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ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

Production of Epoxy Oil From Podocarpus Falcatus Seed (Zigba) Via Epoxidation Reaction Using Sulphuric Acid Catalyst

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This is to certify that the thesis prepared by *Yigezu Mekonnen*, entitled: *production of epoxy oil from podocarpus falcatus seed via epoxidation reaction using sulphuric acid catalyst* and submitted in partial fulfilment of the requirement for the degree of Master of Science Chemical and Bio Engineering under Process Engineering stream complies with the regulations of the University and meets the accepted standards.

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I declare that this thesis entitled "*production of epoxy oil from podocarpus falcatus seed via epoxidation reaction using sulphuric acid catalyst* " has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. I have followed all ethical and technical principles of scholarship in the preparation, data collection, data analysis and compilation of this Thesis. Any scholarly matter that is included in the Thesis has been given recognition through citation. The work was under the guidance of *Dr.Beteley.T (Assistant Professor)* instructor in Addis Ababa University, School of Chemical and Bio Engineering.

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ABSTRACT

Epoxidized vegetable oils are the most surprise importance because of their sustainable, renewable and environment friendly nature and they are substituted the petrochemical resource's. The main objective of this study was investigating the production of epoxidized oil from Podocarpus falcatus seed through epoxidation reaction via sulphuric acid as homogeneous reaction with perfomic acid. The physicochemical characteristics of seed, oil and epoxidized oil of Podocarpus falcatus were investigated using standard analytical methods. The proximate compositions of the seeds were as follows: moisture (6.02%), ash (2.25%), crude fat (65.73%), seed density (1.04 g/m^3), volatile matter (86.46), and fixed carbon content (5.3%). In addition to this, physicochemical characteristics of Podocarpus falcatus oil were moisture content (2.2 %), viscosity (30.5 m.Pa. s) acid value (3.11 mg KOH/g, free fatty acid (1.54 mg KOH/g). saponification value (181.93 mg KOH/g) specific gravity (0.922). iodine value (107.18 g I_2/ g 100 oil %). and refractive index (1.468). The experiments were carried out by Design-Expert 7.0.0 three-level-three-factor Box -Behnken Design and it was applied for experimental design and statistical analysis of results. A total of 15 experiments were conducted at conditions of reaction temperature 50, 60 and 70^{o}C, molar ratio of hydrogen per oxide to oil 1.1, 1.4 and 1.7 and 3, 4.5 and 6 hours of reaction time. From the analysis of experimental results, the individual and interaction effects were studied and the optimal epoxidation reaction process conditions, which will maximize the percentage of conversion and selectivity were found to be 63 °C reaction temperature, 1.4:1 molar ratio of hydrogen per oxide to oil and 4 hours of time reaction, which gave 70.9% and 90.07 percentage of conversion and selectivity respectively. The product of epoxidized podocarpus falcatus oil were characterized by identifying the structure, functional group and composition of podocarpus falcatus seed oil, in comparison to epoxidized podocarpus falcatus oil, using Fourier Transform Infrared Spectroscopy and proton Nuclear magnetic resonance spectroscopy.

Keywords; *podocarpus falcatus; Epoxidation; Epoxidized podocarpus falcatus oil, performic acid*

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ACRONYMS

ANOVA	Analysis of Variance
AOAC	Association of Official Analytical Chemists
ASTM	American Society for Testing and Material
AV	Acid Value
BBD	Box -Behnken Design
DB	Double bond
EA	Elemental analysis
EPFO	Epoxidized podocarpus falcatus Oil
FA	Fatty Acid
FFA	Free Fatty Acid
FT-IR	Fourier Transform Infrared Spectroscopy
GCMS	Gas Chromatography Mass Spectroscopy
HV	Hydroxyl value
^{1}HNMR	Nuclear Magnetic Resonance
ISO	International Standards Organization
IV	Iodine Value
OCC	Oxirane oxygen content
PFA	perfomic acid
Ppm	Parts per million
PVC	Poly Vinyl Chloride
SV	Saponification value

CHAPTER ONE
INTRODUCTION

1.1. Background

Epoxides are organic compound or group of hydrocarbons containing oxygen, called oxirane, cyclic ethers with a reactive three-membered ring, can be derived from vegetable oils and petroleum-based chemicals and recently very fast cultivating in commercial interest increasing from year to year. Since Epoxide group have high reactivity of the oxirane ring than double bond, thus providing a more energetically favorable site for reaction, and the reaction is occurred at moderate condition. Therefore, having this high reactivity of oxirane ring leads Epoxides group to have application used as a renewable raw material for manufacturing of products such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers (Deshpande, 2013).

Most of the Epoxides used industrially are derived from both of the vegetable oils and petrochemicals. Developing alternatives production of Epoxides from the petrochemical have serious drawbacks in terms of biodegradability, initial processing cost, energy consumption and health hazards. Consequently, there is a strong need to develop novel bio-based product from cheaper, available resources and renewable feedstock. This achieved via vegetable oils, for development and production of epoxy oil, is gaining importance because of its sustainable, renewable and eco-environment friendly nature. The modified oils can serve as feedstock that can replace petroleum derived materials in many applications and used to reduce the stress from synthetic chemical industries on the environment (Gupta et al, 2015).

The natural renewable polyunsaturated vegetable oils have unique and excellent properties such as high viscosity index, high lubricity, high flash point, low evaporative loss, high bio-degradability and low toxicity and an attractive natural resource for the synthesis and production of Epoxidized vegetable oil production since they have low and stability cost, ready availability in nature in large quantity, and have capability of potential biodegradability (Ni, Fong, & Salimon, n.d.). In general, most of the Epoxidized vegetable oil produced from feed stocks come from edible oils since they are mainly produced in many regions and the properties of epoxidized vegetable oils produced from these oils are much suitable to be used as the epoxidized petroleum product

substitute (Rongpeng Wang, 2014). One important plant oil that can be used for raw material of these epoxide vegetable oil which contain oil yield more than 63 % is *Podocarpus falcatus*.

Podocarpus falcatus are the family of *Podocarpaceae* and belongs to the gymnosperms which mean that no fruit layer is produced, the seeds are borne "naked" inside the cone. It is native to East and South Africa and each seed is almost round and up to 2 cm in diameter (Leaflet & Version, 2017). Traditionally *Podocarpus falcatus* seed oil were utilized in trahditional way with inefficient methods of oil extraction for house hold consumption which is ordinary oil in Chercher Eastern highland of Ethiopia around Arsi zone like Asella an Shashemene and Haraghe zone like Kersa and Hirna . This needs to be extract by using different extraction method in order to optimized its yield for different application such as for food as edible oil, medicine as treatment for gonorrhea and epoxy oil for different uses (Br & Addo, 2015)

Podocarpus falcatus has largest oil content ranged from 52.97 to 57.43 % on dry basis depending on the moisture content and distribution area of the podocarpus plant cultivation(Feleke, Haile, Alemu, & Abebe, 2012). Due to having this high value amount of oil content *podocarpusfalcatus* kernel oil greater oil content than other an edible crop oil such as niger seed (40%) and other tropical zone trees like *Terminalia bellirica* (47%), *Trichilla emetica* (51%), *Solanum nigrum* (34%) and *Balanites aegyptica* (46–50%) (Dhellot et al. 2006). *Podocarpus falcatus* kernel seed oil have higher percentage of unsaturated fatty acid which indicates that the oil is non-drying, edible and not used for making soap and its iodine value range from 121 mg/100g to 130 mg/100g and this value comparable to IV values of other seed oils, such as soybean (124-139 g/100g) and sunflower (110-144g/100g (Of, 2016) (Daniel 2015). Therefore, the indication having such amount of iodine value and higher percentage of unsaturation fatty acid is that this oil used for the production of epoxy oil in the presence of catalyst.

The best method of the reaction that used to make and improve vegetable oil as renewable resources chemically or catalytically that replace raw material in order to use material derived petroleum based is called Epoxidation reaction. Epoxidation reaction is reaction occurred between double bond and it opens up a wide variety of reactions that can be carried out under mild conditions. It occurs when a cyclic ether is formed at sites of ethylenic unsaturation (C=C) located along the Fatty acid chains by the addition of an active oxygen atom to get three-member cyclic ring (Gamage, Brien, & Karunanayake, 2009). The formation of epoxy oil can be achieved via

action of catalyst since the reaction between the olefinic compounds (unsaturated fatty acid, alkyl ester, or oil) and organic peroxy acid [RC (=O) OOH, oxygen transfer reagent] is slow without catalyst and also its conversion to epoxide oil. This can be done though either homogeneous catalytic system such as sulfuric acid, nitric acid, *p*-toluene sulfonic acid, or heterogeneous catalytic system like tungsten based catalyst, titanium(iv)-grafted silica catalyst, methyl trioxorhenium (vii), amorphous $Ti.SiO_2$ etc.(Patil & Waghmare, 2013).

1.2. Statement of problem

Most of the country of the world are an importer of fossil fuel and products based on fossil fuels of epoxide oil and spends a substantial amount of its foreign currency reserves on these fossil fuel-based products. Based on the current of epoxide oil production issues which derived from petroleum based especially Ethiopian government importing and uses these epoxy materials for plastic industry, coating and additives that leads to problems related with increase in the price and depletion of fossil reserves, decreasing the foreign currency of the country and increasing fluctuation of oil price from time to time. Due to these, the replacement going to be done to investigate the substitution and use a renewable material on the area of the attention that increase the demand and upgrading the scale of the epoxy oil which has a benefit economically and also used as a raw material for chemical industry. Therefore, conversion of vegetable oils to epoxy oil can bring advantages to country in economical as well as making them no longer dependent on the outside depleted sources. In addition to this vegetable oil has attracted much attention as increasing epoxides demand that serve as primary chemicals and intermediates in many industries as a feedstock for material applications. The production for epoxy oil have a challenge during removing of peracids from epoxy oil and the other side reaction also occurred like degradation of oxirane. However, most of the epoxidized oil is edible oil like soya been, cotton seed and rice bran oil and largest industrial epoxidized vegetable oil is soya been oil which is genetically modified but not natural.

One important plant, that satisfy the above point of view *podocarpus falcatus*, which is native and cultivated to East and South Africa especially in Ethiopia gown in Arsi, Wollega, Bale and Jimma, which is underutilized for any application in industry and not used for production of edible oil commercially as well as it can be strong renewable crop seed feed stock of novel oil based for industrial. It prefers a warm and humid climate, in dry areas plantations fail and tolerates moderate frost but not drought. This plant oil contained unsaturated fatty acid 88 % and oil yield from 63% and the fruit is edible around the rural area but it is very resinous and also cannot used for soap preparation.

It also has high amount iodine value which related with unsaturated fatty acid used to obtain high conversion of epoxy oil.

1.3. Objectives of the research

1.3.1 General objective

The general objective of this research is to study the production process of epoxy oil from locally available raw material, *podocarpus falcatus* seed kernel oil, through epoxidation reaction by using homogeneous catalyst, Sulfuric acid.

1.3.2. Specific objectives

The specific objectives are the Following:

- To investigate the physiochemical property of the extracted oil like moisture content, specific gravity, acid value, Free fatty acid and Iodine value.
- To investigate the main and interaction effect of Epoxidation reaction parameters namely reaction temperature, hydrogen per oxide to oil ratio, and reaction time.
- To generate model equation relating the independent variable and determine the optimal operating condition aiming for maximum degree of epoxidation by using BoxBehnken Design
- To characterize epoxidized *p. falcatus* oil by FT-IR and HNMR test.
- To study the behavior of epoxidation reaction of kinetics reaction model for epoxidized *podocarpus falcatus* oil.

1.4. Significance of the study

This paper is aimed at having the potential to produce epoxidized podocarpus falcatus oil from easily local available of renewable one which makes participate in production of epoxide material from *podocarpus falcatus* seed. By doing so it is interested for the industry to have beneficial for the farmers who are going to prepare a farm of this plant and has benefits to many stakeholders whose produce epoxide which substitute an importer of fossil fuel and products based on fossil fuels in the economy. In our country the government spent more of its foreign currency on the epoxy oil for plastic industries. By looking these expensive material, one can resist this problem and overcome to produce such a material from existing vegetable oil other than petroleum-based oil and can significantly reduce their carbon footprint by employing bio based product.

The relevance of the production and use of epoxy oil, which have the following advantages:

- ✓ The podocarpus falcatus oil can be used as an ingredient in producing different types of polymer filler based on its application so, different epoxy oil industry will be benefited and also substitutes import and saves foreign currency.
- ✓ Production of oil from podocarpus falcatus seed kernel will contribute for minimizing price of imported cost and also generates an income for epoxy oil processing industries.
- ✓ Epoxy oil production from podocarpus falcatus kernel oil program can also be helpful to creates job opportunity for the society.
- ✓ The result of this study will be used as a base line information for future study since the oil has also an application in pharmaceutical industry and also used as edible oil.

CHAPTER TWO
LITERATURE REVIEW

Petroleum based products are ubiquitous in our everyday lives. Throughout the history of human civilization, the use of naturally occurring polymeric materials such as cotton, wool, silk, starch, and leather has developed and synthetic polymers such as nitrocellulose or vulcanized natural rubber were also derived from these natural polymeric materials. In the 20th century witnessed exponential growth of synthetic polymers, which is Bakelite, that was accompanied with a booming petrochemical industry. But these petroleum chemical industry products are non-biodegradable, unsustainable and have a volatile commodity market. In order to increasing the growing societal concerns about sustainability, decreasing depletion of fossil raw materials, and a perceived negative environmental impact of petroleum-based polymers in the last two decades, the development of bio-based polymers called vegetable oils as bio-material sources, *i.e.*, polymers derived from renewable feed stocks were emerged (Rongpeng Wang, 2014). They are used as precursors for many chemical materials such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizers and stabilizer for polymers (Of, 2016). These products of chemical materials are derived from epoxide oil through epoxidation reaction in the presence of catalyst.

Epoxy resin which is categorized by three ring members known as the epoxide or ethoxy line groups were first produced in in the late of 1930s and early of 1940s in Europe and United states respectively (Rapid, 2013). Due to the presence of oxirane, *i.e.,* high reactivity of oxirane in molecule Epoxide vegetable oils, are impart of thermal and photo stability to polymer composite and advantage associated to good performance with low production cost. The application of epoxy fatty acid are used to advance flexibility, elasticity, and toughness and to impart stability of polymer towards heat and UV radiation and are used directly as plasticizers and as stabilizers for that are compatible with polyvinyl chloride (PVC) and PVC resins respectively (Patil & Waghmare, 2013).

The unsaturated fatty acids which contain many double or triple bond between two carbon atoms, *i.e.*, reactive sites, present in vegetable oils modification can be done through chemically to value added product by complex reaction called Epoxidation of vegetable oil reaction by using peracid it convert to epoxy functional group (Saurabh, et al, 2011). The epoxidation of vegetable oils has been studied during the past few years owing to the commercial importance of these compounds

as additives of polymers, lubricants and detergents. Epoxidation reactions are usually carried out using peracids formed *in-situ*, by reaction of carboxylic acid with concentrated hydrogen peroxide. The hydrogen peroxide serves as oxygen donor for the Oxirane ring formation. Since the by-product of oxidation with hydrogen peroxide is water, it is taken as an environmentally friendly and high oxygen content oxidant in comparison with similar oxidants such as N_2O and NaClO (Oyama 2008; Rios et al. 2011).

The epoxidation reaction is used to insert the three- member oxirane ring in the unsaturated portion of the oil molecule, which increases its complexity and chemical reactivity with a variety of compounds such as amines and carboxylic acid. The conversion of unsaturation to epoxy groups can be directly monitored by determining the oxirane oxygen content, and indirectly by determining the iodine value.(Singh et al, 2015)

2.1. Current demand production of epoxidized vegetable oil in oil Industries

Since the 1950s, epoxidized vegetable has grown to a major research and technology area in several institutions and industries. A large variety of products based on fats and oils have been developed since then for different uses, such as specialties for polymer applications, biodiesel, surfactants, emollients for home and personal-care industries, pesticides and biodegradable mineral oil replacements for lubricants. However, for some time we have observed a shift toward an increasing use of natural plant oils for bioenergy and biofuels. This increase originally started in Europe years ago with the development of biodiesel from rapeseed, to be followed later on with further development based on other plant oils, such as palm and soybean. Epoxidized soybean oil (ESO) as a plastic additive has a relatively stable market of approximately 100,000 tonnes/year (Rongpeng Wang, 2014).

American region is the largest market in the global epoxidized soya been oil market in terms of value and this trend is expected to projected to continue till 2026. Countries in this region such as U.S. A, Canada and Mexico are achieving symbolic increase in the use of epoxidized soybean oil in the plastizers application industry. This growth is due to the easy availability of raw materials in large quantities and at lower costs which is driving the demand for epoxidized soya been oil in this region (Saurabh et al, 2011).

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The Epoxidized Soya Been Oil market in the Europe is predicted to register the faster growth rates in the world. This is mainly attributed to the growth of food and beverages, health care, adhesives and sealants end user industries in the emerging and developed economics such as Germany, France, U.K, Italy and Turkey. Europe is reportedly the second largest market in terms of the values of the global epoxidized soya been oil market in 2014 with Germany being the main contributor (Milchert et al, 2015).

2.2 Review on Sources for epoxide oil Production

2.2.1. Petrochemical Oil

The synthesis of epoxy resin oil is feasible from different natural materials such as petroleum, wood biomass, industrial lignin and starch. Traditionally, epoxy and other plastic production processes produced from petroleum resources to assist in the reaction. Currently, most organic polymers are produced from intermediate chemicals derived from non-renewable resources of petroleum or natural gas(Mohammad Hossein Tavassoli Kafrani A, 2016). However, petroleum use is large and creates significant problems such as air pollution, promotion of the greenhouse effect, and depletion of petroleum reserves. Therefore, environmental concerns, as well as instability in the petrochemical market, have recently increased in using more sustainable and renewable chemical resources(Celikbag, 2015).

Concerns over diminishing fossil fuel reserves, rising oil prices, and environmental impacts, have all contributed to the large research efforts made to develop and secure renewable energy sources such as biofuels and epoxide. Epoxide of long chain unsaturated fatty acids, is one of the promising alternatives (or extenders) to conventional petroleum-based epoxy oil. The epoxide vegetable of alternative source of energy has a number of advantages including, but not limited to, being renewable, environmental benign, having less CO_2 emissions on life cycle analysis basis, and lower toxicity (Mehdi, 2010). In addition to this, energy demands increase and fossil fuel reserves are limited, there has been a growing interest in the utilization of renewable resources as an alternative to petroleum-based polymers. Consequently, much attention has been focused on the development of polymeric materials from vegetable oils, a sustainable resource. Vegetable oil, which is readily available and is a comparatively inexpensive material, can be used to synthesize various types of polymers. Today, one of the most important epoxidized vegetable oils is epoxidized soybean oil (ESO), and its worldwide production is about 200,000 t/year. Several

derivatives of vegetable oils are used as polymerizable monomers in a radiation curable system due to their environmentally friendly character and low cost when compared to products from petroleum(Saremi & Babanalbandi, 2012).

2.2.2. Vegetable Oil

Oils and fats of vegetable and animal origin have been the most important renewable feedstock of the chemical industry. They are composed of complex mixtures of different triglycerides, which are esters of glycerol and fatty acids. Triglycerides are one of the most important raw materials for bio-based thermosetting polymers. Classical and well-established oleochemical transformations occur preferentially at the ester functionality of the native triglycerides, such as hydrolysis to free fatty acids and glycerol and transesterification to fatty acid methyl esters(Biermann et al., n.d.). Vegetable oils are the fats and lipids containing triglyceride molecules. It represents one of the cheapest and most abundant biological feedstock available in large quantities and its use as starting material offers numerous advantages such as low toxicity and inherent biodegradability(Saurabh et al, 2011).

Vegetable oils are the renewable feedstocks of epoxide oil that have excellent properties such as high viscosity index, high lubricity, high flash point, low evaporative loss, high bio-degradability and low toxicity. One of the most effective modifications of triglycerides is the epoxidation reaction, in which the C=C double bonds are converted to oxirane (epoxide) rings which are highly strained and very reactive(Salih, Ahmad, & Ibrahim, 2015). With regard to their use they can easily undergo variety of reactions to give important chemical compounds for polymer synthesis as base oils for different purposes and raw material for various chemical industry such as alcohols, glycols, alkanol amines, carbonyl compounds, olefinic compounds and polymers like polyesters, polyurethanes, and epoxy resin (Ni et al., n.d.).

Vegetable oils are triglycerides in which C_{18} carboxylic acids are dominant and the part of a larger family of chemical compounds known as fats i.e. derived from glycerides and lipids and they are saturated and unsaturated which are used as raw materials for polymer applications and lubricants (Idah, 2014). High share of fatty acids with a short or medium chain length (mainly 12 and 14 carbon atoms: C_{12}, C_{14}) these are particularly suitable for further processing to surfactants for washing and cleansing agents as well as cosmetics. Triglycerides are unsaturated; those typically contain stearic, oleic, linoleic and linolenic acids in varying amounts. From these

namely oleic (18:1), linoleic (18:2) and linolenic (18:3) are called unsaturated acids (Gamage, 2009). In the figure 2.1 they represents as follows; (a) oleic acid; (b) linoleic acid; (c) linolenic acid; (d) erucic acid; (e) ricinoleic acid; (f) vernolic acid; (g) 10-undecenoic acid.

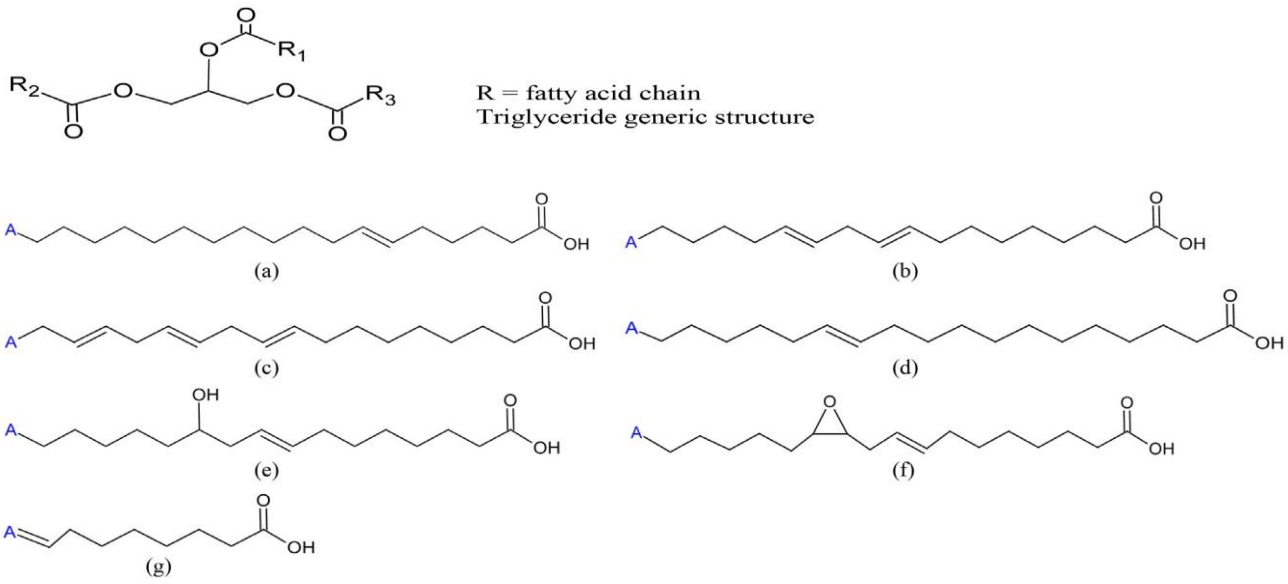

Figure 2.1**.** General triglyceride structure and Fatty acids commonly used in polymer chemistry

Edible, non-edible oil and drying oils of vegetable oils are a raw material source of polymeric material precursors that can be modified and polymerized to exhibit various types of advantages and functionalities in order to use these natural products to produce novel polymers and polymer precursors for increasing the number of its potential applications(Adekunle, 2015). Vegetable oils can be classified in either by source or by use. By source: most, but not all vegetable oils are extracted from the fruits or seeds of plants, and the oils may be classified by grouping oils from similar plants, such as "nut oils". By use, oils from plants are used in cooking, for fuel, for cosmetics, for medical purposes, and for other industrial purposes. Polymers have its own life cycle based on vegetable oils, in order to maximize the yield of vegetable where the biomass from plant-derived resources is extracted. consequently, the extracted, degummed and neutralized if necessary the bleached or deodorized oil is submitted to chemical modification with the aim of enhancing and modifying its reactivity towards a given type of polymerization approach. The polymers are then made available to the consumers, and once used, they become waste, which after degradation and assimilation is reused as biomass and the cycle starts again(Samarth & Mahanwar, 2015).

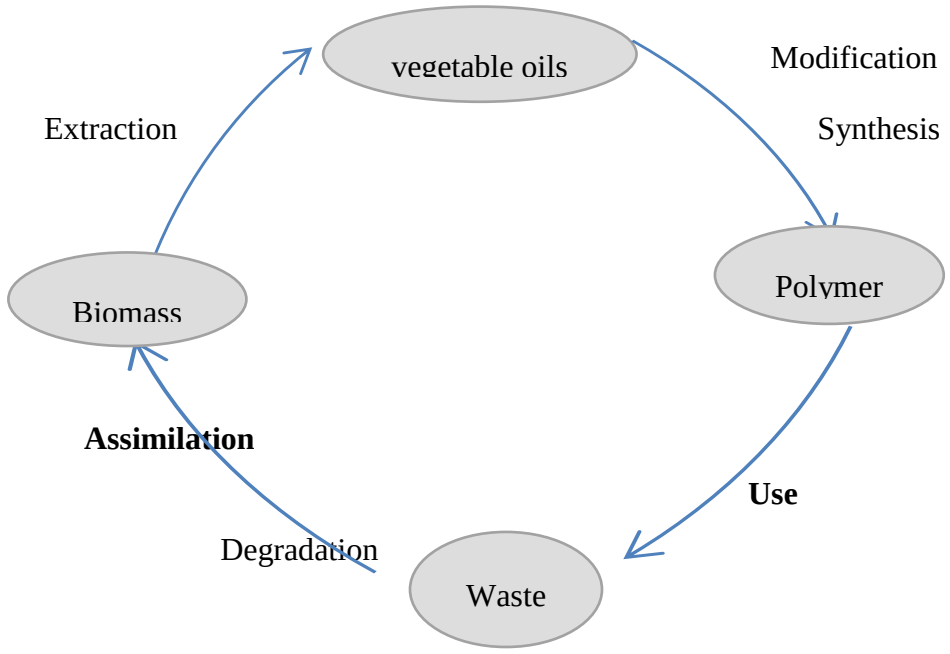

Figure 2.2. Life cycle of polymeric material based on vegetable oils.

2.2.3 Podocarpus falcatus seed oil

Ethiopia, one of the sub Saharan African country region, is known for its biodiversity resulted of having abundant wild plants and cultivated native trees species with great silvicultural and commercial potential as food tree crops, oil tree crop and industrial tree crop. Among these, oil bearing tree species of Ethiopia, *Podocarpus falcatus*, consists of diets, with linoleic, oleic and linolenic acids as examples of unsaturated fatty acids. So utilization of these oil bearing tree species will not only reduce the nation expenditure of the country foreign currency through import substitution but also cannot improve the livelihood of the rural people through availing healthy edible oil, maintain the environmental balance and improving household income(Hundessa, 2014).

Podocarpus falcatus belongs to the family *podocarpceae* and is the two-coniferous species naturally growing grows at 1500-2500 m altitude above sea level in areas with mean annual rainfall of 1200-1800 mm. It is an evergreen tree reaching up to 46 m in height with long, cylindrical trunk. It is a multipurpose plant with wider range of socio economic and environmental importance. Suitable for manufacture of furniture, bakery boards, shelving or fittings where a bright, clean-colored wood is desirable. The timber is also used as standard building timber, for flooring and roofing and it is suitable for firewood. The bark contains 3-6% tannin and is used for tanning

leather, the fruit is edible and oil from the seeds is used for medicinal purposes. The large, dense crown makes it suitable for shade and windbreaks and the attractive shape has made it popular as an ornamental tree in cities, it is locally the most preferred timber for butter and cheese boxes and other food containers. Various organisms use it as part of their habitat. It is also useful for fire wood, charcoal and paper pulp(Leaflet & Version, 2017).

Podocarpus falcatus seed is one of the source of edible oil but still now its toxicity not well done and it is very resinous, which extracted by traditionally method using hot water in the rural area of the Ethiopian country and nutritional security for the rural poor family, especially those who cannot afford the cost of edible oil in the market(Tadele & Fetene, 2013). Therefore, it may use as a new potential industrial oilseed crop (Daniel, 2015).

Podocarpus falcatus have high parentage of oleic acid (e.g. Oils rich in monounsaturated fatty acids). Having this component its generally more stable to oxidative rancidity and stable as deep-frying oils (Mohammed *et al*., 2003). An oil having high percentage of oleic acid or monounsaturated fatty acid have many applications such as plant based lubricants, greater affinity towards metal surfaces, and fairly high viscosity could be exploited to minimize metal to metal contact, control temperature, reduce wear of vital engine components under boundary, hydrodynamic lubrication conditions and as feedstock for the oleochemical industry(Hundessa, 2014).

Figure 2.3: *podocarpus falcatus* seed

2.3. Extraction, composition and properties of podocarps seed oil

Extraction of *P. falcatus* kernel oil can be done using different methods. Aqueous method and Solvent extraction using solvents can be applied according to the desired output. The oil extracted from *P.falcatus* seeds by solvent extraction yield of up to 57.93% has been reported((Feleke et al., 2012). In other review by it was found that aqueous method extraction yielded somewhat more than oil (63%). *P. falcatus* seed oil of fatty acid mostly composed of 9,12-octadecadienoic acid, 9-octadecenoic acid, Methyl stearate, Methyl 5,11,14-eicosatrienoate and others. In a fully epoxidized oil, the linolenic acid with three double bonds (positions 9, 12, and 15), is more reactive than linoleic, which contains two double bonds per molecule(N B Samarth et al., 2016). The physicochemical characteristics of *P. falcatus* seed as follows: moisture (5.73), ash (2.44), crude fat (63.73), crude protein (18.27), crude fiber (3.91) and carbohydrate (by difference) (11.66%), hundred kernel mass (16.51g) and kernel density (1.02g/ml). The mineral composition (mg/kg) of *P. falcatus* seed showed the zinc and iron contents (0.02) and iron (0.01), respectively. The tannin and saponin contents are 2.37and 11.46mg/100g-1, respectively (Daniel, 2015).

Table 2.1. physical and chemical properties of p. falcatus kernel seed oil

Property of *p. falcatus* Oil	**Value**
Saponification value, mg KOH/g oil	113.4-221.44
Iodine value, g I2 /100 g oil	121.73-130.95
Refractive Index at 25^0C	1.47
Peroxide MEq /g oil	9.13-12.76
Acid value mg KOH/g oil	2.18-2.28
Specific gravity	0.89-0.96
Free fatty acid mg KOH/g oil	1.28-2.54
Crude fat %	63.73

(Sources Daniel 2015)

2.4. Synthetization of epoxidized oil via epoxidation reaction and ring opening

From time to time attention of the industrial sector and researchers have received increasing for production bio-based polymers that can be substitute petroleum based. These polymers or their monomers are derived from renewable resources of plant oil called vegetable oil. Vegetable oil is one of the interesting renewable monomers and typically containing fats and oil. Fat and oil composed of triglyceride molecules i.e., major component in all of these plant oils, and contain both saturated and unsaturated fatty acid (Saithai, et al, 2013).

The chemistry and technology of oils and fats derived industrial products i.e. oleochemicals run parallel to those of petrochemicals. These Oleochemicals can be derived from splitting (hydrolysis) or transesterification of natural fats and oils such as fatty acids (FA), mono-alkyl (mostly methyl) fatty esters (biodiesel substitute for diesel fuel), and glycerol. By means of simple industrial reaction, fatty materials are available from vegetable oils may be used for of chemical conversion

and for production of pure chemical compound. These reaction is called epoxidation reaction by using catalyst (Biermann et al., n.d.).

An epoxidation reaction is the general process for the synthesis of the epoxide groups where in an alkene is reacted with an organic peroxy acid. This reaction accomplished by two methods i.e., in situ or ex situ process, during for preparation or generation of peracids in epoxidation reaction. In-situ epoxidation using hydrogen peroxide as oxygen donor and acetic or formic acid as the per oxygen carrier has achieved commercial importance. With hydrogen peroxide and acetic acid, however, acid catalysts, such as sulfuric acid or strong cation exchange resins, are needed to speed up peracid formation, whereas performic acid formation requires no strong acid(Saurabh et al., 2011). The reaction is always carried out under isothermal condition. Where as in the case of *ex situ*, initially the mixture of the formic or acetic acid is stirred for some time to form per acid before adding to reactor that contains oil (Gebremedhn Tekeste, 2017)

Proton donors such as water, alcohols, and acids are used in performing ring opening of epoxy oil. Among these, water is the cheapest one and easily can open epoxy groups in the presence of acids such as formic acid, acetic acid, and perchloric acid leading to the formation of two secondary hydroxyl groups per each epoxy group(Ulven, 2014). The other and most requiring strong acid is Ring opening by alcohols is performed in the presence of acids such as sulfuric acid and results in the formation of one secondary hydroxyl group per epoxy group. In addition to mono alcohols, diols such as ethylene glycol and 1,3-propanediols can be also used to open epoxy groups in order to the introducing two hydroxyl groups per epoxy group(Mohammad Hossein Tavassoli Kafrani A, 2016).

2.4.1. Non-catalytic and catalytic system of epoxidation reaction

In large industrial scale the process of non-catalytic epoxidation is performed, in which the unsaturated fatty compound reacts with a peroxycarboxylic acid (typically peracetic or performic acid) obtained by the acid-catalyzed oxidation with hydrogen peroxide called *Prilezhaev* epoxidation process. The combination of hydrogen peroxide and sulfuric acid with acetic acid and formic acid were used for formation of peracetic acid and performic acid respectively. In this case a typical *in situ* and *ex situ* epoxidation of oleic acid process are applied(Wolfgang Stah, 2002).

The *in-situ* generation of peracids is mostly preferred because, when the organic peroxyacid is preformed, there are some safety issues associated with its storage since the concentrated peroxyacid is unstable and explosive. Moreover, the *in-situ* process operates with a lower concentration of aliphatic acids. On the other hand, the presence of an acid during in situ epoxidation causes the opening of the oxirane ring with formation of undesirable secondary products. In *ex situ* process, the acid is eliminated from preformed peracid by neutralizing it with a buffer or filtering. With preformed peroxyacetic acid, the conversions, yields and selectivity were higher than those with the *in situ* formed peroxyacetic acid(Meshram, Puri, & Patil, 2011).

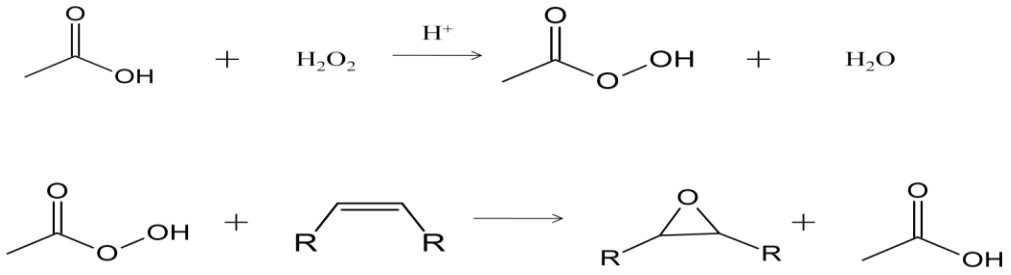

Figure 2.4. *In situ* peracid epoxidation reaction

2.4.2. Established techniques of epoxidation reaction

There are different stablished methods of epoxidation reaction namely; Epoxidation by Conventional or chemical treatment Method; Epoxidation using acid ion exchange resin(AIER); Epoxidation using enzymes and Epoxidation using metal catalyst(Saurabh et al., 2011)

2.4.2.1 Conventional Chemical Treatment

It is the most widely used process of epoxidation. For safety point of view these epoxidations are usually carried out using peracids formed in-situ, by reacting a carboxylic acid with concentrated hydrogen peroxide(Sodvwlfl et al., 2004). This process performs industrially on large scale.

2.4.2.2. Epoxidation using acid ion exchange resin

In this method Peroxy acid is obtained by reaction of H_2O_2 with carboxylic acid ($HCOOH/CH_3COOH$). The peroxy acid interacts with the catalyst by way of entering the pores of the catalyst. Thus, when AIER loaded into the reactor its pores get filled with peroxy acid. It leads to low oxirane degradation as triglyceride couldn't enter into the gel type structure of acid ion exchange resin (Saurabh et al., 2011). The epoxy ring opening reaction occur either by acid

catalysis in the presence of water associated with aqueous solution of H_2O_2 used. The hydrolysis of the ester groups during epoxidation reaction in oils is the main side reaction. In the case of hydrolysis, a carboxylic acid functional group is formed(Zeleke & Ayana, 2017).

2.4.2.3. Epoxidation using enzymes

This type of epoxidation consists on using an immobilized enzyme, the lipase B of *Candida antarctica* as catalyst. This process is selective and takes place under mild conditions, giving high epoxidation yields suppressing completely the undesirable ring opening. The reaction system consists of an aqueous phase containing the hydrogen peroxide, an organic phase containing usually toluene as solvent, the oil, and free fatty acid and immobilized enzyme as solid phase readily separable(Téllez, 2009). The reaction mechanism is in two steps: first, the unsaturated fatty acid or ester is converted into an unsaturated peroxycarboxylic acid by the reaction of the enzyme with hydrogen peroxide. Then, it is epoxidized by an intermolecular pathway without the participation of the enzyme. In this reaction, both carboxyl group and the unsaturation are in the same molecule (Gebremedhn Tekeste, 2017).

2.4.2.4. Epoxidation using metal catalyst

In this case the peracid oxidant is obtained in situ when a carboxylic acid (usually acetic acid) reacts with hydrogen peroxide in the presence of mineral acids that act as catalysts. From process, environmental safety and efficiency point of view epoxidation of vegetable oils in one step, i.e., with peroxy acid generated in situ from carboxylic acid (formic/acetic acid) with hydrogen peroxide in the presence of acid catalyst is widely used on an industrial scale. However, the use of a mineral acid as catalyst in epoxidation is inefficient because of problems associated with separation of the catalyst from the reaction product(Zeleke & Ayana, 2017).

2.5. Parameters affecting epoxidation reaction

The production of epoxide oil during epoxide reaction can be affected by different parameters. The main factors which highly affects include, reaction temperature, amount of hydrogen peroxide and reaction time, agitation speed, catalyst and purity of reactants.

2.5.1. Reaction temperature

High reaction temperature with the increasing time and gives the high numbers oxirane value. Thus, higher reaction temperature caused simultaneous rise in rate of epoxidation and oxirane ring opening reactions. Reaction at lower temperature shows lower rate but gave more stable oxirane ring and caused a decrease of the iodine number (Nugrahani,& Wibowo, 2017). Increasing of the temperature from 30 to 60 °C caused a decrease of the iodine number, while the value of the epoxy number rapidly decreased above 60 °C for the formation of epoxidized rapeseed oil.

In the case of epoxidation of rapeseed oil an influence of temperature on the changes in the epoxy number demonstrates that the temperature of 60 °C is the most advantageous for formation of epoxidation since, the value of the epoxy number decreases above 60 °C (Milchert & Smagowicz, n.d.).

Effect of temperature for epoxidizing of Rice bran oil methyl ester using the catalyst resin Amberlite IR -120 (20% (w / w)), at a temperature of 60 °C and a reaction time of 5 Hours, the Oxirane oxygen greater with a high of 3.9%. At temperatures higher and the required reaction time is shorter, i.e., at temperatures of 60 °C, Oxirane oxygen content somewhat decreased with the value of 3.83% at reaction time 4 hours, while the temperature reaction of 85 °C, Oxirane Oxygen is lowered to 3.8% was at reaction time is shorter, i.e. 2 hours. For the Soybean Oil epoxidation catalyst Amberlite IR -120 (5%) at a higher temperature, i.e. 75 °C, reaction time of short six hours increased by 5.88% Oxirane Oxygen while at temperatures of 60 °C, the reaction time of 10 hours, lowered Oxirane Oxygen of 5.68%. however, the reaction time is getting longer than 1 hour up to 5 hours and the temperature is higher, namely at 85 °C, then the Oxirane Oxygen has decreased, it is likely to occur because of the side reactions such as ring opening oxirane (the ring epoxy cleavage). Furthermore, the effect of temperature on the IV is opposite to the Oxirane Oxygen(Nugrahani,et al, 2017).

2.5.2. Amount of hydrogen peroxide and reaction time

Amount of hydrogen peroxide and reaction time has influence on the rate of the reaction and the degree of epoxidation (conversion). An excess of hydrogen peroxide relative to the number of unsaturated bonds is necessary. This permit reaching full conversion of double bonds and compensation of hydrogen peroxide loss, caused by its decomposition at temperatures above 50

°C. The challenge is to shorten the reaction time. Too long a reaction time (6 to 12 h) and excess of hydrogen peroxide lead to increased level of carboxylic peracids in the final product(Milchert et al, 2015). Peracids could be a potential problem for reasons of safety and contamination of the final product. The reaction rate increased with increasing hydrogen peroxide concentration between 10–50 wt. %. The optimal conditions (91% conversion, 5.99% epoxide content in product) for peracetic epoxidation of soybean oil were found to be: 0.5 mole of glacial acetic acid and 1.1 mole of hydrogen peroxide (30%) per mole of ethylenic unsaturation, 750C, 8 hour, 5 wt% of the resin catalyst.

Effect of the ratio of Hydrogen Peroxide to Unsaturation fatty acid during Epoxidation of Palm Kernel Oil Fatty Acids increasing the moles of hydrogen peroxide, the oxirane conversion rate increase followed by decreasing of iodine value. The maximum relative conversion is at 1.46 mol of hydrogen peroxide (75%). For higher concentration of hydrogen peroxide at the same conditions; temperature and reaction time, the reaction rate becomes constant. An increase in hydrogen peroxide concentration will increase the oxirane conversion rate. However, the stability of oxirane ring produced in a very high concentration of H_2O_2 is very poor, thus increasing the production of diol and α-glycol as side products(Fong, & Salimon, 2014).

2.5.3. Amount of the peracids

The effect of the formic acid to unsaturation fatty acid mole ratio has influence on the rate of reaction and degree oxirane oxygen content and iodine value during of epoxidation reaction. The conversion of double bond is significantly increased when the formic acid mole ratio increased results IV value dropped. since formic acid is acted as an oxygen carrier in epoxidation reaction the formation of performic acid was increased when raised the formic acid mole ratio of same amount of hydrogen peroxide. Oxirane ring cleavage could perform by acid-catalyzed ring opening in the presence of water. During the epoxidation reaction, the presence of water in the aqueous phase owing to the reduction of hydrogen peroxide to water by *in situ* epoxidation. The epoxidation rate is increased when the formic acid molar ratio increased. However, the oxirane ring was not stable in high formic acid content and it tends to promote the hydrolysis of the epoxide, thereby decreasing the final yield(Performic et al., 2015).

In the case of fatty acid palm kernel oil the concentration of formic acid increase to 0.87mol, the oxirane conversion rate increase to its highest (72%). However, when the formic acid

concentration is further increased, percent of Oxirane Oxygen content and the iodine value decrease significantly and oxirane ring degraded from high concentration of formic acid. The amount of formic acid used per mole of unsaturation recommended is 1 mole and less. This ratio used not only for economic reasons but also to reduce by-products such as dihydroxy and dihydroxyformoxy derivatives that can reduce the oxirane production(Ni et al., n.d.).

2.5.4. Catalyst and purity of reactants

Homogeneous catalysts increase the reaction rate several times faster than heterogeneous catalysts acid catalysts due to less mass transfer limitations. During epoxidation of mahua oil, From the Catalytic loading of two different acids, i.e., H_2SO_4 and HNO_3, H_2SO_4 is found to be more effective in terms of conversion to oxirane carried out at moderate temperature range of 55- 65 °C. Higher temperatures and higher sulphuric acid concentrations reduced reaction time and resulted in higher oxirane content with lesser cleavage to glycol(Patil & Waghmare, 2013b). H_2SO_4 is more effective in terms of oxirane conversion and resulted in higher oxirane with very less oxirane cleavage by in situ technique. The order of effectiveness of catalysts was found to be sulphuric acid > phosphoric acid > nitric acid > hydrochloric acid(Patil & Waghmare, 2013).

Impurities present in vegetable oil like hydrolysis of glycerides, and free fatty acids, also affect the epoxidation reaction significantly.

2.5.5. Agitation speed

String rate can also affect the rate of reaction and used to eliminate the effect of resistance to mass transfer of performic acid (PFA) from aqueous phase to organic phase and ensure that the reaction was kinetically controlled.

Generally, if the catalyst is heterogeneous higher agitation speed is required than that of homogeneous catalyst to eliminate the effect of mass transfer limitations, investigates the effect of mass transfer resistance, the reaction was performed at different stirring speeds ranging from 200 to 2500 rpm. The oxirane formation rate was not substantially affected by stirring speeds beyond 1500 rpm, and hence it can be safely assumed that the reaction is free from mass transfer resistance beyond 1500 rpm under the given conditions of temperature and catalyst loading(Milchert et al., 2015).

2.6. Characterizing an epoxy oil

The method is used to optimize the formation of epoxy groups through the analysis of periodic oxirane or epoxy group, iodine value, and hydroxyl group. Epoxy number, is used to estimate the fractional conversion, yield, and the selectivity of transformation to epoxidized oil/ fatty acids/ ester. The structures of the products are confirmed by thin layer chromatography (TLC), Fourier transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) analysis.

2.6.1 Oxirane number (ON)

The Oxirane Number defines the content of epoxy groups in epoxidized oil. A number of methods have been developed to measure epoxides in oxidized oils of oxirane number, although all have associated challenges. The most widely used method to determine concentrations in epoxidized oil is the hydrogen bromide (HBr) method, involving direct titration of oil with HBr−acetic acid solution (AOCS Method Cd 9-57). The method involves the determination of oxirane oxygen by potentiometric titration. It is based on the reaction between perchloric acid and bromide, with the transformation of latter in the hydrogen bromine that by interaction with the oxirane group forms bromidrina. The equivalence point, determined by titration, is detected at an excess of perchloric acid(Xia, et al, 2015). In the epoxidation reaction, double bonds are converted into oxirane groups (Figure 1-4). Therefore, it is useful to measure the changes in IV (ΔIV) and OOC (ΔOOC) over the course of the epoxidation process because it can give an indication about the conversion of double bonds into the oxirane groups. Furthermore, in order to obtain a product with the maximum OOC, the reaction must be stopped once it reaches the maximum OOC, since after that, the OOC reduces as a result of side reactions(Mohammad Hossein Tavassoli Kafrani A, 2016).

2.6.2. Hydroxyl value (HV)

The hydroxyl number (mg KOH/g sample) is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl content per gram of sample according to ASTM E 222-00, that counts the epoxy functional group and the primary and secondary alcohol functional groups in the molecule(DR. Galen J. Suppes, 2009). This method is reliable and reproducible if carried out under standardized conditions, but it is time-consuming, labor intensive, reasonably sensitive, largely dependent on the skills of the analyst, uses large amounts of sample and reagents, and some of them (pyridine, acetic anhydride) are hazardous and difficult to dispose off (Flôres & Unisc, 2006).

The HV characterization was used to monitor the extent of transesterification (or degree of substitution) of sucrose with FAME/ oil. It is determined by the titration of residual unreacted acetic anhydride left from the reaction of the free OH groups of the sample with an excess of acetic anhydride (DIN EN ISO 4629). In epoxidation reaction, side reactions such as ring opening by water can occur. This results in a formation of secondary hydroxyl groups and a decrease in oxirane oxygen content (OOC) of the epoxidized oil. Therefore, measurement of the OH of an epoxidized oil can give an estimation of such side reactions(Mohammad Hossein Tavassoli Kafrani A, 2016).

2.6.3 Iodine value (IV)

The Iodine Number gives a measure of the average degree of unsaturation of oils and fats: the higher the iodine value, the greater the number of C=C double bonds. By definition, the Iodine Number is expressed in terms of centigrams of iodine per gram of sample (weight percent of absorbed iodine). One of the most commonly used methods for determining the iodine value of oils and fats is "Wijs method"(Iso, 1999).

2.7. Kinetics of epoxidation reaction

In many reaction to measure and express how fast chemical reactions can occur is determined by kinetics of the reaction is one that can expressed by several parameters with disappearance of reactants and appearance of products (Fogler, 2004). As the others reaction there is also kinetic reaction involved in the epoxidation reaction. In moreover, the kinetic epoxidation reaction depends on the catalytic operated in the reaction and also epoxidation methods vary from case to case depending on the nature of reactants and catalysts used for epoxidation (Cai et al., 2008). Catalytic reactions are often broken down into a number of steps including diffusion steps and elementary reaction steps. It is assumed that the diffusion steps can be ignored as intensive mixing of the reactor has been shown to make the resistance to mass transfer negligible (Cooney, et al, 2011).

Generally, in epoxidation reaction there are two steps considered: (i) formation of peracids, and (ii) reaction of peracids with the unsaturated double bond. In this case the first step is considered rate determining, and the concentration of peracids is assumed constant throughout the reaction (Dinda et al, 2008).

2.8. Industrial application of epoxidized vegetable oil

From recent time it has been a growing trend in utilizing epoxidized vegetable oils in various applications. In industry, Fatty epoxides are used directly as plasticizers that are compatible with polyvinyl chloride (PVC) to improve flexibility, elasticity, and toughness and to impart stability of polymer towards heat and UV radiation. The high reactivity of oxirane ring enables epoxides to act as raw material for a variety of chemicals, such as alcohols, glycols, alkanol amines, carbonyl compounds, olefinic compounds and polymers like polyesters, polyurethanes, and epoxy resin (Ni et al., n.d.).

In other cases, Epoxidized vegetable oil compounds are well known as typical non-metallic stabilizers for PVC. The primary stabilization effect of epoxy plasticizers is that it acts as acceptors for the liberated hydrogen chloride. The importance of these epoxy compounds is due to their co-stabilizing effect in combination with almost all stabilizer system, but especially in combination with metal carboxylate stabilizers. Furthermore, these substances also have a lubricating section. Vegetable oil as a lubricant is preferred not only because they are renewable raw materials but also because they are biodegradable and non-toxic. They also acquire most of the properties required for lubricants such as high index viscosity, low volatility and good lubricity and are also good solvents for fluid additives. However, vegetable oils have poor oxidative and thermal stability, which is due to the presence of unsaturation. This unsaturation restricts their use as a good lubricant. The primary use of vegetable oil in coatings is as drying oil. Vegetable oil derivatives as value added polymers/monomers have found enhanced applications as environment friendly hyperbranched or waterborne coating materials that offer improved performance and reduction or elimination in the use of volatile organic solvents(Nikesh B Samarth & Mahanwar, 2015).

Moreover, epoxidized fatty acids are monomers suited for ring opening polymerizations and polyether polyols derived from epoxidized fatty acid compounds may substitute the petrochemical compounds in various applications. P. falcatus, is an underutilized unsaturated and naturally contained epoxidized plant oil that can be used as applications for binder in coating and preferentially in photo curing coating. Epoxy coating has been widely used as a protection layer for steel in concrete structures, due to its good process ability, electrical insulating properties, good performance in chemical resistance and strong adhesion to heterogeneous materials. They are two

ways that epoxy coatings react to decrease the corrosion of a metal substrate which was subjected to an electrolyte; either become a physical barrier layer to control the attack from deleterious species or serve as a source for corrosion inhibitors to protect the steel surface in resisting attack by species such as chloride anions(Communication, 2013).

2.9. Gaps in the Literature Retrieval

Academic papers covering the social impact of the use of epoxidized vegetable oils sources in epoxidation process for manufacturing were not identified. In addition, none of the institutional documents that were retrieved analyzed the social impact of using this material, which indicates that a thorough knowledge of the topic is missing.

Researchers findings of the iodine value and other chemical properties of vegetable oil which related to the use of different vegetables oils are available but a gap on feeding position of these materials in epoxidized industries were noticed. Therefore, more researches on mechanisms of feeding these alternative materials and their effects must availability also be investigated in order to increase the reliability of findings and to give a knowledge and evidence for process engineers all over the world.

More details about the costs related to the use of petrochemical in epoxidation process are required in order to see the economic benefits petrochemicals in detail; in fact, few findings of this topic emerged from the institutional journals and this highlights another gap in the literature.

Another gap which was noticed during literature retrieval was a detailed study of the different vegetables oils found in Ethiopia for use in epoxidation processes. One document which dealt in detail with a lot of renewable resources and their residues for use in Ethiopian plastics and related industries was found and reviewed thoroughly, but this was deemed insufficient for a comprehensive knowledge of the different properties of epoxidized materials.

CHAPTER THREE
MATERIALS AND METHODS

3.1. Characterization of Physio Chemical Property of kernel seed and Refined *P. Falcatus Oil*

3.1.1. Materials and Reagents

The major materials will be used during the experimental work were p. falcatus seed, potassium iodide, diethyl ether, sulfuric acid, Potassium hydroxide, sodium thiosulphate, and formic acid, hydrogen per oxide, wijj's solution, glacial acetic acid, cyclohexane, starch, Hexane, ethanol and starch. Podocarpus falcatus seed was acquired from Leka Dullacha Eastern wollega of Oromia. All the other chemicals were analytical reagent grade and bought from different chemical stores in Addis Ababa.

The major Engineering material elements used during the experimentations were includes crusher, dyer, extractor (soxheletor unit), centrifuge, and the others equipment's are glass reactor equipped with a magnetic stirrer, water bath, condenser, separating funnel, balance, oven, magnetic stirrer, Bunsen burner, Muffle furnace, different size conical and Erlenmeyer flasks, beakers, measuring cylinders, burette, micropipettes, filter paper, GC/MS, FTIR and ^{1}HNMR spectroscopy

Extraction of p. falcatus seed oil were done with soxhelet apparatus, p,falcatus seed oil refining, characterization of the refined oil, synthesized of the epoxidized oil and analysis of the reaction mixture were done at School of Chemical and Bio Engineering Laboratory. The other characterization of the catalyst such as elemental analysis, FTIR, fatty acid and NMR analysis of the epoxidized oil as well as *p. falcatus* seed oil were done at faculty of natural science Addis Ababa university department of chemistry, Arat Killo.

3.1.2. Methods

P. falcatus seeds were first cleaned from dirt, dust, sand, small stones and washed manually. Then *P. falcatus* seeds were dried for two days by sun light. The cleaned and dried seeds were weighted and .991 kg *Podocarpus falcatus* seeds will be further dried in an oven at 105 °C for a hour to remove the rest of their moisture content. Then seeds would had crushed using a coffee grinder with particle size of 0.25–0.75 mm for solvent extraction analysis. The prepared *p. falcatus* seed were then characterized using proximate analysis as ASTM procedure to determine the parameters like moisture content, seed density, crude fat and ash content.

The proximate analysis of the raw *p. falcatus* seed (moisture content, volatile matter, fixed carbon and ash content) was determined using ASTM D1762-84.

To extract the *p. falcatus* seed oil the Soxhlet apparatus was used. A 200g of grinded seed (packed in a filter paper) and 600ml hexane solvent were be placed in the Soxhlet extraction unit. Then the solvent and crushed mixture were heated at constant temperature of 70 °C for 3 hours to extract the oil. After extraction the solid suspension from the supernatant solution will be separated using centrifuge at 4500 rpm for 30 minutes. Finally, the solvent and oil will be separated using rotary evaporator and the solvent will be recovered using condenser.

In order to avoid rancidity and the interference of phosphatides, gums and other complex compounds during epoxidation reaction of oil during storage the degumming was done. The degumming process were done by mixing distilled water 3 weight % of oil at 70 °C with the oil. Then the mixtures were stirred at speed of 350 rpm for 1 h heated at 70 °C. Finally, the mixtures were separated using centrifuge at 3500 rpm for 30 minutes. Then Physicochemical properties (viscosity, acid value, iodine value, refractive index, saponification value, and specific density) were determined.

The overall structure of the experimental works is shown in Figure (3.1).

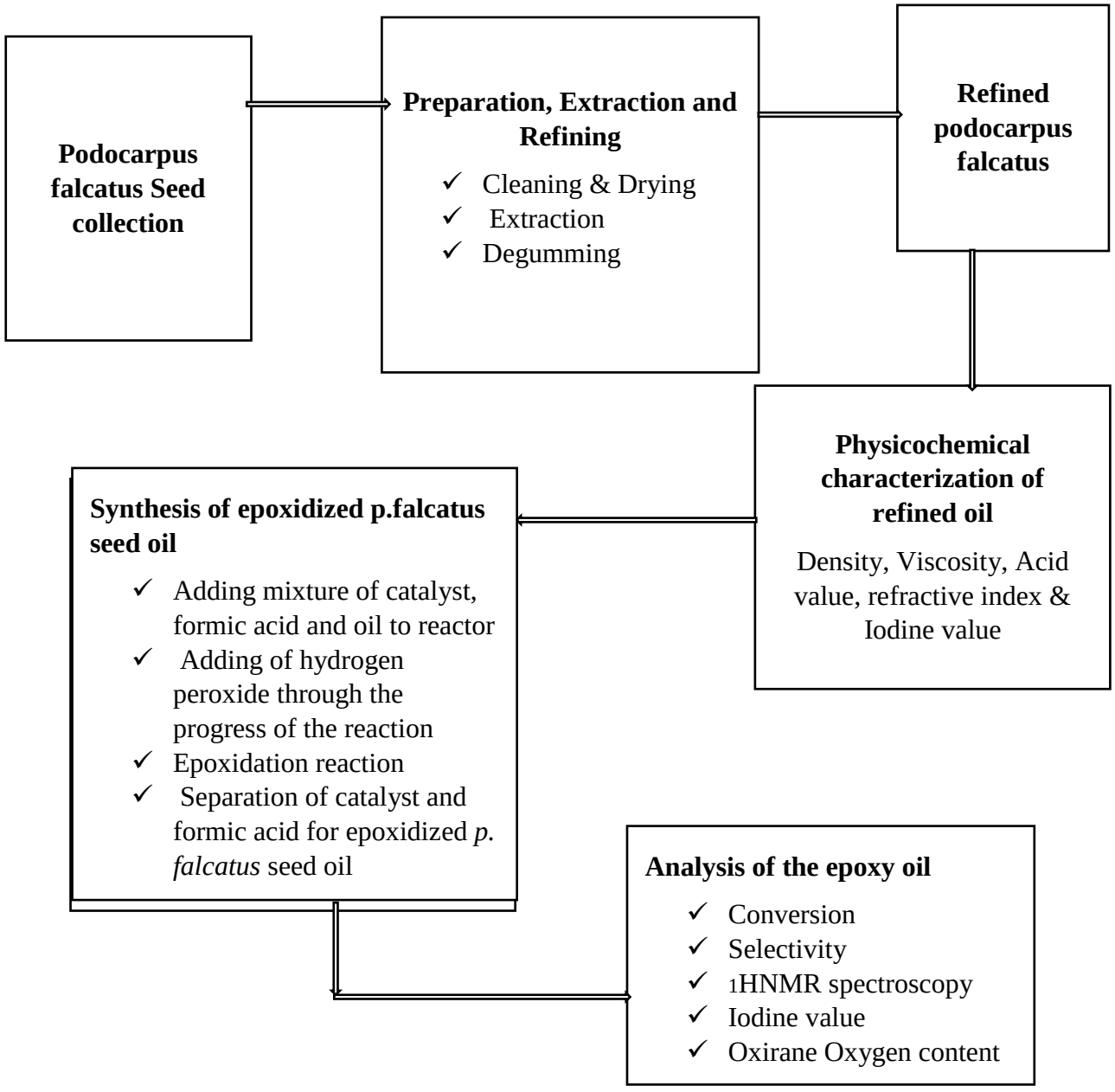

Figure 3.1 frame work of the experiment

I. Moisture content

The *p. falcatus* crushed to desirable size was put into crucible. The crucible was weighed with and without the amount of *p. falcatus*. The crucible with *p. falcatus* was dried in an oven at 105 °C for six hours still achieved constant weight. The sample was removed from the oven and placed in the

desiccator for 15 minutes to cool and re-weighed till constant weight is obtained. Finally, the weight was taken and compared with the initially recorded weight. The percentage weight in the dust was calculated using the formula:

$$\text{moisture content}, \% = \frac{W_2 - W_3}{W_2 - W_1} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

Where;

W*1* is mass of the crucible (g),

W_2 is initial mass of the sample and crucible before drying(g),

W_3 (g) is mass of sample and dish after drying (g)

II. Crude fat

The crude fat analysis was determined by Soxhlet extraction method. Ground sample of 3 g was weighed and added into a filter paper. The paper with sample was placed in 50 ml beaker and dried in an oven for 2 hours at 110 °C. A 250 ml dried beaker was weighed and rinsed several times with petroleum ether. The sample contained in the thimble was extracted with petroleum ether in a Soxhlet extraction apparatus for 8 hours. After the extraction was completed, the extracted fat transferred into a pre-weighed beaker. The beaker with extracted fat was placed in a fume hood to evaporate the solvent on a steam bath until no odor of the solvent was detectable. Then the beaker with content was dried in an oven for 30 minutes at 100 °C. Finally, the beaker with its contents was removed, cooled in a desiccator and weighed.

The amount of fat in the sample was calculated by using the following formula;

$$\text{oil } \% = \frac{M_2 - M_3}{M_2 - M_1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Where; M_1 is mass of crucible

M_2 initial mass of crucible with sample

M_3 final mass of crucible with sample

III. Ash content

Crucible was cleaned and dried at 550 °C for 1 hour and weighed. Ground sample 3 g was weighed. The sample was dried at 120 °C for 1 hour. Then the dried sample will be carbonized over a blue

flame and ignite in a muffle furnace at 550 °C until ash was completed. After ignition, the sample was cooled to ambient temperature and weighed. Finally, total ash content was calculated as follows:

$$\text{ash } \% = \frac{M_2 - M_1}{M} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3$$

Where; M is mass of sample

M_1 mass of beaker

M_2 final mass of beaker with sample

IV. Volatile matter

The muffle furnace was heated until it reaches to a temperature of 925 ℃. The crucible with its cover was preheated in furnace at 925 ℃ for around 10 minutes to remove its moisture content and any physically adsorbed material with in the crucible and the crucible with its cover was put in to desiccator for 1 hours. Then, the crucible and its cover were weighed with *p. falcatus*. Then, the samples were heated at 925 °C in a closed crucible for 7 minutes and 30 seconds. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample. The percentage of volatile matter in the sample was calculated using the formula:

$$Volatile\ matter, \% = \frac{V - Y}{V} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.4$$

Where; V grams of sample before drying and

Y grams of sample after drying

V. Fixed Carbon Content

The fixed carbon content is determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content form 100. The percentage of fixed carbon content in the sample was calculated using the formula:

$$fixed\ carbon\ content, \% = 100 - (M + V + A) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

Where A - Percentage of moisture content (%)

B-Percentage of volatile matter (%)

C - Percentage of ash (%)

VI. Seed density

P. *falcatus* seed density was determined according to the method of Alfonso et al. (1998). One hundred Seeds were weighed and transferred into 100 ml measuring cylinder containing 50 ml of tap water. The displaced volume of was the volume of the seed and immediately the changed in volume recorded.

$$\text{seed density}\left(\frac{\text{g}}{\text{ml}}\right) = \frac{\text{sample of weight (g)}}{\text{sample of volume(ml)}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.6$$

VII. Physio Chemical Analysis of Refined *P. Falcatus Oil*

Extraction podocarpus falcatus oil

The crude oil yield was calculated as follows;

$$\text{yeild of oil \%} = \frac{\text{masss of extracted crude oil (g)}}{\text{total mass of kernel seed}} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.7$$

A. Determination of Moisture Content

The same procedure was used to determine the moisture content of the *p. falcatus seed* as discussed in section I.

B. Viscosity

Vibro viscometer used to determine a viscosity of the oil. The sample was kept in the water bath heated by thermostat until it reached the 20 °C. After maintaining the equilibrium temperature**,** the vibro viscometer tip was inserted in the sample and the reading was taken from the controller. This was done in triplicate and the average dynamic viscosity was recorded. The Kinematic viscosity in mm^2/sec was calculated using formula:

$$\text{kinematic viscosity} = \frac{\text{dynamic viscosity (mpa. sec)}}{\text{density of the oil}\left(\frac{\text{kg}}{\text{m}^3}\right)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.7$$

C. Acid value

The number of mg of KOH required to neutralize the free acids in 1 g of the oil will determined by placing 0.5 g of sample in conical flask containing mixture of ether and ethanol (50 mL; 95% v/v). Standard alcoholic potassium hydroxide solution (0.1 N) was prepared by dissolving KOH (pellet) with 95 %ethanol. The solution was filtered and stored in brown bottle for five days. A

phenolphthalein 1g per 100 ml of 95% v/v ethanol was used us an indicator. Furthermore, a mixture of 1 to 1 ratio (v/v) 95% ethanol and diethyl ether was prepared by mixing 250 ml diethyl ether and 250 ml of ethanol. A weighed quantity of the oil sample was dissolved in 25 ml of 1 to 1 mixture of ethanol and diethyl ether. The solution was titrated with 0.1N ethanolic KOH solution in presence of 5 drops of phenolphthalein as indicator until the end point (colorless to pink) is recognized. The volume of 0.1 N ethanolic KOH for the sample titration was noted. The total acidity (acid number) in mg KOH/ gm was calculated using the following equation:

$$Acid\ value = \frac{V \times N \times 56.1}{W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.8$$

Where V is the volume expressed in milliliter of 0.1N solution of ethanolic KOH

W is mass in gram of the test portion

N is concentration of ethanolic KOH

D. Free Fatty Acid

Free fatty acid value of the oil was determined by introducing 1.0 g of weighted oil into a 250 ml conical flask. A 3 drop of phenolphthalein added to this the sample followed by 20 ml ethanol. The mixture was titrated with 0.1 M KOH solution until a pink color developed. Free fatty acid was calculated as follows;

$$free\ fatty\ acid = \frac{V \times M \times 56.1}{W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.9$$

Where V is Volume of Titre value

M is Molarity of the titrant

W is Weight of oil

56.1 is Acid constant

E. Saponification value

A 2 gm of the sample was taken and added in to 250 ml flask. A 25 ml of alcoholic potassium hydroxide solution was added in to the flask. The flask was connected to reflux condenser and kept on the water bath and boiled gently for 1 hour. After the flask and the condenser were cooled a few drops of phenolphthalein indictor were added and the excess potassium hydroxide was titrated

with 0.5 N hydrochloric acid to the end point, until the pink color of the indictor just disappears. The same procedure was conducted for the blank and the saponification value (SV) expressed as the number of milligrams of KOH required to saponify 1 gm of fat was calculated as follows;

$$SV = \frac{56.1 \times (B - A) \times \text{Normality of the titrant}}{W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.10$$

Where; SV is saponification value in mg KOH/g oil

B Titter value of blank (mL),

A Titter value of sample (mL),

W weight of the sample

F. Specific gravity

Fifty-centimeter cube, capacity of was cleaned and dried in a dry-air oven. Then it was cooled in a desiccator. The weight of the picometre was obtained as W1**.** Then the picometer was filled with clean oil sample, and the weight as recorded as W2 and volume was recorded as V. The specific gravity of the oil was calculated using the formula below;

$$\text{specivic gravity of oil} = \frac{\text{density of oil}}{\text{density of the water}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.11$$

G. Iodine value

The iodine value of oil is the number of grams of iodine absorbed by 100 g of the oil, was determined by using Wiji's solution. For this study Wiji's method was applied to determine the iodine value of oil. A standard Wiji's solution was prepared by dissolving 9 g of iodine trichloride in 300 ml carbon tetrachloride (AR) and 700 ml glacial acetic acid. Allowed the solution to stand for three days before use. To determine the iodine number, first the oil was dissolved in 5ml tetra chloride in a ground in glass stopper conical flask and 25 ml standardized Wiji's solution was added. Then the stopper was replaced at once and the flask had been allowed to stand for 30 minutes at 20 °C in the dark. When the reaction was completed, 15 ml 10% KI solution and 50 ml water were added. Finally, the free iodine was titrated with 0.1N sodium thiosulphate until the color was pale yellow. A few drops of starch solution were added and the titration was continued until the blue color was discharged. The volume of 0.1N thiosulphate was recorded. Similarly, a

blank determination was done for the same length of time and at the same temperature. The result was calculated using equation:

$$\text{Iodine value} = \frac{((\text{B} - \text{s}) \times \text{N} \times 12.69)}{\text{m}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.12$$

Where: B = Volume in mL of standard required for the blank,

S = Volume in mL of standard thiosulfate required for the sample,

N = Normality of the standard thiosulfate solution.

W = Weight in g of the *P. falcatus* seed oil taken for the test.

NB: 12.69 is molecular weight of iodine used to convert from thiosulfate to I.

I. Refractive index

The temperature of refractometer was adjusted to 20 °C and, then several drops of sample were placed on lower prism. Prisms was closed and tightened firmly with screw head. It was allowed to stand for 1– 2 min or until sample comes to temperature of instrument. The instrument and light were adjusted to obtain most distinct reading possible and then refractive index was determined.

H. Fatty acid profile composition of oil

GC analysis was performed with Gas Chromatography system. Samples were injected by a sampler injector at an oven temperature of 325 to 350 °C for a total run time of 38 minutes. The data, was obtained using MS (mass spectroscopy) and processed using Chemstation software, that used to obtain fatty acid composition of oils.

3.2. Experimental Designs

3.2.1 Materials and Reagents

Feed material required for epoxidation of reaction were refined podocarpus falcatus kernel oil, formic acid that used to add oxygen to double bond of fatty acid with hydrogen peroxide and sulphuric acid as a catalyst. It was done on an MSH-D hotplate magnetic stirrer equipped with a magnetic stirrer, condenser and thermometer to control the actual reaction temperature.

In all experiments 500 ml three neck glass reactor equipped with MSH-D hotplate magnetic stirrer in which pneumatic trough with oil was used as oil bath for epoxidation reaction a was used. The

MSH-D hotplate magnetic stirrer can be adjusted to the desired temperature, reaction time and molar ratio of hydrogen peroxide to oil. The batch epoxidation reaction system was employed for *epoxidized podocarpus falcatus* seed oil production as shown in the schematic diagram below.

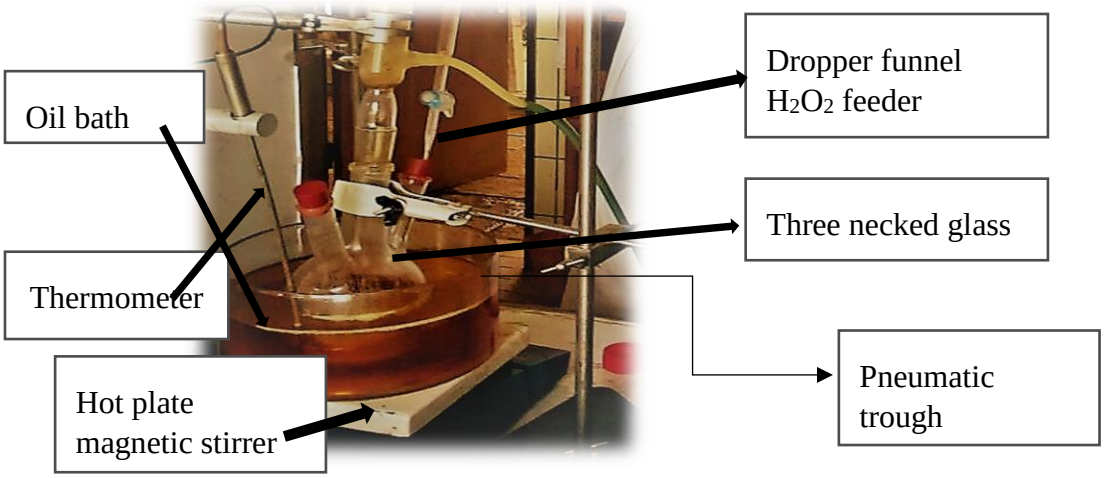

Figure 3.2. experimental set up epoxidation reaction

3.2.2. Methods

Epoxidation of *p. falcatus* seed oil was carried out in a 500 ml three neck glass reactor equipped with MSH-D hotplate magnetic stirrer, and thermometer. *P. falcatus* seed oil will be charged in the round bottom flask with formic acid and the reaction temperature will have maintained at 50-70 °C. In the first step of epoxidation, 30% hydrogen peroxide solution in the presence of small quantities of concentrated sulphuric acid was added into flask slowly through a funnel over 30 minutes. The stirring rate was controlled at 850 rpm so that oil was completely dispersed in the mixture. In the second step, after was charged hydrogen per oxide, the reaction was continued by mixing and controlling the temperature at 50-70 °C for further 3 to 6 hr. After completion of the reaction, the mixtures were cooled down and neutralized by washing with water three times (cool, hot, cool) to remove the residual peroxyformic acid and remove the catalyst. The resulting product was characterized. Then after analysis of physicochemical properties of epoxidized *p. falcatus* oil such as functional group by FT-IR test, ^{1}HNMR spectroscopy was studied, viscosity, oxirane oxygen content, epoxide content and iodine value were determined.

Experimental Design for Epoxidized *p. falcatus* oil Production

Experimental Data analysis has performed by DESIGN EXPERT 7.0.0 software. The experimental design selected for this study are three-level-three-factor Box Behnken Design (BHD) and the parameter variable such as reaction temperature, amount of hydrogen per oxide to oil ratio and reaction time were measured in order to know the percentage of conversion oil to epoxide, and selectivity of epoxide oil. Those three independent variables were studied for the epoxidation reaction process and their interaction effect was analyzed to obtain maximum degree of epoxidation. In order to attain high percentage, yield or epoxide content of epoxidized *p. falcatus* oil the rotational speed kept as constant at 850 rpm, ratio of formic acid to oil constant at 0.5 mole, sulphuric acid at 0.5 ml and the other independent variables were conducted by choosing lower and higher levels of the operating limits of epoxidation reaction process parameter conditions.

This design of the experiment helps us to differentiate the significance of the main and the interaction factors. It also used to develop the mathematical model that will describe the effects of the main and interaction factors on the response. Three level-three-factor BHD was used in the optimization study which requires 15 experiments to be conducted. The fifteen experiments were done and the data was statistically analyzed using Design-Expert Software 7.0.0 to obtain a suitable model equation for the degree of epoxidation as a function of the independent variables. Table (3.1) lists the range and levels of the three independent variables studied. The lower and higher levels are chosen by considering the operating limits of epoxidation reaction process conditions.

Table 3-1: Independent Variables and Levels Used in The BHD for The Epoxidized Oil Production

Variables	**Unit**	**Levels**		
		-1	0	-1
Reaction temperature	^{O}C	50	60	70
Hydrogen peroxide to oil ratio	Mole/mole	1.1	1.4	1.1
Reaction time	Hr.	3	4.5	6

Table 3.2. design layout matrix of epoxidized oil created by Design-Expert 7.0.0.

Std	Run	Factor 1	Factor 2	Factor 3	Response 1	Response 2
		Reaction temperature (50-70°C).	H_2O_2 to oil mole/mole (1.1:1-1.7:1)	Reaction time (3 - 6hr.)	conversion %	Selectivity %
8	1	70.00	1.1	6.00		
9	2	60.00	1.4	3.00		
2	3	70.00	1.4	4.50		
11	5	60.00	1.4	6.00		
1	6	50.00	1.4	4.50		
7	7	50.00	1.4	6.00		
10	8	60.00	1.7	3.00		
12	9	60.00	1.7	6.00		
4	10	70.00	1.7	4.50		
15	11	60.00	1.4	4.50		
13	12	60.00	1.4	4.50		
14	13	60.00	1.4	4.50		
5	15	50.00	1.4	3.00		
3	16	50.00	1.4	4.50		
6	17	70.00	1.4	3.00		

3.3. Physiochemical analysis of epoxy products

3.3.1. Viscosity

Viscosity of epoxidized *p. falcatus* oil was determined as *p. falcatus* oil discussed in section 3.2.6

3.3.2. Iodine value

Iodine value of epoxidized *p. falcatus* oil was determined as *p. falcatus* oil discussed in section 3.2.10. But to determine the saturation conversion of the epoxide oil the initial iodine value of oil was taken. The quality and conversion of epoxy product of podocarpus falcatus oil was determined by this value accordingly of the procedure.

$$conversion\ \% = \frac{Iv_o - Iv}{Iv_o} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.13$$

Where, Iv_o is the initial iodine value

Iv iodine value of epoxy oil

3.3.3. Oxirane oxygen content or epoxide content of epoxidized *p. falcatus* oil

A 0.4g of epoxidized *p. falcatus* oil was mixed with chlorobenzene in a 250 mL Erlenmeyer flask. A magnetic stirring bar was placed into the flask and mix on the magnetic stirrer and dissolved; stirred at a moderate speed to avoid splashing. Then, 5 drops of crystal violet indicator solution were added. After this the solution was titrated with the 0.1 N HBr in glacial acetic acid solution until the deep blue changed to a blue-green endpoint with the stirrer rotating at a moderate speed. The titration was slow down near the endpoint to allow ample time for the reaction to take place. Finally, volume of the titrant used was record. Then oxirane oxygen content was calculated using the following formula:

$$OOC = \frac{V \times N}{W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.14$$

where, V is the volume titrant of (mL) of HBr glacial acetic acid solution,

N (mol/L) is the concentration of HBr glacial acetic acid solution,

W is the mass (g) of the sample.

3.3.4. Selectivity

The overall values of produced epoxidized *p. falcatus* oil was analyzed by calculating the selectivity of the samples. The selectivity implies that total amount of desired epoxidized oil formed per total amount of limiting reactant consumed. It was calculated as follows;

$$S_p = \frac{OOC}{OOC_{th}} \times \frac{IVo}{IVo - IV} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.15$$

$$OOCth = \frac{IV_O/2A_I}{100 + (\frac{IV_O}{2A_I}) \times A_O} \times A_O \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.16$$

Where, S_p is selectivity of the epoxidized oil

OOC is oxirane oxygen content of the epoxidized oil determined by experiment

OOC_{th} is theoretical value of oxirane oxygen content of the oil

A_i (126.9) and A_o (16.0) are the atomic weights of iodine and oxygen respectively and

IV_0 is the initial iodine value of oil sample.

3.3.5. FT-IR spectrum analysis of epoxy product

Fourier Transform Infrared Spectrometry was used to determine functional group by considering a peak at which to represent oxirane groups and peaks of the epoxy groups in the triglyceride molecule. Whereas a weak band representing hydroxyl groups can be of epoxy group.

3.3.6. ^{1}HNMR analysis

Hydrogen nuclear magnetic resonance was used to determine complete conversion of carbon-carbon double bonds in triglyceride of oil to epoxy oil. The value was obtained using conversion of double bond were recorded on Bruker Avance 400 spectrometer (Bruker, Rheinstetten, Germany) operated at 400 MHz using CDCl3 as solvent.

CHAPTER FOUR
RESULT AND DISCUSSION

4.1. Characterization of Physio Chemical Property of kernel seed and Refined *P. Falcatus Oil*

A 4 Kg of the ripen fresh *p. falcatus* seed was collected on December, 2017 from Western Oromia East wollega Zone Leka Dullacha woreda. First it was cleaned from impurities and epicarp (outer cover) and mesocarp (pulp) of the fruits were removed manually. The clean seeds were weighted and *P. falcatus* seeds were further dried in an oven at 105 °C for an hour to remove the rest of their moisture content. Then the dried seed was crushed using a crushing mill with particle size of 0.25 –0 .75 mm for solvent extraction analysis. For this study, from 4 kg of dry fruits .991 kg of kernels (24.75%) of kernels were obtained and the others like epicarp (outer cover) and mesocarp (pulp), discarded as a waste. This result was lower than the 25% reported by (Feleke et al, 2012) and higher than reported by (Daniel Alemu, 2015).

I. Moisture content of *podocarpus falcatus* seed

The moisture content of the sample was obtained using equation 3.1, After drying the seed in the oven at 105 °C for the six hours the *p. falcatus* seed average moisture content was found 6.02%. The moisture content determination of *p. falcatus* seeds conducted laboratory result is given in appendix C of Table (C.1)

From this value we concluded that it was lower than 8.41 reported by Gadissa.H, (2014) and is comparable with that of castor seed 5 to 7 % (A Abdelaziz, M Elamin, 2014). The result was suitable for solvent extraction method and without further drying of the seeds and moisture content of seeds which is an important factor that affects the yield and quality by deteriorating oil extracted. Since, the deteriorating oil extracted decreased the quality and yield of epoxy oil by increasing the acid value. Thus, the value was not affect epoxidized *p. falcatus* oil.

II. Crude fat of *podocarpus falcatus* seed

The crude fat of *P. falcatus* kernel used in this study was analyzed by Soxhlet apparatus and the value was calculated using equation 3.2 and the result was 65.287%.

Most vegetable common oil crop niger seed (40%) and some tropical trees such as *Terminalia bellirica (*47%), *Trichilla emetica* (51%), *Solanum nigrum* (34%) and *Balanites aegyptica* (46–50%), (Dhellot *et al*. 2006) were slightly lower than crude fat of *P. falcatus* seed kernel. Therefore, *p. falcatus* seed have high amount of crude fat and indicates that high amount of oil will obtain from these seed and also high yield of epoxidized oil.

III. Analyses of volatile, ash content, seed density and fixed carbon

The volatile, ash content, seed density and fixed carbon of *podocarps falcatus* were determined accordingly of the equations of 3.3, 3.4, 3.6 and 3.5 respectively.

Table 4.1. Volatile, ash content, seed density and fixed carbon content of p. falcatus seed kernel.

Parameters	**Value**
Volatile matter	86.46%
Ash content	2.25 %
Seed density	1.04 g/cm^3
Fixed carbon content	5.3 %

The *Podocarpus falcatus* was rich in volatiles (86.46%) but low in ash content (2.5%), the fixed carbon content for *Podocarpus falcatus* was 5.3%.

The hundred-kernel weight and the density of *Podocarpus falcatus* kernel were 16.51g and 1.02g/ml respectively. The value obtained for fixed carbon content is very low this due to high contained of crude fat dry based.

IV. Physio Chemical Analysis of Refined *P. Falcatus Oil*

The amount of *p. falcatus* grounded kernel collected from the crushing mill was used for oil extraction. From 0.991 kg of the kernel, 0.6681 liter of *p. falcatus* crude oil was extracted. The yield of oil extracted was calculated using the density and volume of obtained in this study. The yield of p. falcatus oil was 62.2%.

The present study indicated that the oil content higher than the seed that used for production of epoxy such as soya been oil (30-35%), cotton seed oil (25-40%), *v.galmensis (*35-42% (Lson, Chang, & Regional, 1985), rice bran 37% (Tyagi et al., 2012) and *palm oil* (25%).

After refining of the extracted oil by using degumming process, from Soxhlet solvent extraction total amount of crude oil obtained was 0.6681 liter. From this liter of crude oil 102.5 liter (15.34%) was removed during the refining and purification process. Higher amount of suspended solid such as wax and gum were removed by centrifuging. About 20.043 ml distilled water was used for degumming process.

After refining by degumming process, the free fatty acid (which may be built up due to enzymatic processes (lipase) resulting from damage to the seed) of crude oil was not much high since the presence of free fatty acids, water and other impurities are chiefly responsible for the rancidity of oils, thus making saponification of the oil very difficult. and hence it can use directly for epoxidation reaction without further purification, because the possibility of soup formation is low.

After oil the purified its moisture content, density, acid value, viscosity, free fatty acid, saponification value and iodine value were determined.

A Moisture content of *podocarpus falcatus* oil

The moisture content of the oil was calculated using equation (3.1). The *Podocarpus falcatus* purified oil average moisture content was found to be 2.2%. This result was good for epoxidation reaction without any drying in oven since drying at high temperature get the oil composition change their content in to other, may decrease its iodine value and change its phase. there will be a substantial loss in seeds moisture content which in turn will harden the seed particles, leading to more difficult oil flow (Soetaredjo, *et al*, 2008).

B. Viscosity of *Podocarpus falcatus* oil

By using Vibro viscometer dynamic viscosity of oil was determined to be 30.5 m.Pa.s at temperature of 20 °C. Since the viscosity is important in determining optimum handling, storage, and operational conditions. This value is less than the viscosity of cotton seed (74), soya been (32) and clos relation to *v. galmensis* oil (30.2) (Adelola & Ndudi, 2012). It is related to followability of the oil, effective number of the carbon, and degree of unsaturation of fatty acid (Gunstone, 2002). The more the value of the viscosity indicated the more saturation level of the fatty acid which leads to decreases chance oil to undergo epoxidation reaction. Since the value of the viscosity of the *p. falcatus* oil was low, the oil further gone to produce the epoxidized *p. falcatus* oil.

C. Specific gravity of the *podocarpus falcatus* oil

The specific density of oil was then determined in using the relation given in equation (3.11). The specific gravity of purified oil was measured by using pycnometer and found to be 0.922. The specific gravity of 0.922 for P. *falcatus* oil was almost similar with the specific gravity of 0.90 obtained by Feleke, 2012. The specific density *p*. *falcatus* oil respectively agreed well with the data reported for edible oil of common oil seeds (0.91–0.93) such as niger, rapeseed, linseed, sunflower, watermelon seed kernel oil (0.92), *Sterculiastriata* (0.85),Weinert *et al.*, 1990 and shea butter oil (0.92)(Vol & Press, 2006). Specific gravity indicates the purity of oil. As the value increases the purity of the oil increases. Therefore, during epoxidation reaction does not interfere with impurity of the oil since the specific density of the present study was high.

D. Acid value of *podocarpus falcatus* oil

The amount of acid value found in the *Podocarpus falcatus* kernel seed oil was done by titration method. Then a titration volume was taken for acid value calculation. Acid value was 3.11 mg/KOH.

From this value, the acid value of *p. falcatus* kernel seed oil resulted in lower than some the other vegetable oil. The lower the acid value of an oil, the fewer free fatty acids it contains which makes it less exposed to the phenomenon of rancidification. The present study value was lower than 4.0 which is reported by Gadissa.H, 2014. So, it was possible to say since the acid value of *p. falcatus* oil obtained in this study was low, the oil was stable and may not go into form rancidity. The oil

that undergo epoxidation reaction incorporated the acidic catalyst, acid value of the oil preferred to be low. Since the acid value of *podocarpus falcatus* oil was low the epoxidation of this oil will take place without any further purification.

E. Free fatty acid of *podocarpus falcatus* oil

Six samples of oil were taken to calculate free fatty acid by using titration method in order to increase the accuracy value of titration. The average titration volume was taken for free fatty acid value calculation. The laboratory results are presented in Appendix C. The free fatty acid value of purified *p. falcatus* oil is calculated using equation (3.9) and result was 1.54 mg/KOH

Which indicated that the amount of potassium hydroxide needed to neutralize free fatty acid. This free fatty acid value was lower less than two which does not require further purification of oil and acceptable for epoxidized vegetable oil. The lower the free fatty acid value of the oil the lower its ability to hydrolyze and ability withstand the unsaturated of the oil which will be suitable for epoxidation reaction and increase the shelf life. The higher the acid value the higher the level of free fatty acids which translates into decreased oil quality. The hydrolysis is probably caused by a variety of agents such as; presence of moisture in the oil, elevated temperature (above room temperature) and, most important of all, lipases (enzyme) coming from the source or contaminating microorganisms which case degradation of oxirane number of epoxidized *p. falcatus* oil. The lower the free fatty acid the greater the oil leads to epoxidation reaction.

F. Saponification value of *p. falcatus* oil

The saponification value helps to determine the quantity of potassium (in mg) needed to neutralize the acids and saponify the esters contained in 1g of lipid. Saponification value was calculated through titration using equation 3.10. First the blank level changed from pink to colorless at 32 mL titration volume. The color at which the saponification test changed from pink color to red color was 14.1 mL of titration volume. The value of the saponification value of the *Podocarpus falcatus* seed kernel oil was 181.93 mg KOH/g oil.

The saponification value (181.93 mg KOH/g oil) of *Podocarpus falcatus* seed kernel oil was slightly high. Higher Saponification value means oils of smaller molecules and so their penetrating powers into the epoxidized *Podocarpus falcatus* oil is more, which gives softness to epoxy oil when it is used for paints and coatings. Saponification value is a measure of epoxidation during

storage, and also indicates deterioration of the oils. The smaller saponification value higher deterioration of the oil that leads to impurity interfere of the epoxidation reaction and low in its yield.

The present study indicated that value was lower than those of the common oils such as soya bean (189-195 mg KOH/g oil), Peanut (187 - 196 mg KOH/g oil) and cotton seed oil (189-198 mg KOH/g oil) (Codex, 1993) and olive oil (185-196 mg KOH/g oil) (Vol & Press, 2006). This saponification value of fat and oil was high due to the predominantly high proportion of shorter carbon or carbo carbon double and triple bond chain lengths of triglyceride fatty acids. Having such property of shorten carbon length of oil is used in fabrication of epoxidation of vegetable oil. Low molecular weight (short to medium chain) fatty acids have more glyceride molecules per gram of fat than high molecular weight acids. Each glyceride molecule required three KOH molecules for saponification, hence the more the glyceride molecules the greater the saponification value.

G. Iodine value of *podocarpus falcatus* oil

The importance of determine the iodine value is related with the conversion of unsaturated fatty acid to epoxy oil. The iodine value is an indicator of the degree of unsaturation, a great value of Iodine Value indicating an oil prone to epoxidation. The unsaturated character affects the stability of oils, and, as a result, leads to the appearance of degradation effects during production of the epoxy oil.

The titration was done in triplicate to increase the accuracy which is found in appendix C. The iodine value of the oil was calculated using equation (3.12) was 107.18 g I_2/g100 sample. This iodine number of *p. falcatus* oil determined showed that the oil was a drying type of oil since it was greater than 100 g I_2/g100 sample and can definitely be applied for epoxidized vegetable oil. Having such an amount of iodine value indicated that unsaturation of fatty acid which means that shorten carbon chains of length due to this *p. falcatus* kernel oil was agreed the range production of epoxidized vegetable oil and can go under epoxidation reaction. This value higher than iodine value of rape seed oil (95.12 g I_2/100 g) (Neagu et al, 2013)veronica oil (94.28 g I_2/ g 100 sample) and lower than iodine value of genetically modified of soya been oil (130) (Gebremedhn Tekeste, 2017)

According to (Ayorinde et al. 1988) higher iodine value (which is higher than 85) indicated that the ability to produce epoxides which are used for resins for paint and press-ink formulations. Apart from this, it is also used in a wide range of industrial applications including lubricants, paints and coating(Mohamed et al., 2014). Hence, *p. falcatus* oil had high unsaturation of fatty acids, when it heated the oil are prone to polymerization of the glycerides, causing formation of deposits, and thereby compromising epoxidation reaction.

H. Refractive index of *podocarpus falcatus* oil

Refractive index of *Podocarpus falcatus* kernel seed oil was determined according to the section in 3.2.11. The result refractive index value was 1.468 at a temperature of 20 °C. The value of refractive index was told the ratio of the speed of light in a vacuum to that in the oil under examination and it is related to the degree of unsaturation and the ratio of cis/trans double bonds and can also provide hints on the oxidative damage. And also, it related to which oil is more saponified or un-saponified. The high refractive index the low oleic which contained more double bond of fatty acid.

Refractive index of extracted *podocarpus falcatus* seed oil was more similar to common vegetable oil Niger seed oil (1.46-1.48), olive oil (1.467-1.471), and watermelon seed oil (1.47) and lower than soya been oil (1.4700 – 1.4780) and Sunflower oil (1.5170 – 1.5260) (Vol & Press, 2006)

Refractive index can be used for rapid sorting of fats and oils which are suspected to be adulterated (Olaniyan et al, 2007) as well as one of the important physical characteristics for identification of oils and fats.

I. Gas chromatography mass spectroscopy (GC/MS)

The most abundant and total fatty acid composition of the extracted from podocarpus falcatus seed obtained in this study was determined by GC-MS and is shown in Table 4.4 and Appendix E.

Table 4.2. Fatty acid profile of podocarpus falcatus and saturation level

Fatty acid	IUPAC name of fatty acid	Carbon structure	%total abundance
Palmitic	Hexadecenoic acid	18:0	6.24

Oleic	Cis-9-octadecanoic	18:1n-9	53.49
Linoleic	Cis-9, cis-12-octadecanoic	18:2n-6	31.48
Linolenic	Cis-9, cis-12, cis1-15-octadecatreic	18:3n-3	3.87
Stearic	Octadecanoic	16:0	4.93

From the above table, the result which shown from this table the largest covered area proportion occurred in this fatty acid profile of podocarpus falcatus seed oil was cis-9-octadecanoic which is oleic acid and the next largest one was cis-9, cis-12 octadecadienoic, the others fatty acid composition were lowest when compared to the others. Those compounds had carbon structures between C_{16} and C_{18}, their carbon bonds and saturation levels were different and they were discussed in above table.

We know that the fatty acid profile is a main determinant of the oil quality. And P. *falcatus* fatty acid composition were monounsaturated oleic acid (53.49%), poly-unsaturated linoleic acid (31.48%), linolenic acid (3.87%), saturated palmitic acid (6.24%), and stearic acid (4.93%). It is, however, important to note that the high percentage of mono-unsaturated oleic acid provides a high degree of oiliness. Acids degree of unsaturated fatty acid leads to solidification at low temperature or cloud formation. Oils rich in monounsaturated free fatty (e.g. oleic acid and linoleic acid) are generally more stable to oxidative rancidity and stable as deep-frying oils (Mohammed *et al*., 2003). They have many applications such as plant-based lubricants and as feedstock for the oleo chemical industry such as epoxidized vegetable oil.

The total percentage of unsaturated fatty acid in this study of extracted oil of *podocarpus falcatus* oil was 88.83% which lower than sun flower oil, but higher than the total percent of unsaturated fatty acid value of Soybean oil, Mustard oil, Palm oil and Coconut oil for values 81.14, 86.18, 53.30 and 7.12% respectively (Chowdhury, *et al*., (2007)).

4.2. Experimental Design Results

Epoxidized *podocarpus falcatus* oil was produced according to the procedure discussed in the section of 3.2.13. The production of this *podocarpus falcatus* epoxidized oil was carried out at 50

°C, 60 °C, 70 °C of temperature, at different reaction time of 3hr, 4.5hr, 6hr and at different level of hydrogen peroxide to oil ratio of 1.1:1, 1.4:1, and 1.7:1 by the taken of constant value of *p. falcatus oil*, sulphuric acid, formic acid and rotational speed of magnetic stirrer.

Fifteen experiments were done at this different value of different parameter of the epoxidized *p. falcatus* seed oil. In addition to this for these produced epoxidized oil its conversion, epoxide content and selectivity was done. At optimum value by considering its selectivity and conversion the FTIR and ^{1}HNMr analyses, oxirane value, and viscosity were done

The overall epoxidation of this oil was carried out a 500 ml capacity glass reactor which was equipped with a magnetic stirrer. The magnetic stirrer rotational speed, reaction time and temperature were adjusted to the desired conditions. The statistical analysis of the epoxidized *p. falcatus* oil synthesis is discussed in the following sections.

4.2.1 Statistical analysis on factors affecting formation of epoxidation of *p. falcatus* oil

The main parameter affecting the formation or production epoxidation process studied in this paper were reaction temperature, amount of hydrogen per oxide to oil ratio and reaction time. Having these three variables, the selected experimental design used to analysis of epoxidation was Box – Behnken design. Since it is commonly used experimental design models for three level three factor experiments. The experimental design selected for this study is the Box-Behnken Design (BHD) and the response variable measured is the double bond conversion of *podocarpus falcatus* seed oil and selectivity of epoxidized oil.

Design-Expert Software 7.0.0 is used to screen out insignificant factors and identify significant factors. Also, it used in the least squares regression analysis of variance (ANOVA). The statistical software program is used to generate the model equation, interaction effects of the independent variables and surface plots using the fitted equation obtained from the regression analysis holding one of the independent variable constants. The actual double bond conversion and selectivity of *p. falcatus* oil of the epoxidized *p. falcatus* oil produced at different process parameters was determined by using the chemical characterization method of determination of iodine value Wiji's method and by determining iodine value and oxirane oxygen content respectively. The detail calculations and results were discussed in sections below and in Appendix C.

Table 4.3. Experimental and predicted value of conversion and selectivity of epoxidized *podocarpus falcatus* oil**.**

	Process parameters			**Response variables**			
St. No	Reaction Temperature (^{O}C)	H_2O_2 to oil ratio (mole/mole)	Reaction time (hr)	**Conversion %**		**Selectivity %**	
				Experimental Conversion	Predicted conversion	Experimental selectivity	Predicted selectivity
1	50.00	1.10	4.50	63.00	64.15	80.74	81.37
2	70.00	1.10	4.50	61.40	63.41	75.00	74.88
3	50.00	1.7	4.50	67.25	65.24	87.86	87.98
4	70.00	1.7	4.50	64.07	62.92	84.08	83.45
5	50.00	1.4	3.00	59.80	60.35	74.07	73.14
6	70.00	1.4	3.00	68.46	68.15	87.92	87.73
7	50.00	1.4	6.00	71.90	72.21	91.18	91.37
8	70.00	1.4	6.00	61.90	61.35	64.82	65.75
9	60.00	1.10	3.00	64.92	63.22	78.11	78.42
10	60.00	1.7	3.00	62.49	63.95	84.69	85.51
11	60.00	1.10	6.00	67.62	66.17	76.86	76.05
12	60.00	1.7	6.00	64.36	66.06	84.44	84.13
13	60.00	1.4	4.50	70.89	70.92	90.03	90.07
14	60.00	1.4	4.50	70.89	70.92	90.03	90.07
15	60.00	1.4	4.50	70.98	70.92	90.14	90.07

4.2.2. Adequacy check for the developed model

The results showed from the ANOVA variance that built up the regression equation model for production epoxidized *p. falcatus* oil of its conversion and selectivity was depends on the linear

terms, on the quadratic terms and also on the interactions of variables. The quality, accuracy, and reasonability of the model developed could be evaluated from their coefficients of correlation and highly significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared.

Coefficient of variation, the standard deviation expressed as a percentage of the mean; predicted Residual Error sum of squares, which is a measure of how the model fits each point in the design; the R- squared, measure of the amount of Varian around the mean explained by the model; Adj R-squared, a measure of the amount of variation in new data explained by the model, and Adequate precision, this is a signal to disturbance ratio due to random error. A ratio greater than 4 is desirable. Here the ratio of 7.007 and 34.372 of conversion and selectivity respectively indicated that it was an adequate signal. Therefore, the model could be used to navigate the design space., presented table 4.4, below, are used to decide whether the model can be used or not.

Table 4.4. Model adequacy measures for conversion of double bond and selectivity of Epoxidized oil.

Responses	Std. Dev	Mean	Coefficient Variance.	R-Squared	Adj R-Squared	Pred R-Squared	Adeq Precision
Conversion	2.07	66.00	3.14	0.9037	0.7303	-0.5409	7.007
Selectivity	0.91	82.67	1.10	0.9949	0.9856	0.9179	34.372

For conversion a negative "Pred R-Squared" implies that the overall mean is a better predictor of response than the current model. But for the selectivity the "Pred R-Squared" of 0.9179 is in reasonable agreement with the "Adj R-Squared" of 0.9856. The value of R-squared for the developed correlation is 0.9949. It implies that 99.49% of the total variation in the percentage of conversion is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values of the three epoxidation reaction process variables to the percentage of selectivity is shown in Figure 4-1. The results in Figure 4-1 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit.

In order to check whether the quadratic model is the right model or not, it was crucial to perform analysis of variance (ANOVA). This it depends on based on a 95% confidence level, F – value is a test for comparing model variance with residual (error) variance and the probability, P-values were used to check the significance of each coefficient of regression model equation and their values are presented in table 4.7 and 4.8.

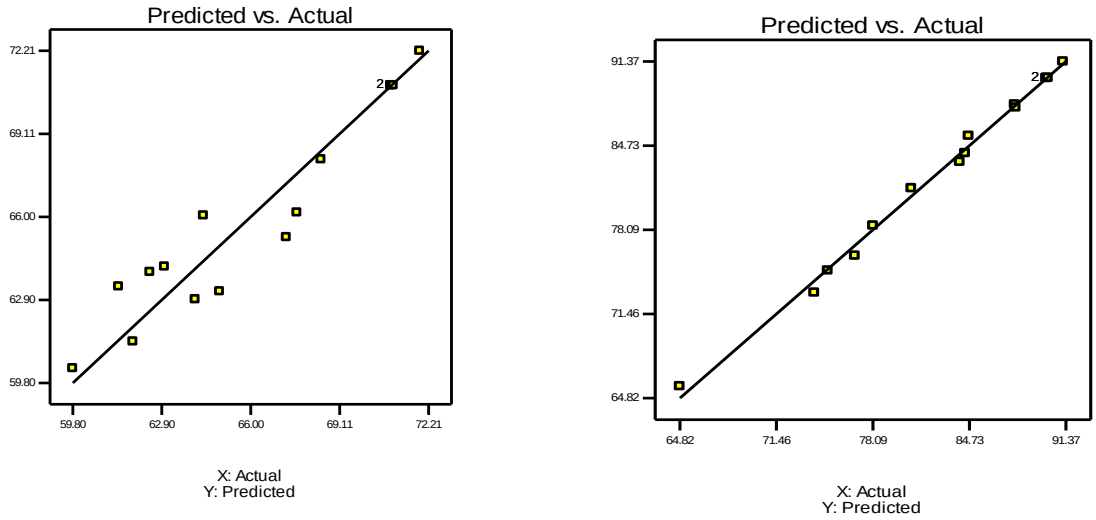

Figure 4.1. Predicted versus actual percentage of (a) conversion of double bond (b)selectivity of the epoxidized *p. falcatus* oil

The P-values of corresponding coefficient should be less than or equals to 0.05. It is calculated by model mean square divided by residual mean square. This is the bench mark for checking the significance of the proposed model. The smaller the p- values are, the bigger the significance of the corresponding coefficient.

A test that used to comparing model variance with residual (error) variance is F- Value. If the variances are close to each other, the ratio will be close to one and it is less likely that any factors have a significant effect on the response. Here the Model F-value of selectivity and conversion was 107.48 and 5.21 respectively, for both it implies the model is significant. There was only a 0.01% chance for selectivity and 4.61 chance for conversion that a "Model F-Value" this large could occur due to noise, personal error or disturbance. Values of "Prob > F" less than 0.0500 indicate model terms were significant. A Values greater than 0.1000 indicate the model terms are not significant. In the case of selectivity percentage of epoxidized *p. falcatus* oil the factors such as A, B, C, A^2, B^2, C^2 and AC were significant model terms. The "Lack of Fit F-value" of 343.51

implies the Lack of Fit was significant. There was only a 0.29% chance that a "Lack of Fit F-value" this large could occur due to noise.

Table 4.5**.** Analysis of Variance for Selectivity of Epoxidized *P. Falcatus* Oil

Source	**Sum of squares**	**DF**	**Mean Square**	**F-Value**	**Prob > F**	**Remark**
Model	805.67	9	89.52	107.48	< 0.0001	ss
A	60.67	1	s60.67	72.84	0.0004	s
B	115.12	1	115.12	138.21	< 0.0001	ss
C	7.01	1	7.01	8.42	0.0337	s
A^2	86.41	1	86.41	103.75	0.0002	s
B^2	40.42	1	40.42	48.53	0.0009	s
C^2	121.29	1	121.29	145.62	< 0.0001	ss
AB	0.97	1	0.97	1.16	0.3304	n
AC	404.21	1	404.21	485.30	< 0.0001	ss
BC	0.25	1	0.25	0.30	0.6073	n
Residual	4.16	5	0.83			
Lack of Fit	4.16	3	1.39	343.51	0.29	ns
Pure Error	8.067E-003	2	4.033E-003			
Cor Total	809.84	14				

Note: s means significant ss means highly significant and n non-significant.

In the case of determining the model for conversion of double bond in *p. falcatus* oil the only factors coded such as A, C, A^2, B^2, AC were significant model terms.

From the point of view, those coded factors showed that the reaction temperature, molar ratio of hydrogen peroxide to oil, reaction time, interaction between reaction temperature and reaction time, square of the reaction temperature, square molar ratio of hydrogen per oxide to oil and square

of reaction time were affect the percentage conversion and selectivity of converted of double bond in *p. falcatus* significantly.

Table 4.6. Analysis of Variance for Selectivity of Epoxidized *P. Falcatus* Oil

Source	Sum of Squares	**DF**	Mean Square	F-Value	Prob> F	Remark
Model	201.51	9	22.39	5.21	0.0419	significant
A	*4.68*	1	4.68	*1.09*	0.03443	
B	*0.19*	1	0.19	*0.044*	0.8421	
C	*12.78*	1	12.78	*2.97*	0.01452	ss
A^2	*36.90*	1	36.90	*8.59*	0.0326	significant
B^2	*54.13*	1	54.13	*12.60*	0.0164	significant
C^2	*18.59*	1	18.59	*4.33*	0.0920	
AB	*0.62*	1	0.62	*0.15*	0.7187	
AC	*87.05*	1	87.05	*20.26*	0.0064	significant
BC	*0.17*	1	4.30	*0.040*	0.0492	significant
Residual	21.48	5	7.16			
Lack of Fit	*21.47*	3	2.700E-0.003	*2651.03*	0. 4	non significant
Pure Error	*5.400E-003*	2				
Cor Total	222.98	14				

4.2.3. Effect of epoxidation reaction process variables

The overall screened conversion and selectivity for epoxidized *podocarpus falcatus* seed oil conducted in this study. The effect of reaction temperature, molar ratio of hydrogen per oxide to double bond the oil and reaction time on the conversion and selectivity of epoxidized *p. falcatus* oil of was studied and evaluated for best epoxidized conditions. Based on the analysis of variance,

were significantly affected by various interactions between the process variables. In addition to the interaction effect, significant individual process variables that affect selectivity and conversion are reaction temperature, molar ratio of hydrogen per oxide to double bond the oil and reaction time. Their effects result demonstrated that the advantage of using BHD surface response for experimental data analysis in capturing the interaction between variables that affects the epoxidation reaction beside these only reaction temperatures and the reaction time affects the conversion in double bond and reaction temperature, time and hydrogen peroxide to oil molar ratio affects the selectivity of epoxidized oil.

4.2.4. Effect of individual process variables

Effects of temperature on conversion of double bound and selectivity of epoxidized oil

Both percentage selectivity and conversion of epoxidized *p. falcatus* oil is highly significantly affected by reaction temperature. As shown figure 4.2 analysis influence of temperature on the conversion change of epoxy percentage that demonstrated the temperature of epoxidation reaction was the most important. From this figure, it is evident that increase in the temperature favored epoxidation reaction and a maximum of 71.9% conversion of iodine value was obtained at 50 °C after a reaction time of 6 hours. Nevertheless, as the temperature increase from 50 to 60 °C the conversion was highly increased while it was reached the design space at 60 °C the percentage of conversion then starts to drop as the temperature tend to increase above the center limit. This indicated that as temperature increase from 50 to 60 °C iodine degradation rate was increased. These results related with the formation of peroxyformic acid in a more rapid epoxidation rate and also in higher rate of degradation. From these we conclude that the epoxidation of *p. falcatus* oil it seemed that the free radical chain of polymerization because the a soon as the reaction begin while the formation of the polymerized or epoxidized of *p. falcatus* occurred. And also, from statistical analysis of conversion the squared power of the temperature indicated that as the gap of the temperature increased the conversion of double bound to epoxy oil highly affected by the temperature. This idea also the same for the selectivity of epoxidized *p. falcatus* oil.

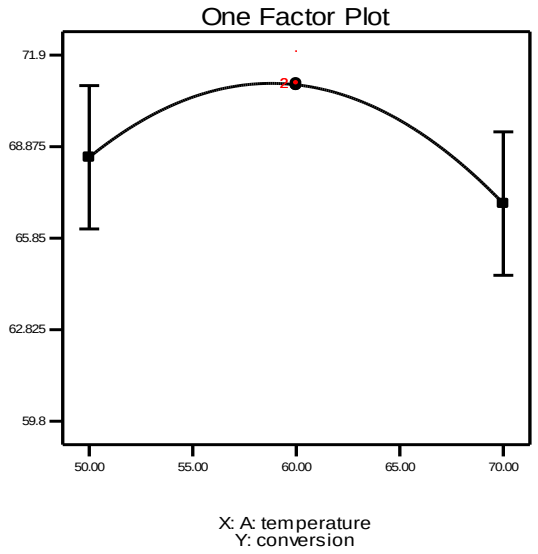

Figure 4.2. Percentage of conversion versus temperature at molar ratio of hydrogen per oxide to oil 1.4 and reaction time of 4.5 hr.

In addition to effects of temperature on conversion, the selectivity of epoxidized oil significantly affected by reaction temperature. It can be seen from the figure 4.3 that with increasing reaction temperature until it reaches its center value would result increasing in the percentage of selectivity, the percentage of selectivity then starts to drop as the temperature tend to increase above the center limit. Since selectivity has directly relation with oxirane value of epoxy number that means at lower temperature its value was higher than at higher temperature. This due to higher rate of ring opening (oxirane cleavage) of the product which is reactions at lower temperatures had lower rates but gave a more stable oxirane ring. Based on these results, an optimum level of epoxidation could be obtained at reaction temperature of 60 °C at which epoxide degradation would be minimal. Moreover, higher operating temperatures are not preferred as the addition of hydrogen peroxide which is an exothermic reaction would lead to an explosion

In other case Figure 4.3 shows with the low temperature (50 °C and 60 °C), the selectivity (%) getting up, but from the temperatures of 60 °C the selectivity has decreased, it is because the temperature of the higher possible side reaction, so lowering the selectivity. According to this study the results of effect of temperature on the selectivity was agreed with epoxidation of rape seed oil (Nugrahani et al, 2017) that the epoxidation results show high Temperature 60°C

until with the increasing time and the high numbers oxirane and percentage of selectivity, then experienced a decline.

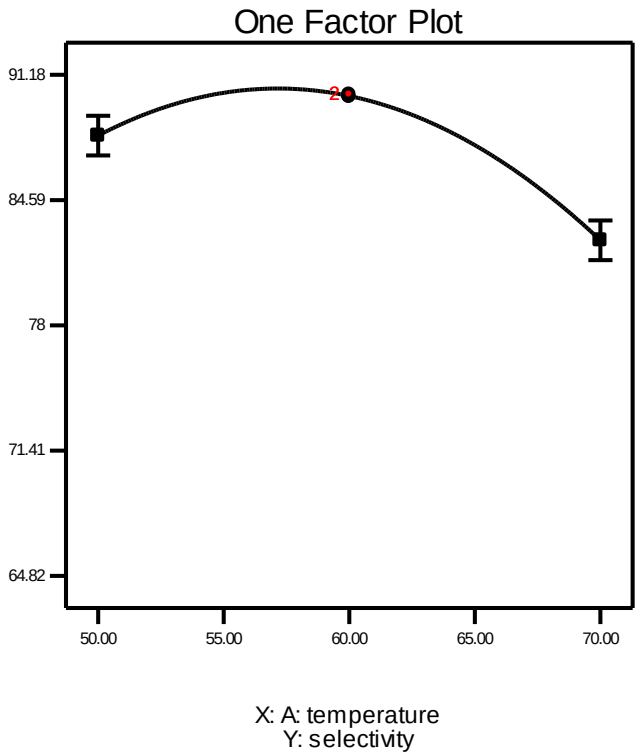

Figure 4.3 Percentage of selectivity versus temperature at molar ratio of hydrogen per oxide to oil 1.4 and reaction time of 4.5 hr.

Effect of molar ratio of hydrogen peroxide to double bond of *p. falcatus* oil

On this study of epoxidation reaction process, in order to determine the influences of H_2O_2 to double bond of fatty acid *podocarpus falcatus* oil the syntheses were carried out 1.1:1 to 1.7:1 at reaction temperature and time of 60 °C and 4.5 hours respectively. As it is shown in table 4.8 the effects of molar ratio of hydrogen peroxide to oil on conversion of double bond based on iodine value is insignificant. However, the selectivity of epoxidation reaction process significantly disturbed by molar ratio of H_2O_2 to oil. As figure 4.4 shown, as molar ratio of H_2O_2 to oil increases the selectivity percentage was increased. This is due to using 30 weight % of hydrogen peroxide concentration cases reaction rate increased. But the stability of oxirane ring was very poor at low H_2O_2 concentration. The oxirane ring cleavage was performed in the presence of formic acid and

water (water produced by performic acid generated *in situ* reaction). The reaction environment contains water and organic acid which will cause the decomposition of the epoxy group as a result of the hydrolysis and acylation in acidic condition.

According to the report (Milchert et al, 2015) an excess of hydrogen peroxide relative to the number of unsaturated bonds is necessary in order to permits reaching full conversion of double bonds, selectivity of oxirane oxygen but compensation of hydrogen peroxide loss, caused by its decomposition at temperatures above 60 °C. On the bases of changing epoxy number and oxirane value it is found that the molar ratio of H_2O_2 to oil equal to 1.7 was the most advantageous by using formic acid in order to forming the perfomic acid and in this case high epoxy number or oxirane value was achieved. In general, with an increase in hydrogen peroxide-to- unsaturation molar ratio, there was a progressive increase in the rate of oxirane formation due to increasing of selectivity. However, the correlation between decrease in the final iodine value and the corresponding increase in the final oxirane value were relatively less when the ratio was increased beyond particular magnitude.

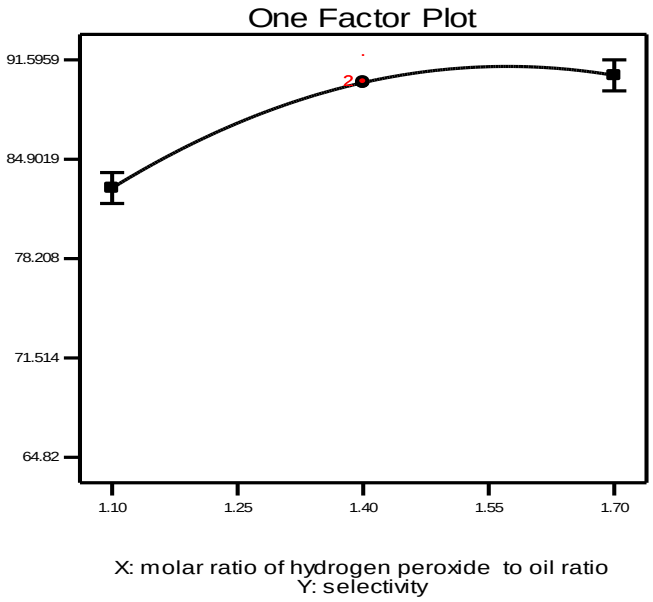

Figure 4.4 Effects of Molar ratio of H_20_2 to oil on selectivity of epoxidized oil

Effects of reaction time on epoxidation reaction process

Iodine value, oxirane value and its conversion and selectivity of epoxidized oil are significantly affected by reaction time. The influence of reaction time in this profile of epoxidation reaction process was studied in the range of 3 to 6 hours at a temperature of 60 °C and 1.4;1 Molar ratio of H_2O_2 to oil. As shown in figure 4.5 (a) as the reaction time increases the conversion of the double bond in fatty acid of *podocarpus falcatus* seed oil was increased but it is not significantly affected. From figure 4.5 (b) as the reaction time increases the selectivity of oxirane value in fatty acid of *podocarpus falcatus* seed oil was increased until it reached its optimum value and starts to decrease when the reaction time obviously increases above limit center. From this result we found that the selectivity of oxirane oxygen content or number of epoxy in oil high at the middle of reaction time and lower at higher reaction time and temperature. This is due to formation of hydrolysis or oxirane degradation at higher reaction time. With further increases in reaction time the Oxirane Oxygen Content which have direct relation with selectivity of epoxidized *podocarpus falcatus* oil decreased which was attributed to more by-products, water being formed and the undesirable oxirane-ring opening reactions or oxirane ring cleavages.

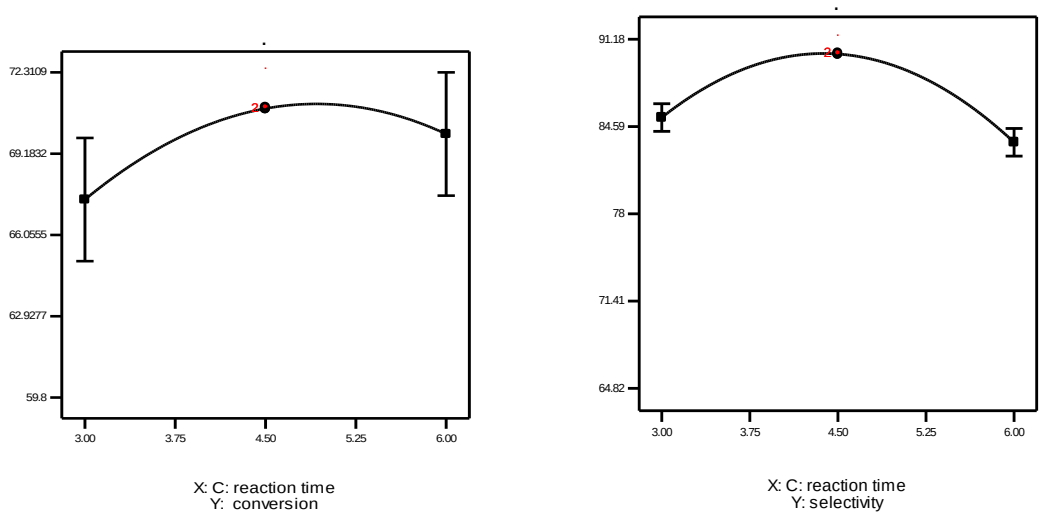

Figure 4.5. Effects of reaction time on epoxidation reaction (a) conversion of double bond (b)selectivity of the epoxidized *p. falcatus* oil.

According to (Nugrahani et al., 2017) At temperatures higher than the required reaction time is shorter, number of epoxy content obtained was high at reaction time 4 hours, while the

temperature reaction of 85 °C and shorter time , Oxirane Oxygen content amount obtained was low during the epoxidation of soya been oil.

4.2.5. Effect of interaction between process variables

The best way of showing the effects of interaction between this parameter for the conversion and selectivity of epoxy content of the oil are to generate response surface plots of the equation. The three dimensional i.e. interactions, contours and response surfaces effect, is the most important and an interaction occurs when the conversion and selectivity of epoxy content of the oil is different depending on the settings of two factors. From this point of view, the only interaction effects that affect the conversion of double bond was reaction temperature with reaction time and their response surface plotted in figures 4.6.

From general points figure 4.6 below, as an increase in amount of reaction time was found to increase the percentage of conversion and decrease at higher temperature of the epoxidation reaction. From the three interaction effects shown in the figures at higher range of reaction time, reaction temperature at the center point and molar ratio of hydrogen per oxide to oil at center point, always resulted in the percentage of conversion higher than when using lower or higher reaction temperature and higher molar ratio of hydrogen per oxide to oil.

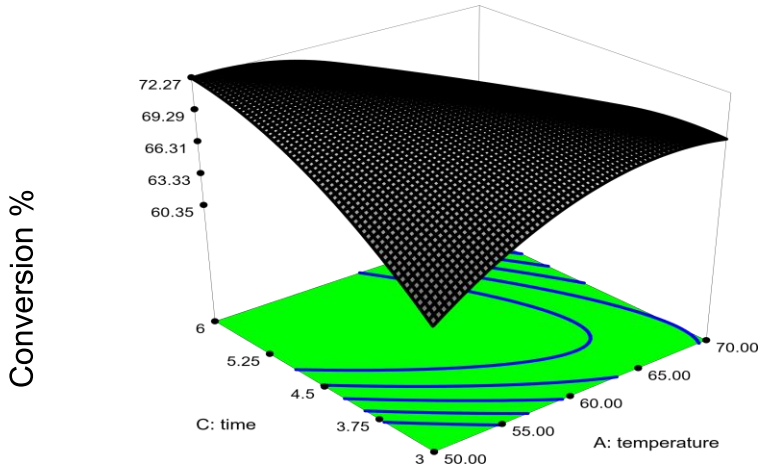

Figure 4.6. Surface plot of the interaction effect of reaction temperature and reaction time versus percentage of conversion when the molar ratio of hydrogen per oxide to oil is 1.4.

In addition to conversion, selectivity of oxirane content was significantly affected by interaction between the process variables. Among these variable reaction temperature and time more significant and other were non-significant.

As shown from figure 4.7 percentage of selectivity of epoxy content and temperature of epoxidation reaction had relationship at higher temperature the epoxy content was low. With the same to this the oxirane oxygen contents also affected by reaction time of epoxidation reaction as it discussed in previous section. This indicated that from the three interactions at lower range of reaction time, reaction temperature at the center point and molar ratio of hydrogen per oxide to oil at center point, resulted in the percentage of selectivity of oxirane value higher than when using lower or higher reaction temperature and higher or lower molar ratio of hydrogen per oxide to oil and higher reaction time. This due to at lower temperature and at center point of reaction time the oxirane rapidly formed but the iodine value was low. This is simply lower iodine value and higher epoxy content of epoxidized oil at medium reaction temperature and medium reaction time will drive the reaction forward and medium molar ratio of hydrogen per oxide to oil was ensure the epoxidation reaction goes to maximize the value which resulted in lower iodine value and rate of hydrolysis of the product.

However, in the case of economical beneficiary is that at higher range of reaction time, the observations showed that using a combination of higher reaction time, higher amount of molar ratio of hydrogen per oxide to oil and higher reaction temperature is not advantageous in order to increasing the percentage of conversion and selectivity of oxirane value.

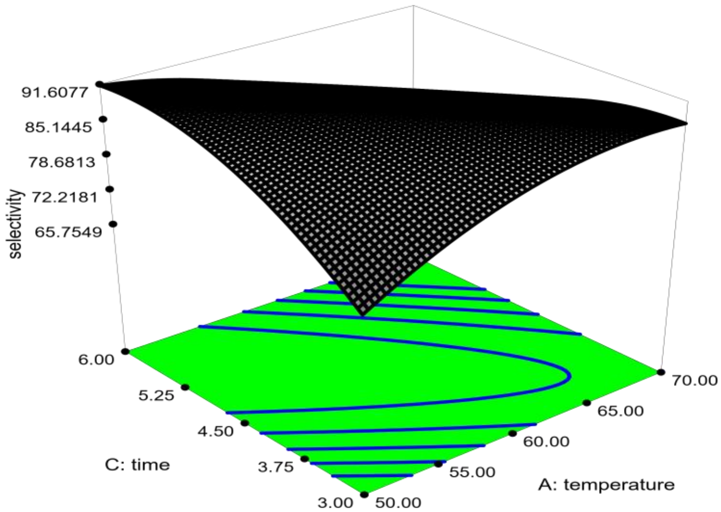

Figure 4.7**.** Surface plot of the interaction effect of reaction temperature and reaction time versus percentage of selectivity when the molar ratio of hydrogen per oxide to oil is 1.4.

4.2.6. Development of regression model equation

The application of RSM gives an empirical relationship between the response function and the independent variables. The mathematical model equation relationships that correlates the response (conversion of double bond and selectivity) to the epoxidation reaction process variables in terms of actual value after excluding the insignificant terms was given below. The predicted model for percentage of degree of conversion and selectivity in terms of the coded factors is given in equation 4.2. and 4.3 respectively.

$$conversion = -4274.63878 + 6.39743 \times A + 32.96345 \times C - 0.31100 \times A \times C - 0.031613 \times A^2 - 3125.51020 \times B^2 \ldots \ldots \ldots \ldots 4.2$$

$$\text{selectivity} = -3779.77696 + 6.95094 \times \text{A} + 6133.89269 \times \text{B} + 57.10690 \times \text{C} - 0.67017 \times \text{A} \times \text{C} + 1.40500 \times \text{A} \times \text{B} - 0.048377 \times A^2 - 2700.98639 \times \text{B}^2 - 2.54731 \times \text{C}^2 \ldots \ldots \ldots \ldots 4.3$$

where A = reaction temperature

B = molar ratio of hydrogen per oxide to oil

C = reaction time

4.2.7. Optimization of process variables for epoxidation reaction

In this study optimization of the process variables was used to obtain the highest percentage of conversion and selectivity of epoxidized *p. falcatus* oil using developed model regression. The goal of these optimization was to maximize economic benefit or increasing epoxidized oil yield by increasing the selectivity and by minimizing process cost. Based on the above analysis in order to obtain the best maximum percentage of conversion and selectivity, the predicted combination of parameters was as follows: temperature of 63.1 °C, molar ratio of hydrogen peroxide to oil 1.4:1 and reaction time of 4.02 hrs. and all these variables are in range. Under these conditions, the model predicted of conversion and selectivity are 70.92 and 90.07 % respectively with a desirability value of 1.00. The more closely the response approaches the ideal intervals or ideal values, the closer the desirability is to 1.00.

The model validations have been determined as optimum levels of the process parameters to achieve conversion and selectivity of 70.92 and 90.0667 % respectively. Optimum conditions predicted by the model using desirability ramp and triplicate experiments were conducted using the optimized epoxidation process conditions and the results are closely related with the data obtained from optimization analysis using desirability functions. Therefore, the numerical optimization can be taken as optimal value because the predicted value is close enough with actual value since desirability is 1.00.

In general speaking, the experiment conducted on the production of epoxidation of *podocarpus falcatus* seed oil shows that complete succession for synthesis epoxidation of *p. falcatus* oil from *podocarpus falcatus* oil can definitely be achieved and optimum percentage of conversion of double bond of oil to epoxidized oil and its selectivity can be obtained from the synthesis of *p. falcatu*s oil using homogeneous catalyst *i.e.* sulphuric acid via epoxidation reaction.

4.3. Characterization of epoxidized *p. falcatus* oil

The epoxidized *p. falcatus* oil characterized by iodine value, oxygen oxirane content, viscosity FT-IR test and ^{1}HNMR analysis. From these result of iodine value and oxygen oxirane content attached at appendix C. since their values are direct relation with calculation of conversion and

selectivity of the product epoxy oil which are discussed in statistical analysis of the epoxidation formation in section 4.4.

4.3.1. Viscosity of epoxy of *podocarpus falcatus* oil

Viscosity of the epoxy oil of *p. falcatus* was determined according to section 3.5.1 and its value was 240 m.Pa.s. at 20^{O}C. The values is lower than viscosity of epoxidized soya been oil (430 m.Pa.s.) and linseed oil (800 m.Pa.s.) both at 25 °C temperature(Wang & Schuman, 2013). In this case the viscosity is used to determine the followability and saturation level of epoxy oil. In general speaking, the viscosity of the oil is always very lower than epoxidized one. Which means that it very saturated and more viscous. In this study when we compared to the two oil the epoxidized one higher than raw oil of *p. falcatus* seed. Physically, this indicated that the raw oil of *podocarpus falcatus* oil more unsaturated than the epoxidized oil. Hence, the conversion of the double bond p. falcatus fatty acid related with iodine value of the oil, the less iodine value the more viscous of the oil and vice versa. Therefore, the less iodine value showed that the oil was undergone the epoxidation reaction and the epoxidized *p. falcatus* oil was formed.

4.3.2. FTIR Spectrum analysis of epoxidized *p. falcatus* oil.

The synthesis and characterization of epoxidized *p. falcatus* oil was analyzed in this work with special focus on the characterization of the desired product at optimum condition by FTIR (Fourier transform infrared spectrometry) spectrum analysis. The analysis of the *p. falcatus* oil and epoxidized *p. falcatus* oil was carried out with analytical grade Potassium Bromide pellets using the transmission mode with the range of 4000 to 400 cm^{-1} wave number. All the spectra were recorded with 4 cm^{-1} resolutions.

Epoxidized *p. falcatus* oil was characterized by FTIR shown in Fig.4.9, in order to monitor the disappearance of double bonds and formation of epoxy groups comparing with raw *p. falcatus* oil shown in figure 4.10. For *p. falcatus* oil the characteristic peaks at 3009, 1653 and 721 - 726 cm^{-1} were attributed to the stretching vibration of the double bonds: **C=C-H**, **C=C**, **cis-CH=CH**, respectively. After epoxidation reaction was carried out the total diminishing of **C=C-H** stretching peaks at 3009 cm^{-1} occurred which indicated that almost complete consuming of double bonds band at 3009 cm^{-1} or almost all the **C=C-H** had taken part in the epoxidation reaction. Also, there was decrease in the intensity of the other important unsaturated bond signals in comparison with

the unreacted oil, giving reliable support of its chemical transformation to an oxirane ring (Meshram et al., 2011).

In addition to this, there were some decreased value occurred bands at 1653 cm^{-1} of **-C=C-** double bond, this indicates that not all **C=C** bound bonds are consumed after epoxidation reaction. For this reason, no 100 % was converted in to epoxidized podocarpus oil and the only 71.9 % was converted based on the iodine value.

The presence of new peaks in the FTIR spectrum of Epoxidized podocarpus oil at 1237- 1251 cm^{-1} and 823.2 cm^{-1}, attributed to the epoxy group, confirmed the success of the epoxidation reaction of podocarpus oil. According to (Mohamed et al., 2014) this bands were useful in the formation of **C-O-C** epoxy functional groups at 1210-1320 cm^{-1} absorption band region. The other new peak at the 3388 cm^{-1} was attributed to the hydroxyl functional group, derived from the epoxy functional group via partial epoxy ring opening reaction. Therefore, The intensity of this band indicates the extent of hydrolysis of epoxidized podocarpus oil .The epoxy ring opening reaction could occur either by acid catalysis in the presence of water associated with aqueous solution of H_2O_2 used (N B Samarth et al., 2016).

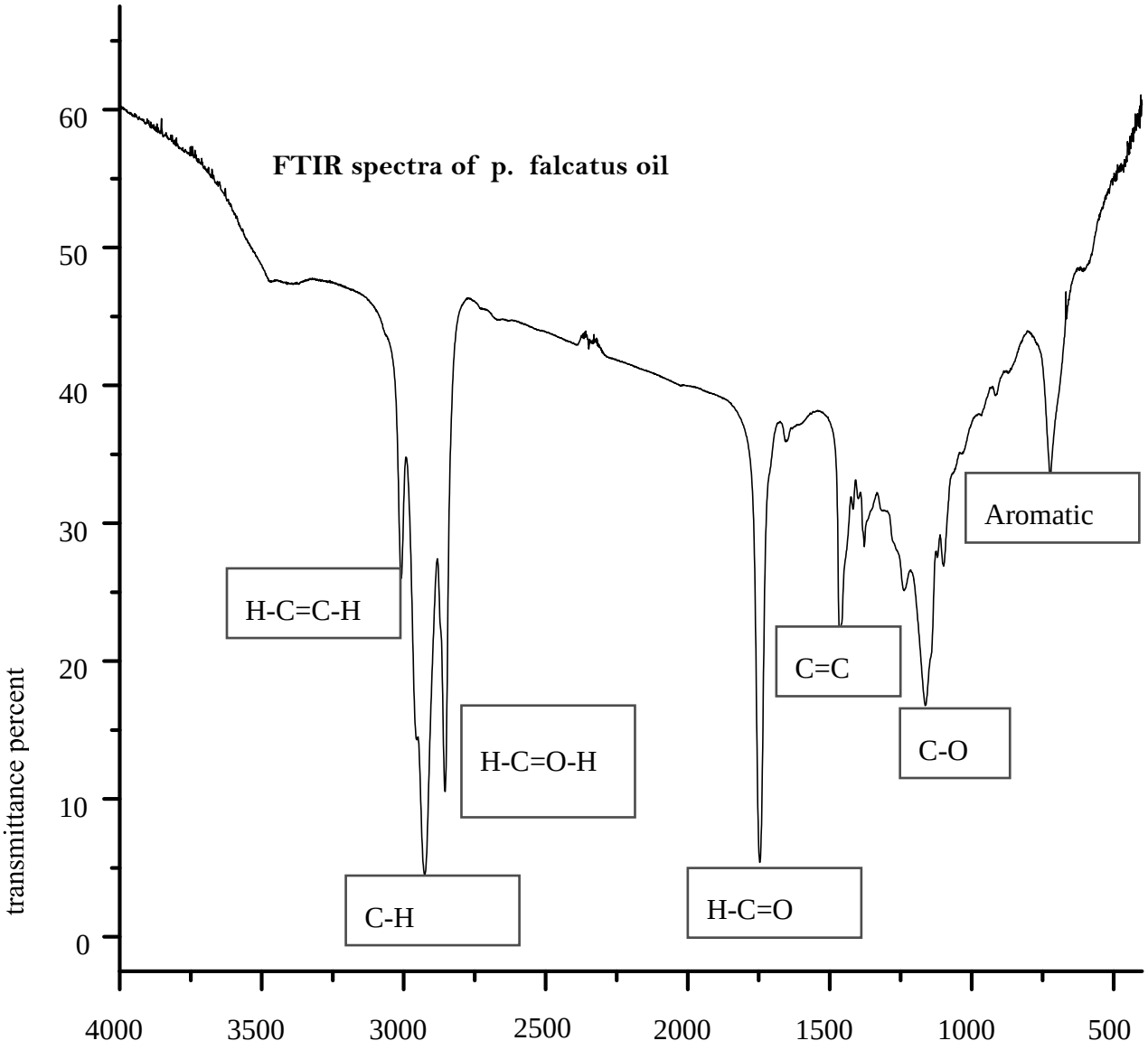

Figure 4.8. FTIR spectroscopy of *p. falcatus* oil

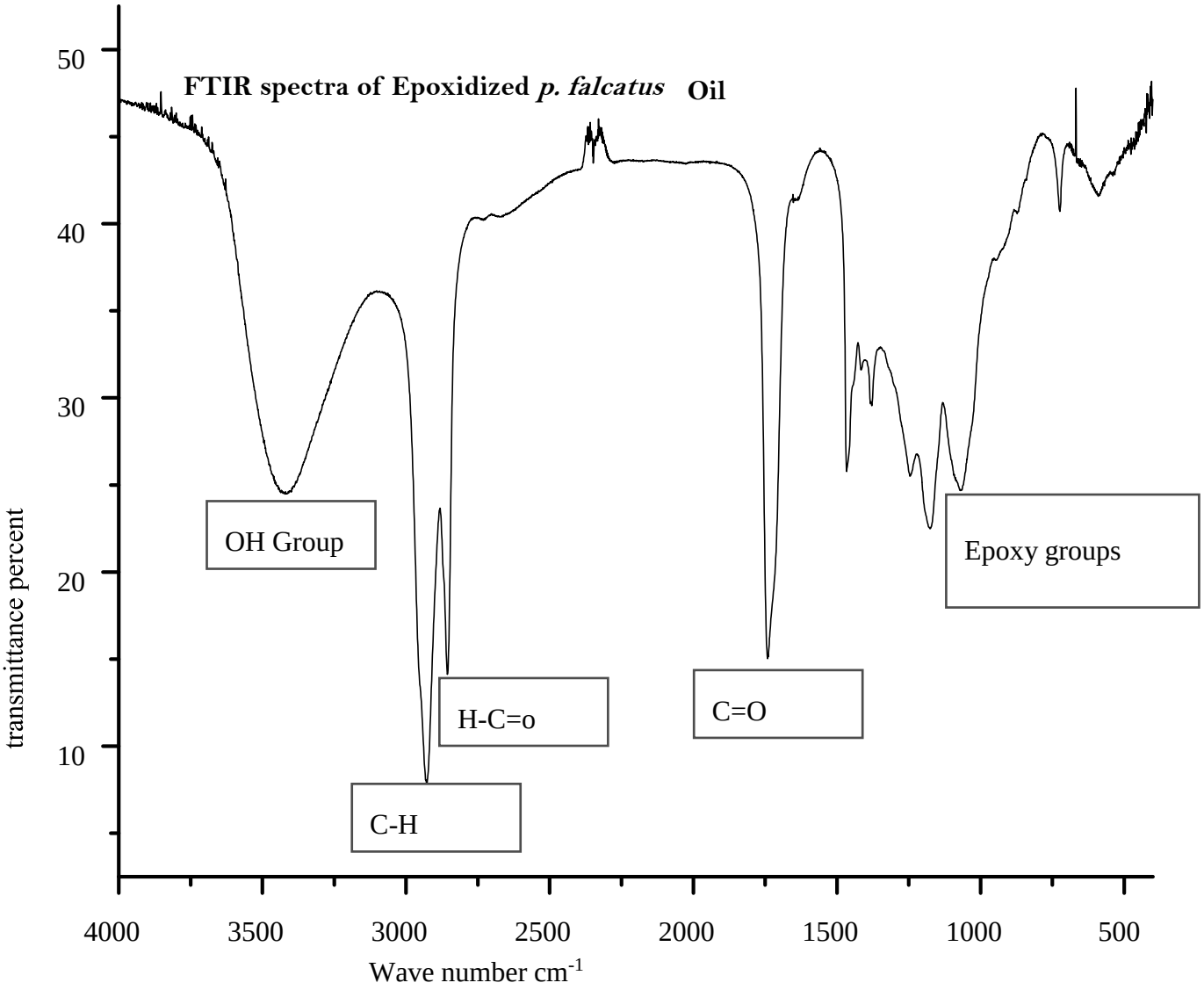

Figure 4.9. FTIR spectroscopy of epoxidized *p. falcatus* oil

4.3.3. ^{1}H-NMR spectrum analysis of epoxidized *p. falcatus* oil.

Hydrogen Nuclear magnetic resonance (^{1}HNMR) has been applied to the study of epoxides in both raw oil and epoxidized podocarpus oils. In this study it is used to tell double bond of the oil disappeared and new signal peak of epoxy ring appeared during epoxidation reaction process. The characterization of the epoxidized *p. falcatus* oil and epoxidized *p. falcatus* oil was carried out using ^{1}H-NMR spectroscopy shown in figure 4.10.

As it shown from figure 4.10 of ^{1}HNMR of podocarpus oil at signal peak between δ 5.48 and 5.23 ppm corresponding the occurrence to double bond (olefin protons) peak in *podocarpus falcatus*

seed oil. This indicated there was backbone of glycerol carbon which is **HC=CH (**methyl proton signals**)** which have great role for production epoxy oil by addition of hydrogen peroxide in order to convert this double in to epoxy functional group of three cyclic ring oxirane. In figure 4.10 of ^{1}HNMR of epoxidized *podocarpus falcatus* oil which is after epoxidation reaction some decreased signal peaks and new signal peak of proton appeared. Thus, from this figure We observe that there is a decrease of the peak area at δ 5.48-5.23 ppm of olefin compound (double bond) and it shows the disappearance **HC=CH** occurred due to addition of hydrogen peroxide to this double and the conversion of this double bond to epoxidized was indicated. In addition to this since all signal peak between 5.48 and 5.23 is totally not disappeared it agrees that in this study 71.9 % conversion of this double was achieved based iodine value.

The new signal peak appeared in epoxidized *p. falcatus* oil were between δ 2.9 to 3.1 ppm. Those peaks assigned the formation of epoxy peaks in epoxidized *p. falcatus* oil. The proton signal centered at δ 3.00 was evident for the presence of epoxy protons. This was further substantiated by the disappearance of the olefinic proton signals in the region between δ 5.48 -5.23. The broad intense signal observed in the region δ 1.26-1.63 is due to the presence of many methylene groups. Furthermore, the proton signal at δ 0.89 was characteristics of terminal methyl groups. The methylene hydrogens alpha to carbonyl groups **(-CH2-C(O)-O-)** appear at 2.35 ppm. The region of δ 4.1-4.4 ppm peak occurred in both *p. falcatus* oil and epoxidized *p. falcatus* oil as a q due to the coupling of adjacent two protons of the **CH_2** group and cis coupling of the Proton attached to next sp^2 hybridized carbon atom due to the presence of secondary and primary glyceral (**-CH-CH2-O**-) proton at δ 5.10 -5.20 and 4.10-4.30, respectively.

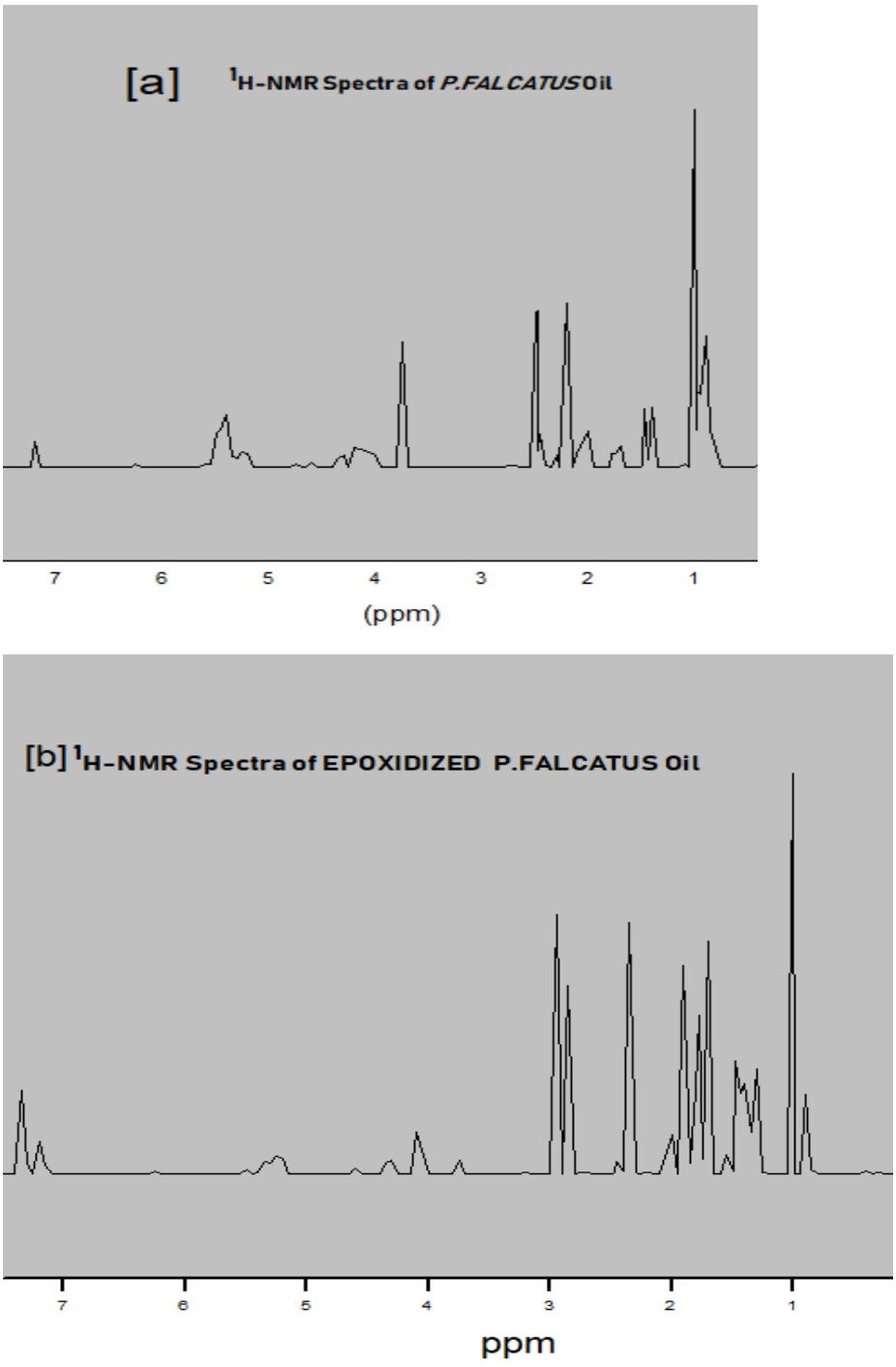

Figure 4.10. [1]HNMR spectra analysis for (a) *p. falcatus* oil (b) Epoxidized *p. falcatus* oil

4.4. Selecting the Kinetic model for epoxidation of podocarpus falcatus oil

In this study of epoxidation reaction there was only two steps involved: the first one is formation of peroxyformic acid, and the other is reaction of peroxyformic acid with the unsaturated double

bond of the *p. falcatus* oil since the reaction involved was homogeneous catalytic reaction. In the case of heterogeneous catalytic reactions are often broken down into a number of steps including diffusion steps and elementary reaction steps. From these two steps reactions the following assumptions were taken.

- ✓ the first step was considered rate determining, since the concentration of perfomic acid and H_2O_2 were assumed constant throughout the reaction.
- ✓ The kinetics model study was based on conversional of double bond from iodine value.

(i) Formation of a peroxy acid

$$CH_3COOH + H_2O_2 \underset{K2}{\rightleftarrows} CH_3COOOH + H_2O \quad \text{……..……..……..(1)}$$

(ii) formation of Epoxidized oil

$$CH_3COOOH + R_1\text{-}C{=}C\text{-}R_2 \xrightarrow{K3} R_1\text{-}CH\ (OH)\ CH\ (OCOCH_3)\text{-}R_2 + CH_3COOH \quad \text{……..(2)}$$

In order to determine the order of the reaction let us drive the general equation for epoxidation reaction for the two steps.

$$\frac{d[DB]}{dt} = K_3\,[DB]_1^n\,[FAA]_2^n \quad \text{……..3}$$

Where, [DB] = Molar Concentration of Double Bond

[FAA] = Molar Concentration of Performic Acid

K_3 = Reaction rate constant

1^n = Reaction order with respect to double bonds concentration.

2^n = Reaction order with respect to Performic Acid concentration.

Since rate determining was lowest rate steps the concentration of performic is remain constant because the first reaction steps slower than the second.

Therefore, $K_3 \times [FAA]_2^n$ = constant = K

$$\frac{d[DB]}{dt} = k[DB]^n \quad \text{……4}$$

$$[DB] = [DB]_O(1\text{-}X) \quad \text{……5}$$

Substituting equation (5) into equation (4)

$\frac{d[DB]_o\,(1-X))^n}{dt}$= k($[DB]_O$(1-X))^n …….6

$\frac{dX}{dt}$ = k (1-X)^n …….. 7

Then integrating the equation $\int \frac{dX}{(1-X)}$=kdt

By guessing the pseudo first order, second order and so on we can obtain best fitting the equation for epoxidation reaction.

From experimental data by varying the time reaction at constant reaction time and molar ratio of hydrogen peroxide to oil the experimental conversion was determined and result was given in the following table.

Table 4.7. Data for conversion versus time at constant temperature and Hydrogen peroxide to oil ratio for pseudo first order reaction

Conversion	Time	Reaction temperature	Hydrogen peroxide to oil ratio
0.522	2	60	1.4
0.605	3	60	1.4
0.662	4.5	60	1.4
0.692	5	60	1.4
0.723	6	60	1.4

Cases for selecting best data fitting for equation of $\int \frac{dX}{(1-X)}$=kdt

Case 1. First order reaction

Integrating the equation (7) and Integration at t=0 → X=0 and t=t → X=X become

$\ln(\frac{1}{1-x})$ = Kt …….8

By generating the data and drawing the graph for $\ln(\frac{1}{1-x})$ versus time simply we can determine the slope of the graph if it make straight line.

Table 4.8. Data for conversion versus time for first order reaction

Time	**X**	$(\frac{\mathbf{1}}{\mathbf{1-x}})$	$\mathbf{ln}(\frac{\mathbf{1}}{\mathbf{1-x}})$
2	0.522	2.096	0.74
3	0.605	2.53	0.93
4	0.662	2.96	1.0804
5	0.692	3.247	1.177
6	0.723	3.61	1.284

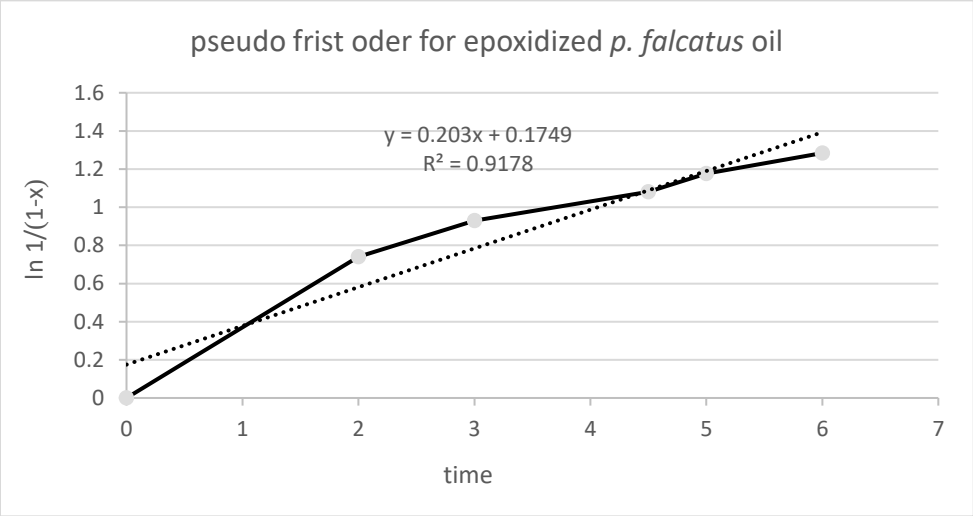

Figure 4.11. kinetics model for pseudo first order epoxidized reaction

From the figure 4.14 we conclude that the first order reaction is not accepted since the graph of $\ln(\frac{1}{1-x})$ versus time is not straight line. Therefore, in this study the kinetic model for epoxidized *p. falcatus* oil was not first order based on conversion relative to iodine value.

Case 2. Pseudo Second order reaction

Integrating the equation (7) become

Integration at t=0 → X=0 and t=t → X=X

$\frac{X}{1-X}$= Kt ……9

By generating the data and drawing the graph for$\frac{X}{1-X}$ versus time simply we can determine the slope of the graph if it make straight line.

Table 4.9. Data conversion versus time at constant temperature and Hydrogen peroxide to oil ratio for pseudo second order reaction

Time	**X**	$(\frac{X}{1-x})$
2	0.522	1.09
3	0.605	1.503
4	0.662	2.02
5	0.692	2.242
6	0.723	2.62

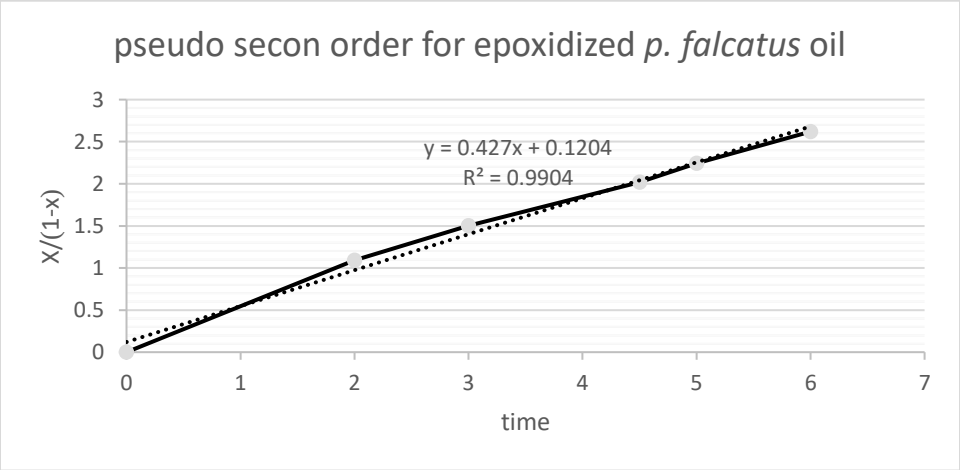

Figure 4.12. kinetics model for pseudo second order epoxidized reaction

From the figure 4.15 we conclude that the second order reaction is accepted since the graph of $\frac{X}{1-X}$ versus time is straight line and also the R^2 value was 0.99 almost close to 1. The kinetic model for epoxidized *p. falcatus* oil is second order based on conversion relative to iodine value. Generally, by comparing the R^2 value of pseudo first order and second order of the epoxidized oil for the second order R^2 value is closer to one than for first order. Therefore, the pseudo second order was represented the rate equation for kinetic study of epoxidation of *p. falcatus oil.*

Therefore, we can determine the k-value and kinetic model. The slope of the graph of $\frac{X}{1-X}$ vs t is the k- value of the reaction order.

The slope of the graph is equal to 0.3825. Therefore, the value of k = 0.3825 $\frac{L}{mol.\text{hr}}$.

Then k= 0.3825 L/mol.hr.= 1.0625×10^{-4} $\frac{L}{mol.\text{sec}}$. then the rate equation will be;

$$\mathbf{-r_{DB} = d[DB]/dt = 1.0625\times10^{-4}\,[DB]^2\,\frac{L}{mol.sec}}$$

Finally, the rate equation for epoxidized *p. falcatus oil* was pseudo second order in concentration of double bond of the oil.

CHAPTER FIVE
CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this research epoxidized vegetable oil was produced from podocarpus falcatus oil by using epoxidation reaction. The reaction was carried out with perfomic acid in the presence of 98 % of concentrated sulphuric acid as homogeneous catalyst acid. The effect of process variables such reaction temperature, molar ratio of hydrogen peroxide to double bond of oil and reaction time on conversion of the carbon double bond of oil to epoxidized p. falcatus oil based on iodine value and its selectivity was investigated.

This study examined based on analysis experimental results showed that, the two process variables namely reaction temperature and time are exhibited significant interaction effect on the percentage of conversion and selectivity. This shows that the capability of the design of experimental analysis in successfully capturing these effects and investigated their optimum condition. A reaction temperature of 63 °C, molar ratio of hydrogen per oxide to oil 1.4:1 and reaction time of 4 hours an optimal value of 71.9% percentage of conversion and 90.98 % of selectivity.

The FTIR analysis was found to be useful in confirming the disappearance of –C=C- and formation of C-O-C epoxy functional groups at 1237-1251 cm^{-1} and 823.2 cm^{-1}absorption band region. The formation of hydroxyl compound which characterized the epoxidized *p. falcatus* oil was further confirmed by using the FTIR test. The result showed that the absorption band of hydroxyl group was detected at the region 3388 cm^{-1}. ^{1}HNMR was powerful tool and support the successful synthesis of epoxidation reaction for evidence on investigation of the number of double bonds (unsaturation) which was used to correlate it with the epoxy number and epoxidation percentage of the oils.

The development of reaction kinetics based on conversion of double bond of the oil with time reaction based on iodine value test at constant reaction temperature and molar ratio of hydrogen peroxide to oil was investigated. In this study the kinetics of epoxidation reaction favor's both the two consecutive reactions of epoxidation (i.e., reaction of hydrogen peroxide and formic acid in the presence of acid catalyst to form per-formic acid and reaction of per-formic acid with oil to

produce epoxidized oils). In this case the final rate equation for epoxidized *p. falcatus* oil is second order with respective to concentration of double bond of the oil.

In general concluding, economically efficient epoxidized vegetable oil obtained from p. falcatus oil can be widely used in present the possibility for the production of oil derivatives through a cleaner technology in oleo chemical industry applications in such as plasticizers, lubricants, paint formulations, polymers etc.

5.2. Recommendation

Producing epoxidized vegetable oil from renewable resources is becoming an important issue for the whole world. Therefore, the work needs to be continued for scaling up of epoxy oil production from plant of p. *falcatus*. This research would like to suggest further investigations to the following recommendation;

- Further researches have to be carried out to increase the conversion and selectivity of epoxidized *p. falcatus* oil from *p. falcatus* seed by using enzymatic epoxidation which are capable of converting vegetable oil into epoxy oil.
- Further researches have to be carried out by using heterogeneous catalyst in order to avoid the environmental pollution rather homogeneous.
- Further study on improvement of the epoxidation process parameters catalyst loading, molar ratio of formic acid to oil and speed of agitator on percentage of conversion and selectivity is also suggested.
- The government should involve in epoxy production from non-edible oil plant *i.e. podocarpus falcatus* seed is not competitive for edible because most the epoxidized vegetable oil plants are from edible oil.
- An economic feasibility analysis of the overall conversion process is necessary for the purpose of commercialization.

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APPENDICES

Appendix-A composition *podocarpus falcatus* oil

Table A-1 *P. falcatus* oil characteristics

Property of Oil	**Value**
Iodine value, gI2 /100g oil	121 – 130
Saponification value, mg KOH/g oil	113.4 – 221.44
Acid value	2.18 – 2.82
Free fatty acid	1.28 – 2.54
Smoking point	14.78 – 17.38
Fire point	3.9 – 4.12
Flash point	3.61– 3.7
Refractive Index at 25^0C	1.4740 – 1.4860

(Source: (Daniel 2014)

Table A-2 Fatty acid composition of the major fatty oils and fats

Sr. No.	Name of the Oil	Density	S. V	I. V	%Fatty Acid Composition					
					C14	C16	C18	C18:1	C18:2	C18:3
1	Castor	0.945-0.965	177-187	83-86	……	2	1	7	5	…….
2	Coconut	0.917-0.919	251-263	7.5-10.5	13.0-19.0	8.0-11.0	1.0-3.0	5.0-8.0	0-1.0	……
3	Groundnut	0.910-0.915	188-195	84-100	…….	6.0-9.0	3.0-6.0	52.0-60.0	13.0-27.0	……..
4	Mustard	0.906-0.910	169-176	98-110	…….	1.5	0.4	22	14.2	6.8
5	Soybean	0.916-0.922	189-195	128-143	tr.0.5	7.0-11.0	2.0-6.0	22.0-34.0	43.0-56.0	5.0-11.0
6	Sunflower	0.915-0.919	188-194	125-140	……	3.0-6.0	1.0-3.0	14.0-35.0	44.0-75.0	……
7	Cottonseed	0.915-0.926	191-196	103	0.4	20	2	35	42	……
8	Palm	0.921-0.925	196-205	48-58	0.5-2.0	32.0-45.0	2.0-7.0	38.0-52.0	5.0-11.0	……
9	Linseed	0.931-0.938	189-196	170-180	……	4.0-7.0	2.0-5.0	12.0-34.0	17.0-24.0	35.0-60.0

ρ: specific gravity, **I. V.:** Iodine value, **S.V.:** Saponification value,**:** Myristic acid ,

C_{16} : Palmitic acid, **C_{18}:** Stearic acid, **$C_{18:1}$:** Oleic acid , **$C_{18:2}$:** Linoleic acid ,

$C_{18:3}$: linolenic acid ,_ (Source: (Gunstone 2004)

Appendix B: Infrared spectroscopy correlation table

Table B-1. Infrared Spectroscopy Correlation

Simplified Infrared Correlation Chart			
	Type of Vibration	Frequency (cm^{-1})	Intensity
C-H	Alkanes (stretch)	3000-2850	s
	-CH3 (bend)	1450 and 1375	m
	-CH2- (bend)	1465	m
	Alkenes (stretch)	3100-3000	m
	(out-of-plane bend)	1000-650	s
	Aromatics (stretch)	3150-3050	s
	(out-of-plane bend)	900-690	s
	Alkyne (stretch)	~3300	s
	Aldehyde	2900-2800	w
		2800-2700	w
C-C	Alkane not interpretatively useful		
C=C	Alkene	1680-1600	m
	Aromatic	1600 and 1475	-m
C≡C	Alkyne	2250-2100	-m
C=O	Aldehyde	1740-1720	- s
	Ketone	1725-1705	s
	Carboxylic Acid	1725-1700	s

	Ester	1750-1730	s
	Amide	1670-1640	s
	Anhydride	1810 and 1760	s
	Acid Chloride	1800	s
C-O	Alcohols, Ethers, Esters, Carboxylic Acids, Anhydrides	1300-1000	s
O-H	Alcohols, Phenols		
	Free	3650-3600	m
	H-bonded	3500-3200	m
	Carboxylic Acids	3400-2400	m
N-H	Primary and Secondary Amines and Amides		
	(stretch)	3500-3100	m
	(bend)	1640-1550	M
C-N	Amines	1350-1000	m-
C=N	Imines and Oximes	1690-1640	-w
C≡N	Nitriles	2260-2240	¯m
X=C=Y	Allenes, Ketenes, Isocyanates, Isothiocyanates	2270-1950	M
N=O	Nitro (R-NO2)	1550 and 1350	¯s
S-H	Mercaptans	2550	w
S=O	Sulfoxides	1050	s

(Source: http://en.wikipedia.org/wiki/Infrared_spectroscopy_correlation_table**)**

Appendix C: Experimental result

Table C-1. Moisture content determination for *Podocarpus falcatus* seed

	Samples of	Weight				
Run	W_2	W_3	W_2-W_3	W_2-W_1	Moisture Content %	Average moisture content
1	53.641	53.501	0.14	2.241	6.247	
2	53.753	53.61	0.143	2.353	6.077	
3	53.562	53.420	0.142	2.162	6.568	**6.02**
4	53.425	53.312	0.113	2.025	5.58	
5	53.385	53.271	0.111	1.985	5.592	

Table C-2 Moisture content of extracted oil

	Samples of	Weight				
Run	W_2	W_3	W_2-W_3	W_2-W_1	Moisture Content %	Average moisture content
1	54.965	54.904	0.061	2.665	2.25	
2	55.475	55.412	0.063	3.175	1.99	
3	55.213	55.146	0.067	2.913	2.3	**2.2**
4	55.71	55.635	0.075	3.41	2.2	

Table C-3 Free Fatty Acid Value of *p, falcatus* oil

Run	**Titration , ml**	**Free fatty Value**	**Color Change**
1	0.75	1.67	Gray to P ink
2	0.72	1.61	Gray to P ink
3	0.71	1.57	Gray to P ink
4	0.65	1.44	>>
5	0.68	1.51	>>
6	0.62	1.49	>>
Average value	**1.5483**		

Table C-4 Blank titration for Iodine value of *p. falcatus* oil

Run	**Titration Volume,**	**Colour Change**
Blank ml		
1	36.8	Blue to colorless
2	36.2	Blue to colorless
3	35.3	Blue to colorless
Average value	**36.1**	

Table C-5**.** Titration for iodine value of *p. falcatus* oil

Run	Mass of the sample	Titrant volume ml	Iodine value 100g/oil	Color change
1	0.219	14.8	111.255	Blue to pale yellow
2	0.249	15.	108.55	>>
3	0.286	13.2	101.735	>>
Average value			**107.18**	>>

Table C-6 Experimental processes conditions for epoxidized oil production

Run	Reaction temperature (^{o}C)	Hydrogen peroxide(g)	Amount of Catalyst(g)	Reaction Time(hrs)	Speed (rpm)	Formic acid(g)
1	65	1.85	0.276	4.5	850	1.14
2	85	1.85	0.276	4.5	850	1.14
3	65	2.85	0.276	4.5	850	1.14
4	85	2.85	0.276	4.5	850	1.14
5	65	2.35	0.276	3	850	1.14
6	85	2.35	0.276	3	850	1.14
7	65	2.35	0.276	6	850	1.14
8	85	2.35	0.276	6	850	1.14

9	75	1.85	0.276	3	850	1.14
10	75	2.85	0.276	3	850	1.14
11	75	1.85	0.276	6	850	1.14
12	75	2.85	0.276	6	850	1.14
13	75	2.35	0.276	4.5	850	1.14
14	75	2.35	0.276	4.5	850	1.14
15	75	2.35	0.276	4.5	850	1.14

Table C-7 Iodine value of the epoxidized oil

Run	Mass(g)	Titration volume(ml)	Iodine Value
Blank	……..	36.1	
1	0.262	27.9	39.66
2	0.325	25.5	41.33
3	0.581	19.9	35.1
4	0.309	26.6	38.51
5	0.405	22.3	43.1
6	0.653	31.7	33.8
7	0.248	30.2	30.12
8	0.265	27.6	40.83

9	0.242	29	37.6
10	0.211	29.3	40.2
11	0.445	23.9	34.705
12	0.365	25.1	38.2
13	0.486	21	31.2
14	0.326	28	31.2
15	0.36	27.3	31.1

Table c-8. Oxirane oxygen containing value of epoxidized

Run	Mass(g)	Titration volume(ml)	Oxirane oxygen content
1	0.446	9.0	3.22
2	0.4635	8.5	2.92
3	0.454	10.3	3.74
4	0.4288	9.1	3.41
5	0.445	7.9	2.83
6	0.465	11	3.8
7	0.458	11.9	4.15
8	0.474	7.5	2.54
9	0.4238	8.5	3.21

10	0.4133	8.6	3.35
11	0.475	9.7	3.29
12	0.466	10.0	3.44
13	0.4858	12.2	4.04
14	0.418	10.5	4.04
15	0.445	11.5	4.05

Appendix D. calculation part

Ratio of input material for epoxidation reaction of *p. falcatus* oil

Knowing the necessarily material added into in the epoxidation reaction which is used to produce epoxidized *p. falcatus* oil is important. Therefore, the amount of hydrogen per oxide, formic acid and sulphuric was calculated as follows using the process parameters. For all reaction steps amount of oil added was 13.8 gram. The determined molecular mass of podocarpus oil was 279.2994g/mole.

Then,

$$\text{mole of oil (n)} = \frac{\text{mass of oil}}{\text{molecular mass}} = \frac{13.8\ g}{\frac{279.2994 g}{mol}} = 0.049 mole$$

i. **The amount of hydrogen peroxide required when the molar ratio of hydrogen peroxide to oil ratio 1.1:1**

$$1.1 = \frac{\text{n Hydrogen peroxide}}{\text{n oil}} = \frac{\frac{mass\ of\ hydrogen\ peroxide}{molecular\ mass\ of\ hydrogen\ peroxide}}{\frac{mass\ of\ oil}{molecular\ mass}}$$

$$1.1 = \frac{m\ H_2O_2}{\frac{13.8\ g}{279.2994\ g/mol}}$$

So, m of H_2O_2 = 1.844 gram

ii. **The amount of formic acid required when the molar ratio of formic acid to oil ratio 0.5:1;**

$$0.5 = \frac{n\ formic\ acid}{n\ oil}$$

$$0.5 = \frac{m\ CH3OOH}{\frac{13.8\ g}{279.2994\ g/mol}}$$

So, mass of CH_3OOH=1.14 gram

The mass of sulphuric acid during epoxidation reaction was 2 % of podocarpus falcatus oil added. But the different required amount of hydrogen per oxide is calculated for all experiments. The tabulated result for different processes parameter was given in appendix C

Purification of the Crude Oil

The total amount of crude *p. falcatus* oil obtained from extraction is 0.6681 liter

out of 0.991kg of *p. falcatus* seed kernel.

Degumming

It is the removal of phosphatides, gums and other complex compounds the extracted crude

Jatropha oil. Hence, based on the method discussed in previous chapter; 3% of distilled water by volume is required for degumming the crude *p. falcatus* oil.

Amount of distilled water required = amount of *p. falcatus* oil×3%

=0.6681liter×0.03

=0.020liter or 20ml

Physio- Chemical Properties of Purified Oil

Saponification Value

The saponification number was determined by using titration. I prepared the solution with the required concentration. Since we don't know the exact concentration, we have to standardize the solution. Hence, primary and secondary standardization was used.

Mass of KOH=N × equivalent weight × Volume of solution in liter

=0.5mol/lit × 56.11g/mol × 1lit

=28.055gm

Mass of HCL= N×equivalent weight×Volume of solution in liter

=0.5×36.5×1

=18.25gm

V_{HCL}=m/ρ=18.25/1.16 =15.73ml

0.53 gm of sodium carbonate was dilute in 100ml distilled water was used as a primary standard with a known concentration which is 0.1 normality.

25ml solution of sodium carbonate was taken and titrated with HCL solution to determine the concentration using 3 drops of methyl orange as indicator. The Volume was noted as the end point appears.

$V_1N_1=V_2N_2$…… Equation. c.1

$N_2= (V_1N_1)/V_2 =25\times0.1/5.4 =0.46$

Another experiment was done to validate the concentration;

$N_2=25\times0.1/5.5=0.4545$

$N_3=25\times0.1/5.4 =0.46$

Then the average concentration becomes;

NHCL=0.46

Molecular weight of *p. falcatus* oil

Table D1: Molecular Weight of Fatty Acids

Fatty Acids	Elementary Formula	Constitutional Formula	Corresponding Fatty acid composition (%)	Molecular weight
Linoleic	$C_{18}H_{32}O_2$	$CH_3(CH_2)_{12}$	31.48	280
Oleic	$C_{16}H_{34}O_2$	$CH_3(CH_2)_{14}$	53.49	282
Linolenic	$C_{18}H_{30}O_2$	$CH_3(CH_2)1_0$	3.87	278
Palmitic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{14}$	6.24	284
Stearic	$C_{16}H_{36}O$	$CH_3(CH_2)_{16}$	4.93	240

Molecular mass of Triglyceride = Molecular mass of Oleic Acid + Molecular mass Linoleic Acid + Molecular mass Linolenic Acid + Molecular mass + Molecular mass Palmitic Acid + Molecular mass Stearic Acid

Molecular mass of fatty acid = (280 × 0.3148) + (282 × 0.5349) + (278 × 0.0387) + (284×0.0624) + (240×0.0493) = 279.2994g/mole

Molecular mass of Triglyceride = 3* Molecular mass of fatty acid

= 837.898 g/mole

Appendix –E. The main experimental photo

p. falcatus seed kernel grinded kernel Soxhletor extraction

Extracted *p. falcatus* oil epoxidation process epoxidized *p. falcatus* oils

Figure-E-1. Experimental photos

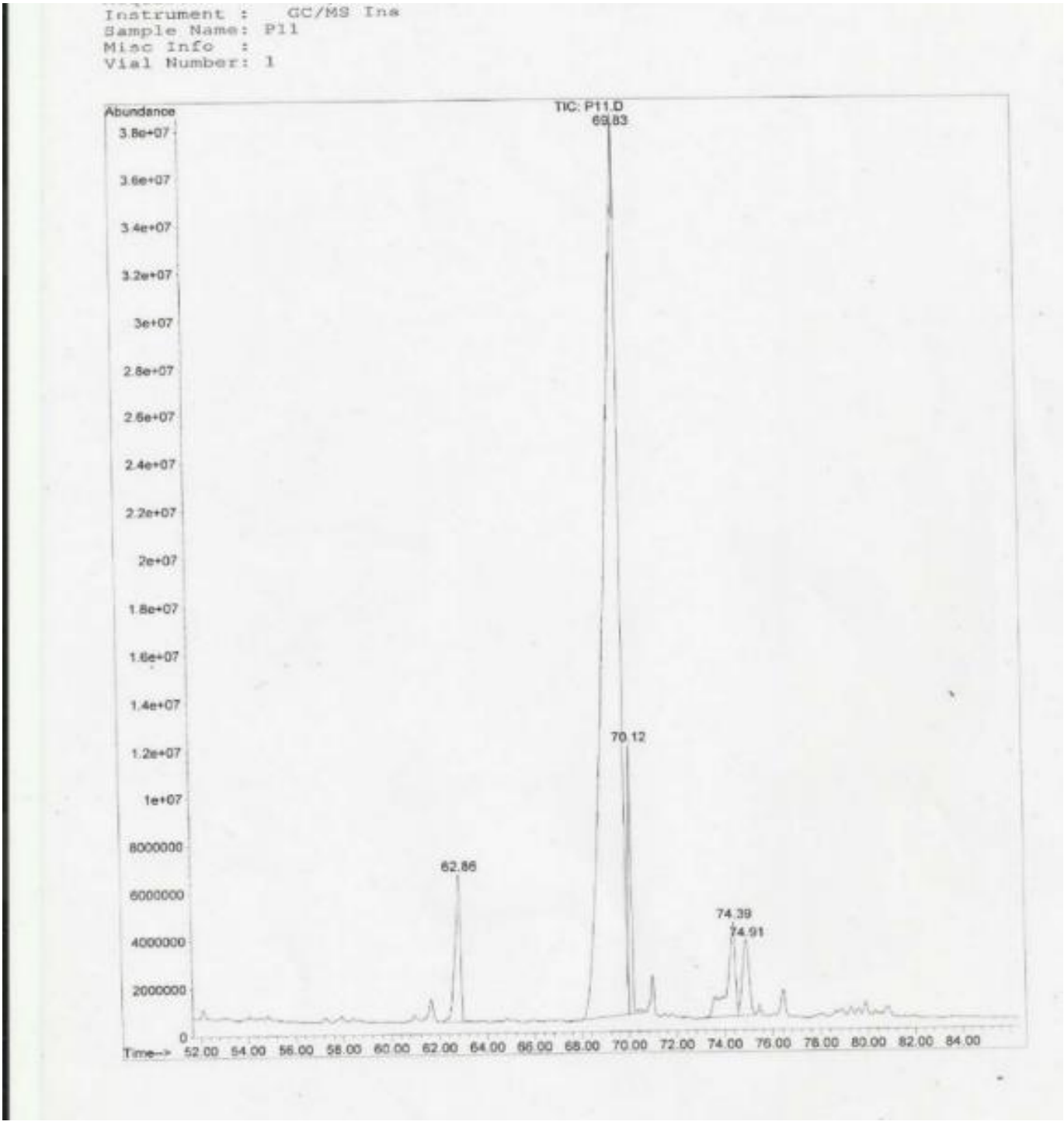

Figure E-2. GC/MS analysis of *p. falcatus* oil