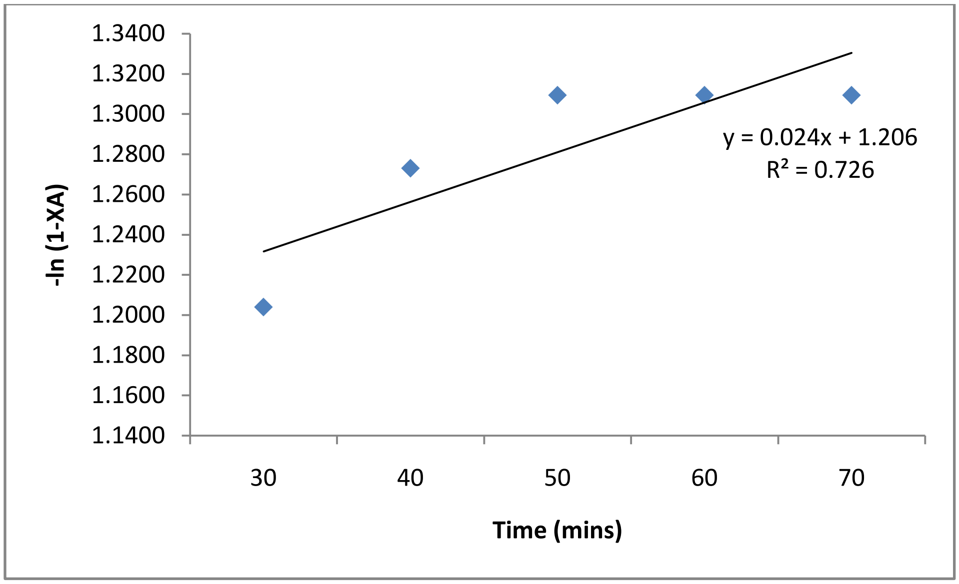
Appendix 14d: Verification of Second order behaviour for transesterification of *cyperus esculentus m*ethyl ester at 30^{o}C

Appendix 15a: *Cyperus esculentus* methyl ester @50^{o}C

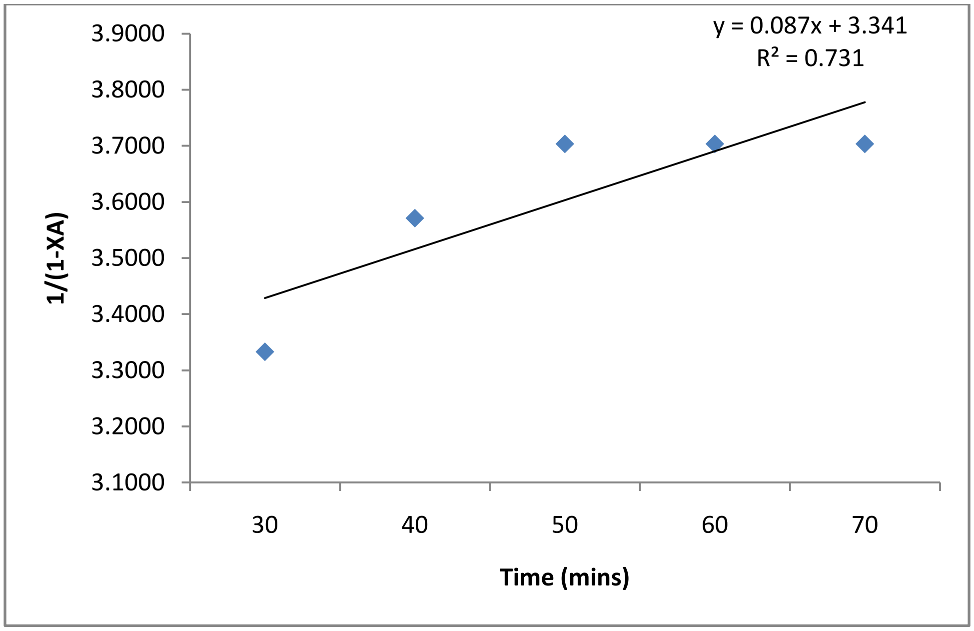
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.700	0.300	1.2040	3.3333
40	0.720	0.280	1.2730	3.5714
50	0.730	0.270	1.3093	3.7037
60	0.730	0.270	1.3093	3.7037
70	0.730	0.270	1.3093	3.7037



Appendix 15b: Verification of zero order behaviour for transesterification of *cyperus esculentus m*ethyl ester at 50^{o}C



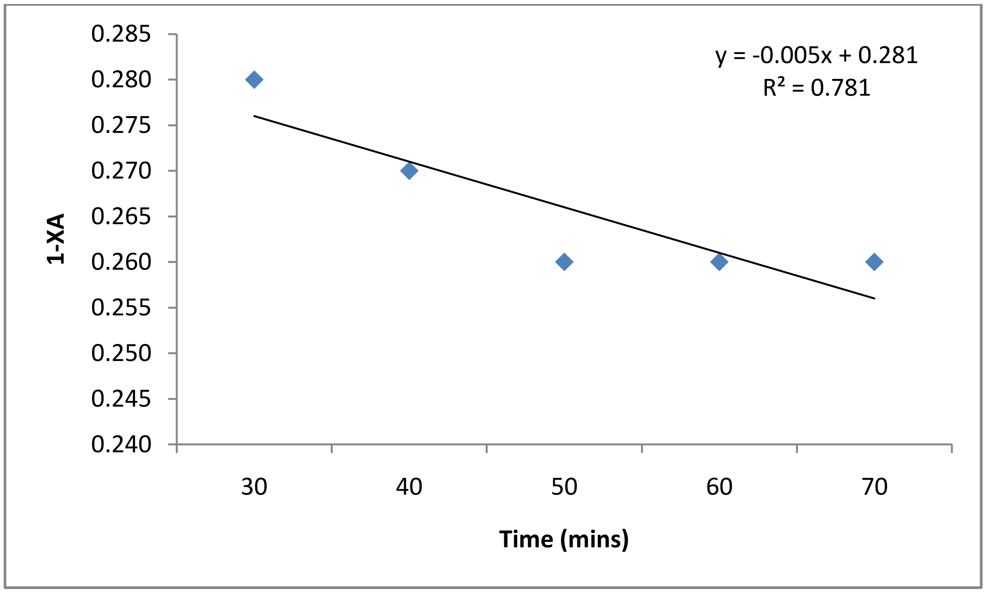
Appendix 15c: Verification of ist order behaviour for transesterification of *cyperus esculentus* methyl ester at 50^{o}C



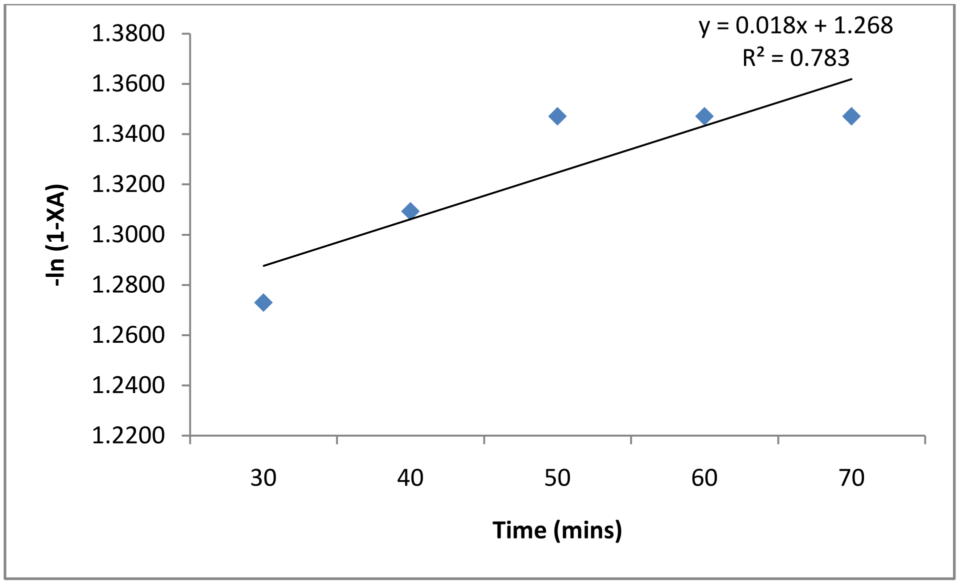
Appendix 15d: Verification of Second order behaviour for transesterification of *cyperus esculentus m*ethyl ester at 50^{o}C

Appendix 16a: *Cyperus esculentus* methyl ester @70°C

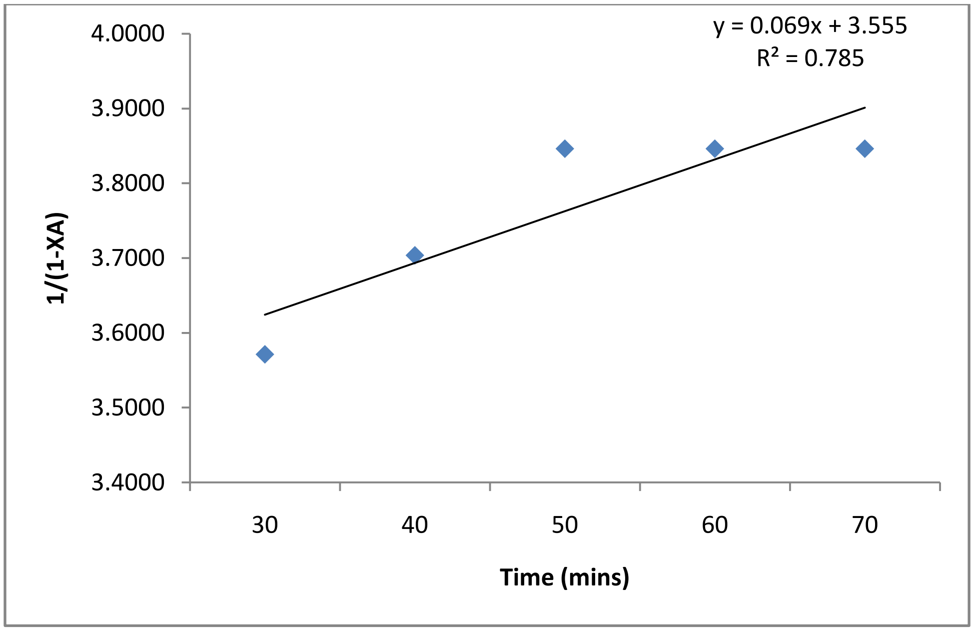
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.720	0.280	1.2730	3.5714
40	0.730	0.270	1.3093	3.7037
50	0.740	0.260	1.3471	3.8462
60	0.740	0.260	1.3471	3.8462
70	0.740	0.260	1.3471	3.8462



Appendix 16b: Verification of zero order behaviour for transesterification of *cyperus esculentus* methyl ester at 70°C



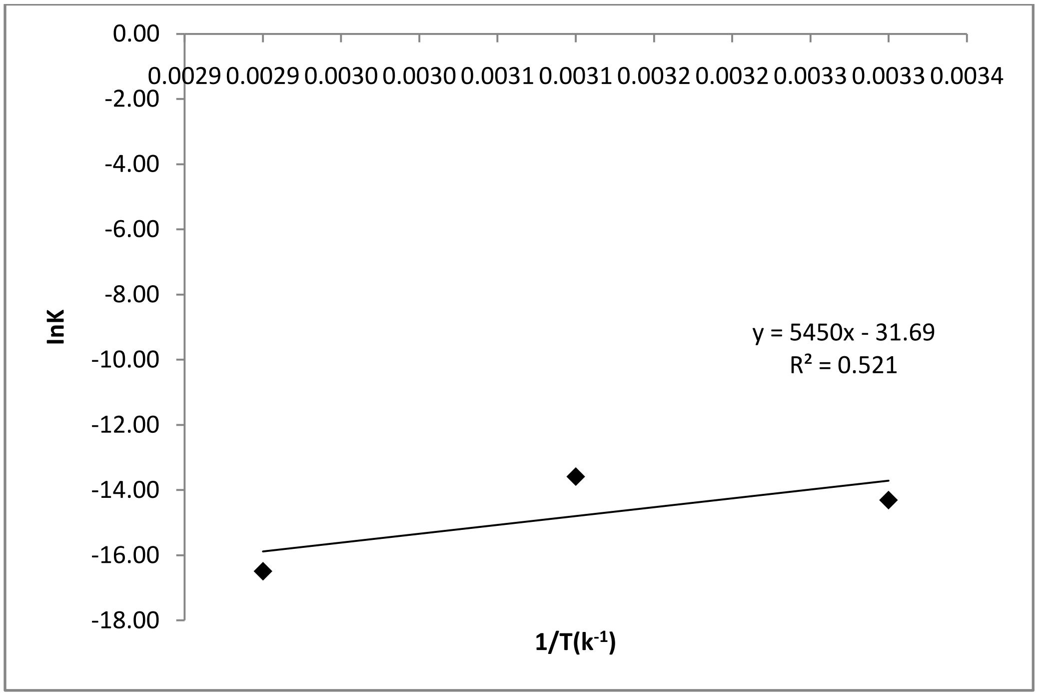
Appendix 16c: Verification of ist order behaviour for transesterification of *cyperus esculentus* methyl ester at 70^{o}C



Appendix 16d: Verification of Second order behaviour for transesterification of *cyperus esculentus m*ethyl ester at 70^{o}C

Appendix 17a: Determination of rate constants (K) for a second order reaction at different temperatures for *Cyperus esculentus* methyl esters

Temp °C	Temp k	1/T (k^{-1})	K	InK
30	303	0.0033	0.00000061	-14.31
50	323	0.0031	0.00000087	-13.59
70	343	0.0029	0.00000069	-16.49



Appendix 17b: Determination of activation energy from plot of Ink versus 1/T

Slope = $-E_a/R$

Slope = -5450K

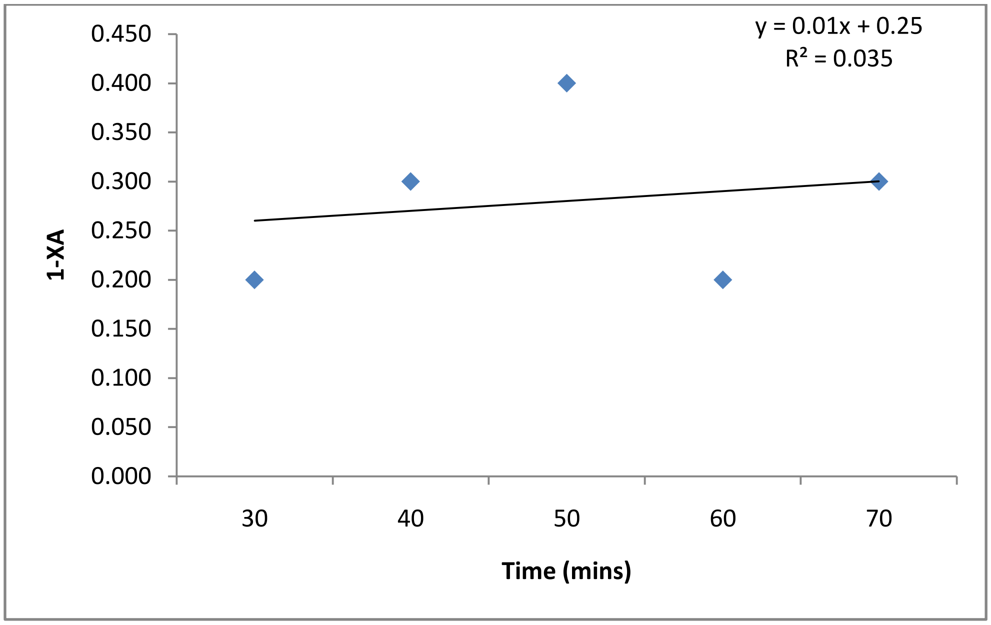
R =8.314J/K.mol

E_a = (8.314J/K.mol x 5450K)

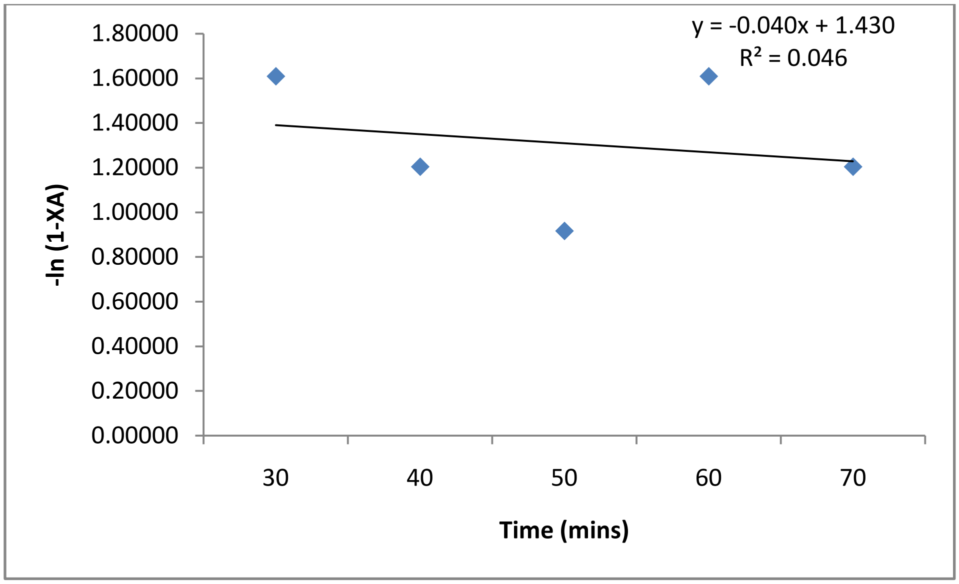
Activation energy = 45311.3 KJ/mol

Appendix 18a: *Sesamum indicum* ethyl ester @30°C

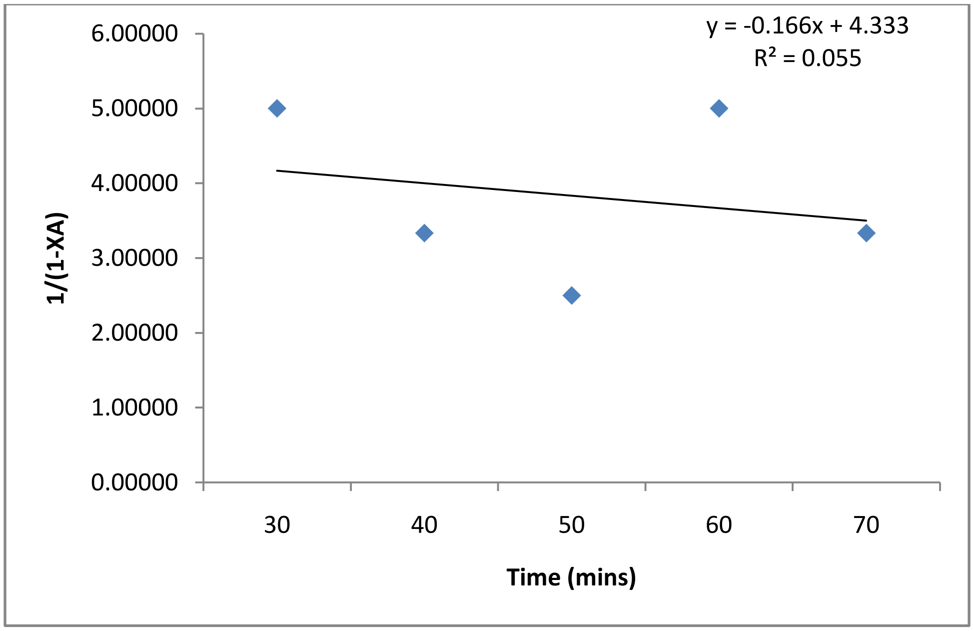
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.800	0.200	1.6094	5.0000
40	0.700	0.300	1.2040	3.3333
50	0.600	0.400	0.9163	2.5000
60	0.800	0.200	1.6094	5.0000
70	0.700	0.300	1.2040	3.3333



Appendix 18b: Verification of zero order behaviour for transesterification of *Sesamum indicum* ethyl ester at 30°C



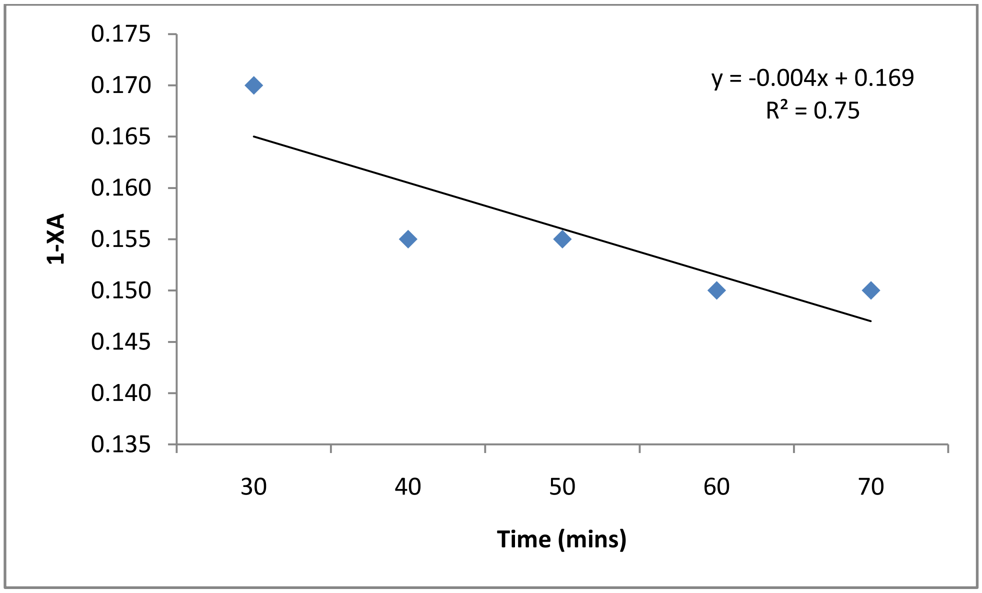
Appendix 18c: Verification of ist order behaviour for transesterification of *Sesamum indicum* ethyl ester at 30^{o}C



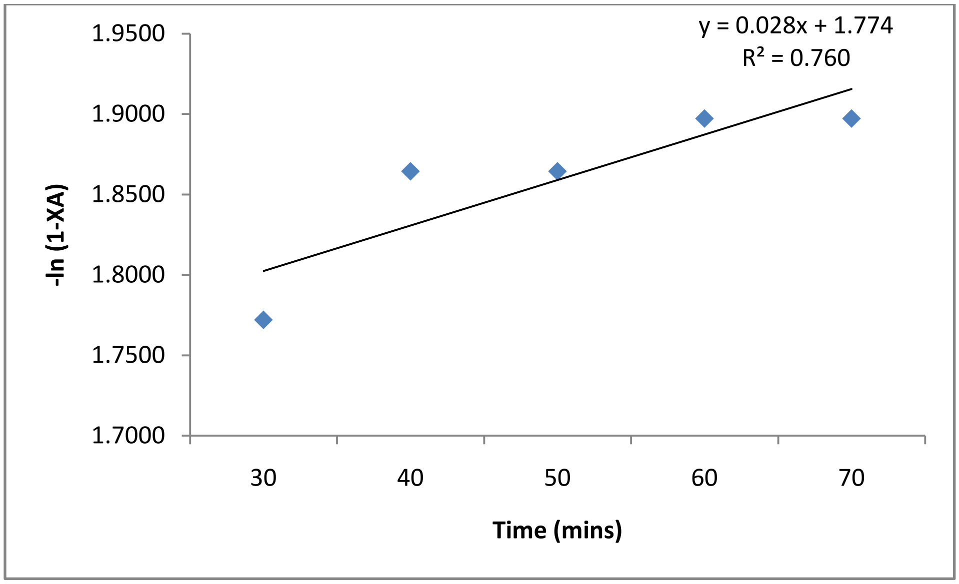
Appendix 18d: Verification of Second order behaviour for transesterification of *Sesamum indicum* ethyl ester at 30^{o}C

Appendix 19a: *Sesamum indicum* ethyl ester @50^{o}C

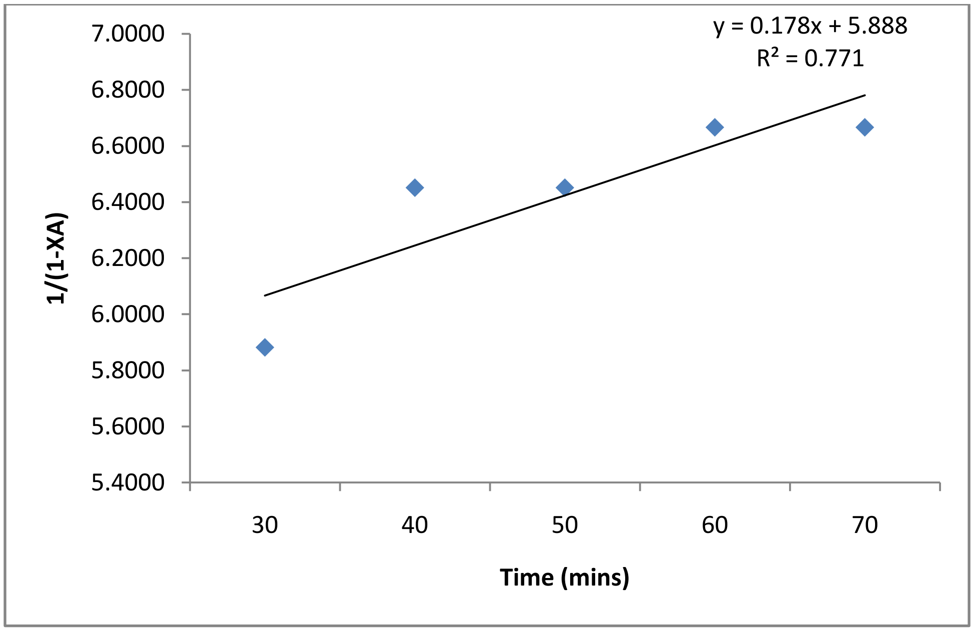
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.830	0.170	1.7720	5.8824
40	0.845	0.155	1.8643	6.4516
50	0.845	0.155	1.8643	6.4516
60	0.850	0.150	1.8971	6.6667
70	0.850	0.150	1.8971	6.6667



Appendix 19b: Verification of zero order behaviour for transesterification of *Sesamum indicum* ethyl ester at 50^{o}C



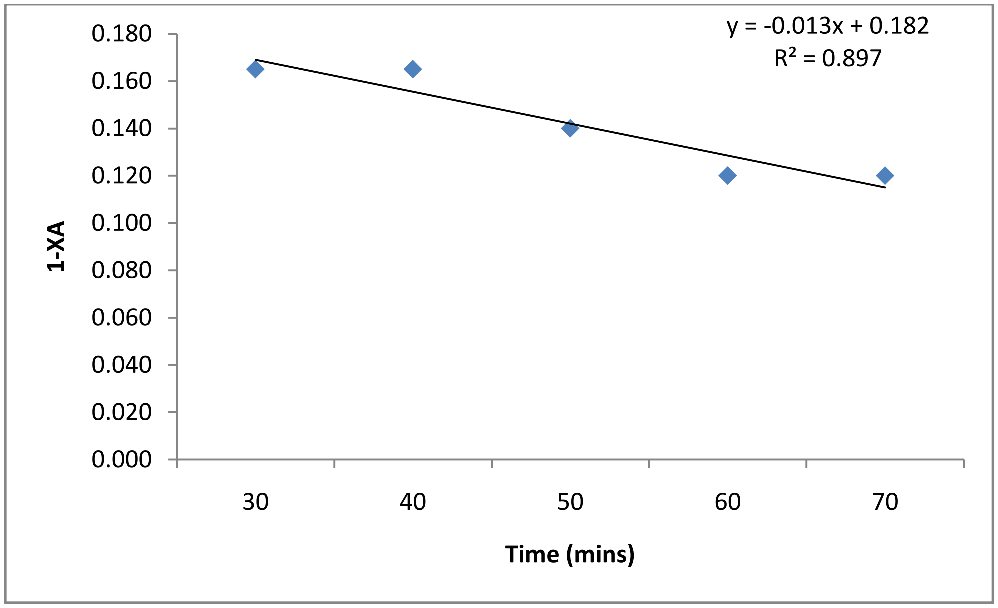
Appendix 19c: Verification of ist order behaviour for transesterification of *Sesamum indicum* ethyl ester at 50^{o}C



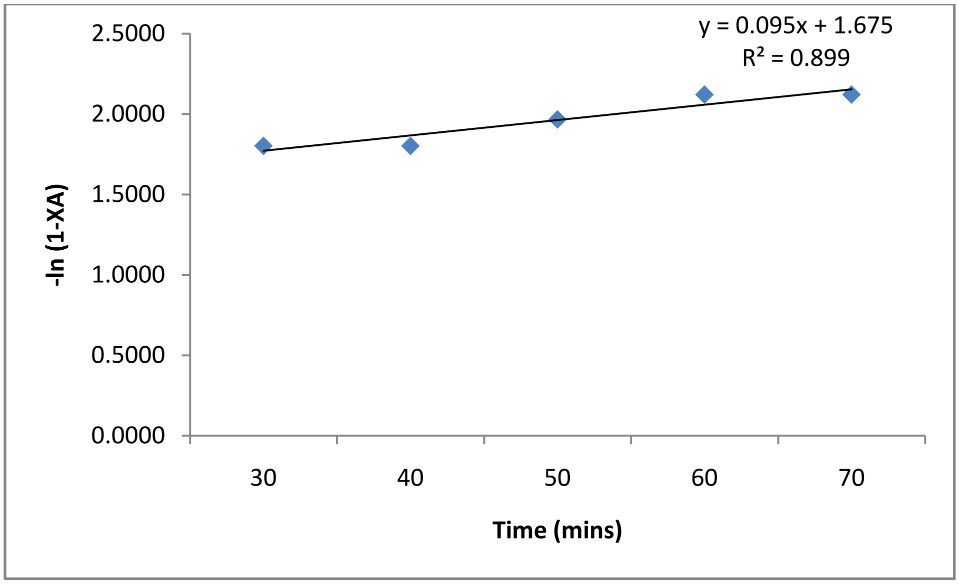
Appendix 19d: Verification of Second order behaviour for transesterification of *Sesamum indicum* ethyl ester at 50^{o}C

Appendix 20a: *Sesamum indicum* ethyl ester @70^{o}C

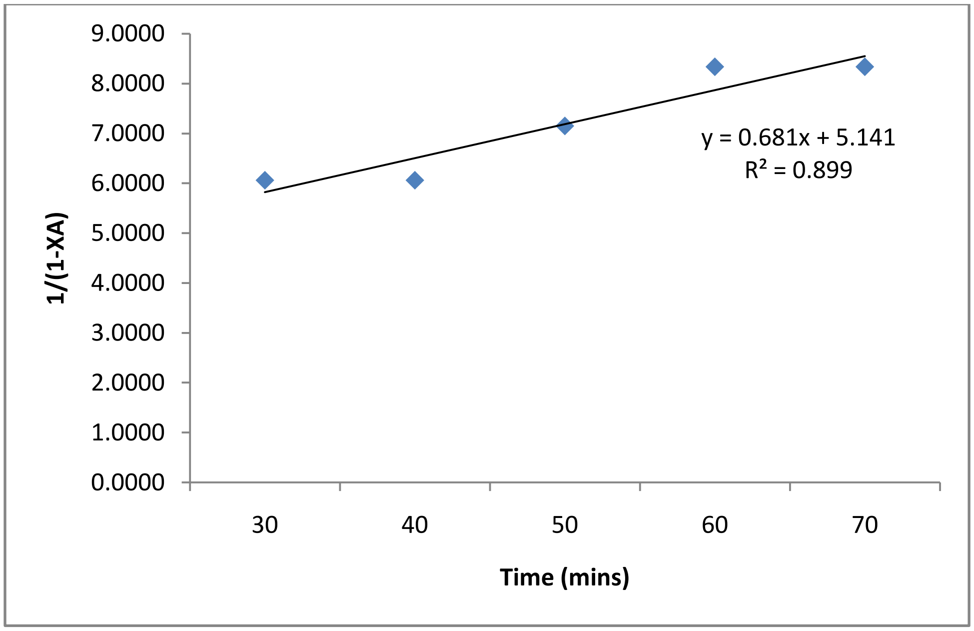
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.835	0.165	1.8018	6.0606
40	0.840	0.160	1.8326	6.2500
50	0.860	0.140	1.9661	7.1486
60	0.880	0.120	2.1203	8.3333
70	0.880	0.120	2.1203	8.3333



Appendix 20b: Verification of zero order behaviour for transesterification of *Sesamum indicum* ethyl ester at 70^{o}C



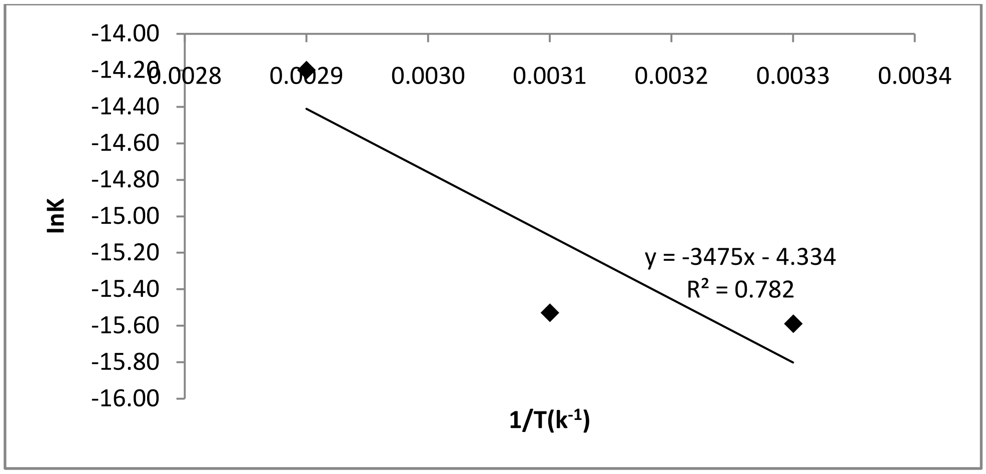
Appendix 20c: Verification of ist order behaviour for transesterification of *Sesamum indicum* ethyl ester at 70°C



Appendix 20d: Verification of Second order behaviour for transesterification of *Sesamum indicum* ethyl ester at 70°C

Appendix 21a: Determination of rate constants (K) for a second order reaction at different temperatures for *Sesamum indicum* ethyl esters

Temp ^{o}C	Temp k	1/T (k^{-1})	K	InK
30	303	0.0033	0.0000017	-15.59
50	323	0.0031	0.00000018	-15.53
70	343	0.0029	0.0000069	-14.20



Appendix 21b: Determination of activation energy from plot of Ink versus 1/T

Slope = $-E_a/R$

Slope = -3475K

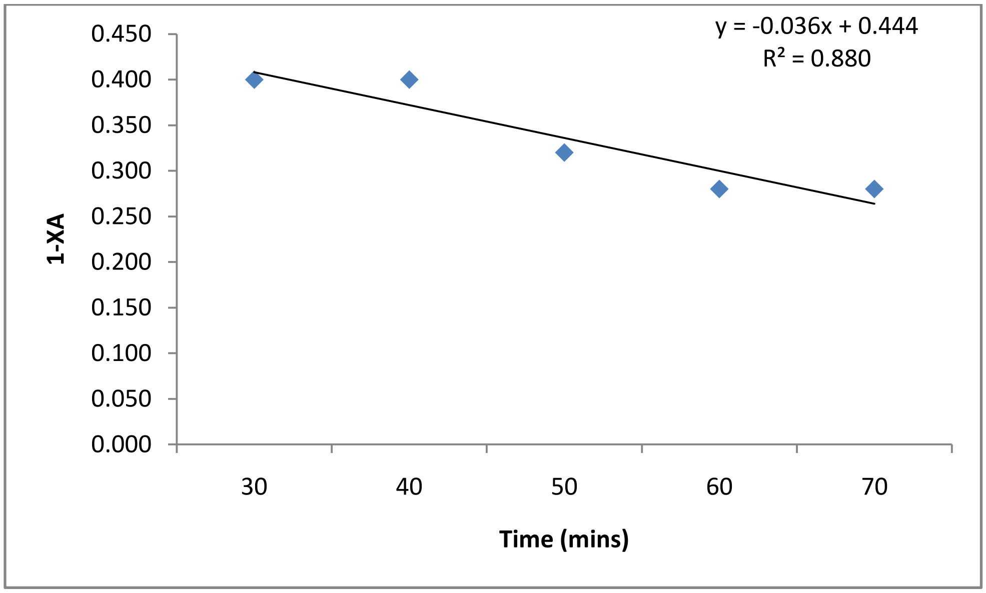
R =8.314J/K.mol

E_a = (8.314J/K.mol x 3475K)

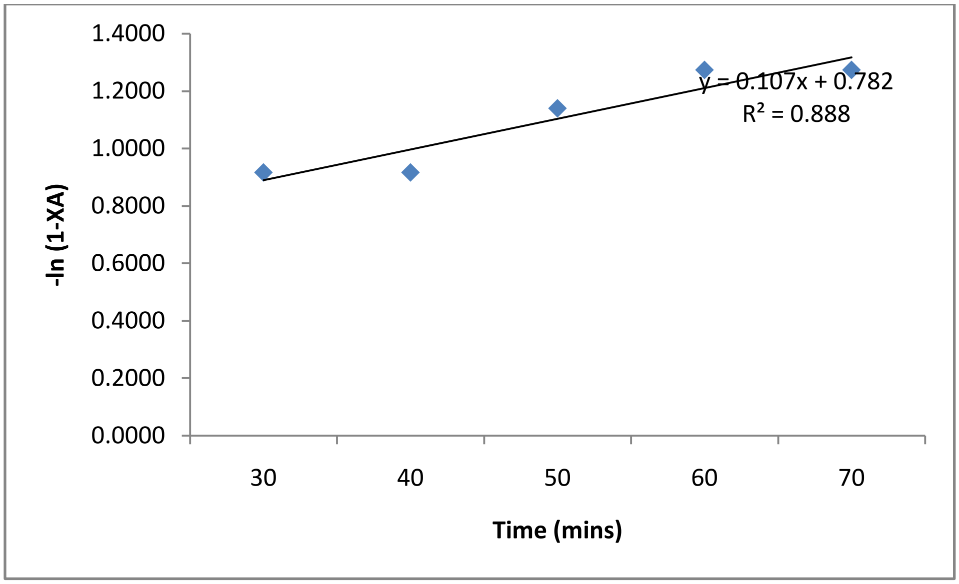
Activation energy = 28891.15KJ/mol

Appendix 22a: *Sesamum indicum* methyl ester @30^{o}C

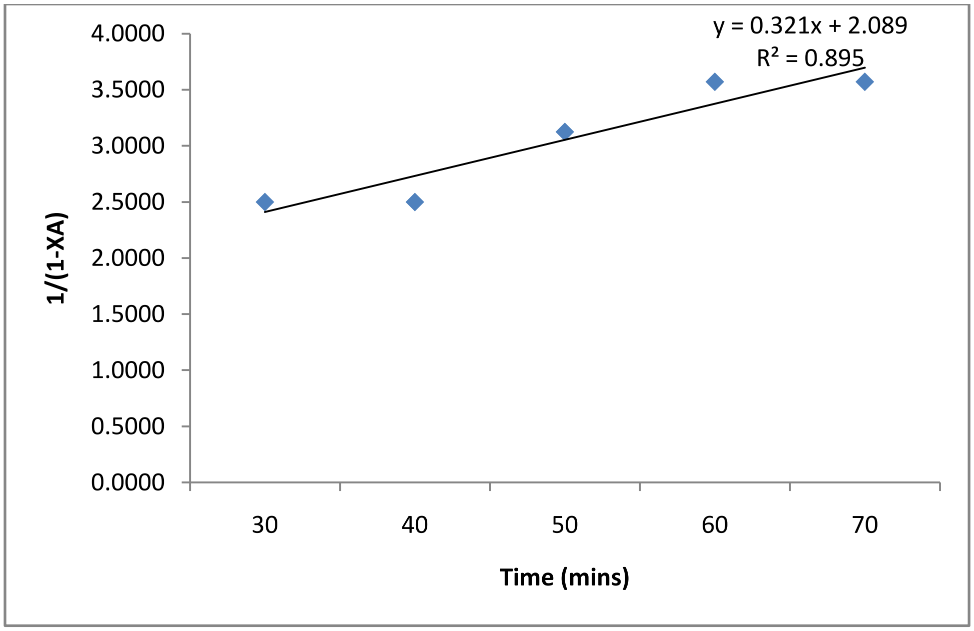
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.600	0.400	0.9163	2.5000
40	0.600	0.400	0.9163	2.5000
50	0.680	0.320	1.1394	3.1250
60	0.720	0.280	1.2730	3.5714
70	0.720	0.280	1.2730	3.5714



Appendix 22b: Verification of zero order behaviour for transesterification of *Sesamum indicum* methyl ester at 30^{o}C



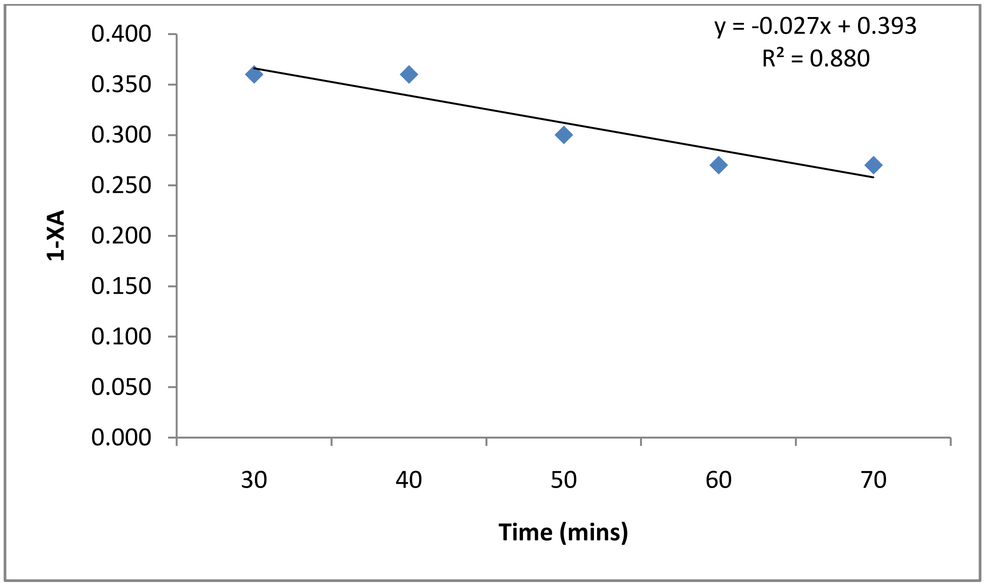
Appendix 22c: Verification of ist order behaviour for transesterification of *Sesamum indicum m*ethyl ester at 30^{o}C



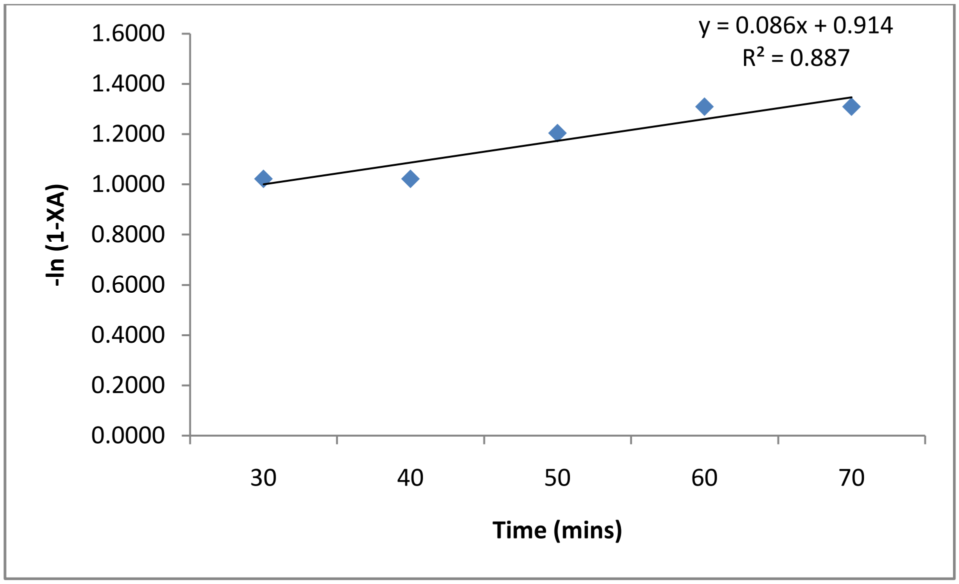
Appendix 22d: Verification of Second order behaviour for transesterification of *Sesamum indicum* methyl ester at 30^{o}C

Appendix 23a: *Sesamum indicum* methyl ester @50°C

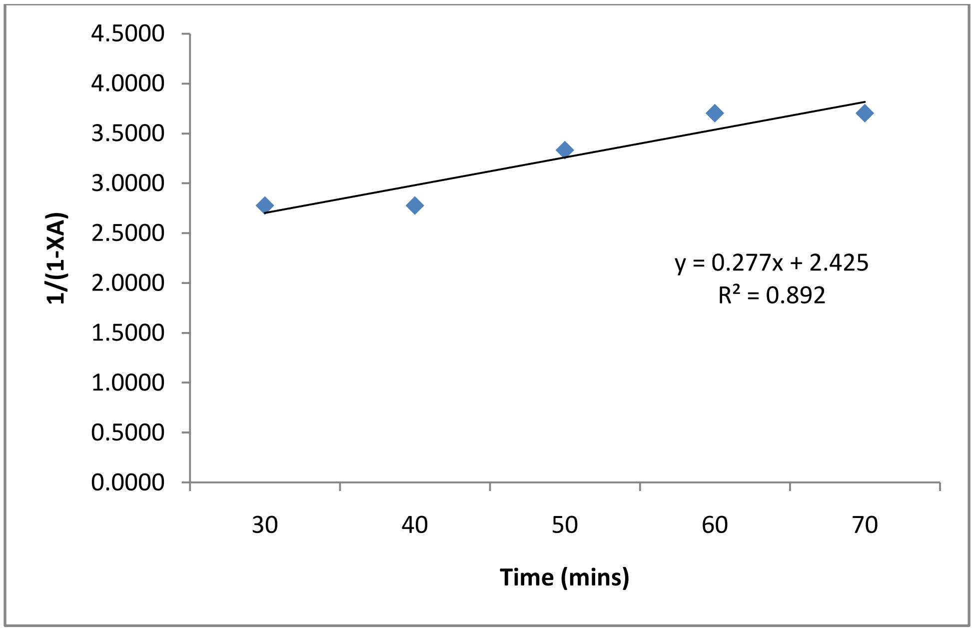
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.640	0.360	1.0217	2.7778
40	0.640	0.360	1.0217	2.7778
50	0.700	0.300	1.2040	3.3333
60	0.730	0.270	1.3093	3.7037
70	0.730	0.270	1.3093	3.7037



Appendix 23b: Verification of zero order behaviour for transesterification of *Sesamum indicum* methyl ester at 50°C



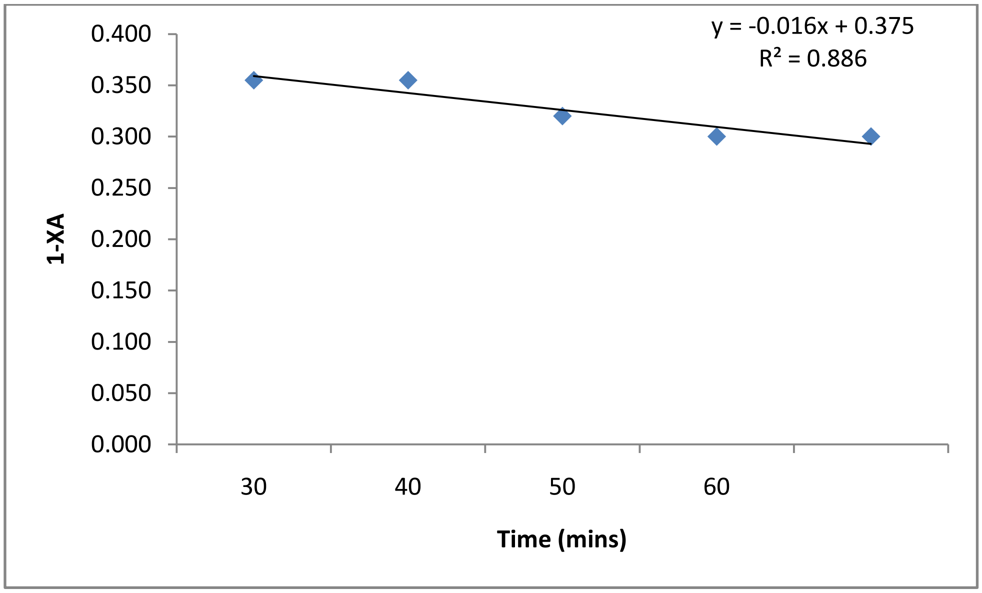
Appendix 23c: Verification of ist order behaviour for transesterification of *Sesamum indicum m*ethyl ester at 50^{o}C



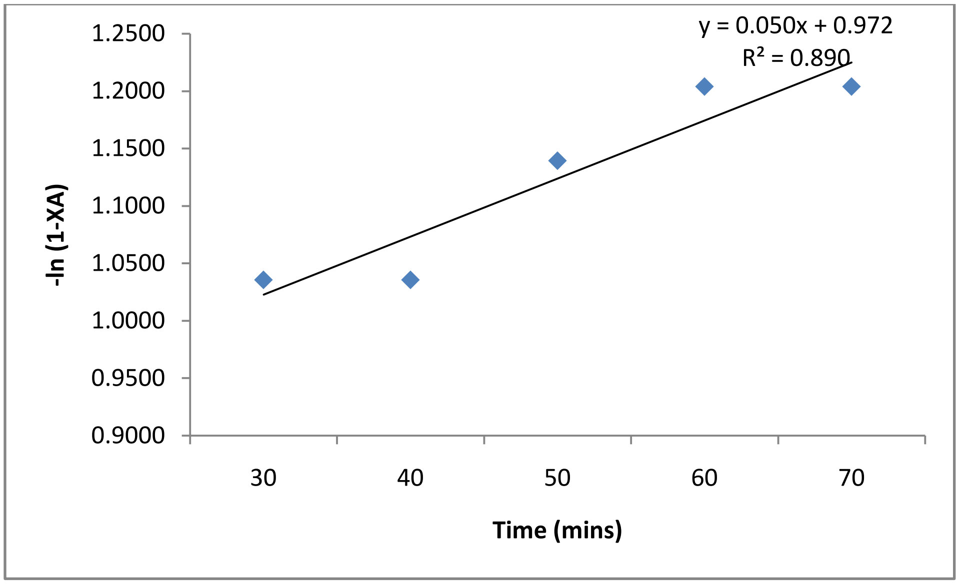
Appendix 23d: Verification of Second order behaviour for transesterification of *Sesamum indicum* methyl ester at 50^{o}C

Appendix 24a: *Sesamum indicum* methyl ester @70^{o}C

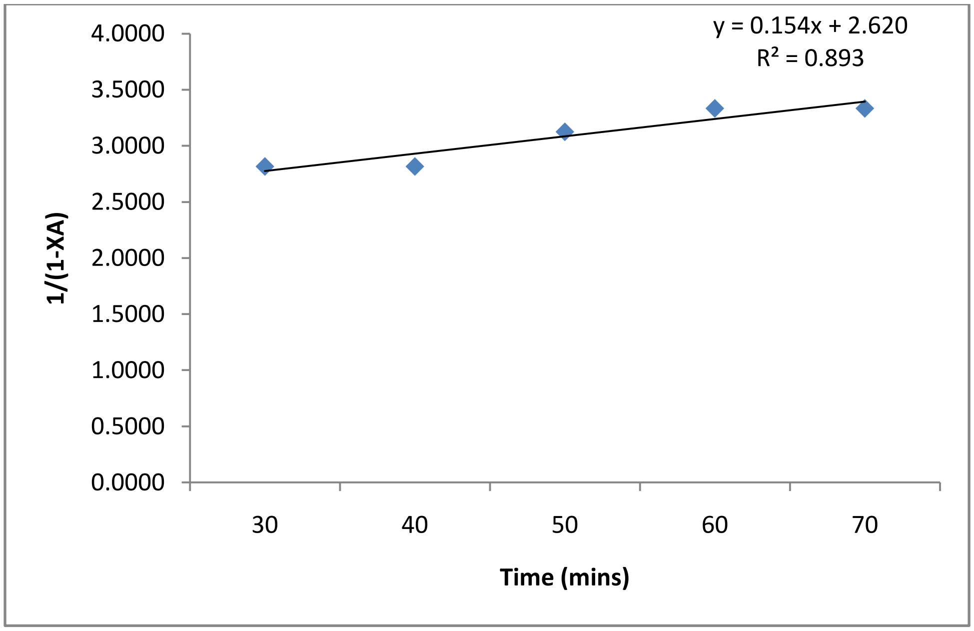
Time (mins)	XA	1-XA	-ln (1-XA)	1/(1-XA)
30	0.645	0.355	1.0356	2.8169
40	0.645	0.355	1.0356	2.8169
50	0.650	0.350	1.0498	2.8571
60	0.700	0.300	1.2040	3.3333
70	0.700	0.300	1.2040	3.3333



Appendix 24b: Verification of zero order behaviour for transesterification of *Sesamum indicum* methyl ester at 70^{o}C



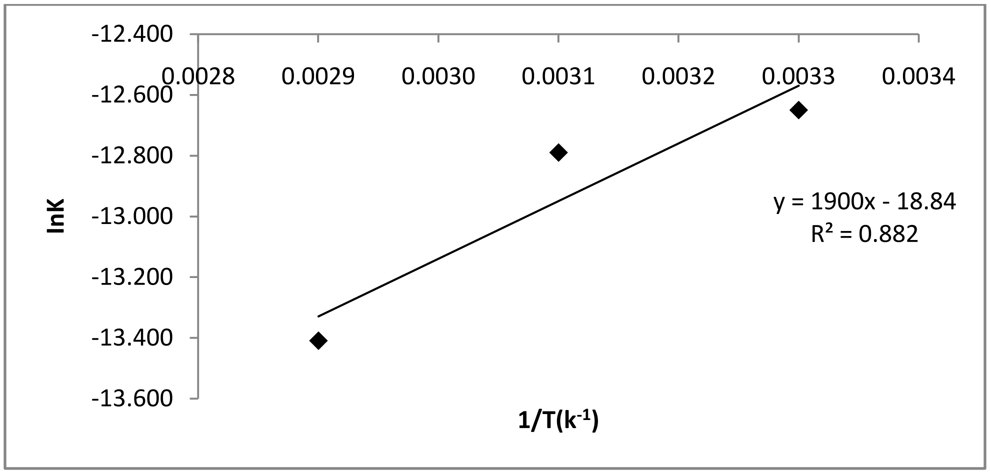
Appendix 24c: Verification of ist order behaviour for transesterification of *Sesamum indicum* *m*ethyl ester at 70^{o}C



Appendix 24d: Verification of Second order behaviour for transesterification of *Sesamum indicum* methyl ester at 70^{o}C

Appendix 25a: Determination of rate constants (K) for a second order reaction at different temperatures for *Sesamum indicum* ethyl esters

Temp ^oC	Temp k	1/T (k^{-1})	K	InK
30	303	0.0033	0.0000032	-12.650
50	323	0.0031	0.0000028	-12.790
70	343	0.0029	0.0000015	-13.410



Appendix 25b: Determination of activation energy from plot of Ink versus 1/T

Slope = $-E_a/R$

Slope = -1900K

R =8.314J/K.mol

E_a = (8.314J/K.mol x 1900K)

Activation energy = 16796.6KJ/mol

Appendix 26: FTIR peaks of *Colocynthus vulgaris* ethyl ester B100 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4336.12	4260.9	4338.05	4337.09	O-H unbonded
Absent	3863.55	3855.83	3846.19	O-H unbonded
Absent	3748.78	3741.06	3741.06	O-H unbonded
3476.81	3473.91	3536.6	3537.57	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2930.93	2925.15	2930.93	2929.97	C-H stretch of methyl and methylene groups
2867.28	2860.53	2869.21	Absent	C-H stretch of alkanes (alkyl groups)
2348.41	2305.01	Absent	2403.38	-
Absent	2035.01	2296.33	2295.37	-
Absent	Absent	Absent	2036.38	Alkyne C≡C symmetrical bending
1739.85	1738.89	1737.92	1736.96	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	1529.6	1527.67	1527.67	C=C stretch of Arenes and alkene
1449.55	1453.41	1448.59	1448.59	C-H bond assymetric bending
Absent	1368.54	1367.58	Absent	C-H bond assymetric bending
Absent	1236.41	Absent	1238.34	C-O stretch of esters, carboxylic acids and ethers
1167.94	1167.94	1167.94	1168.9	C-O stretch of esters, carboxylic acids and ethers
Absent	1045.45	Absent	Absent	C-H Bending out of plane for alkenes
715.61	721.4	714.65	Absent	C-H Bending out of plane for alkenes
448.46	Absent	407.96	Absent	C-H deformations for alkyl groups

Appendix 27: FTIR peaks of *Colocynthus vulgaris* ethyl esters/diesel blend B20 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4327.44	4332.25	4332.26	4336.12	O-H unbonded
Absent	4259.93	3868.37	4260.9	O-H unbonded
Absent	Absent	3740.1	3746.85	O-H unbonded
3366.86	3414.12	3477.77	3475.84	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2931.9	2925.15	2930.93	2925.15	C-H stretch of methyl and methylene groups
Absent	2859.56	2867.28	2858.6	C-H stretch of alkanes (alkyl groups)
2439.38	2359.98	2296.33	2397.6	Alkyne C≡C symmetrical bending
1744.67	1743.71	1740.81	1742.74	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1600.01	1614.47	1625.08	1635.69	C=C stretch of Arenes and alkene
Absent	Absent	1531.53	Absent	C=C stretch of Arenes and alkene
1454.38	1455.34	1527.67	1454.38	C-H bond assymetric bending
1371.43	1374.33	1371.43	1366.61	C-H bond assymetric bending
Absent	1236.41	1239.31	1234.48	C-O stretch of esters, carboxylic acids and ethers
1166.01	1163.11	1166.97	1163.11	C-O stretch of esters, carboxylic acids and ethers
Absent	1105.25	1045.45	1105.25	C-H Bending out of plane for alkenes
720.44	720.44	719.47	720.44	C-H Bending out of plane for alkenes
441.71	Absent	424.35	425.3	C-H deformations for alkyl groups

Appendix 28: FTIR peaks of *Colocynthus vulgaris* ethyl esters/diesel blend B50 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
Absent	4336.12	4337.09	4335.16	O-H unbonded
4256.07	4260.9	4260.9	4259.93	O-H unbonded
Absent	3744.92	Absent	3755.53	O-H unbonded
Absent	3511.53	3492.24	3468.13	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2930.93	2925.15	2924.18	2925.15	C-H stretch of methyl and methylene groups
Absent	2857.64	2857.64	2858.6	C-H stretch of alkanes (alkyl groups)
Absent	2727.44	2729.37	2730.33	-
2351.3	2385.06	2301.15	2350.34	-
Absent	2311.76	Absent	Absent	-
Absent	2032.08	2034.97	2033.04	Alkyne C≡C symmetrical bending
1741.78	1741.78	1741.78	1739.85	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	Absent	1601.93	1620.26	C=C stretch of Arenes and alkene
Absent	Absent	Absent	1506.46	C=C stretch of Arenes and alkenes
1453.41	1455.34	1451.48	1454.38	C-H bond assymetric bending
1371.43	1370.47	1368.54	1369.5	C-H bond assymetric bending
Absent	1236.41	1235.45	1235.45	C-O stretch of esters, carboxylic acids and ethers
1166.97	1164.08	1162.15	1165.04	C-O stretch of esters, carboxylic acids and ethers
Absent	1105.25	1106.21	1105.25	C-O stretch of esters, carboxylic acids and ethers
718.51	725.26	725.26	726.22	C-H Bending out of plane for alkenes
Absent	Absent	Absent	589.27	C-H deformations for alkyl groups
431.1	Absent	409.89	417.6	C-H deformations for alkyl groups

Appendix 29: FTIR peaks of *Colocynthus vulgaris* methyl esters B100 (cm^{-1}) at different temperatures

28^{0}C	100^{0}C	150^{0}C	200^{0}C	Description
Absent	4336.12	4336.12	Absent	O-H unbonded
Absent	4260.9	4260.9	Absent	O-H unbonded
Absent	4206.89	4206.89	Absent	O-H unbonded
Absent	3984.1	3984.1	3743.96	O-H unbonded
Absent	3480.66	3460.66	3556.85	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2929	2926.11	2926.11	2925.15	C-H stretch of methyl and methylene groups
2863.42	2859.56	2859.56	2857.64	C-H stretch of alkanes (alkyl groups)
Absent	2680.18	2680.18	Absent	-
Absent	2409.17	2409.17	2419.78	-
2348.41	2300.19	2300.19	2307.9	-
Absent	2036.9	2036.9	Absent	Alkyne C≡C symmetrical bending
1740.81	1740.81	1740.81	1741.78	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	Absent	Absent	1654.01	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	1599.04	1599.04	1527.67	C=C stretch of Arenes and alkene
1449.55	1453.41	1453.41	1524.78	C-H bond assymetric bending
1366.61	1366.61	1366.61	1365.65	C-H bond assymetric bending
1166.61	1235.45	1235.45	1237.38	C-O stretch of esters, carboxylic acids and ethers
Absent	1165.04	1165.04	1164.08	C-O stretch of esters, carboxylic acids and ethers
711.76	720.44	720.44	723.33	C-H Bending out of plane for alkenes
442.68	408.92	408.92	401.21	C-H deformations for alkyl groups
Absent	Absent	Absent	388.67	C-H deformations for alkyl groups

Appendix 30: FTIR peaks of *Colocynthus vulgaris* methyl esters/diesel blend B20 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4331.3	4332.26	4332.26	4336.12	O-H unbonded
Absent	Absent	4178.92	4260.9	O-H unbonded
3804.72	3875.12	3864.51	3768.07	O-H unbonded
Absent	3742.03	Absent	Absent	O-H unbonded
3401.58	3414.12	3400.62	3480.66	O-H stretch alcohols, Hydroperoxides and carboxylic acids
Absent	2930.93	2924.18	2924.18	C-H stretch of methyl and methylene groups
Absent	Absent	2859.56	2858.6	C-H stretch of alkanes (alkyl groups)
Absent	2404.35	Absent	Absent	-
2346.48	2293.44	Absent	Absent	Alkyne C≡C symmetrical bending
Absent	1810.25	2052.33	2050.4	-
1744.67	1738.89	1743.71	1741.78	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1605.79	1635.69	1621.22	1636.65	C=C stretch of Arenes and alkene
Absent	1527.67	Absent	Absent	C=C stretch of Arenes and alkene
1452.45	1453.41	1455.34	1454.38	C-H bond assymetric bending
1371.43	1369.5	1375.29	1366.61	C-H bond assymetric bending
Absent	Absent	1237.38	1235.45	C-O stretch of esters, carboxylic acids and ethers
1165.04	1167.94	1163.11	1163.11	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	1105.25	1106.21	C-O stretch of esters, carboxylic acids and ethers
Absent	1033.88	1038.7	Absent	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	911.4	Absent	C-H Bending out of plane for alkenes
719.47	720.44	719.47	721.4	C-H Bending out of plane for alkenes
441.71	422.42	417.6	424.35	C-H deformations for alkyl groups
Absent	Absent	Absent	406.99	C-H deformations for alkyl groups

Appendix 31: FTIR peaks of *Colocynthus vulgaris* methyl esters/diesel blend B50 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4331.3	4335.16	4337.09	Absent	O-H unbonded
Absent	4256.07	4260.9	Absent	O-H unbonded
Absent	4195.31	Absent	3855.83	O-H unbonded
Absent	Absent	Absent	3741.06	O-H unbonded
3474.88	3480.66	3474.88	3530.81	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2930.93	2934.79	2926.11	2924.18	C-H stretch of methyl and methylene groups
2871.14	2867.28	2858.6	2856.67	C-H stretch of alkanes (alkyl groups)
2346.48	2333.94	2286.69	2311.76	Alkyne C≡C symmetrical bending
Absent	2035.93	2039.79	Absent	-
1741.78	1736.96	1739.85	1738.89	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1605.79	Absent	1619.21	1527.67	C=C stretch of Arenes and alkene
1451.48	1447.62	1452.45	1454.38	C-H bond assymetric bending
Absent	1518.99	Absent	Absent	C-H bond assymetric bending
1365.65	1362.75	1366.61	1372.4	C-H bond assymetric bending
Absent	Absent	1237.38	Absent	C-O stretch of esters, carboxylic acids and ethers
1166.01	1167.94	1166.01	1167.94	C-O stretch of esters, carboxylic acids and ethers
717.54	722.37	720.44	722.37	C-H Bending out of plane for alkenes
454.25	415.67	417.6	420.5	C-H deformations for alkyl groups

Appendix 32: FTIR peaks of *Sesamum indicum* ethyl ester B100 (cm^{-1}) at different temperatures

28^{0}C	100^{0}C	150^{0}C	200^{0}C	Description
4339.02	4338.05	4339.02	4339.02	O-H unbonded
Absent	4259.93	4261.86	4261.86	O-H unbonded
Absent	3456.55	3461.38	3459.45	O-H stretch alcohols, Hydroperoxides and carboxylic acids
Absent	Absent	3209.66	3193.26	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2929	2927.08	2925.15	2926.11	C-H stretch of methyl and methylene groups
2867.28	2860.53	2858.6	2858.6	C-H stretch of alkanes (alkyl groups)
Absent	2680.18	2878.25	2679.21	
2346.48	2290.54	Absent	2295.37	
1738.89	1729.24	1735.03	1736.96	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	1515.14	Absent	Absent	C=C stretch of Arenes and alkene
1451.48	1452.45	1454.38	1452.45	C-H bond assymetric bending
1367.58	1387.83	1371.43	1375.29	C-H bond assymetric bending
Absent	1242.2	1239.31	Absent	C-O stretch of esters, carboxylic acids and ethers
1172.76	1175.65	1172.76	1171.79	C-O stretch of esters, carboxylic acids and ethers
Absent	1106.21	1105.25	Absent	C-O stretch of esters, carboxylic acids and ethers
1043.52	1036.77	1036.77	1037.74	C-O stretch of esters, carboxylic acids and ethers
709.83	725.26	725.26	726.22	C-H Bending out of plane for alkenes
455.22	407.96	406.03	405.06	C-H deformations for alkyl groups
Absent	349.13	Absent	Absent	C-H deformations for alkyl groups

Appendix 33: FTIR peaks of *Sesamum indicum* ethyl esters/diesel blend B20 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
Absent	4329.37	4330.34	Absent	O-H unbonded
Absent	Absent	4257.04	Absent	O-H unbonded
Absent	4069.94	4073.79	3737.2	O-H unbonded
Absent	3465.23	3454.62	3455.59	O-H stretch alcohols, Hydroperoxides and carboxylic acids
3366.86	3161.43	Absent	Absent	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2924.18	2926.04	2929.97	2925.15	C-H stretch of methyl and methylene groups
2859.56	2861.49	2862.46	2859.58	C-H stretch of alkanes (alkyl groups)
Absent	Absent	2733.22	Absent	
Absent	2676.32	2677.29	Absent	
2439.38	Absent	Absent	2424.6	
2355.16	2307.9	Absent	2305.01	
Absent	2035.93	2038.83	Absent	Alkyne C≡C symmetrical bending
Absent	1893.2	Absent	1927.92	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1743.71	1741.78	1739.85	1739.85	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1621.22	1603.86	1615.44	1643.41	C=C stretch of Arenes and alkene
Absent	Absent	Absent	1527.67	C=C stretch of Arenes and alkene
1456.3	1457.27	1454.38	1456.3	C-H bond assymetric bending
1374.33	1372.4	1372.4	Absent	C-H bond assymetric bending
Absent	Absent	1236.41	1237.38	C-O stretch of esters, carboxylic acids and ethers
1166.01	1167.94	1168.9	1169.87	C-O stretch of esters, carboxylic acids and ethers
Absent	1034.84	1106.21	1103.32	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	1034.84	1036.77	C-O stretch of esters, carboxylic acids and ethers
Absent	868.96	868.96	Absent	C-H Bending out of plane for alkenes
721.4	722.37	726.22	725.26	C-H Bending out of plane for alkenes
Absent	Absent	588.31	Absent	C-H deformations for alkyl groups
440.75	449.43	Absent	Absent	C-H deformations for alkyl groups
Absent	433.03	Absent	402.17	C-H deformations for alkyl groups

Appendix 34: FTIR peaks of *Sesamum indicum* ethyl esters/diesel blend B50 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
Absent	4334.19	4334.19	4337.09	O-H unbonded
Absent	4258.97	4258	Absent	O-H unbonded
Absent	4172.17	4184.71	Absent	O-H unbonded
Absent	4077.65	Absent	3787.36	O-H unbonded
Absent	3473.91	3466.2	3474.88	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2931.9	2927.08	2930.93	2929.97	C-H stretch of methyl and methylene groups
2874.03	2860.53	2871.14	Absent	C-H stretch of alkanes (alkyl groups)
Absent	2733.22	Absent	Absent	
2347.45	Absent	2332.02	Absent	
Absent	2035.93	2037.86	2042.68	
1740.81	1737.92	1735.03	1735.03	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	1618.33	Absent	Absent	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1454.38	1454.38	1450.52	1449.55	C-H bond assymetric bending
1370.47	1373.36	1365.65	1364.68	C-H bond assymetric bending
Absent	1239.31	Absent	Absent	C-O stretch of esters, carboxylic acids and ethers
1170.83	1170.83	1172.76	1171.79	C-O stretch of esters, carboxylic acids and ethers
Absent	1106.21	Absent	Absent	C-O stretch of esters, carboxylic acids and ethers
Absent	1038.7	1040.63	Absent	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	Absent	880.53	C-H Bending out of plane for alkenes
710.79	724.29	725.26	724.29	C-H Bending out of plane for alkenes
443.64	414.71	Absent	Absent	C-H Bending out of plane for alkenes
421.46	Absent	393.49	392.53	C-H Bending out of plane for alkenes

Appendix 35: FTIR peaks of *Sesamum indicum* methyl ester B100 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4336.12	4336.12	Absent	Absent	O-H unbonded
Absent	4259.93	4261.86	Absent	O-H unbonded
Absent	Absent	3890.55	3736.24	O-H unbonded
3466.2	3469.09	Absent	Absent	O-H stretch alcohols, Hydroperoxides and carboxylic acids
Absent	3300.31	3393.86	3399.65	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2929.97	2926.11	2925.15	2925.15	C-H stretch of methyl and methylene groups
Absent	2858.6	2858.6	2858.6	C-H stretch of alkanes (alkyl groups)
Absent	2677.29	Absent	Absent	
2347.45	2297.3	2287.65	2311.76	
Absent	2036.9	Absent	Absent	
1733.1	1737.92	1739.85	1739.85	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	1635.69	1636.65	1654.98	C=C stretch of Arenes and alkene
Absent	1506.46	Absent	1527.67	C=C stretch of Arenes and alkene
Absent	Absent	Absent	1510.31	C=C stretch of Arenes and alkene
1446.66	1453.41	1453.41	1455.34	C-H bond assymetric bending
Absent	1365.65	1373.36	Absent	C-H bond assymetric bending
Absent	1239.31	1239.31	1236.41	C-O stretch of esters, carboxylic acids and ethers
1173.72	1179.79	1170.83	1166.97	C-O stretch of esters, carboxylic acids and ethers
Absent	1106.21	1105.25	1104.28	C-O stretch of esters, carboxylic acids and ethers
Absent	1035.81	1033.88	1050.28	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	922	Absent	C-H Bending out of plane for alkenes
716.58	718.51	717.54	723.33	C-H Bending out of plane for alkenes
421.46	416.64	422.42	406.99	C-H deformations for alkyl groups

Appendix 36: FTIR peaks of *Sesamum indicum* methyl esters/diesel blend B20 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4327.44	4331.3	Absent	4334.19	O-H unbonded
Absent	4258	Absent	4258.97	O-H unbonded
Absent	Absent	3744.92	3749.74	O-H unbonded
Absent	3396.76	3514.42	3290.67	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2931.9	2925.15	2924.18	2927.08	C-H stretch of methyl and methylene groups
Absent	2860.53	2858.6	2860.53	C-H stretch of alkanes (alkyl groups)
Absent	2731.29	Absent	2679.21	
2347.45	2303.08	2310.8	2038.83	
1735.03	1738.89	1739.85	1736.96	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1621.22	1612.54	1654.01	1627.97	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	Absent	1527.67	Absent	C=C stretch of Arenes and alkene
1454.38	1455.34	1456.3	1453.41	C-H bond assymetric bending
1371.43	1371.43	Absent	1369.5	C-H bond assymetric bending
Absent	1240.27	1237.38	1238.34	C-O stretch of esters, carboxylic acids and ethers
1170.83	1167.94	1167.94	1166.97	C-O stretch of esters, carboxylic acids and ethers
Absent	1105.25	1104.28	Absent	C-O stretch of esters, carboxylic acids and ethers
Absent	1030.99	1031.95	1037.74	C-O stretch of esters, carboxylic acids and ethers
Absent	872.82	Absent	825.56	C-H Bending out of plane for alkenes
721.4	727.19	723.33	724.29	C-H Bending out of plane for alkenes
460.04	536.23	401.21	408.92	C-H deformations for alkyl groups

Appendix 37: FTIR peaks of *Sesamum indicum* methyl esters/diesel blend B50 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4331.3	4331.3	4335.16	4337.09	O-H unbonded
Absent	Absent	4259.93	4260.9	O-H unbonded
Absent	Absent	4203.99	3736.24	O-H unbonded
Absent	Absent	3853.9	Absent	O-H unbonded
Absent	Absent	3738.17	Absent	O-H unbonded
Absent	3378.43	3471.98	3481.63	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2930.93	2929.97	2926.11	2926.11	C-H stretch of methyl and methylene groups
2871.14	2863.42	2859.56	2859.56	C-H stretch of alkanes (alkyl groups)
Absent	Absent	2678.25	2684.04	
2347.45	2272.22	Absent	2039.79	Alkyne C≡C symmetrical bending
1735.03	1737.92	1735.99	1741.78	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	1639.55	1649.19	1631.83	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	Absent	1529.6	Absent	C=C stretch of Arenes and alkene
1451.48	1448.59	1452.45	1453.41	C-H bond assymetric bending
1371.43	1378.18	1373.36	1367.58	C-H bond assymetric bending
Absent	1223.87	1239.31	1238.34	C-O stretch of esters, carboxylic acids and ethers
1171.79	1171.79	1169.87	1164.08	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	1105.25	1109.11	C-O stretch of esters, carboxylic acids and ethers
Absent	1035.81	1038.7	Absent	C-O stretch of esters, carboxylic acids and ethers
717.54	720.44	722.37	720.44	C-H Bending out of plane for alkenes
443.64	406.03	406.03	408.92	C-H deformations for alkyl groups
421.46	Absent	349.13	Absent	C-H deformations for alkyl groups

Appendix 38: FTIR peaks of *Cyperus esculentus* ethyl ester B100 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4336.12	4337.09	4336.12	4337.09	O-H unbonded
Absent	4256.07	4259.93	4259.93	O-H unbonded
3805.68	Absent	3736.24	Absent	O-H unbonded
3414.12	3474.88	3463.3	3471.98	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2928.04	2929	2925.15	2927.08	C-H stretch of methyl and methylene groups
Absent	2867.28	Absent	2860.18	C-H stretch of alkanes (alkyl groups)
Absent	2693.68	2679.21	Absent	
2348.41	Absent	2289.58	2281.87	
Absent	2040.76	Absent	Absent	
1729.24	1730.21	1736.96	1734.06	C=O stretch of esters, carboxylic acids, aldehydes and ketones
Absent	Absent	1632.8	1642.44	C-H bond assymetric bending
1442.8	1450.52	1456.3	1453.41	C-H bond assymetric bending
Absent	1369.5	1378.18	1371.43	C-H bond assymetric bending
Absent	Absent	1298.14	1237.38	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	1240.27	Absent	C-O stretch of esters, carboxylic acids and ethers
1176.62	1176.62	1174.69	1173.72	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	1106.21	1108.14	C-O stretch of esters, carboxylic acids and ethers
1058.96	1063.78	1035.81	1037.74	C-O stretch of esters, carboxylic acids and ethers
879.57	873.76	866.07	874.75	C-H Bending out of plane for alkenes
717.54	718.51	719.47	719.47	C-H Bending out of plane for alkenes
440.75	417.6	423.39	410.85	C-H deformations for alkyl groups

Appendix 39: FTIR peaks of *Cyperus esculentus* ethyl esters/diesel blend B20 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
Absent	4334.19	4334.19	Absent	O-H unbonded
Absent	4258	4258	Absent	O-H unbonded
4170.24	4187.6	3851.01	Absent	O-H unbonded
3787.36	3769.03	3737.2	3423.76	O-H unbonded
Absent	3460.41	3553.96	Absent	O-H stretch alcohols, Hydroperoxides and carboxylic acids
Absent	Absent	3328.28	Absent	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2929.97	2929	2929.97	2929.97	C-H stretch of methyl and methylene groups
Absent	Absent	2865.35	2865.35	C-H stretch of alkanes (alkyl groups)
Absent	Absent	2724.87	Absent	
Absent	2350.34	2299.22	2273.19	
Absent	2042.68	2019.54	Absent	
Absent	1818.93	Absent	Absent	
1738.89	1735.99	1734.06	1735.99	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1602.9	1631.83	1522.85	1610.61	C=C stretch of Arenes and alkene
1456.3	Absent	1450.22	1454.38	C-H bond assymetric bending
Absent	Absent	1444.73	Absent	C-H bond assymetric bending
Absent	1371.43	1383.97	1377.22	C-H bond assymetric bending
Absent	Absent	1370.47	Absent	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	1234.48	Absent	C-O stretch of esters, carboxylic acids and ethers
1173.72	1171.79	1168.9	1169.87	C-O stretch of esters, carboxylic acids and ethers
Absent	1041.6	1046.42	1033.88	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	Absent	951.9	C-H Bending out of plane for alkenes
Absent	882.46	882.46	818.81	C-H Bending out of plane for alkenes
Absent	722.37	724.29	715.61	C-H Bending out of plane for alkenes
439.78	437.86	424.35	423.39	C-H deformations for alkyl groups

Appendix 40: FTIR peaks of *Cyperus esculentus* ethyl esters/diesel blend B50 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
Absent	4335.16	4335.16	Absent	O-H unbonded
3792.18	Absent	3863.55	3736.24	O-H unbonded
3400.62	3456.55	3473.91	3534.67	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2929.97	2929.97	2925.15	2924.18	C-H stretch of methyl and methylene groups
Absent	2870.17	2858.6	2857.64	C-H stretch of alkanes (alkyl groups)
2347.45	2350.34	2035.93	Absent	
1731.17	1734.06	1737.92	1739.85	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1605.79	Absent	1640.51	1527.67	C=C stretch of Arenes and alkene
Absent	Absent	Absent	1510.31	C=C stretch of Arenes and alkene
1459.2	1450.52	1454.38	1456.3	C-H bond assymetric bending
1373.36	1367.58	1369.5	Absent	C-H bond assymetric bending
Absent	Absent	1236.41	1236.41	C-O stretch of esters, carboxylic acids and ethers
1173.72	1172.76	1166.97	1164.08	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	1106.21	1105.25	C-O stretch of esters, carboxylic acids and ethers
1044.49	Absent	1039.67	1036.77	C-O stretch of esters, carboxylic acids and ethers
717.54	723.33	720.44	719.47	C-H Bending out of plane for alkenes
443.64	Absent	418.57	424.35	C-H deformations for alkyl groups
Absent	409.89	407.96	Absent	C-H deformations for alkyl groups

Appendix 41: FTIR peaks of *Cyperus esculentus* methyl ester B100 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4334.19	4337.09	4336.12	4336.12	O-H unbonded
3805.68	4255.11	4254.14	4258.97	O-H unbonded
Absent	4194.35	4189.53	Absent	O-H unbonded
3475.84	3519.24	3465.23	3473.91	O-H stretch alcohols, Hydroperoxides and carboxylic acids
Absent	Absent	Absent	3291.63	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2929.97	2929.97	2929.97	2926.11	C-H stretch of methyl and methylene groups
2828.24	2868.24	2868.24	2860.18	C-H stretch of alkanes (alkyl groups)
Absent	Absent	2696.57	2680.18	
2346.48	Absent	2334.91	2288.62	
Absent	2041.72	2035.93	2035.93	
1741.78	1734.06	1734.06	1740.81	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1448.59	1448.59	1447.62	1454.38	C-H bond assymetric bending
1362.75	1357.93	1362.75	1363.72	C-H bond assymetric bending
Absent	Absent	Absent	1229.66	C-O stretch of esters, carboxylic acids and ethers
1168.9	1171.79	1170.83	1165.04	C-O stretch of esters, carboxylic acids and ethers
717.54	719.47	Absent	720.44	C-H Bending out of plane for alkenes
421.46	419.53	Absent	406.99	C-H deformations for alkyl groups
Absent	Absent	393.49	Absent	C-H deformations for alkyl groups

Appendix 42: FTIR peaks of *Cyperus esculentus* methyl esters/diesel blend B20 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4331.3	4333.23	4337.09	4336.12	O-H unbonded
Absent	Absent	4260.9	Absent	O-H unbonded
Absent	Absent	3870.3	Absent	O-H unbonded
Absent	Absent	3553.96	3496.09	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2931.9	2929	2929.97	2930.93	C-H stretch of methyl and methylene groups
2873.07	Absent	2864.39	2870.17	C-H stretch of alkanes (alkyl groups)
Absent	Absent	2402.42	Absent	
2348.41	2349.38	Absent	2345.52	
Absent	Absent	2299.22	2048.47	
Absent	Absent	2037.86	1736.96	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1730.21	1736.96	1739.85	Absent	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1600.97	Absent	1524.78	Absent	C=C stretch of Arenes and alkene
1459.2	1453.41	1527.67	1448.59	C-H bond assymetric bending
1371.43	1369.5	1369.5	Absent	C-H bond assymetric bending
Absent	Absent	1234.48	Absent	C-O stretch of esters, carboxylic acids and ethers
1170.83	1171.79	1166.97	1168.9	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	888.25	Absent	C-H Bending out of plane for alkenes
728.15	726.22	719.47	719.47	C-H Bending out of plane for alkenes
440.75	407.96	412.78	420.5	C-H deformations for alkyl groups

Appendix 43: FTIR peaks of *Cyperus esculentus* methyl esters/diesel blend B50 (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4331.3	4335.16	4334.19	4336.12	O-H unbonded
Absent	4258.97	4256.97	4259.93	O-H unbonded
Absent	Absent	4191.46	4204.96	O-H unbonded
3790.25	Absent	Absent	3524.06	O-H stretch alcohols, Hydroperoxides and carboxylic acids
Absent	3467.16	3477.77	3475.84	O-H stretch alcohols, Hydroperoxides and carboxylic acids
Absent	3309.96	Absent	Absent	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2930.93	2925.15	2924.18	2925.15	C-H stretch of methyl and methylene groups
Absent	2859.56	2858.6	2858.6	C-H stretch of alkanes (alkyl groups)
Absent	2678.25	2682.11	2684.04	
2347.45	Absent	2283.79	2306.94	
Absent	2035.93	Absent	2035.93	
1735.03	1738.89	1742.74	1742.74	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1600.97	1640.51	1660.77	Absent	C=C Stretch of Arenes and alcohol
1451.48	1453.41	1454.38	1454.38	C-H bond assymetric bending
1371.43	1366.61	1365.65	1364.68	C-H bond assymetric bending
Absent	1235.45	1235.45	1235.45	C-O stretch of esters, carboxylic acids and ethers
1169.87	1165.04	1162.15	1163.11	C-O stretch of esters, carboxylic acids and ethers
Absent	1042.56	1105.25	1108.14	C-O stretch of esters, carboxylic acids and ethers
Absent	Absent	Absent	896.93	C-H Bending out of plane for alkenes
718.151	720.44	721.4	723.33	C-H Bending out of plane for alkenes
441.71	Absent	Absent	447.5	C-H deformations for alkyl groups
Absent	421.46	431.1	432.07	C-H deformations for alkyl groups
Absent	Absent	402.17	413.74	C-H deformations for alkyl groups
Absent	388.67	Absent	407.96	C-H deformations for alkyl groups

Appendix 44: FTIR peaks of Diesel (cm^{-1}) at different temperatures

28^0C	100^0C	150^0C	200^0C	Description
4327.44	4327.44	Absent	Absent	O-H unbonded
Absent	Absent	Absent	3471.98	O-H stretch alcohols, Hydroperoxides and carboxylic acids
2931.9	2956.01	2956.01	2944.44	C-H stretch of methyl and methylene groups
2359.02	2347.45	2355.16	2332.02	
Absent	Absent	1733.1	1735.03	C=O stretch of esters, carboxylic acids, aldehydes and ketones
1601.93	Absent	1621.22	1640.51	C=C of arene and alkanes
1458.23	1456.3	1457.27	1457.27	C-H bond assymetric bending
1372.4	1372.4	1372.4	1371.4	C-O Stretch of esters and ether
732.73	725.26	725.26	724.29	C-H Bending out of plane for alkenes
425.32	443.64	443.64	443.64	C-H deformations for alkyl groups