ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

Production of Epoxidized Zigba (Podo Carpus Falcatus) Seed Oil Through Carbon Based Sulfonated Catalyst

By Ysacor Mengistu

A Thesis Submitted to The School of Chemical and Bio Engineering Presented In Fulfilment of The Requirement for the Degree of Master of Science in Chemical Engineering (Process Engineering)

Addis Ababa University

Addis Ababa, Ethiopia

June 2019

DECLARATION

I declare that this thesis entitled “Production of Epoxidized Zigba (Podo Carpus Falcatus) Seed Oil Through Carbon Based Sulfonated 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 Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. The work was under the guidance of Dr.Anteneh Marelign (Assistant Professor) Instructor in Addis Ababa University, School of Chemical and Bio Engineering.

Name of the student: Ysacor Mengistu Signature _____

Date of submission: July, 2019

Place: Addis Ababa

This thesis has been submitted for examination with my approval as a university advisor.

Advisor Name: Dr.Anteneh Marelign

Signature:_____

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

ADDIS ABABA

THESIS APPROVAL SHEET

Student:

Ysacor Mengistu	_____	_____
Name	Signature	Date

This is to certify that the thesis prepared by **Ysacor Mengistu**, entitled: Production of Epoxidized Zigba (Podo Carpus Falcatus) Seed Oil Through Carbon Based Sulfonated Catalyst and submitted in partial fulfillment of the requirement for the degree of Master of Science Process engineering complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Approved By:

Advisor: Dr..Anteneh Marelgn	_____	_____
Name	Signature	Date
External Examiner: Dr..Sintayehu Nibret	_____	_____
Name	Signature	Date
Internal Examiner: Dr. Abubeker Yimam	_____	_____
Name	Signature	Date
Chair Holder/Coordinator: Dr. Abubeker Yimam	_____	_____
Name	Signature	Date

Abstract

Epoxidation is reaction of the carbon–carbon double bond of fatty acids of vegetable oils. Recent environmental awareness and reduction of world fossil fuel reserves have enforced the need to look for a replacement of mineral oils with environmental friendly and nontoxic vegetable base oils such as epoxy oil. In this study epoxy oil was produced from seed oil using locally available raw material, podo carpus falcatus (‘zigba’) by carbon-based sulfonated catalyst. This bio-based catalyst was used for epoxidation reactions of podo carpus falcatus seed oil and the study was undertaken by preparing both carbon-based acid catalyst from rice husk at carbonization temperatures (400, 500, 600 ℃) and extraction of vegetable oil from podo carpus falcatus seed. The prepared sulfonated solid acid catalysts were characterized using: bulk density, total acid density, elemental analysis (CNHS), absorbance for methyl orange solution, and (Fourier Transform Infrared Spectroscopy) FT-IR. Based on the above characterization, the catalyst prepared from rice husk at temperature of 600 ℃ was selected for further investigation for epoxidation reaction of podo carpus falcatus seed oil. Podo carpus falcatus seed oil and epoxidized podo carpus seed oil were characterized by acid value (4 mmol KOH/l), Iodine value (121 g/100 g of I_2), Gas Chromatography Mass Spectroscopy (GC-MS), FT-IR, Nuclear Magnetic Resonance (NMR) and including other physical properties (density, specific gravity, and kinematic viscosity).The epoxidation reaction experiment was performed at reaction temperatures of 65, 75 and 85 ℃, hydrogen peroxide to the podo carpus falcatus seed oil with molar ratio of 1.5 :1, 2.5:1 and 3.5:1, acetic acid to podo carpus falcatus seed oil molar ratio 0.5:1 and reaction times of 2, 4, and 6 hours. The optimal value of oxirane oxygen content 3.788 % was obtained at 71.89 °C reaction temperature, in 5.1 hours reaction time, and 1.94:1 hydrogen peroxide to oil molar ratio. The relative conversion of double bond was 90.89%. Epoxidized podo carpus falcatus prepared from podo carpus falcatus seed have a good physiochemical and functional properties for epoxidized podo carpus production. and the carbon-based sulfonated catalyst works successfully for epoxidation of podo carpus falcatus seed oil.

Key words: Epoxidation, Rice husk, podo carpus falcatus seed oil, sulfonated solid acid catalyst, oxirane oxygen content,

Acknowledgment

First of all, I would like to thank the heavenly father (GOD) for his amazing mercy, care and giving me strength and hope to complete this thesis work successfully.

Moreover, I would like to express my heartfelt appreciation and thank to my Advisor Dr.Anteneh Marelign first believing in me to do this research and for his amazing humble welcoming, timely response, for his sustainable and appreciable guidance, tireless advising, for sharing his knowledge, skill, experience and fine-tuning up to the successful completion of this thesis and thank you for showing me how to became good person additional to your knowledge and skill.

I would like to say thank you to engineer Ray Cann for his much-needed guidance with the English language (which is not my first or most comfortable language) and trying to embed good grammar and spelling into a highly complex technical subject. Also, for supporting me in every step of my work, not giving up, and giving me moral, material and financial support.

I would also like to thank Mr. Eleyas and the Chemical Engineering Laboratory staff members especially Ato Hintsasilasie, Akiliu GebereHaweria, Samson Adisu and Azeb Tibebu for their technical assistance, kind heart and support during my work.

I wish to express my deepest gratitude to my families whose guidance, encouragement, wisdom, motivation, and expectations are indispensable to my achievements and will serve as a continuous inspiration for my future career.

The last but not the least, I would like to thank you all of my friends for your invaluable support and encouragement.

Contents

LIST OF TABLES

LIST OF FIGURES

ACRONYMS

AAIT	Addis Ababa institute of technology
AC	Activated Carbon
ANOVA	Analysis of Variance
AOAC	Association of Official Analytical Chemists
ASTM	American Society for Testing and Material
ATM	Atmospheric
AV	Acid Value
BBD	Box -Behnken Design
BC	Biochar
CBSC	Carbon Based Sulfonated Catalyst
CHNSa	Carbon Hydrogen Nitrogen Sulfur Analysis
DB	Double bond
EA	Elemental analysis
EN	European committee for standardization
EPCFO	Epoxidized Podo Carpus falcatus Oil
FA	Fatty Acid
FFA	Free Fatty Acid
FT-IR	Fourier Transform Infrared Spectroscopy
GCMS	Gas Chromatography Mass Spectroscopy
HV	Hydroxyl value
ISO	International Standards Organization
IV	Iodine Value
NMR	Nuclear Magnetic Resonance
ON	Oxirane Number
Ppm	Parts per million
PVC	Poly Vinyl Chloride
RSM	Response Surface Methodology
TAD	Total Acid Density

CHAPTER ONE

INTRODUCTION

1.1. Background

Vegetable oils mostly contain fluid hydrophobic compounds (at room temperature) extracted from milled grains from different plants such as sunflower, canola, soybean, Jatropha, palm, rape seed, peanut, and cottonseed (Access, 2015). These oils are composed of lipids, mainly triacylglycerols with different fatty acids composition. The most common are caprylic, capric, lauric, myristic, palmitic, palmitoleic, stearic, oleic, linoleic, α-eleostearic, ricinoleic and vernolic. Melting point of oils is very high which is due to high amount of carbons present in the fatty acid chain, and also a lower number of double bonds between carbons and trans configuration of these bonds (Ahmad et al., 2019). Other hydrophobic compounds also present in considerable amounts in several vegetables such as sterol, carotene, phospholipids and tocopherol (Brittany holt, 2016).

Vegetable oils are mainly used as emulsifiers, lubricants, plasticizers, surfactants, plastics, and resins. The main advantages of vegetable oils are biodegradable, having low toxicity, renewability, and no volatile organic chemicals. Modified oils have several relevant industrial applications such as lubricants, surfactants, emulsifiers and biopolymer. They also symbolize an excellent source for the obtainment of valuable compounds such as unsaturated fatty acids, phytosterols, squalene, pigments, antioxidants, vitamins, waxes, glycolipids and lipoproteins. They can also provide us appropriate sources for applications in other fields such as food, and pharmaceutical. (Erhan, 2005)

The demand for new biodegradable, and less toxic materials has given rise to the extensive exploration of renewable resources, both in academe and in industry. Epoxidation is one of the most significant functionalization reactions of the carbon–carbon double bond of fatty acids of vegetable oils. This functionalization can be obtained through environmental friendly procedures such as catalyzed chemical oxidation with hydrogen peroxide or by enzymatic oxidation. Epoxidized vegetable oils offer promising economical renewable materials for many industrial applications since they share many of the characteristics of conventional petroleum-based epoxy thermosets.

The epoxy group, often called the oxirane ring, is highly reactive and undergoes ring opening reactions. It cleaves readily to polyols by alcoholysis in the presence of alcohols/ thiols, and by

hydrolysis in the presence of acid catalysts. Epoxy resins are also chemically compatible with other materials and tend to wet surfaces easily, making them particularly well suited as binders in composites applications. They are therefore regularly used as adhesives, coatings, encapsulating materials, casting materials, potting compounds, and so on (Martin, 2010).

Catalysts based on biomass have advantages such as low cost and surface chemical properties that can be tailored appropriately. Among the desirable characteristics of the catalyst support is stability, inertness, reusability, high surface area, porosity and appropriate chemical structure (Ding, Rosén, & Bolton, 2012). The carbonization process from bio-mass(Rice husk ,corn cob and ,rice husk) usually produces sulfonated carbon with high surface area and high acid site content (Geng et al., 2015). Environmentally benign sulfonic acid modified solid acid catalysts have been successfully applied for various organic transformations such as etherification, dehydration, oxidation, acetylation and sialylation reactions (Rios et al., 2015).

1.2. Statement of the Problem

Recent environmental awareness and reduction of world fossil fuel reserves push us to look for a replacement of mineral oils with the biodegradable fluids such as vegetable base oils and certain synthetic fluids in epoxy oil formation. The nontoxic and readily biodegradable characteristics of vegetable oil-based epoxy pose less danger to soil, water, flora, and fauna in case of accidental spillage or during disposal, and Epoxy oil is used extensively for rubber, polymer, cosmetic and leather factory in Ethiopia. The problems related with this petroleum product of epoxide are non-degradable, shifting toward higher value and depletion of fossil fuel, instability of world political condition, and high demand of the oil as a whole all over the world. In recent years, investigation concerning the benefits of renewable raw materials have intensified the efforts for producing sustainable epoxide oil fabrication sources from vegetable oils. Podo carpus falcatus tree is found in the central and eastern highlands of Ethiopia. Where the weather situation is moist and wet, mainly found in Weyna Dega and Dega agroclimatic zones in Gonder, Gojam, Wolega, Shoa, Harerge, Arsi, Bale, Sidamo and Kefa. And an interesting aspect of this seed oil is that the oil contains as the major unsaturated fatty acid (around 81 % Oleic, linoleic and linolenic) of the oil due to its huge amount of unsaturation present in this seed oil, it's very suitable for many industrial applications (D. Alemu, 2015).

Epoxidation is the reaction between double bonds in olefinic compounds (unsaturated fatty acid, alkyl ester, or oil) and organic peroxy acid [RC (=O) OOH, oxygen transfer reagent] to obtain (three-membered) cyclic ethers called epoxidized oils. In industry, the epoxidation of plant oils has been already carried out using a homogeneous catalyst with a per carboxylic acid, obtained by oxidation with hydrogen peroxide, and sulfuric acid, as a catalyst. However, several drawbacks are associated with using sulfuric acid and all of the homogeneous catalyst, such as equipment corrosion, the release of toxic residues causing environmental issues, purification and separation of desired product and recovery of the catalyst. Therefore, continuous efforts have been made by researchers around the world to replace the conventional homogeneous acid catalysts by environmentally friendly and efficient heterogeneous catalyst (Corma, 1995). Until present times, the heterogeneous catalyst from cheap material is not widely used for epoxidation reaction of vegetable oil. In addition to overcome problems associated with homogeneous catalyst, heterogeneous catalyst is renewable, abundant, cheap can be produced directly from biomass compared to other solid acid catalysts.

Carbon-based sulfonated catalysts (CBSC) is among heterogeneous catalyst, and its own stable carbon skeleton and $-SO_3H$ group, high selectivity and insoluble in most acidic/basic conditions as well as organic solvents and in spite of this advantage, the carbon-based sulfonated catalyst is not widely used especially for epoxidation reactions. (Silva et al., 2017).to produce carbon-based sulfonated catalyst biomass-based material can be used such as rice husk is one of the biomass products, and Rice husk is treated as waste and mostly used power plant sites, and it's by product, rice husk ash, leads to a serious environmental problem. Therefore, it is important to make full use of the husk without leaving any product. Recently, rice husk is used as precursors to produce activated carbon. Rice husk is a great environment threat causing damage to land and surrounding area where it is dumped. Therefore, in this study rice husk is used for production of carbon-based sulfonated Catalyst to solve the problem related to rice husk as environmental pollutant.

1.3. Objective of the Research

1.3.1 General Objective

The overall objective of this research is to produce epoxy oil from locally available raw material, podo carpus falcatus seed oil, through carbon based sulfonated catalyst from rice husk.

1.3.2 Specific objectives

- To prepare sulfonated carbon catalyst from rice husk.
- To determine the physiochemical property podo carpus falcatus seed oil.
- To investigate the catalytic performance of prepared catalyst for epoxidation of podo carpus falcatus oil.
- To investigate the primary and interaction effects of parameters by using Response Surface Methodology (RSM).
- To optimize model equation by using Box Behnken Design.

1.4. Significance of the Study

This research is extremely important for countries like Ethiopia which has no source of petroleum. So, this epoxidized podo carpus falcatus seed oil can be used in the place of petroleum products and epoxy oils which are imported from foreign countries and hence save valuable foreign exchange. This study enables the for both researchers and the investors to explore substitution of mineral Oils (petroleum oil) by using locally produced epoxidized 'zigba' (podo carpus falcatus)

1.5. Scope of the Study

This thesis work covers activation, carbonization and sulfonation of rice husk, extraction of oil from podo carpus falcatus seed oil and production of epoxidized podo carpus falcatus seed oil through prepared carbon-based sulfonated catalyst.

CHAPTER TWO

2. LITERATURE REVIEW

Currently, attempts to develop partially or totally biodegradable polymers of semi-synthetic or bioorigin are being encouraged as viable alternatives to synthetic non-biodegradable polymers. It is evident that biodegradable polymers will become the pre-eminent polymeric materials in the near future and will be eco-friendly. There is considerable scope for the use of biodegradable polymers in the medical and agricultural sectors, as disposable packaging materials and as binders for paints and composites (Gawrilow, 2004). Tailoring the composition of these polymers for slower or faster rates of biodegradation, depending upon the usage conditions and their mode of disposal after use is also possible by means of appropriate molecular engineering (Renge V.C., 2012).

Recycling is an attractive solution for petroleum-based polymer even though only a small percentage of polymers are actually recyclable. Recently, this problem has become so severe, particularly in the packaging and medical sectors, that many countries have banned their use in such applications. However, consumers have come to expect the advantages of easily processed and inexpensive products and the need for biodegradable polymers has become more attractive (Brittany holt, 2016)

2.1. Vegetable oil

Renewable oils come from two major sources; animal and plant (mostly oil seed crops). Vegetable oils are becoming increasingly dominant over animal fats and oils as it contributes approximately 85 % of the total oil used. Vegetable oils are triglycerides of various fatty acids. They are termed fatty esters of glycerol (triglycerides) because they contain a glycerol chain attached to three different fatty acids chains (Land- & Er-, 1997).

The fatty acid portion is approximately 90 % of the total oil weight while 10 % of the weight is the glycerin portion (Beltrán & Boyacá, 2011). the four major vegetable oils in the world which contribute approximately 84 % of the total vegetable oils and 70 % of the total fat and oils were palm, soybean, canola, and sunflower oils (Gordon, 2005). These major vegetable oils are composed primarily of five fatty acids; palmitic, stearic, linoleic, oleic, and linolenic. The stereochemistry of the double bonds, their degree of unsaturation, and the length of these fatty acid chains are the most important factors affecting the physical and chemical properties

of oils. The mean proportion of Fatty Acid compositions for these major vegetable oils and their iodine values are shown in Table 2.1 while the structures of these common Fatty Acids are shown in Figure 2.1.

Table 2-1 Proportion of the main fatty acids (C-atoms:double bonds) found in the four major vegetable oils

Fatty acid type	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Iodine range	Value
Canola oil	4.0	1.8	60.9	21.0	100-115	
Palm oil	44.3	4.3	39.3	10	50-60	
Soybean oil	10.6	4.0	23.3	53.7	123-139	
Sunflower oil *	5.0	3.9	65.0	25	125-140	

Source: Rios et al., 2005

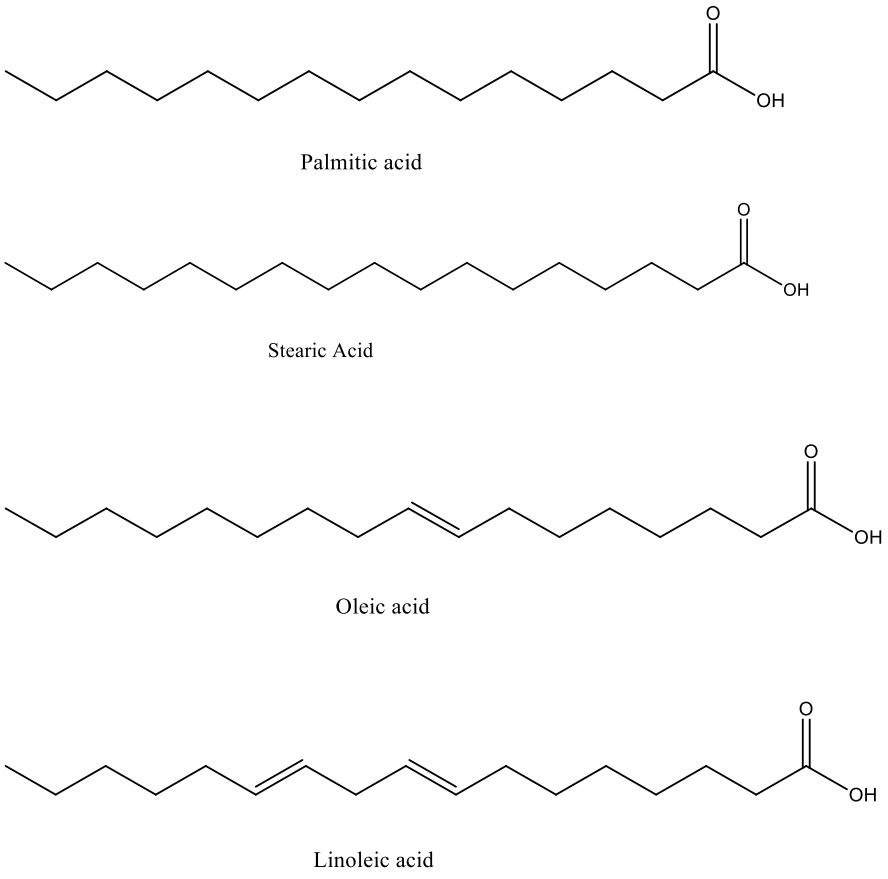


Figure 2-1 Chemical structure of the four major fatty acids found in vegetable oil.

In food industries, a balance between high saturated and high unsaturated vegetable oil is important. High consumption of oils with high saturated Fatty acids has been linked to many health problems like high cholesterol and heart diseases. On the other hand, oils with high unsaturated Fatty Acids are relatively unstable to oxidative deterioration, hence low shelf life. To improve the shelf life of oils with high degree of unsaturation, hydrogen is added to unsaturated Palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid bond through a chemical process known as hydrogenation. This process reduces the amount of double bonds and improves the shelf life, but the hydrogenation process increases the amount of saturated fat that has also been linked to cardiovascular disease (O. & M.B., 2006). Vegetable oil with high oleic proportion is usually the balance between high saturated and unsaturated fatty acids. Oilseed crop breeding programs have modified the Fatty acid composition to achieve high oleic acid content. For example sunflower oleic acid content has increased over the years to up to 70-80 % from its traditional low oleic acid content of 20 % Therefore, the food and health concerns, oxidative stability, and the need for high quality bio-based resin will always dictate the future composition of fatty acids in various vegetable oils (Chappell, 1998),

Currently, attempts to develop partially or totally biodegradable polymers of semi-synthetic or bio-origin are being encouraged as viable alternatives to synthetic non-biodegradable polymers. It is evident that biodegradable polymers will become the pre-eminent polymeric materials in the near future and will be eco-friendly. There is considerable scope for the use of biodegradable polymers in the medical and agricultural sectors, as disposable packaging materials and as binders for paints and composites (Gawrilow, 2004). Tailoring the composition of these polymers for slower or faster rates of biodegradation, depending upon the usage conditions and their mode of disposal after use is also possible by means of appropriate molecular engineering (Renge V.C., 2012).

Recycling is an attractive solution for petroleum-based polymer even though only a small percentage of polymers are actually recyclable. Recently, this problem has become so severe, particularly in the packaging and medical sectors, that many countries have banned their use in such applications. However, consumers have come to expect the advantages of easily processed and inexpensive products and the need for biodegradable polymers has become more attractive (Brittany holt, 2016).

2.2. Epoxidation Reaction

The epoxidation reaction of vegetable oils is a very sluggish reaction. To increase the reaction rate and to achieve a substantial selection the choice of the catalyst for the epoxidation reaction is of at most importance (Gordon, 2005)

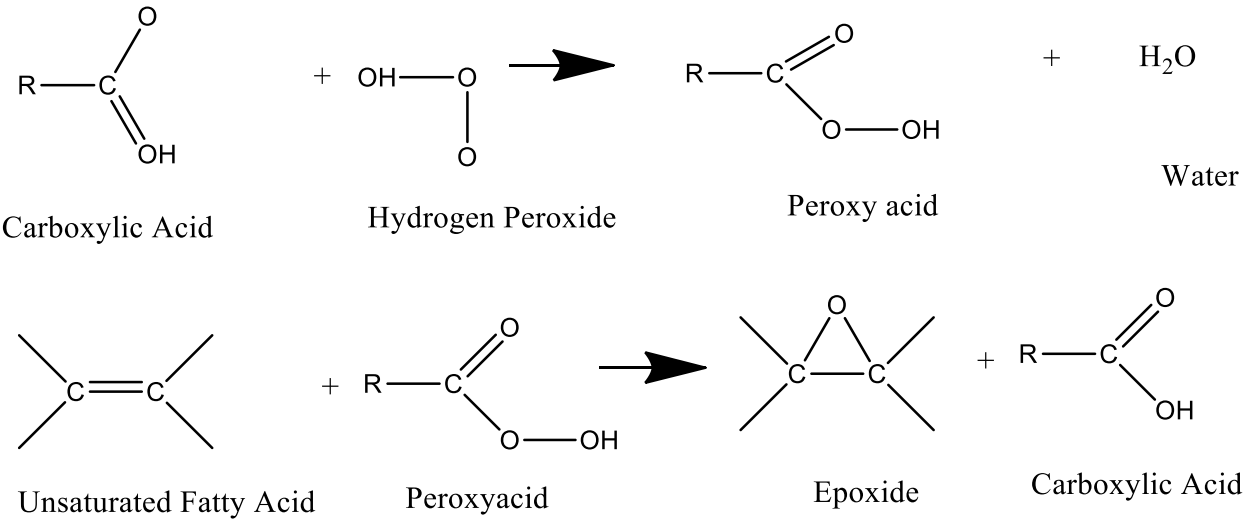


Figure 2-2. Epoxidation of Vegetables oil

The classification of catalysts as heterogamous or homogenous is important. Catalysts operate in the same phase as where the reaction occurs (homogenous catalyst) or in a different phase (heterogeneous phase) Most of the processes involving homogenous catalysts occur in a liquid phase whereas for heterogeneous catalysts, the catalyst is usually in a solid form, and the reaction occurs either in the liquid or gaseous phase. The phase difference between heterogeneous catalysts and the reaction medium makes it ideal for cheap separation and reutilization of the catalyst. In addition, heterogeneous catalysts are typically more tolerant to extreme operating conditions than their homogenous analogues (Eider, 2017)

The preparation of epoxy resins from a large number of vegetable oils such as sunflower, cotton-seed, linseed, Vernonia, soybean, and castor oil. vegetable epoxy resin are low viscosity materials used in conjunction with industrial epoxy resins to reduce viscosity and to increase the molecular mass of the latter as a reactive diluent can also act as a solvent for the resin system, it enables the production of high-solid and low VOC (volatile organic compound) coatings.(Bodanese-zanettini, 2012)

2.3. Podo carpus falcatus seed oil

Podo carpus falcatus belongs to the family '*podo carpceae'* and is the two coniferous species naturally growing up to 45 m high and 250 cm trunk diameter in Ethiopia. It is a multipurpose plant with wider range of socio economic and environmental importance. and one of the most promising products from the tree is the oil extracted from the seeds. the local people prefer oil obtained from the Podo carpus falcatus tree to the ordinary oil they purchase from shops. The cake, which results from the extraction of oil from the seeds, has a potential to be used as a source of animal feed directly or mixed with other feed items. (Teketay, 2005) .

The seed of Podo carpus falcatus tree is greenish –blue ovoid in shape, about 1-1.85 cm long and 1-1.25 cm in diameter. The average moisture content of Podo carpus falcatus kernel is 8.31 %, while average oil content was 52.96 % on dry basis. The specific density (0.89), saponification value (189.3 KOH mg per gram of oil) and refractive index (1.47) of the oil extracted from seed of Podo carpus falcatus (Feleke, 2005).

Podo carpus falcatus seed which is extracted by traditional method in the rural area of the country. The seed provides an important source of edible oil and nutritional security for the rural poor family, especially those who cannot afford the cost of edible oil in the market. (A. Alemu, 2019).

Figure 2-3 Podo carpus falcatus tree, Addis Ababa, around 'Gurd Shola "

2.4. Composition of Podo Carpus Falcatus Seed Oil

Physio-chemical composition of podo carpus falcatus seed oil is be shown on table 2.2 and the most important parameter is crude fat and moisture content of the seed oil and among the different parameter listed below the crude fat show 64 % on dry bases .the oil present on the seed helps to develop many industrial oil such as emulsifier ,plasticizer and epoxy oil product .

Table 2-2 physio- chemical property of podo carpus falcatus seed oil

No.	Parameters	Values
1	Moisture content (%)	5.84
2	Ash % (db)	2.69
3	Crude protein % (db)	18.60
4	Crude fat % (db)	64
5	Crude fiber % (db)	4.21
6	Total carbohydrate % (db)	12

Source: (D. Alemu, 2015)

Where 'db 'means dry bases

2.5. Epoxy Oil formation

Compounds such as vegetable oils, fatty acids, di/polyhydroxy compounds, epichlorohydrin and catalysts are required for the preparation of vegetable oil-based epoxies. The epoxy formation methods are similar to those of conventional petrochemical-based epoxy resins.The epoxy resins are usually synthesized by direct reaction of the aromatic and or aliphatic diols and epichlorohydrin through polycondensation reaction. Epoxidized oil is generally synthesized by in situ peroxidation with organic and inorganic peroxides, with halohydrins and molecular oxygen.

A large number of vegetable oils such as linseed, soybean, safflower, sunflower, canola, crambe, meadowfoam, lesquerella, rapeseed, rubber seed, castor, tung, coriander, olive, mahua, Annona squamosa, Pongamia glabra and Mesua ferrea L. fatty acids are used in the preparation of a variety of vegetable oil-based epoxies (N.Karak, 2012).Vegetable oil represents one of the cheapest and most abundant biological feed stocks available in large quantities. Its use as starting material offers

numerous advantages such as low toxicity and inherent biodegradability. Thus, the economic value of the vegetable oil could be increased by converting the vegetable oil into epoxidized vegetable oil. The increasing level of awareness regarding environment is driving the development of sustainable green materials (N.Karak, 2012).

Petrochemical based resins such as epoxy, polyester and vinyl ester find a number of engineering applications due to their advantageous material properties such as high stiffness and strength. However, these resins have serious drawbacks in terms of biodegradability, initial processing cost, energy consumption and health hazards. Consequently, there is a need to develop novel bio-based product from renewable feed stock. Hence a number of researchers have studied vegetable oils as alternative feedstock to substitute petroleum (Tayde et al., 2012).

2.6. Methods for epoxidation of vegetable oil

2.6.1. Conventional Method

Conventional method is the most widely used process for 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.(Dinda, Patwardhan, Goud, & Pradhan, 2008) epoxidation kinetics of cottonseed oil using a hydrogen peroxide catalyzed by liquid inorganic acids i.e. HCl, H_2SO_4, HNO_3 and H_3PO_4. carboxylic acid CH_3COOH and HCOOH as oxygen carrier and they found that acetic acid is more effective oxygen carrier than formic acid. Out of all liquid inorganic acid studied as catalyst, H_2SO_4 was found to be most efficient and effective (Tayde et al., 2012).

The epoxidation of the soybean oil and jatropha oil is done by conventional method. And the epoxidation reaction at 50 ℃ and atmospheric pressure for about 10 hours. The maximum reaction conversion was 83.3 % for epoxidation of soybean oil as catalyst (Jia et al., 2011). Similarly, Cai et al. (2008), worked on the kinetics of in-situ epoxidation of soybean oil, sunflower oil and corn oil by peroxyacetic acid catalyzed H_2SO_4. In this work they found that soybean oil has moderate conversion rate and lowest activation energy for epoxidation using peroxyacetic acid (Glass & Meyer, 2011) and 87.4 % for epoxidation of jatropha oil.

An epoxidation reaction of vegetable oils by using conventional homogeneous catalyst in the presence of this side reaction in commercial preparation of fatty epoxide diminishes their attractiveness as a starting material for further elaboration, as producers may require expensive purification (Piazza et al., 2003) In order to optimize the process, mahua oil studied with various parameter and factors including catalyst type, temperature, and reactants molar ratio and mixing speed on the epoxidation reaction. Also, they stated that the economic value of mahua oil could be increased by converting oil to epoxidized mahua oil. They used H_2O_2 as oxygen donor and glacial acetic acid as oxygen carrier in the presence of catalytic inorganic acid i.e. H_2SO_4 and HNO_3. And this study showed that Sulfuric acid is the best inorganic catalyst for this system producing a high conversion of double bonds to oxirane groups when the epoxidation reaction performed at the intermediate temperature of 55 ℃ to 65 ℃ to reduce the hydrolysis reaction (Goud et al., 2006).

2.6.2. Acid Ion Exchange Resin

Acidic Ion Exchange Resin (AIER) is an insoluble gel type catalyst in the form of small yellowish organic polymer beads. 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 (acid ion exchange resin) loaded into the reactor its pores get filled with peroxy acid. It leads to low oxirane degradation as triglyceride couldn't enter in to the gel type structure of AIER (Piazza et al., 2017).

It is investigated that the conversion of unsaturated fatty acids to oxirane ring using peroxy acid either peroxy formic acid or peroxyacetic acid in the presence of AIER shows different conversion for different vegetable oil. Petrovic et al. worked on the epoxidation kinetics and side reactions of soybean oil in toluene with peroxyacetic acid and peroxy formic acid in the presence of AIER as a catalyst. They found that peroxyacetic acid is less efficient than peroxy formic acid.

Acidic ion exchange resin can be used as catalyst to synthesize peroxy acids followed by in-situ epoxidation of vegetable oils (Aller, 2017) worked on in-situ epoxidation of karanja oil with aqueous hydrogen peroxide and acetic acid in presence of Amberlite IR-120 acidic ion exchange resin as catalyst. The variables studied were stirring speed, hydrogen peroxide to ethylenic unsaturation molar ratio, acetic acid to ethylenic unsaturation molar ratio, temperature and catalyst loading. The effects of this parameter on the conversion to epoxidized oil were studied at the optimum condition for the maximum oxirane content was established. They reported that the

intermediate temperature in the range of 55 ℃ to 65 ℃ gives maximum conversion of double bonds to oxirane groups and the reaction time was minimized. Further, they added the molar ratio of acetic acid to karanja oil 0.5 mol and a mole ratio of 1.5 for hydrogen peroxide to oil was the optimal concentration for the epoxidation reaction (Coud et al., 2006). Mungroo et al. worked on the epoxidation of canola oil with H_2O_2 as oxygen donor, acetic acid as oxygen carrier and AIER (22 % loading) as catalyst. The heterogeneous catalyst, AIER, was found to be reusable and exhibited a negligible loss in activity and the formation of epoxy adduct of canola oil was confirmed by Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectral analysis (Mungroo, 2008).

2.6.3. Enzymatic Method

To avoid side reactions and make the process more environmentally friendly it is preferred to use enzyme catalyst, immobilized Candida Antarctica lipase, which was used as the catalyst; the epoxidation reaction can be improved by adding the lipase step wisely. Enzymatic catalyst for epoxidation is a good alternative to chemical treatment. The main limitation however is the low stability of the lipase under the reaction conditions. The parameters affecting the lipase activity and operational life time during chemo-enzymatic epoxidation of fatty acids were investigated (Tzialla et al., 2010). It is found that in bio catalyzed reactions, enzymatic activity may also be lost due to elevated concentrations of hydrogen peroxide or to temperature effects. However, some recent papers have shown that Candida Antarctica B lipase remained stable above 50 °C, although this was not favorable, mainly due to the decomposition of hydrogen peroxide.

They studied epoxidation of plant oils such as rapeseed, sunflower, soybean and linseed using immobilized lipase catalyst. They find that the epoxidation using lipase biocatalyst was very selective and epoxidation conversion rate was exceeding 90 % worked on the optimization of chemo-enzymatic epoxidation of soybean oil. In this work, they find that the rate of reaction is affected by the concentration of lipase biocatalyst. Along with the catalyst loading (not more than 4 wt% of catalyst loading) reaction temperature, molar ratio of hydrogen peroxide to ethylenic unsaturation, oleic acid concentration and solvent concentration (Vlček & Petrović, 2006).

Rosana de Cassia et al. worked on the Chemo Enzymatic Epoxidation of Sunflower Oil Methyl Esters. They investigated that the chemo-enzymatic epoxidation of the methyl esters of sunflower oil with lipase from Candida Antarctica B and aqueous H_2O_2 in the presence and absence of an

acyl donor. The biphasic system (CH_2Cl_2/H_2O) comprised Candida Antarctica B lipase (CALB, 1000 u g^{-1}) and 30 % (v/v) aqueous hydrogen peroxide. In some cases, the conversion was higher than 99%. The best results were obtained for the biphasic system after 16 h of reaction, at 30 °C, using 10 mol of octanoic acid in relation to 1 g of the oil, 6 mL of dichlo methane and 5 mL of water (Schneider, 2009).

2.6.4. Metal Catalyst Method

Researchers and scientist are always in search of some new method and techniques to improve the existing technology. In the same line many workers and co-workers have given their contribution to increase the oxirane content and improve the efficiency of epoxidation reaction. Various metal catalysts such as titanium, molybdenum, tungsten can used for epoxidation of vegetable oils. 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. Several drawbacks must be improved in the peracid process, including:

(i) the selectivity to epoxidized products is relatively low due to acid catalyzed oxirane ring-opening;

(ii) the separation of acidic byproducts, whose presence may be detrimental for further applications, is not easy;

(iii) the handling of highly concentrated hydrogen peroxide and strong acids is dangerous and causes corrosion problems.

Thus, several articles have dealt with the setting up of catalytic processes aimed at overcoming such disadvantages, using more sustainable compounds and technologies. Campanella et al. worked on the epoxidation of soybean oil and soybean methyl esters with hydrogen peroxide in dilute solution (6 wt %) using an amorphous heterogeneous Ti/SiO_2 catalyst in the presence of tert-butyl alcohol. Under the experimental conditions employed in this work, no degradation of the oxirane ring was observed. Recently, it has been shown that the incorporation of Ti on an amorphous silica support produces oxidation catalysts that are highly effective in epoxidation reactions with hydrogen peroxide (Wade, 2002).

Table 2-3 Summary of epoxidation processes and conditions for various types of vegetable oil reported in the scientific literature.

Epoxidation process	**Vegetable oil**	**Batch size (gram)**	**Process variable**			**Conversion (%)**	**Reference**
			Temperature (℃)	H_2O_2 Addition (Molar ratio)	Reaction Time (hours)		
Conventional	Soybean	150	45,55,65 and 75	12	12	83	(Homrich, 2012)
	Jatropha	No defined	30,50,70and 85	0.5	3.5,4.5 and 10	35-88	(Saurabh, 2011)
	Cottonseed	No defined	30,45,60 and 75	0.5	4	80	(Dinda et al., 2008)
AIER	Canola	22.6	40,55,65and 75	0.5	7	50-90.8	(Mungroo et al., 2008)
	Canola	50 and 300	50-60	0.5	5	95-98	(Espinoza, 2013)
	Soybean	100	30,60 and 75	0.5	8	73.1-97and 7	(Sinadinović, 2001)
	Sucrose ester of fatty acid	170	55-56	Variable	No defined	99.4-99.9	(Uses, 2007)
Chemo enzymatic	Rubber, neem	40 and 1000	50-60	1and 2.5	5.5and 8	86-91	(Gamage, 2009)
	Soybean	25	50	0.083	24	50-98.9	(Vlček & Petrović, 2006)
	Soybean, Sunflower, linseed, rapeseed	7.8	Room temperature	54 µL every 7.5 min	16	88-99	(Hopulele, 2006)
Metal catalyzed	Fatty acid	11.7	30	2	2	31-96	(Manley, 2013)
	Soybean	30	Room temperature	No defined	1-2	16-92	(Gerbase, 2002)

Note. The temperature reported was the batch temperature, except where noted otherwise

2.7. Factors affecting epoxidation reaction

There are many factors which influence the formation of epoxidized oil, few of them are the suitability of vegetable oil for production of epoxidized oil, catalyst loading and characteristics of catalyst, molar ratio of hydrogen peroxide related to oil, time, and temperature is the most influential one, additional to this agitation speed also considered as factor, when the catalyst is heterogeneous.

Epoxides are an important class of industrial chemicals that have been widely used as raw materials for production of epoxy resin, paints, surfactants, medicines and so on, or the efficient intermediates in organic syntheses. Their selective synthesis is attractive to both academic research and industrial production Especially, the epoxidation of alkene is one of the main routes for the production of epoxides (Zong, Kharismadewi, Ra, & Shim, 2012).

2.7.1 Effects of temperature and reaction time

The effect of temperature related to epoxidation reaction is found that when temperature increased, the epoxidation rate increased. And, at lower temperatures the relative percentage conversion to oxirane continuously increased within the experimental time limit. However, at higher temperature the relative percentage conversion to oxirane attained a maximum, after which it gradually decreased. This indicates that an increase in temperature not only increased the epoxidation rate but also increased the rate of hydrolysis (oxirane cleavage) of the product. Reaction at lower temperatures gave lower epoxidation rate but led to lesser ring opening. It is clear that time required for the attainment of the maximum relative conversion at different temperatures was different. These results suggested that an optimum level of epoxidation could be obtained within a shorter time at moderate reaction temperature (Dinda et al., 2008).

Epoxide from Waste Cooking Oil (WCO) and epoxidation catalyzed sulfuric acid reached a maximum content of 3.1 % within temperature of 60 °C for 5 the. effects of temperature have been conducted by previous research of the epoxidation reaction such on cotton seed (Dinda et al., 2008), plum seed oil (Shagal, 2013), castor oil (Purwanto et al., 2006), while epoxidation of soybean oil was succeeded at temperature of 50 °C at 5 h. This epoxidation of WCO by peroxyacetic acid generated in situ hydrogen peroxide and glacial acetic acid in the presence inorganic acids as catalysts were not more efficient to convert double bonding of WCO become epoxidized WCO than it was compared to the epoxidation of cottonseed oil generated 70.4 % of

oxirane conversion with 2 % of H_2SO4 (Silviana, Anggoro, & Kumoro, 2017) The challenge is to shorten the reaction time. Too long 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).

2.7.2. Effect of hydrogen peroxide

Epoxidation rate increased as the concentration of H_2O_2 in the system increased. Because the excess amount of oxygen will be provided by hydrogen peroxide and the maximum conversion to oxirane was obtained. But, the stability of the oxirane ring was very poor at this high mole ratio. On the other hand, at low concentrations of H_2O_2, oxirane ring was quite stable. It was also observed that the formation and stability of oxirane will depend on the amount of hydrogen peroxide. Therefore, the optimum value of hydrogen peroxide is required to attain the higher formation of oxirane and stability (Dinda et al., 2008).

2.7.3. Catalyst loading

A catalyst accelerates the rate of a chemical reaction towards chemical equilibrium, but is not altered itself. It can afford an alternative chemical pathway, which provides lower activation energy so the reaction can proceed at an accelerated rate. After the reaction is stopped, it can be recovered in its original form from the mixture without having been subjected to a chemical change for this reason, the catalytic material does not appear as one of the reactants or products in an overall balanced chemical equation.

Table 2-4 Comparison between heterogeneous and homogeneous catalysts

Criterion	**Heterogeneous catalyst**	**Homogeneous catalyst**
Catalyst phase	Generally solid. Metal or metal oxide	Metal complex
Recyclability	Easy	Difficult
Selectivity	Variable	Usually high
Stability	Stable at high temperature	Decomposed
Solvent	Often not required	Required
Application	Wide	Limited

The catalyst's role is to lower the amount of energy needed to form one or more transition states between the reactants and the product. Nevertheless, both the forward and reverse reactions will be altered by a catalyst and there should be no change in the equilibrium position (Alsaiari, 2017).

2.8. Carbon-Based Solid Acid Catalyst

Sulfonated (SO_3H-bearing) carbon materials have been reported to act as strong solid acid catalysts. Hara's group first prepared sulfonated carbon catalysts via the sulfonation and carbonization of polycyclic aromatic hydrocarbons (Hara et al., 2004). These catalysts showed excellent activity in a series of acid catalyzed reactions, although, they were not stable enough and the aromatic molecules leached out above 100 ºC (Lu & Love, 2005). The problem could be overcome by selecting saccharides as carbon precursor (Mo et al., 2008). The controlled carbonization and sulfonation of these materials resulted in stable carbon structures with a high SO_3H group density. Carbon-based solid acid catalysts could also be obtained by sulfonation of carbon nanotubes or mesoporous carbon materials (X. Y. Liu et al., 2010).

Activated carbon by using chemical activation by using NaOH is widely used as a catalyst support in a variety of industrial and environmental applications for its chemical stability, high specific surface area, and low cost (Peng, 2005). An early experimental result from Hara's group showed that heating activated carbon in H_2SO_4 only produced a carbon material with a very low SO_3H group density (less than 0.15 $mmol \cdot g^{-1}$), a fact attributed to the chemical inertness of AC (Onda, 2013) reported the generation of a sulfonated carbon material with a SO_3H density of 0.44 $mmol \cdot g^{-1}$ by treatment of activated carbon with concentrated H_2SO_4 (Hu, 2015). The obtained carbon material in this case was quite stable and showed evident catalytic activity for the hydrolysis of cellulose. Recently, another paper from Hara's group described the preparation of a porous sulfonated carbon catalyst with high specific surface area by carbonization and sulfonation of $ZnCl_2$-impregnated wood powders (Kitano et al., 2009).

A porous carbon-based solid acid catalyst possessing a SO_3H density of 0.64 $mmol \cdot g^{-1}$ and a specific surface area of 602 $m^2 \cdot g^{-1}$ was synthesized by sulfonating activated carbon in an aryl diazonium salt reduction process. In the esterification reaction of acetic acid with ethanol, AC-SO_3H showed inferior catalytic activity to the commercial catalyst, Amberlyst-15, because the former's SO_3H density is much lower than the latter's (4.60 $mmol \cdot g^{-1}$). However, AC-SO_3H possessed evident advantages in the esterification of decanoic acid, which was probably due to

the high specific surface area and a large number of mesopores of the activated carbon. And this study results suggest that AC-SO3H may have potential applications in the acid-catalyzed reactions of large organic molecules (X. Y. Liu et al., 2010).

2.9. Activated carbon from rice husk

Activated carbon is highly porous in its structure, non-hazardous, carbonaceous material having a high surface area. The activated carbon can be used as adsorbent to adsorb different substances including dyes and heavy metals. It is capable to attract molecules to its internal surface.one of the main characteristics of activated carbon is their adsorption capacity.

Activated carbon is highly porous carbon which has been treated to increase its adsorption performance. Rice husk consists high cellulose and lignin content, can be used as source of carbons to produce activated carbon (Kane et al., 2016). In the grinding process, rice husks will be separated from rice grains and are known to be the residual or waste material which always burned by the farmers after the milling process. From the total of dry milled grain 20-30 %. rice husks will be obtained (Dewandono et al., 2018).

Rice husk is a promising feedstock for industrial application, due to its wide abundance and composition. Similar to other lingo-cellulosic materials, rise husk comprises of cellulose, hemicellulose, lignin and ash. More importantly, this biomass waste possesses unique properties, such as high silica content, high porosity, light weight and high external surface area. These properties makes it an ideal biomass waste for use as a potential metal as adsorbent (Touhami et al., 2017).

Among the most promising solid catalysts are the carbon- based sulfonated catalysts possess a carbon supporting framework and can provide a high density of strong acid sites (-SO_3H group); they also resist water deactivation during the transesterification reaction. Furthermore, Carbon based sulfonated catalyst have other acid groups such as the carboxylic group (-COOH) and hydroxyl group (–OH), thus differing from conventional solid acids bearing a single functional group. Owing to the extensive sources of raw material, cheap price and simple preparation, rice husk is widely used for catalyst preparation (Touhami et al., 2017).

Activated carbon derived from alkali treated rice husk indicated good adsorption capacity for methylene blue in aqueous solutions (Lin et al., 2013), and for nitrogen adsorption/desorption (Liu

et al., 2016). Activated carbon has several important usages including solution purification, removal of tastes and odors from domestic and industrial water supplies, vegetable and animal fats and oils, alcoholic beverages, chemicals and pharmaceuticals and in the waste water treatment. It is a versatile product with good market demand (Ahiduzzaman & Sadrul Islam, 2016).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The major raw materials used during the experimental work were podo carpus falcatus (zigba) seed, rice husk , sodium thiosulphate, sodium hydroxide, hydrochloric acid, sodium chloride, sulfuric acid, formic acid, hydrogen per oxide, sodium chloride, Nitrogen gas, hanus solution, glacial acetic acid, cyclohexane, starch, potassium iodide, Potassium hydroxide, Hexane, ethanol and starch. Podo carpus flacatus seed from local market around 'gurd shola' and rice husk was acquired from 'Bahir Dar' 'werta' and All the other chemicals were analytical reagent grade and bought from different chemical stores around 'cherkos' in Addis Ababa.

3.2 Equipment

The equipment's used during the experimentations includes maffle Furnace with modified nitrogen gas cylinder , Soxhlet apparatus, three neck glass reactor, water bath, condenser, crusher (Jaw crasher ,coffee grinder) separating funnel, vacuum pump, balance, oven, magnetic stirrer, oven, rotary vacuum, evaporator different size conical and Erlenmeyer flasks, beakers, measuring cylinders, burette, micropipettes, GC-MS, FTIR, and NMR.

Preparation of the rice husk, pyrolysis of the rice husk, washing and sulfonation of the char and characterization of bio-char catalyst such as bulk density, acid density and activity of the catalyst was done at School of Chemical and Bio Engineering Laboratory (AAiT) and Addis Ababa Science and Technology (ASTU). Extraction of podo carpus falcatus seed oil using Soxhlet apparatus; the extract was separated with simple distillation and further with rotary vacuum evaporator, podo carpus falcatus seed oil refining, characterization of the refined oil, synthesized of the epoxidized oil and analysis of the reaction mixture was also done at School of Chemical and Bio Engineering Laboratory. The other characterization of the catalyst such as elemental analysis, FTIR, fatty acid composition of the refined oil (GC/MS) and NMR analysis of the epoxidized oil as well as podo carpus falcatus seed oil were done at Faculty of Natural Science Department of Chemistry, Arat Kilo. The experimental works is shown from Figure 3.1-3.3

3.3 Raw Material Preparation

1. Extraction of oil from podo carpus falcatus seed oil

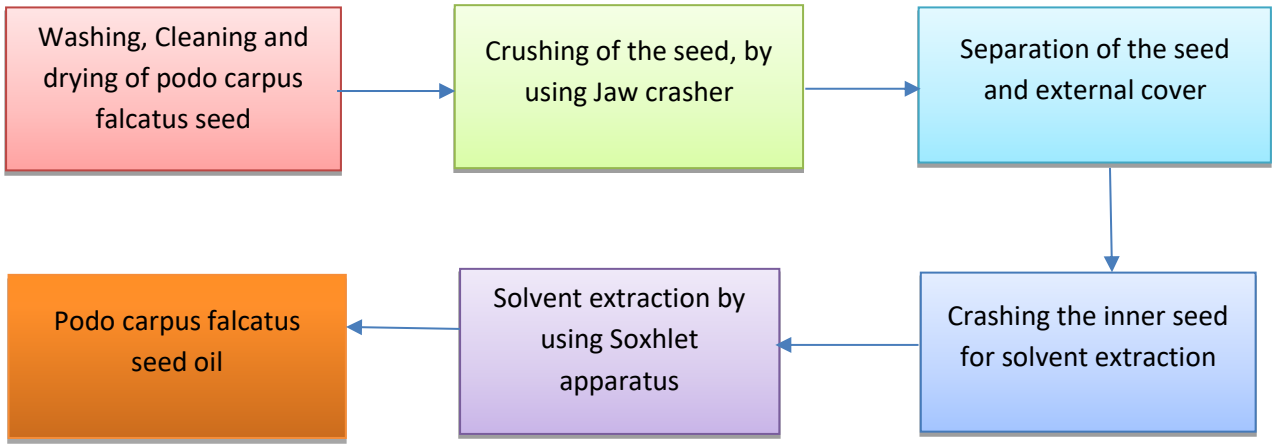


Figure 3-1. Extraction of podo carpus falcatus seed oil

2.Preparation of carbon-based catalyst

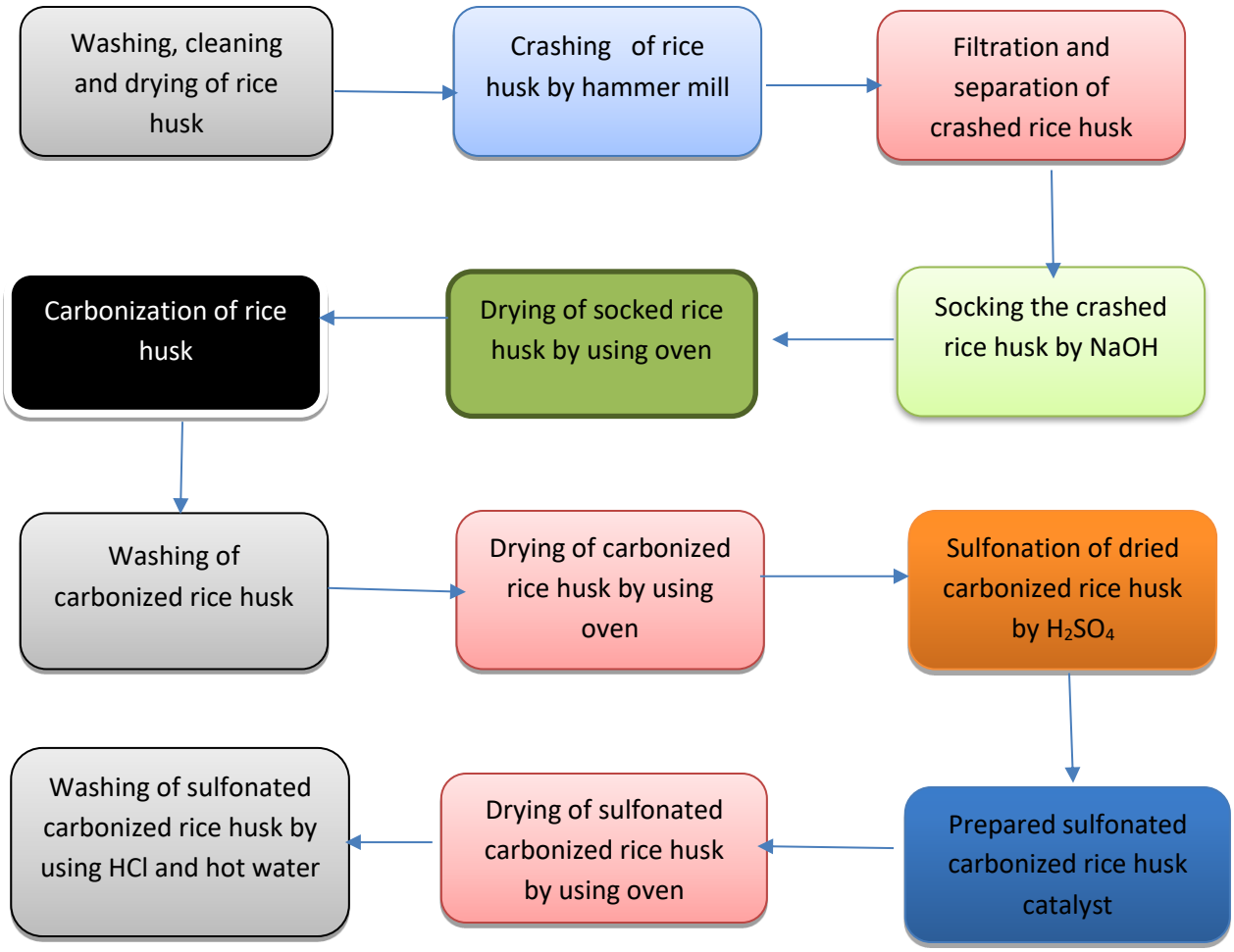


Figure 3-2. preparation of carbon-based catalyst from rice husk

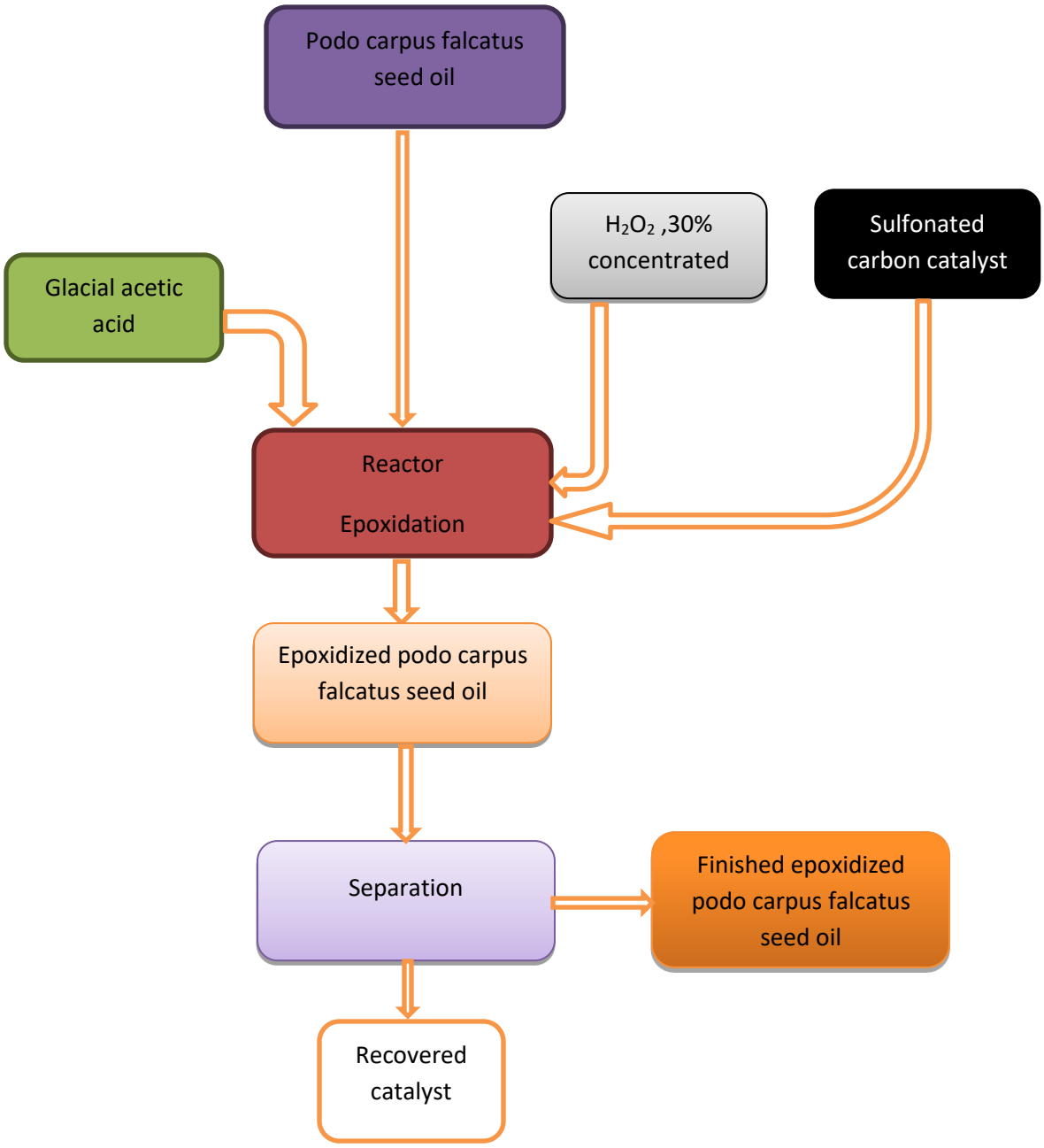


Figure 3-3. The overall structure of the experimental works

3.3. Experimental Method

3.3.1. Carbon Catalyst Support preparation from rice husk

The rice husk, collected from the local market, was washed and filtered to remove dust any undesirable waste such as mud and other sand substance. The washed rice husk was then sun dried for 4 hours. Dried and cleaned rice husk was crushed using a roller mill and sieved in order to obtain a desirable size fraction (0.5 -1.4 mm). The rice husk was then dried in an oven for 12 hours at 105 ℃ to reduce its moisture content (9.41-10.31 %). The dried rice husk was stored in air tight plastic bags and in a clean space for further analysis. When the rice husk was dry, it was socked in 0.1 M of NaOH solution for one day, dried to 105 ℃ for 8 hours. The dried saw dust rice husk was pyrolyzed in a Muffle furnace at different temperature ranges under Nitrogen gas flow rate is adjusted based on the amount of nitrogen available in the maffle furnace (1.1 up to 1.2 Atmospheric pressure) and the chamber was heated, to initiate carbonization process. The pyrolysis process was undertaken at temperatures of 400, 500 and 600 ℃ for constant time of two hours under nitrogen gas atmosphere. Then, the char produced was discharged from the furnace and cooled by using a desiccator for 10 minutes washed first by a 0.1 M solution of hydrochloric acid then followed by hot distilled water (80 ℃) several times to remove the ash content of the char until the pH of the washed water was neutral and this experiment was carried out at the Addis Ababa Science and Technology Institute.

Rice husk (a)

Size reduction of rice husk by juice blender (b)

Filtration of soaked rice husk (c)

carbonization of rice husk (d)

Figure 3-4. Carbon Based sulfonated catalyst Support preparation from rice husk

3.4. Sulfonation of bio-chars

The sulfonation was applied for all prepared bio-chars. The bio-chars prepared at different temperature were then impregnated by sulfuric acid (98 % of H_2SO_4; 102-153 ml of sulfuric acid for 10-15 g of char) heating to 150 ℃ under nitrogen flow for 15 hours. The final catalyst was washed with plenty of hot water (80 ℃) to remove the homogeneous sulfuric acid until the pH of the washed water became neutral and no sulfate ions were detected by measuring the pH of the hot water after its cool to atmospheric temperature and the sulfonated catalysis will remain on the bottom of measuring cylinder. The samples were dried at 105 ℃ for 4 hours to remove moistures from the samples in the oven. The bio-chars prepared at different temperatures can be designated as; C-SO_3H- 400, SO_3H- 500 and SO_3H- 600 ℃, this experiment (Sulfonation) was done in School of Chemical and Bio-Chemical Engineering (Addis Ababa institute of Technology)

Figure 3-5 . Sulfonation of activated carbon under nitrogen gas

3.5. Catalyst and Rice Husk Characterization

3.5.1 Proximate Analysis of the Rice Husk

The proximate analysis of the raw rice husk mainly moisture content, volatile matter, fixed carbon and ash content) was determined using ASTM; D1762-84 (Reapproved 2007). The measurement was done three times and the average was taken to reduce the errors due to many factors such as errors due to human measurement errors, equipment calibration errors or failure, and. machine efficiency.

3.5.1.1. Moisture content

The raw rice husk, crushed to a desirable size, was put into a dried and clean ceramic crucible. The crucible was weighed with and without the sample of raw rice husk. The crucible with rice husk dust was dried in an oven at 105°C for 8hrs. The sample was removed each 2 hours from the oven every 2 hours and placed in the desiccator for 30 minutes to cool and then re-weighed until constant weight was obtained. Finally, the weight was taken and compared with the initially recorded weight. The percentage weight in the dried rice husk was calculated using the formula:

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

Where: W_1 is the original weight of rice husk before drying and

W_2 is the weight of the dried rice husk after drying

3.5.1.2. Volatile matter

The crucible with its cover was preheated in oven at 150 ℃ for 10 minutes to remove its moisture content and any physically absorbed material, kept in desiccators for 10 minutes. Then, the crucible and its cover were weighed with and without the amount of rice husk dust. Then, the samples were heated at 925 °C for 7 minutes and 30 seconds in muffle furnace. 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:

$$\text{Volatile matter (\%)} = \frac{B-C}{B} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Where: B grams of rice husk before drying and

C is grams of the rice husk after drying at 925 ℃

3.5.1.3. Ash content

The crucible was preheated in oven to 150 ℃ for 10 minutes to remove its moisture content and any physically absorbed material within the crucible, kept in desiccator for 10 minutes. Then, the crucible was weighed with and without the amount of rice husk dust. The sample was heated at 650°C in an open crucible for 1 hour 30 minutes in a furnace. The weight of the sample before heating and after heating was used to determine the amount of ash content present in the sample. In this test, the amount of residual substance is equal to the ash present in the sample. The percentage of ash in the sample was calculated using the formula:

$$\text{Ash (\%)} = \frac{D}{B} \times 100 \quad \text{.....3.3}$$

Where: B grams of rice husk before drying and

D is grams of residue (sample remain after burn)

3.5.1.4. Fixed Carbon Content

The fixed carbon content is determined by subtracting the sum of volatile matter content and ash content fron100. The obtained value is the amount of fixed carbon present in the sample expressed in percentage. The percentage of fixed carbon content in the sample was calculated using this formula by assuming there is negligible amount of error due to the existence of another unknown element.

$$\text{Fixed Carbon content (\%)} = 100 - (B + C) \quad \text{.....3.4}$$

Where: B -percentage of volatile matter (%)

C-percentage of Ash (%)

3.6. Bulk Density of the Char

Bulk density is defined by the volume of the container used to hold the sample—this volume includes pore space within and between the sample particles inside the container. To measure bulk density, a container of known volume is weighed empty, filled with sample, and then weighed again; the mass of the sample is divided by the volume of the container. Bulk density is heavily dependent on how the sample particles pack into a container. Bulk density measurement standards, such as (ASTM, 2013) for densified particulate biomass fuels and(Procedures, n.d.) for solid waste fractions have to be very specific about how the sample is poured and leveled, and if any kind of pressure or tapping procedure is used (Brewer, 2012). ASTM D2584 for activated carbons the practice of tapping the container to ensure repeatable sample packing is why bulk density is

sometimes called "tap density." The bulk density of the material was obtained by weighting a certain gram of the produced bio-char and transferring it into a 10 ml graduated cylinder. The cylinder was tamping with a rubber pad while char was being added until the entire original sample was transferred to the cylinder. Tamping was continued for 5 minutes until there was no further settling produced. The volume was recorded and the bulk density was calculated on the dry basis:

$$\text{Bulk density: } \frac{\text{weight of sample (g)}}{\text{volume of sample (ml)}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 3.5$$

3.7. Bulk Density of the catalyst

The bulk density of catalyst the material was obtained by weighting a certain gram of the produced catalyst and transferring it into a 10 mL graduated cylinder. The cylinder was tamping with a rubber pad while char was being added until the entire original sample was transferred to the cylinder. Tamping was continued for 5 minutes until there was no further settling produced. The volume was recorded and the bulk density of catalyst was calculated on the dry basis:

$$\text{Bulk density of catalyst: } \frac{\text{weight of catalyst (g)}}{\text{volume of sample (ml)}} \ldots\ldots\ldots\ldots\ldots\ldots \; 3.6$$

3.8. Acid Density of the Catalyst

The total acidity groups as well as amount of SO_3H group, were determined by using back titration for total acid density and direct titration for SO_3H acid density following the method reported in the literature (Ouyang, 2014). The catalyst was pre-dried in the oven at 110 °C for at least two hours prior to analysis. In a typical analysis, 0.05 g of sample was put in a beaker containing 20 ml of 0.01 M NaOH, and the mixture was stirred for 60 min at room temperature. An excessive amount of NaOH was used in order to completely neutralize all acidic functional groups in the sample. After separation of the solid catalyst and supernatant solution by using filtration the NaOH solution or supernatant solution (containing the sample) as the analyte and then titrated in the presence three drop of phenolphthalein as indicator using 0.01 M HCl as the titrant. The titration was continued until the end point (pink to colorless) is recognized. The total acid density was calculated using formula:

$$\text{Total Acid Density (TAD)} = \frac{(V_{NaOH} \times N_{NaOH} - V_{HCl} \times N_{HCl})}{\text{Mass of the catalyst}} \ldots\ldots\ldots\ldots\ldots\ldots \; 3.7$$

The content of -SO_3H group: The amount of SO_3H was determined similar to total acid density determination except the analyte was NaCl instead of NaOH and that of titrant was NaOH which is different from HCl used in total acid density determination. The titration was continued until the end point (colorless to pink) is recognized. The SO_3H amount was calculated using formula: (Ouyang et al., 2014)

$$AD_{-SO3H} = \frac{(\text{Volume of NaOH used for titration} \times \text{Normality of NaOH})}{\text{Mass of the Catalyst}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.8$$

Where: AD-SO_3H is acid density of -SO_3H group

3.9. Ultimate Analysis (CHNSs)

The Ultimate Analysis used to determine the elemental composition of the sample. It is based on the principle of Dumas method which involves the complete and instantaneous oxidation of the sample by flash combustion. The results are in percentage composition of Carbon, Hydrogen, Nitrogen and Sulphur. From these results the oxygen composition is determined by subtracting the sum of Carbon, Hydrogen, Nitrogen, and Sulphur compositions from 100. The Ultimate Analysis was carried out in EA 1112 Flash CHNS/O- analyzer device. The samples were fed into the analyzer along with carrier gas (helium) flow rate of 120 ml/min, reference flow rate 100 ml/min, and excess supply of oxygen at flow rate 250 ml/min. The reaction of oxygen with other elements (namely carbon, hydrogen, nitrogen, and sulfur) present in the sample produces carbon dioxide, water, nitrogen dioxide, and sulfur dioxide respectively. The combustion products were separated by a chromatographic column and are detected by the thermal conductivity detector which gives an output signal proportional to the concentration of the individual components of the mixture. This determines equivalent compositions of elements in the sample (Kudzin & Waśkowski, 2004).

Figure 3-6. Ultimate Analysis Instrument

3.10 Absorbance of the catalyst

The absorbance of the catalyst of the sample was evaluated by using variation of methyl orange concentration in aqueous solution. Methyl orange was used as a model solution because it was possible to measure its concentration by using UV–visible spectroscopy, and to monitor the variation under different carbonization temperature, carbonized rice husk dosage and solar intensity remain constant (3-gram carbonized rice husk). So first the methyl orange solution prepared at different concentration (5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L) by dissolving the Adsorption tests were performed in a set of Erlenmeyer flasks (250 ml) where 100 ml of methylene orange solutions with initial concentrations of 50–500 mg/l were placed in these flasks. equal mass of 0.1 g of the prepared activated carbon with particle size of 200 μm was added to each flask of the dye (methyl orange) with distilled water (Tan, Hameed, & Ahmad, 2007)..

Figure 3-7. UV -spectroscopy and methyl orange solution preparation

Consequently, measure the absorbance of the dye solution with UV-spectroscopy and prepare a linear absorbance versus concentration standard curve of Methyl orange and by comparing the initial and final absorbance of the carbonized catalyst by using the initial and final concentration of the methyl orange solution.

Table 3-1. Relationship between methyl orange concentrations with their Absorbance

Sample	Initial Methyl Orange Concentration(mg/l)	Absorbance
1	0	0
2	5	0.233
3	10	0.4713
4	15	0.7096
5	20	0.9479
6	25	1.1862

After the standard curve was plotted, there is a relationship between Absorbance and concentration of methyl orange solution. 15mg/l of synthetic methyl orange solution was from the prepared solution is chosen to compare the significant absorbance. Change after the plugin of prepared Catalyst. And all sample is mixed for 1hour with magnetic stirrer and sample will filter out by using centrifugation by using (universal 320R) and the centrifugation speed is 6000 revolution/ minutes for 5 minutes.

3.11. Fourier Transform Infrared Spectroscopy

The infrared spectrum was recorded by passing a beam of infrared light through the sample. The functional group analysis of the sulfonated carbon catalyst was carried using Fourier-Transform Infrared (FTIR) spectroscopy. The FTIR spectra were recorded on spectrum 65 FT-IR (Perkin Elmer) equipped with KBr beam splitter. Diffuse reflectance system (DRS) was used for powder samples and NaCl plate for liquid samples by thin film deposition technique. A regular scanning range of 400-4000 cm^{-1} was used for 20 repeated scans at a spectral resolution of 4 cm^{-1}. All the

spectra were recorded and processed using essential FTIR software. This experiment was done on Chemistry Department, Addis Ababa University.

Figure 3-8. (Perkin Elmer & Inc, n.d.) and Ethiopian Pharmaceutical plc

3.13. Preparation, Purification & Characterization of podo carpus falcatus seed oil

3.13.1 Preparation of Podo carpus falcatus Seed

Podo carpus falcatus seeds were first cleaned from dirt, dust, sand, small stones and washed manually. Then the prepared Podo carpus falcatus seeds were sun dried for one day. The clean seeds were weighted. Then the dried seed was crushed using a Jaw crasher. External cover will be separated by using sieve. The internal seed were crushed to increase the extraction efficiency of the oil. the internal seed with particle size of 0.5 – 1.0 mm for solvent extraction analysis (D. Alemu, 2015).

Figure 3-9. Jaw crusher: Addis Ababa Institute of Technology, School of Chemical - Bio Engineering (Mechanical Operation Laboratory)

3.13.2 Extraction of Podo carpus falcatus seed oil

Soxhlet extraction apparatus method was applied for podo carpus falcatus seed oil extraction. For Soxhlet extraction 140 gram of grinded podo carpus falcatus seed (packed in a filter paper) and 600 ml hexane solvent was placed in the Soxhlet extraction unit.

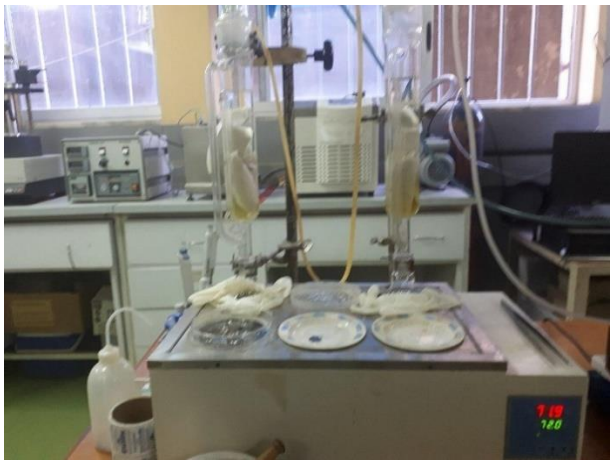


Figure 3-10. Soxhlet extraction of podo carpus falcatus seed oil

Then the solvent and crushed mixture was heated at constant temperature of 72℃ for 5 hours in round bottom flask to extract the oil. After extraction the huge amount of oil and solvent is separated with simple distillation; additional to this rotary vacuum evaporator to concentrate

purified oil and the solvent was recovered. The yield of oil extracted will be calculated using the equation given below:

$$\text{Yield of podo carpus falcatus seed oil} = \frac{\text{mass of crude oil extracted}}{\text{total mass of seed kernel}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots 3.9$$

3.13.3. Determination of Moisture Content

To determine the moisture content of the podo carpus falcatus seed oil we have to use available methods. by using direct moisture analyzer instrument (MB45) the sample holder must be cleaned properly and measured exact one gram of the oil sample and add on sample holder and wait for 10 minutes for one run, and this experiment on 100 ℃. And Finally, the weight was taken and compared with the initially recorded weight. The percentage weight in the podo carpus falcatus seed oil was calculated using the formula:

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.10$$

Where: w_1 is the original weight of podo carpus seed oil before drying and

w_2 is the weight of the podo carpus seed oil after drying

Figure 3-11. Moisture analyzer instrument (MB45)

3.13.4 Determination of Density

The density of podo carpus falcatus seed oil was determined using density meter (DMA 4100M). The oil was injected using syringe to the density meter and the density meter was recorded for density and specific gravity of crude oil (API) at 20 ℃

Figure 3-12. determination of density of podo carpus falcatus seed oil

3.13.5. Determination of Kinematic Viscosity

Vibro viscometer was used to determine a viscosity of the oil. The sample holder must be cleaned and dried well. 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 was calculated using formula:

$$\text{Kinematic Viscosity} = \frac{\text{Dynamic Viscosity}}{\text{Density}} \quad \text{.....3.10}$$

Figure 3-13. Vibro viscometer

3.13.6 Determination of Acid value

Standard alcoholic (potassium hydroxide is diluted using ethanol rather than distilled water) potassium hydroxide solution (0.1 N) was prepared by dissolving KOH (pellet) with 95 % ethanol. The solution was filtered and stored closed bottle. A phenolphthalein (1g per 100 ml of 95% v/v ethanol) was used as 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 3 drops of phenolphthalein as indicator until the end point (colorless to pink) is recognized. The volume of 0.1 N ethanolic KOH (V) for the sample titration was noted. The total acidity (acid number) in mg KOH/ gm was calculated using the following equation:

$$\text{Acid Value} = \frac{56.1 \times V \times N}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.11$$

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

N is concentration of ethanolic KOH

m is mass in gram of the test portion

3.13.7 Determination of Iodine value

Iodine value was determined by AOAC (official method no.920.158, 2000), about 0.50 g of sample, 10 mL of chloroform and 25 mL of Hanus solution iodine were added into a 500 mL conical flask; and then the solution was left to stand in the dark for 60 minutes with occasional shaking. Then after, 20 mL of potassium iodide (15 %) was added, shaken thoroughly and distilled water (100mL) was added to rinse down any iodine on the stopper. The solution was then titrated with 0.01N thiosulfate solution using starch as indicator (1 mL) till fade in color.

Hanus Method for iodine determination

Determination of the excess halogen by addition of potassium iodide aqueous solution and titration of the liberated iodine with a standardized sodium thiosulphate solution.

Reagents are Glacial acetic acid free from ethanol, Carbon tetrachloride analytical reagent quality. Iodine monobromide (IBr) must be pure, Potassium iodide prepared 100 gram /1iter of aqueous solution. This must contain no free iodine or iodate. Sodium thiosulphate 0.1 N accurately standardized aqueous solution. Starch solution (10 g/l aqueous dispersion) recently prepared from natural soluble starch.

Preparation of the Hanus Reagent Into a brown glass bottle (brown bottle is used ,because the reaction is highly light sensitive) weigh 10 g of iodine monobromide and dissolve it in 500 ml of acetic acid.

The weight of fat to be taken (in gram) [about 25/I. V. (expected iodine value)] into a glass scoop weigh the appropriate quantity accurately to within 0.001 g. Insert the scoop with contents into a ground-necked bottle, add 10 ml of carbon tetrachloride and dissolve. Then, add exactly 25 ml of the reagent and insert the stopper. Shake gently, and place in the dark for 1 hour. Add 20 ml of the potassium iodide solution and 100 ml of distilled water. Titrate with the aqueous thiosulphate solution, using starch solution as indicator, continuing the titration until the blue color just disappears after very vigorous shaking. (Paquot, 1978)

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

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 Podo carpus falcatus seed oil taken for the test.

Note that: 12.69 is molecular weight of iodine.

3.13.8. Determination of Epoxy-Group Oxygen

Weigh accurately, to the nearest 0.1 mg, 0.3 to 0.5 g of the prepared sample into a conical flask and Dissolve it in 10 ml of benzene. Introduce the magnetic stirring bar and add not more than 0.1 ml of the indicator solution. Fix the stopper and the burette in such a manner that the tip of the burette just touches the surface of the solution (in order to avoid loss of hydrogen bromide). Begin stirring and titrate, rapidly at first and then more slowly near the end point, with the hydrogen bromide acetic solution until a bluish-green color persists for 30 seconds (control the speed of the stirrer so as to avoid splashing) (Paquot, 1978).

$$\text{Oxirane Oxygen Content (OOC, \%)} = \frac{1.6*V*N}{Wm} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.13$$

Where: V is the number of ml of the standardized hydrogen bromide acetic solution used for the titration,

N is the exact normality of the hydrogen bromide acetic acid solution used,

m is the mass, in g, of the test portion

3.13.9. Gas Chromatography Mass Spectroscopy (GC/MS)

Gas chromatography-mass spectroscopy (GC-MS) is one of the so-called hyphenated analytical techniques. As the name implies, it is actually two techniques that are combined to form a single method of analyzing mixtures of chemicals. Gas chromatography separates the components of a mixture and mass spectroscopy characterizes each of the components individually.

In general, chromatography is used to separate mixtures of chemicals into individual components. Once isolated, the components can be evaluated individually. In all chromatography, separation occurs when the sample mixture is introduced (injected) into a mobile phase. In liquid chromatography (LC), the mobile phase is a solvent. In gas chromatography (GC), the mobile phase is an inert gas such as helium. The mobile phase carries the sample mixture through what is referred as a stationary phase. The stationary phase is usually a chemical that can selectively attract components in a sample mixture (Sasaki, 2012).

GC/MS analysis was done first by preparing the podo carpus falcatus seed oil (5Micro liter) for injector by preparing standard solution by the ratio of 50ml oil sample with one liter of di-chloro methane and inject with sample holder with Agilent GC/MS – system – 7820A. Sample analysis was carried out on packed column- Agilent Technologies (30 m × 0.250 mm, 0.25 μm). Samples were injected by a sampler injector at an oven temperature of 325 to 350 ℃ for a total run time of 18 minutes. The data, obtained using GC/MS - Agilent Technologies EMS detector and processed using Chem station software, were used to obtain fatty acid composition of oils. And this experiment done at Chemistry Department. Addis Ababa University.

Figure 3-14. Gas Chromatography Mass Spectroscopy (GC/MS) analyzer of podo carpus falcatus seed oil

3.13.9 Nuclear Magnetic Resonance (NMR) spectroscopy Analysis

The NMR spectra of Podo Carpus falcatus seed oil and epoxidized podo carpus falcatus seed oil was recorded on Bruker Advance 400 spectrometer (Bruker, Rheinstetten, Germany) operated at 400 MHz using CDCl3 as solvent.

Figure 3-15. NMR- Spectroscopy

3.14. Experimental Design for Epoxidized podo carpus falcatus seed oil production

In this work the epoxidized podo carpus falcatus seed oil was produced using purified podo carpus falcatus seed oil, hydrogen per oxide, formic acid and sulfonated carbon catalyst. Experimental data analysis was done using Design- Expert 7.0.0 software.

The experimental design selected for this study was response surface methodology, three-level-four-factor Box-Behnken Design (BBD) and the response variable measured was the percentage of conversion. In addition to this analysis of physicochemical properties of epoxidized podo carpus falcatus seed oil such as FTIR, NMR spectroscopy was done at Chemistry Department, Arat Kilo, Addis Ababa University.

The four independent variables studied for the epoxidation reaction process were reaction temperature time, molar ratio of hydrogen per oxide to oil and catalyst loading. The independent variables interaction effect was analyzed to obtain maximum percentage of conversion double bond in podo carpus falcatus seed oil.

Four-level-three-factor BBD was used in the optimization study which requires 29 experiments to be conducted. The 29 experiments were done and the data was statistically analyzed using Design-

Expert Software 7.0.0 to obtain a suitable model equation for the percentage conversion of double bond as a function of the independent variables.

Table 3-2. Independent variables and levels used in the Box-Behnken Design for the epoxidized oil production

Variables	**Units**	**Levels**		
		-1	**0**	**1**
Reaction temperature	℃	65	75	85
Time	hr.	2	4	6
Hydrogen peroxide to oil ratio	mole /mole	1.5	2.50	3.50
Catalyst loading	Wt.%	2	4	6

Below in Table 3-5 the complete experimental design matrix of BBD for the factorial design was shown. The order in which the runs were made was randomized to minimize systematic errors.

Table 3-3. Experimental design matrix

Run	**Actual factor**			
	Time (hr.)	**Temperature (℃)**	**Catalyst loading (Wt. %)**	**H_2O_2 to oil ratio (mole/mole)**
1	4.00	75.00	6.00	2.50
2	2.00	65.00	4.00	2.50
3	4.00	85.00	2.00	2.50
4	4.00	75.00	6.00	2.50
5	4.00	75.00	4.00	1.50
6	4.00	75.00	2.00	1.50
7	6.00	65.00	4.00	3.50
8	4.00	75.00	4.00	3.50
9	2.00	85.00	4.00	1.50
10	4.00	75.00	4.00	1.50
11	6.00	75.00	4.00	3.50
12	6.00	75.00	4.00	3.50

13	4.00	85.00	4.00	2.50
14	2.00	75.00	4.00	2.50
15	4.00	75.00	4.00	2.50
16	4.00	65.00	2.00	2.50
17	4.00	75.00	2.00	2.50
18	4.00	85.00	6.00	2.50
19	6.00	75.00	2.00	2.50
20	4.00	85.00	4.00	2.50
21	4.00	65.00	6.00	1.50
22	4.00	65.00	4.00	1.50
23	4.00	75.00	2.00	3.50
24	4.00	65.00	4.00	3.50
25	6.00	85.00	4.00	2.50
26	2.00	75.00	4.00	2.50
27	6.00	75.00	6.00	2.50
28	2.00	75.00	4.00	2.50
29	6.00	75.00	2.00	2.50

3.14.1 Experimental Setup

The epoxidation of feed material (mixture of podo carpus falcatus seed oil, peroxy acid and sulfonated carbon catalyst) was done on an MSH-D hotplate magnetic stirrer equipped with a magnetic stirrer, condenser and thermometer to control the actual reaction temperature. For epoxidation reaction, a 100 ml three neck glass reactor equipped with MSH-D hotplate magnetic stirrer was used in all experiments. The MSH-D hotplate magnetic stirrer can be adjusted to the desired temperature, reaction time is used based on the experiential run and rotational speed will fix to 1500 rpm. The batch epoxidation reaction system was employed for epoxidized podo carpus falcatus seed oil production as shown in the figure below.

Figure 3-16. Preparation of sample for each run(a) and experimental setup of epoxidation reaction(b)

3.14.2 Feed Material Requirement

20 ml of purified podo carpus falcatus oil was used for each run. Hence, the amount of hydrogen per oxide, formic acid and catalyst was calculated as follows using the process parameters. The amount of hydrogen peroxide required when the molar ratio of hydrogen peroxide to oil ratio is 1.5:1;

$$\frac{n\ Hydrogen\ peroxide}{n\ Oil} = 2.5$$

Substituting mass for mole: $\frac{\frac{\rho H2O2\ X\ VH2O2}{MH2O2}}{\frac{\rho oil\ X\ Voil}{Moil}} = 2.5$

$$: \frac{\frac{\frac{1.11g}{mol} * VH2O2}{\frac{34.01g}{mol}}}{\frac{\frac{0.912g}{ml} * 20ml}{\frac{837.89g}{mol}}} = 2.5$$

Solving for VH_2O_2 = 1.67 ml

The amount of acetic acid required when the molar ratio of acetic acid to oil ratio 0.5:1;

$$\frac{n\ Acetic\ acid\ (AC)}{n\ OIL} = 0.5$$

$$\frac{\frac{\rho ac * Vac}{MAc}}{\frac{\rho OIL * Voil}{Moil}} = 0.5$$

$$\frac{\frac{1.05g}{ml}*Vac}{\frac{60.052}{\frac{0.912g}{ml}*20ml}{814.89g/mol}} = 0.5$$

Solving for Vac =1.24ml

The amount of Catalyst required when the ratio of catalyst weight to oil 4;

Moil = $\rho\ oil * Voil$

Moil = 0.912 g/ml *20 ml

Moil = 18.24 gram

$$\frac{mass\ of\ catalyst}{mass\ of\ oil} = 4\%$$

Mass of catalyst = mass of oil *4%

Mass of catalyst = 18.24*4%

= 0.7296 gram

The amount of hydrogen peroxide and required catalyst is calculated for all experimental run the tabulated result for all experimental run was given in appendix C-1

CHAPTER FOUR

4. RESULT AND DISCUSSION

This section summarizes the results obtained from the experiments performed in the laboratory. Specifically, it will discuss synthesis and characterization of sulfonated solid acid catalyst from rice husk and epoxy oil production on podo carps falcatus seed oil starting from extraction of podo carps falcatus seed.

4.1. Raw Rice Husk Preparation and Catalyst Characterization

4.1.1 Proximate Analysis of raw Rice husk

The proximate analysis was performed on the fine-ground rice husk samples to determine the weight fractions of volatiles, ash, and fixed carbon in the rice husk. Because rice husk is a highly volatile fuel, the values of volatiles and ash were determined on a dry matter basis. The fixed carbon was then obtained by subtracting from 100 the sum of volatile matter and ash contents.

By Analyzing the number of components in the raw material is important to determine whether the raw material can be used for catalyst purpose or not. Proximate analysis was carried out using moisture analyzer, drying oven, and muffle furnace and the result recorded was shown in figure 4.1. The detailed calculation part is also included under Appendix-A. (The analysis was based on average values of three replicates, the weight percent were on dry basis)

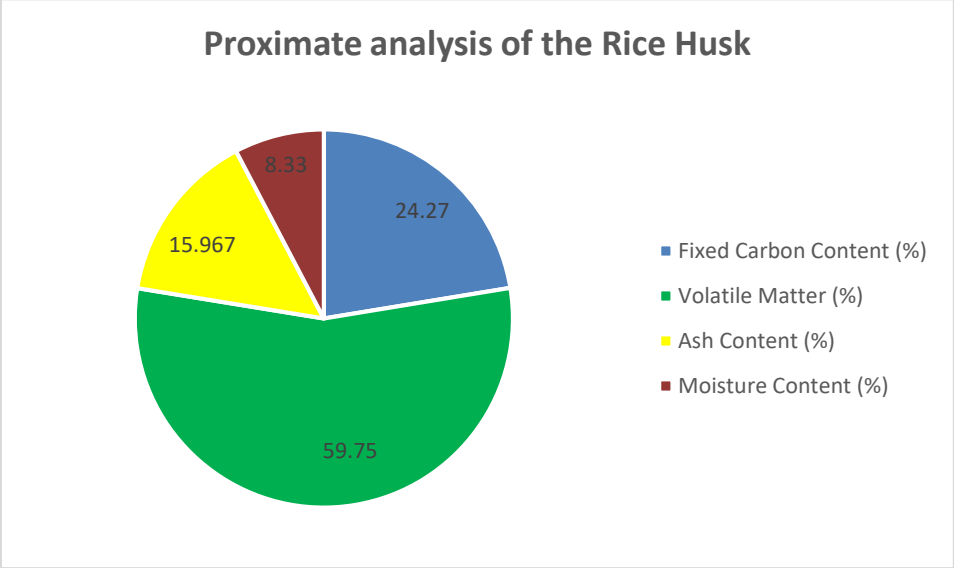


Figure 4-1. Proximate analysis of Rice husk

As shown in the Figure 4-1 the total amount of moisture content, volatile matter, ash content, and fixed carbon content were 8.33 %, 59.75 %, 15.967 %, and 24.27 % respectively. The rice husk sample was rich in high volatiles matter and high fixed carbon content. Bio- mass with higher fixed carbon content and high volatile has higher bio-char yield and higher surface area for attachment of the sulfonate group during sulfonation reaction (Lee, 2016).

4.1.2 Bulk density of Carbonized and Sulfonated Catalyst

The bulk density of rice husk has direct relationship to the performance of carbonization temperature (400,500, and 600℃). Sulfonated rice husk when bulk density of the rice had low bulk density of rice husk may reduce its residence time in the reactor. And will give resulting- in a lower conversion efficiency. High bulk density it may also give rise to poor mixing characteristics and a non-uniform temperature distribution, both of which create unfavorable operating conditions of the thermochemical conversion of raw rice husk along with carbonized and Particle Size Distribution (Mohanta, Kumar, & Parkash, 2012).

The bulk density of row rice husk is measured and 0.312g/ml is obtained. the bio-chars, as well as catalysts, is shown in Table 4-1. The bulk density of bio-chars(Carbonized) rice husk for C-400, C-500 and C-600 was 0.209, 0.214 and 0.238 gm/ml respectively is shown in the Table 4.1.and The bulk density of catalysts prepared sulfonated bio-chars i.e. C-SO_3H- 400, C-SO_3H- 500, and C-SO_3H- 600 was 0.252, 0.263 and 0.292 gm/ml respectively .

Table 4-1. Bulk Density of Bio-Char and Sulfonated Bio-Chars

Sample type	**Bulk density(g/ml)**
Rice husk	**0.312**
C-400	0.209
C-500	0.214
C-600	0.238
C-SO_3H-400	0.252
C-SO_3H-500	0.263
C-SO_3H-600	0.292

The bulk density of the bio-chars (Carbonized) rice husk is lower than that of prepared catalysts. Because, sulfonation reaction is sophisticated, many reactions may occur during sulfonation of bio-chars such as complete carbonization of the bio-chars. Therefore, as long as the bulk density of the bio-chars is lower than that of catalysts sulfonation reaction is the dominant reaction than other possible reactions. The carbonization temperature also shows significant effect on the bulk density of the catalysts this carbonization and sulfonation such behavior could be attributed to the following reasons. Total pore volume increased with increasing carbonization temperature, it was expected that the bulk density of the catalyst samples would increase, as the increase in the pore size would allow the sulfonic groups to be more easily incorporated onto the carbon matrix.

4.1.3. Acid Density of the Catalyst

The total acid density and amount of sulfonate (SO_3H) group for chars and catalyst were determined using back titration and direct titration methods. The results are shown in Table 4-2

Table 4-2. Total density carbonized Sample and -SO_3H group of Sulfonated catalysts

Carbonized sample	Total acid density (mmol/g)
C-400	2.10
C-500	2.32
C-600	2.57

Table 4-3. Acid density and the amount of sulfonated Carbonized Catalyst

Sulfonated Carbonized Sample	Total acid Density (mmol/g)	The amount of -SO3H group
C-SO3H-400	3.465	0.47
C-SO3H-500	3.828	0.54
C-SO3H-600	4.240	0.62

The total acid density of the bio-chars increases as carbonization temperature increases; because when the temperature increase the pore size will expand ,and have possibility to adsorb sulfonate group more as compared with lower temperature ,and this study support agree with previous study on carbon based catalyst and (Cheng & Li, 2018). The performance of carbon based sulfonated

carbon material could catalyze the hydrolysis of cellohexaose more effectively than SO_3H-bearing resins. This was because phenolic OH and COOH groups in the carbon material functioned as adsorption sites. And this study suggests when the carbonization temperature reach 600℃ gives maximum yield of total acid density and attached more sulfonate group.

4.1.4. Ultimate Analysis (CHNS)

Ultimate Analysis was performed on the fine-ground oven-dried rice husk samples to determine the elemental composition. The weight fractions of carbon, hydrogen, nitrogen, sulfur, chlorine, and ash were determined, and the weight fraction of oxygen in the rice husk samples was calculated by the difference. Carbon, hydrogen, and nitrogen weight fractions were determined using a EA 1112 Flash CHNS/O- analyzer device.

Table 4-4. Ultimate analysis for Carbonization and Sulfonated Catalyst

Sample	Carbon (%)	Nitrogen (%)	Hydrogen (%)	Sulfur (%)
Row Rice Husk	52	6.8	3.1	0
C-400	72.8	11	2.4	0
C-500	79.25	14	2.2	0
C-600	81.3	16	2.1	0
C-SO_3H- 400℃	61.86	17.26	2.32	1.9
C-SO_3H- 500℃	60.76	24.164	1.81	2.2
C-SO_3H- 600℃	58.02	31.89	0.478	2.9

4.1.5. Absorbance of the Carbonized Rice Husk

Based on this experiment the efficient catalyst was selected based on its highest removal efficiency of methyl orange from solution and the removal efficiency with its surface area, this means among prepared Bio-char which is synthesized at different Temperature.

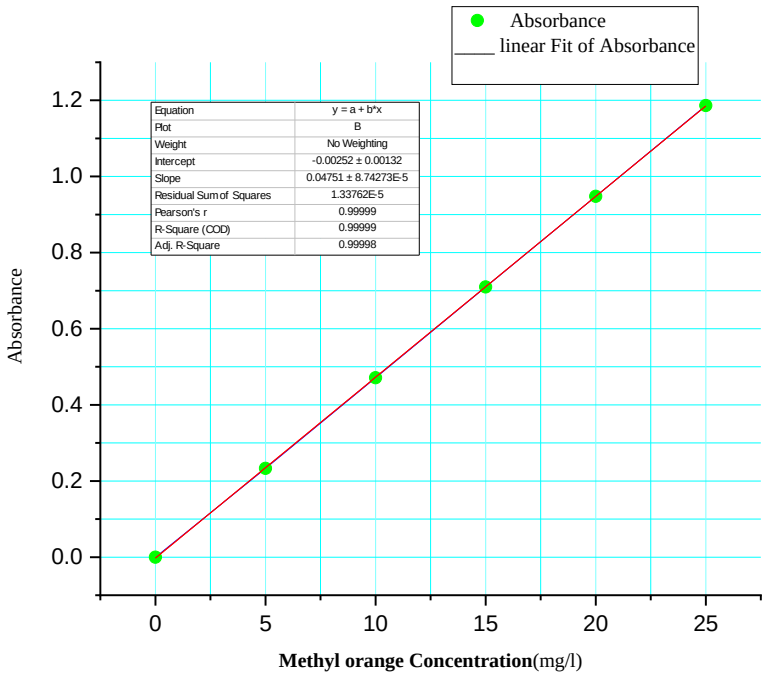


Figure 4-2. Absorbance verses Methyl orange concentration

Based on this observation the on the below table 4-5 Bio-char at C-600 showed better performance among the two, therefore by referring the bulk density, total acid density, and ultimate analysis also confirmed that the Bio-char which is prepared at C-600 showed better quality among them in order to check other performance of this Bio-Char FTIR is performed in the section below for both Bio-Char and sulfonated catalyst for C-600℃

Table 4-5. Removal Efficiency of carbonized samples at different pyrolysis temperature

Sample	Dosage of sample (gram)	Initial concentration (mg/l)	Initial Absorbance	Final Absorbance	Efficiency of Removal (%)
C-400	3	15	0.7096	0.2342	67
C-500	3	15	0.7096	0.1561	78
C-600	3	15	0.7096	0.1397	80.3

4.1.6. FT-IR analysis of activated rice husk and sulfonated activated rice husk

The rice husk which is carbonized and sulfonated were qualitatively analyzed by FTIR spectroscopy. Rice husk is mainly composed of cellulose, hemicellulose, lignin and waxes. The lignocellulosic structure consists of alkenes, esters, aromatics, ketones and alcohols. Figure 4.3

shows the rice husk Carbonized and then Activated by using NaOH. A sharp peak at 789- 792 cm-1 related to O-Si-O stretching vibrations of silica group is observed this result agree with (Ludueña, 2011) and .The silica related peak remained following both the carbonized and sulfonation processes as expected (Figure 4.4.). It is important to note that the silica was not removed from the carbon-based materials in both processes. Since, silica proved to maintain the mesoporous structure which otherwise will cause the carbon composites to collapse (Adrian & Janaun, 2012)

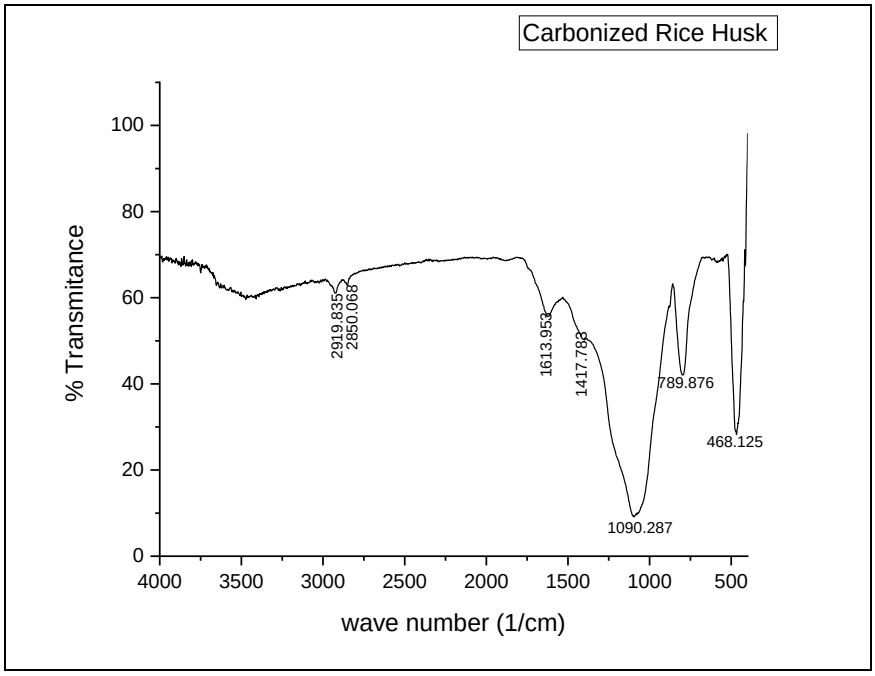


Figure 4-3. FT-IR analysis for (Carbonized) activated rice husk

These newly appearing absorption bands at 1011 cm-1 and 1080 cm-1 represent the asymmetric stretching respectively of S=O bonds of sulfonic acid (SO_3-H) which agree with (Sani, 2015) The sulfonation process was achieved in this case by a covalent attachment of $–SO_3H$ to the carbon framework through substitution of hydrogen in the C-H bond according to (C. Liu et al., 2019).FTIR spectrum and this result suggest that the Sulfonated Rice husk can work to Catalyze epoxidation reaction.

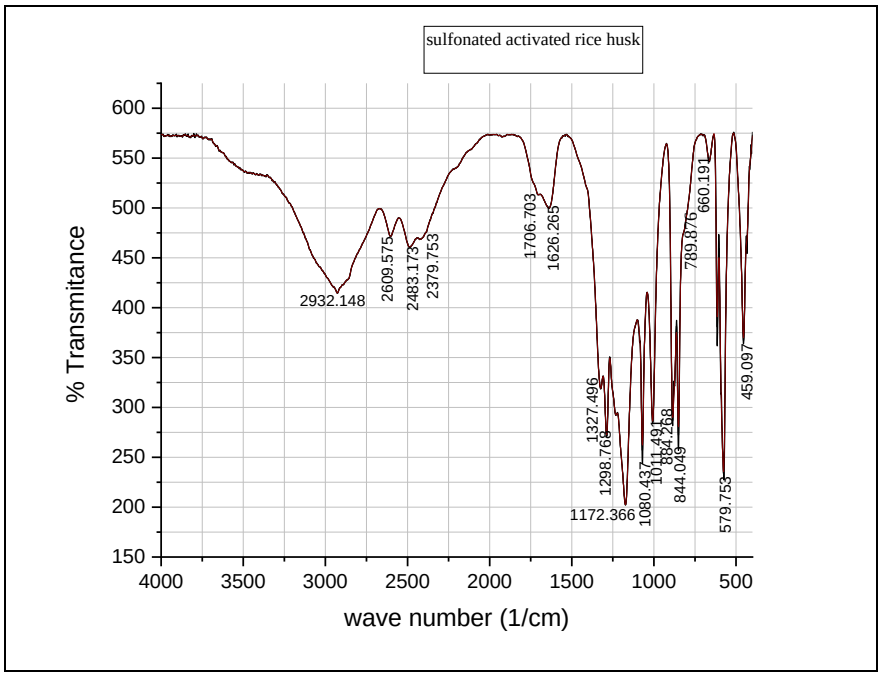


Figure 4-4. FT-IR analysis for a carbonized and Sulfonated rice husk

4.2. Characterization of Podo Carpus Falcatus Seed Oil ('Zegba' Oil)

4.2.1 Podo carpus falcatus Seed Preparation, Oil Extraction, Purification and Characterization

About 1.3 kg of podo carpus falcatus seeds were taken for this research work. First it was cleaned from impurities thus, 15 g wastes were removed. Therefore 1.25 kg cleaned podo carpus falcatus seeds were gained and the cleaned seeds was crushed using Jaw crushing mill to separate the external cover with inside seed, further crashed the internal seed by coffee grinding mill to get particle size of 0.5-1mm for solvent extraction analysis.

Podo carpus falcatus seeds Oil Extraction

From 1.25 kg of the kernel, 0.8 liter of podo carpus falcatus seeds oil was extracted using Soxhlet solvent extraction method by using hexane as a solvent. The yield of oil (Oil Content of the seed) was 58%. The total amount of crude oil obtained from Soxhlet solvent extraction first separated by using simple distillation and further purified by using Rotary Vacuum Evaporator

Yield calculation

The total amount of podo carpus falcatus seed oil obtained from solvent extraction is 0.8 liter out of 1.25 kg of podo carpus falcatus seed.

The density of the Podo Carpus falcatus seed oil = 912 kg/m3

The mass of the oil extracted will be calculated using the following equation:

$m=\rho * V$

Where: **m** is mass of the oil

ρ density of the oil

V volume of the oil

m = 912kg/m3* 0.8liter *1m3/1000 liter

= 0.7296kg

Yield of the oil = $\frac{0.7296kg}{1.25kg} * 100$ = 58%

4.2.2 Physicochemical Properties of Purified podo carpus falcatus Oil

The physiochemical properties were determined by analyzing of density, specific gravity, moisture content acid value, iodine Value, viscosity of the podo carpus falcatus seed oil. According to A.O.A.C. official methods were followed for characterization. The moisture content of the oil, density of the oil, viscosity of oil and acid value of the oil was determined.

Table 4-6. Physicochemical Properties of Purified podo carpus falcatus Oil

Property	Value
Density	912 kg/m^3
Specific gravity	0.9124
Dynamic viscosity	64.3 m.Pa.s at 21.9 ℃
Kinematic viscosity	6.98* 10^4 m^2/s
Moisture content	0.6%
Acid Value	4.0 %
Iodine Value	121 gI_2/100gram oil

The values of this physicochemical was shown in Table 4-6. The Fatty acids composition of the purified podo carpus falcatus oil was less than two which is acceptable for epoxidation reaction which doesn't need neutralization of crude podo carpus falcatus Oil for further purification. The lower the acid value of the oil, the lower its ability to hydrolyze which will be suitable for synthesis of EPFAO (epoxidized podo carpus falcatus seed oil) and increase the shelf life.

The moisture content, acid value, and iodine value of podo carpus falcatus seed oil are 0.6 %, 4 mol/gram and 121gram I_2/100gram oil respectively. These values are good character for the oil used in epoxidation reaction process according to (Gamage et al., 2009) . According to (Biermann & Boas, 2010). The moisture content of oil must be below 1.5 % and higher iodine value (>78) of the oil is better for epoxy oil production. And this physiochemical result suggests that podo Carpus falcatus seed oil is suitable for production of Epoxidized oil.

4.2.3. Gas Chromatography Mass Spectroscopy (GC/MS)

The fatty acid composition of podo carpus falcatus oil investigated by using Gas Chromatography Mass Spectroscopy (GC-MS) analyzer and the result is shown in table 4.7

Table 4-7. GC-MS result of major components of podo carpus falcatus seed oil

Peak	**Retention time**	**Area %**	**Library/ID**
14	11.4457	12.0592	Hexadecanolic acid
15	13.3449	9.4736	9-Octadecenoic acid
16	13.4317	64.8253	6,9-Octadecadienoic acid
17	13.4834	11.8969	stearate
18	16.1344	0.692	Methyl 18-methylnonadecanoate

The GC-MS identification of compounds from podo carpus falcatus seed oil is presented in the Table 4-7 We can also observe that the higher percentage area is registered for the unsaturated fatty acid (6,9-Octadecadienoic acid and 9-Octadecenoic acid), which is the most important fatty acid for production of epoxides. The GC-MS results also in agreement with iodine value of the

podo carpus falcatus oil where both indicates that podo carpus falcatus oil had higher degree of unsaturation bond

Molecular weight calculation of podo carpus falcatus seed oil

Table 4-8. molecular weight calculation of main component of podo carpus falcatus seed oil

Main components	Area present, %	Chemical formula	Molecular weight (gram/mol)
Hexadecanolic acid (palmitic)	12.0582	$C_{16}H_{32}O_2$	256.4
9-Octadecenoic acid (Oleic acid)	9.4736	$C_{18}H_{34}O_2$	282.47
6,9-Octadecadienoic acid	64.8253	$C_{18}H_{32}O_2$	280.452
Stearate (Stearic acid)	11.8969	$C_{18}H_{36}O_2$	284.84
Total			819

Molecular weight calculation of podo carpus falcatus seed oil: area percent *quality *molecular weight of each component and do the same for all component and add them.

$$\text{Molecular weight} = \sum \text{Each Area percent (abundance)} * \text{Each Molecular weight} \quad \ldots\ldots\ldots\ldots 4.1$$

Molecular mass of fatty Acid = 0.1205*256.4 + 0.0947*282.47+0.648*280.452 + 0.1189*284.94 = 273g/mol

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

= 3*273g/mol

=819g/mol

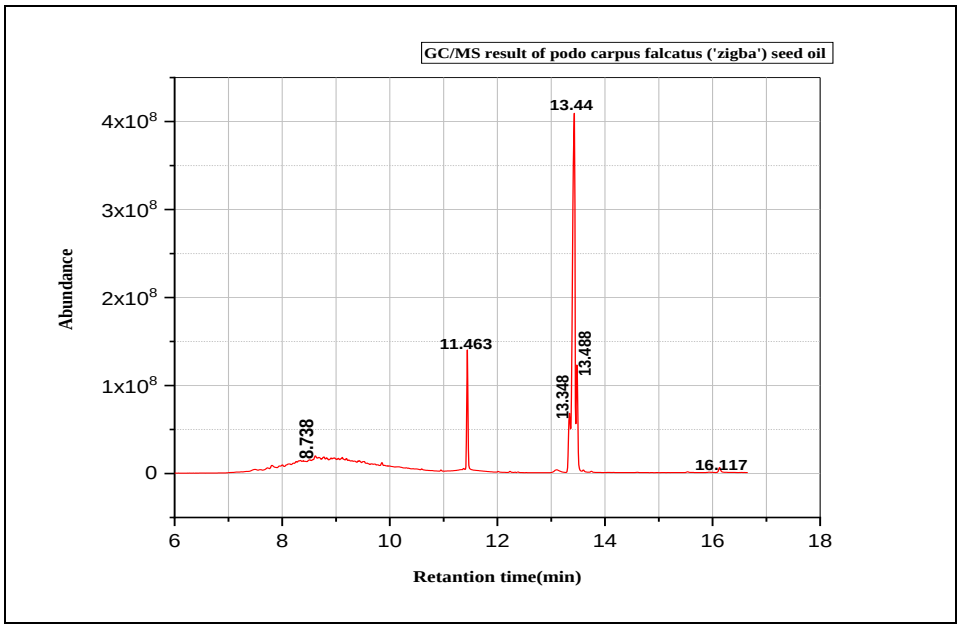


Figure 4-5. GC/MS result of podo carpus falcatus seed oil

4.2.4 Determination of Iodine value

The weight of oil taken for iodine value calculation was 0.3136 and 0.3119g according to (Paquot, 1978) The iodine value of the oil was 121.396gI_2/100gram oil. The iodine number of podo carpus falcatus oil determined shows that the oil has higher degree of unsaturation can definitely be applied for epoxidized podo carpus falcatus oil production. Because according to (Perdue, Carlson, & Gilbert, 1986) higher iodine value (which is higher than 75gram I_2/100gram of oil) indicates the ability to produce epoxides which are used for resins for paint and press-ink formulations.

4.3. Performance of C-SO_3H-600 Catalyst for Epoxidized podo carpus falcatus seed oil Production

The epoxidation reaction was carried out using three neck glass reactor which had 100ml of volume capacity and facilitated with magnetic stirrer to remove external contaminations and the speed was set to 1500 revolution/minute. The speed of the stirrer which maximum in order to increase the contact between the catalyst and the reactant. Further investigation on activity of the catalyst was performed in epoxidation of podo carpus falcatus seed oil studied through statistical and analytical method. The statistical analysis of the epoxidized oil synthesis is discussed in the following sections.

4.4. Statistical Analysis on Factors Affecting Epoxidation

Data analysis has performed by design-expert 7.0 software using Box-behnken design (BHD) method. The response variable measured is conversion of double bond to epoxy ring. There were four factors; time, temperature, catalyst loading, and molar ratio of hydrogen peroxide to molar ratio of podo carpus falcatus seed oil with three levels. This design of the experiment helps us to differentiate the significance of the main and the interaction factors. This program software also used to develop the mathematical model that will describe the effects of the main and interaction factors on the response

A Box-Behnken Design is a three-level quadratic design that does not contain fractional factorial design. The sample combinations are treated in such a way that they are located at midpoints of edges formed by any two factors. The design is rotatable (or in cases, nearly rotatable). One advantage of a Box-Behnken design is that it requires fewer design points than a full factorial CCD and generally requires fewer design points than a fractional factorial CCD. Additionally, a Box-Behnken Design avoids extremes, allowing you to work around extreme factor combinations. Consider using the Box-Behnken Design DOE type if your project has parametric extremes (for example, has extreme parameter values in corners that are difficult to build). Since the Box-Behnken DOE doesn't have corners and does not combine parametric extremes, it can reduce the risk of update failures.

The conversion of double bond and the formation of epoxy ring was done by using process parameter such as Time ,Temperature ,catalyst loading ,and molar ratio of hydrogen peroxide with oil ,the conversion of double bond was done by using Hans method and the formation of epoxy is checked by using epoxy group oxygen checking method (Paquot, 1978) The Box-Behnken Design conditions and their respective responses and the ANOVA are given in Table 4-9 and Table 4-10 respectively

Table 4-9 . Experimental and predicted value for double bond conversion of podo carpus falcatus oil

Std.	Run No.	Time (Hr.)	Temperature ℃	Catalyst Loading (%Wt.)	Molar Ratio of H_2O_2 With Oil	Experimental Conversion (%)	Predict Conversion (%)	Residual
1	12	2.00	65.00	4.00	2.50	0.36	0.38	-0.021
2	9	6.00	65.00	4.00	2.50	0.714	0.73	-0.013
3	24	2.00	85.00	4.00	2.50	0.798	0.78	0.018
4	26	6.00	85.00	4.00	2.50	0.62	0.59	0.026
5	25	4.00	75.00	2.00	1.50	0.68	0.69	-0.01
6	29	4.00	75.00	6.00	1.50	0.677	0.71	-0.029
7	6	4.00	75.00	2.00	3.50	0.89	0.86	0.034
8	15	4.00	75.00	6.00	3.50	0.689	0.68	0.011
9	21	2.00	75.00	4.00	1.50	0.727	0.70	0.031
10	10	6.00	75.00	4.00	1.50	0.6821	0.65	0.032
11	4	2.00	75.00	4.00	3.50	0.61	0.64	-0.030
12	7	6.00	75.00	4.00	3.50	0.819	0.85	-0.028
13	11	4.00	65.00	2.00	2.50	0.55	0.58	-0.028
14	27	4.00	85.00	2.00	2.50	0.765	0.79	-0.024
15	20	4.00	65.00	6.00	2.50	0.602	0.58	0.026
16	8	4.00	85.00	6.00	2.50	0.662	0.63	0.030
17	3	2.00	75.00	2.00	2.50	0.628	0.61	0.016
18	5	6.00	75.00	2.00	2.50	0.89	0.88	0.1
19	2	2.00	75.00	6.00	2.50	0.709	0.72	-0.014
20	16	6.00	75.00	6.00	2.50	0.589	0.61	-0.024
21	17	4.00	65.00	4.00	1.50	0.451	0.44	-0.013
22	19	4.00	85.00	4.00	1.50	0.74	0.77	-0.035
23	22	4.00	65.00	4.00	3.50	0.739	0.71	0.027
24	14	4.00	85.00	4.00	3.50	0.632	0.65	-0.015
25	23	4.00	75.00	4.00	2.50	0.592	0.56	0.030
26	18	4.00	75.00	4.00	2.50	0.586	0.56	0.024
27	13	4.00	75.00	4.00	2.50	0.5431	0.56	-0.019
28	1	4.00	75.00	4.00	2.50	0.583	0.56	0.021
29	28	4.00	75.00	4.00	2.50	0.508	0.56	-0.054

Table 4-10. Experimental and predicted value Epoxy formation of podo carpus falcatus oil

Std.	Run No.	Time (hr.)	Temperature ℃	Catalyst Loading, (%wt.)	Molar ratio of H_2O_2 with oil	Experimental OOC (%)	Predicted OOC%	Residual
1	12	2.00	65.00	4.00	2.50	2.74	2.46	0.28
2	9	6.00	65.00	4.00	2.50	2.71	2.48	0.23
3	24	2.00	85.00	4.00	2.50	1.53	1.30	0.23
4	26	6.00	85.00	4.00	2.50	2.61	2.43	0.18
5	25	4.00	75.00	2.00	1.50	2.78	2.51	0.27
6	29	4.00	75.00	6.00	1.50	2.93	2.55	0.38
7	6	4.00	75.00	2.00	3.50	3.52	3.44	0.077
8	15	4.00	75.00	6.00	3.50	2.84	2.66	0.18
9	21	2.00	75.00	4.00	1.50	2.21	2.47	-0.26
10	10	6.00	75.00	4.00	1.50	1.70	1.88	-0.18
11	4	2.00	75.00	4.00	3.50	1.79	1.82	-0.035
12	7	6.00	75.00	4.00	3.50	3.60	3.56	0.042
13	11	4.00	65.00	2.00	2.50	3.29	3.30	-0.011
14	27	4.00	85.00	2.00	2.50	2.18	2.13	0.050
15	20	4.00	65.00	6.00	2.50	2.10	2.36	-0.26
16	8	4.00	85.00	6.00	2.50	2.12	2.32	-0.20
17	3	2.00	75.00	2.00	2.50	1.70	1.88	-0.18
18	5	6.00	75.00	2.00	2.50	3.20	3.41	-0.21
19	2	2.00	75.00	6.00	2.50	2.43	2.46	-0.032
20	16	6.00	75.00	6.00	2.50	2.02	2.08	-0.060
21	17	4.00	65.00	4.00	1.50	2.05	2.15	-0.099
22	19	4.00	85.00	4.00	1.50	2.23	2.34	-0.11
23	22	4.00	65.00	4.00	3.50	3.34	3.47	-0.13
24	14	4.00	85.00	4.00	3.50	1.92	2.06	-0.14
25	23	4.00	75.00	4.00	2.50	3.21	3.27	-0.060
26	18	4.00	75.00	4.00	2.50	3.13	3.27	-0.14
27	13	4.00	75.00	4.00	2.50	3.45	3.27	0.18
28	1	4.00	75.00	4.00	2.50	3.23	3.27	-0.040
29	28	4.00	75.00	4.00	2.50	3.33	3.27	0.060

The actual experimental data at different epoxidation condition was recorded and given in Appendix C, at Table C-1. The mathematical models were developed to correlate the epoxidation factors with the response conversion.

4.4.1. Development of Regression Model Equation

The mathematical model equation relationships that correlates the response (conversion of double bond and Epoxy Ring Formation (OOC, %)) to the epoxidation reaction process variables like Time, Temperature, Catalyst loading, and molar ratio of hydrogen peroxide with molar ratio of podo carpus falcatus seed oil. in terms of actual value, the insignificant terms were given below. The predicted model for percentage of degree of conversion and epoxy formation (OOC %) in terms of the coded factors and actual factor is given below in Table 4.11. and 4.12 respectively.

Table 4-11. Regression model Equation for conversion

Final Equation in Terms of Coded Factor	Final Equation in terms of Actual Factor
conversion =	conversion =
+0.56 +0.040 * A +0.067 * B -0.040 * C +0.035 * D -0.13 * A * B +0.063 * A * D -0.099 * B * D	-3.83191 +0.41281 * time +0.070346*temprture +0.11449*catalyistloading +0.32551 * mole ratio of H_2O_2 with oil -6.65000E-003 * time * temprture -0.023875 * time * catalyist loading +0.031738 * time * mole ratio of H_2O_2 with oil

Table 4-12. Regression model equation for oxirane oxygen content

Final Equation in Terms of Coded Factors:	**Final Equation in Terms of Actual Factors:**
OOC =	OOC =
+3.27 +0.29 * A -0.30 * -0.19 * C +0.26 * D +0.28 * A * B +0.58 * A * D	-28.15427 +0.026875 * time +0.72767 * temperature +0.038750 * catalyist loading +3.77458 * mole ratio of H2O2 with oil +0.013875 * time * temperature +0.29000 * time * mole ratio of H2O2 with oil

4.4.2. Model Adequacy check

Before the model implemented for different applications it should contain different criteria such as the normal distribution of the error term (residuals) and the residuals verses predicted value of the model data. If the model does not satisfy these criteria, it is not advisable to use the model for different purposes. The correlation of responses of conversion and epoxy (oxirane oxygen) content to the coded value of variables were estimated using non-linear regression in the help of design expert software. The estimated regression coefficients were done through analysis of variance (ANOVA) is provided at Table 4-14 and Table 4-15 for conversion and oxirane oxygen content respectively.*Table 4-13. Regression statistics for conversion and oxirane oxygen (OOC, %) content of podo carpus falcatus seed oil*

Regression statistics	Conversion (%)	Oxirane oxygen content (OOC, %)
R-Squared	0.9526	0.9596
Adjusted R-Squared	0.9053	0.9192
Predicted R-Squared	0.7819	0.8713
Adeq Precision	19.037	16.547
Observation	29	29

For conversion and oxirane oxygen content the "Pred R-Squared" of 0.7819 and 0.8713 are in reasonable agreement with the "Adj R-Squared" of 0.9053 and 0.9192 respectively. and the result suggest that the difference is less than 0.2, then the model is fitting the data and can reliably be used to interpolate. "Adeq Precision" measures the signal to noise ratio and a ratio greater than 4 is desirable. The ratio of signal to noise is 19.037 for conversion and 16.547 for oxirane oxygen content. So, the result suggests an adequate signal for the model can be used to navigate the design space

Table 4-14. Analysis of variance (ANOVA) for conversion of epoxidized podo carpus falcatus seed oil

Source	Sum of Squares	DF	Mean Square	F VALUE	P-VALUE PROB>F	
MODEL	0.46	14	0.027	43.81	< 0.0001	*
A-Time	0.017	1	0.019	22.77	0.0003	*
B-Temperature	0.046	1	0.053	60.63	< 0.0001	*
C-Catalyst Loading	0.012	1	0.019	15.94	0.0013	*
D-Mole Ratio of $H_2O_2$with OIL	0.016	1	0.015	21.46	0.0004	*
AB	0.088	1	0.071	116.09	< 0.0001	*
AC	0.033	1	0.036	43.17	0.0741	**
AD	0.018	1	0.016	23.24	0.0003	*
BC	6.006E-003	1	6.006E-003	7.96	0.0736	**
BD	0.039	1	0.039	51.95	0.0641	**
CD	9.025E-003	1	9.801E-003	11.96	0.0568	
A^2	0.048	1	0.024	63.05	0.0701	**
B^2	0.16	1	6.024E-005	209.93	0.0601	**
C^2	0.012	1	0.046	15.28	0.0916	**
D^2	0.011	1	0.047		0.0722	**
Residual	0.011	14	1.347E-003	1.05		
Lack of Fit	9.061E-003	10	1.367E-003		0.2059	**
Pure Error	1.505E-003	4	1.297E-003			
Cor Total	0.47	28				

Where: (*) represent significant terms and (**) represent non-significant terms

As shown in table 4-14 The Model F-value of 43.81 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case Time, Temprature , Catalyist load , molar ratio of hydrogen peroxide with oil, Time * Temprature , Time*molar ratio of hydrogen per oxide with oil are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 2.41 implies the Lack of Fit is not significant relative to the pure

error. There is a 20.59% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4-15. Analysis of variance for oxirane oxygen content of epoxidized podo carpus falcatus seed oil

Source	Sum of Squares	DF	Mean Square	F VALUE	P-VALUE PROB>F	
MODEL	10.38	14	0.74	11.82	< 0.0001	*
A-Time	0.99	1	0.99	15.73	0.0014	*
B-Temperature	1.10	1	1.10	17.61	0.0009	*
C-Catalyst Loading	0.41	1	0.41	6.61	0.0222	*
D-Mole Ratio of $H_2O_2$with Oil	0.81	1	0.81	12.86	0.0030	*
AB	0.91		0.91	14.55	0.0019	*
AC	1.35	1	1.35	21.46	0.0720	**
AD	0.32	1	0.32	5.09	0.0405	*
BC	0.64	1	0.64	10.21	0.5065	**
BD	0.17	1	0.17	2.75	0.5197	**
CD	2.23	1	2.23	35.51	0.0621	**
A^2	1.71	1	1.71	27.26	0.0521	
B^2	0.33	1	0.33	5.34	0.0677	
C^2	0.41	1	0.41	6.57	0.0725	
D^2	0.82	1	0.082	5.37	0.0614	
Residual	0.061	14	0.015	11.82		
Lack of Fit	11.25	10	0.74		0.0597	**
Pure Error	10.38	4	0.99			
Cor Total	0.99	28				

Where: (*) represent significant terms and (**) represent non-significant terms

As shown in Table 4-15 The Model F-value of 11.82 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case Time, Temperature catalyst loading, molar ratio of hydrogen peroxide with oil, time*temperature, Time*molar ratio of hydrogen per oxide with oil are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), Model reduction may improve your model.

The "Lack of Fit F-value" of 5.97 implies there is a 5.97% chance that a "Lack of Fit F- value" this large could occur due to noise. Lack of fit is bad -- we want the model to fit. This relatively low probability (<10%) is troubling.

The figure 4.7 and figure 4.8 shows predicted values versus actual values which is obtained using the developed correlation and This figure 4-7 and figure 4.8 Showed that the regression model equation gives very close a description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between predicted value of Time ,Temprature ,Catalyist loading ,and molar ratio of Hydrogen peroxide with oil with actaul value of this four factor for epoxidation reaction process variables to the percentage of conversion and epoxy (oxirane oxygen content) .

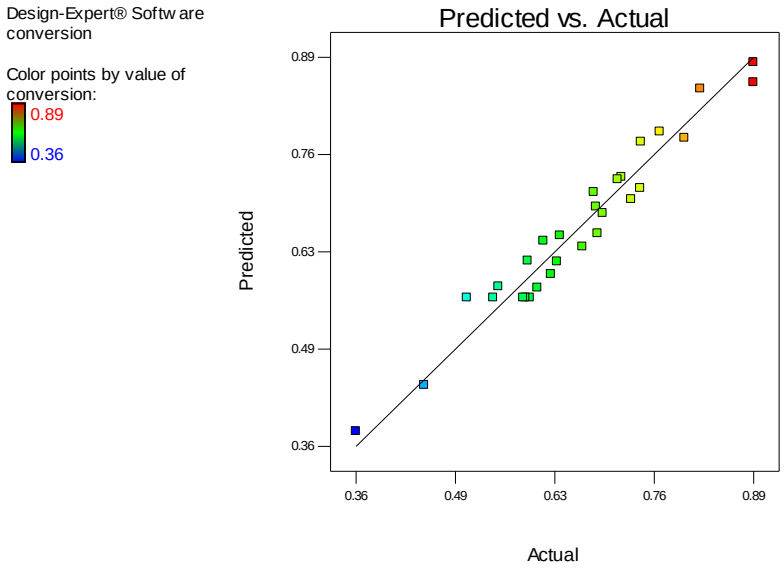


Figure 4-6 Predicted versus actual percentage conversion of the double bond in podo carpus falcatus seed oil.

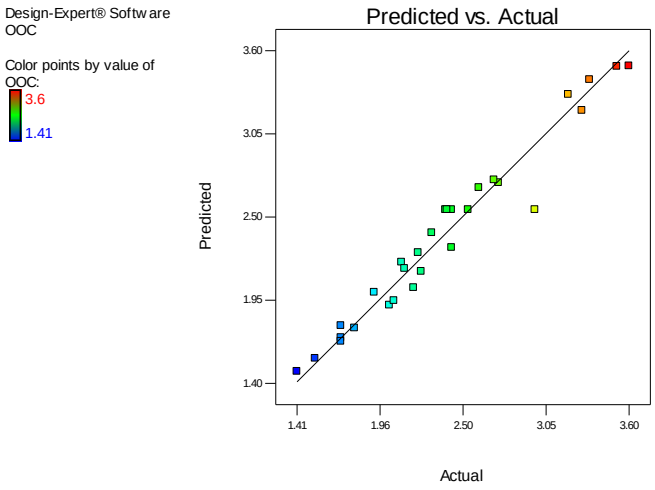


Figure 4-7. Predicted versus actual value of epoxy (oxirane oxygen content) of podo carpus falcatus seed oil

The normal probability plot is a graphical technique for assessing whether or not a data set is approximately normally distributed. The error was normally distributed and assumed a mean of zero. In figure 4-9 the normal probability plot of residual shows the data are distributed normally along center as they lie closely to the straight line and shows no deviation of the variance for conversion and the data set is Match close to normality distributed .a very few outliers which is negligible effect compared with the overall data. The conversion is reasonably distributed and the plot show good approximately normality distributed.

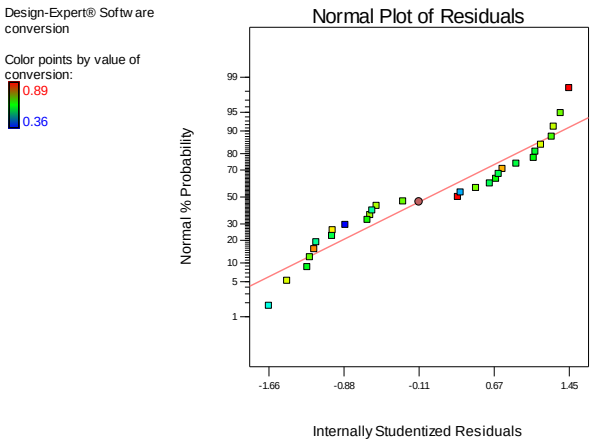


Figure 4-8 Normal probability plot with residuals for conversion

The normal probability plot is a graphical technique for assessing whether or not a data set is approximately normally distributed. The error was normally distributed and assumed a mean of zero. In figure 4-9 the normal probability plot of residual shows the data are distributed normally along center as they lie closely to the straight line and shows no deviation of the variance for conversion and the data set is mach close to normality distributed. A very few outliers which is negligible effect compared with the overall data. The oxirane oxygen content is reasonably distributed and the plot show good approximately normality distributed.

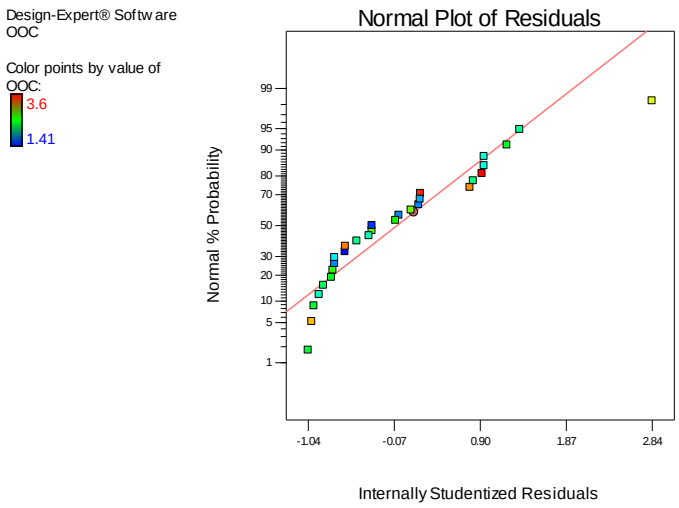


Figure 4-9. Normal % probability plot verses residual for oxirane oxygen content

4.5. Effect of Variables on Conversion

The epoxidation reaction of extracted podo carpus falcatus seed oil is checked by varying four process variables such as time , temperature ,catalyst loading and molar ratio of hydrogen peroxide with podo carpus falcatus seed oil the sulfonated catalyst is prepared from rice husk by activated in sodium hydroxide at different temperature and followed by sulfonated using sulfuric acid in nitrogen gas atmosphere the effect of each process variable to conversion of double bond to epoxy ring is given and the formation of epoxy (oxirane oxygen content) in figure 4-11 up to figure 4-14.

4.5.1. Effects of Reaction Time on Conversion of Double Bond and Oxirane oxygen Content

Figure 4-11 shows the experimental data for the epoxidation of podo carpus falcatus seed oil at different reaction time. The iodine value are especially important properties in the characterization of epoxidized vegetable oils. Because the iodine value indicates the remaining unsaturation after the epoxidation reaction, the oxirane oxygen content indicates the epoxy groups present in the products. In the preparation of polymers, epoxy resins with a lower iodine value and higher oxirane oxygen content are desired. The reductions in iodine values indicated the consumption of the unsaturation during the epoxidation, but they did not represent solely conversion to epoxy groups because epoxy ring degradation generates side products

The influence of reaction time in this profile of epoxidation reaction process was studied in range from 2 to 6 hours in all the experiments, the volume of the oil was kept 20ml, peracetic acid and hydrogen peroxide, and catalyst based on the run order. When reaction time reached around 4 hours the epoxidation reaction gives maximum conversion, after it reached 4 hours the product yield (conversion) was found to be around 81.4 % to 84.5 %.and the oxirane oxygen content is 3.45 OOC %.

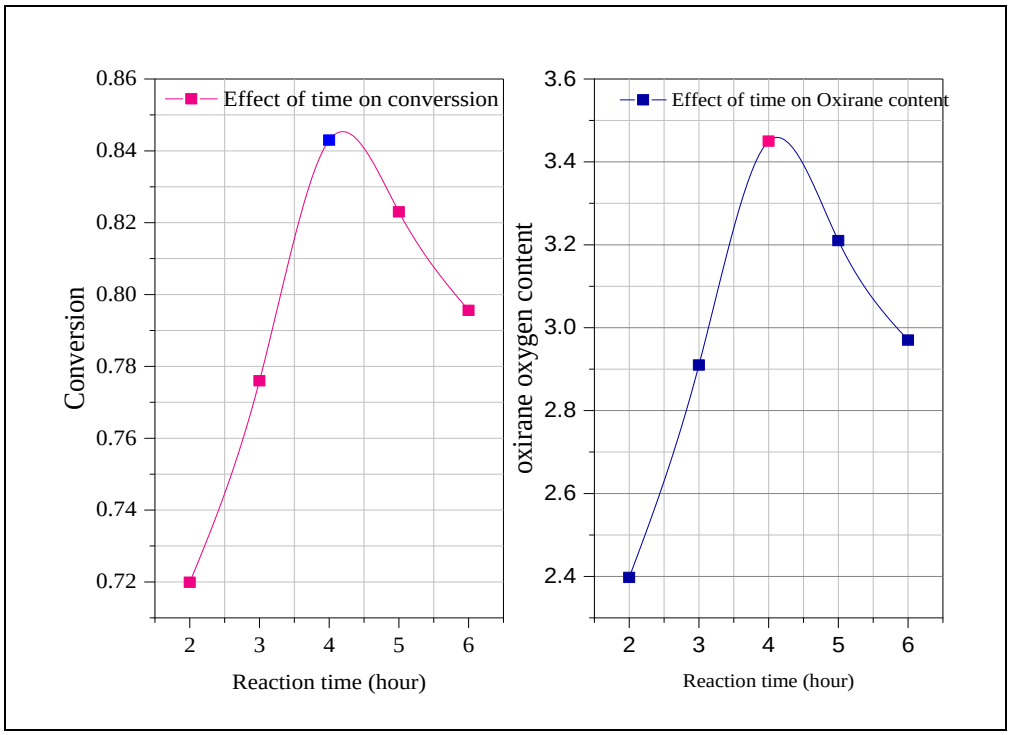


Figure 4-10. Effect of reaction time on conversion and oxirane oxygen content

The oxirane oxygen content OOC of epoxidized podo Carpus falcatus seed oil determines conversion of double bonds in vegetable oil into oxirane rings and reactivity. Hourly measurement is required to monitor OOC level during epoxidation process. The produced epoxidized podo carpus falcatus seed oil had oxirane oxygen content of 5.32–5.82% and relative conversion to oxirane of 76.2.–84.4%. More reaction time leads to degradation of oxirane oxygen content. As oxygen supplied by the hydrogen peroxide depleted, the epoxy formation ended earlier than anticipated. These undesirable reactions contributed lower oxirane oxygen content.

4.5.2. Effects of Reaction Temperature on Conversion and Oxirane Oxygen Content

Increasing temperature showed a favorable effect on the formation of peracetic acid. This resulted not only shown in more rapid epoxidation, but also in higher rate of hydrolysis (oxirane

cleavage) of the product. Reaction at lower temperatures gave lower epoxidation rate but led to lesser ring opening. The time required for attainment of the maximum OOC value at different temperatures (65, 75,and 85 ℃) is performed and when the temperature approaches to 75℃ gives better conversion of double bond and also show more oxirane formation for this specific oil type and this result suggest that for maximum oxirane formation and double bond conversion 75℃ is preferable.

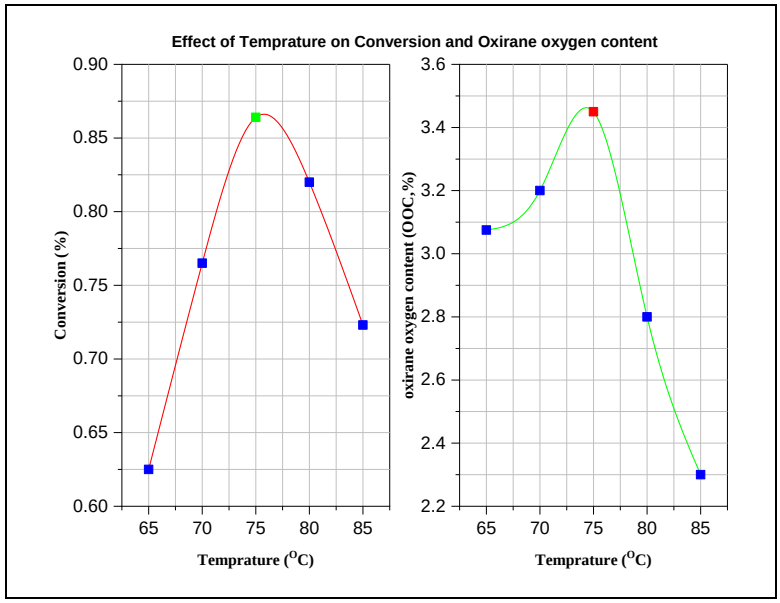


Figure 4-11 Effect of Temperature on conversion and oxirane content

In Figure 4-12 where conversion became maximum and the oxirane content also reach its maximum value and this conform that the almost all double bond occur in the podo carpus falcatus seed oil convert to epoxy ring. when its reach 75℃ apart from this temperature it was observed that the difference in conversion for different temperature and this result correspond with previous studies according to Eider, 2017. This is because more oxirane was formed at lower temperature while at 75℃, the oxirane content became moderate and conversion seems to be maximum because once the double bond is broken and epoxy formed, but when we increase the double bond broken as it is, but the formed epoxy bond will break and the conversion only shows us how much the double bond break and 3.45 OOC % is formed when the temperature reach 75℃, which is related with the decrease of iodine value or conversion but temperature have direct relationship and it affect the overall epoxidation reaction as much as possible the temperature must be kept at 75℃, and oxirane contents at different temperature were observed.

4.5.3. Effect of catalyst loading on conversion and oxirane content of epoxidized podo carpus falcatus seed oil

The effect of the catalyst amount on the epoxidation of podo carpus falcatus seed oil is represented in Figure 4-13. The catalytic activity of sulfonated activated rice husk (C-SO_3H-600℃,) has been investigated in the epoxidation of podo carpus falcatus seed oil.

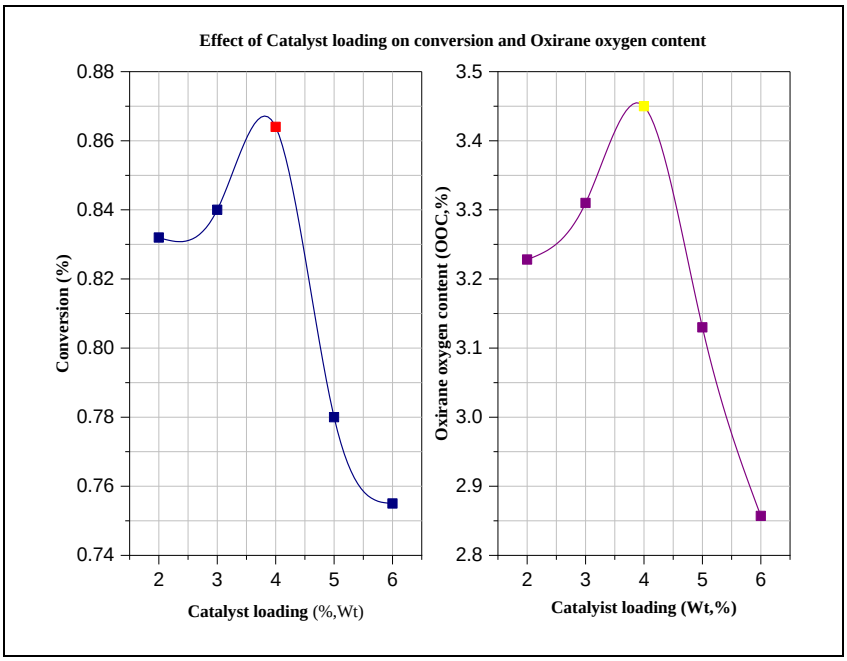


Figure 4-12. Effect of Catalyst Loading on Conversion and Oxirane oxygen Content

figure 4-13 suggest that the catalytic activity for epoxidation of vegetable oil is solely dependent on the catalysis loading .and its shows the catalyst loading is work effectively when we add moderate amount of sulfonated catalyst ,because heterogeneous catalyst they need more free space to mix with the oil and at the same time the contact area became high when the catalyst freely exposed to the oil ,but when we add more solid heterogeneous catalyst the solid became stick each other and they form coagulate .therefore the proper amount of catalyst should be add for each experiment based on the oil ratio ,and sulfonated activated rice work for epoxidation reaction successfully and when the catalyst loading 4%,wt.its give conversion 86.4 which is maximum and 3.45 OOC % number of oxirane content and this result suggest that the Catalyst loading should be 4 % by weight corresponding to podo Carpus falcatus seed oil.

4.5.4. Effect of hydrogen peroxide on conversion and oxirane content of epoxidation reaction

The epoxidation rate increased as the concentration of H_2O_2 in the system increased. But, the stability of the oxirane ring was very poor at this high mole ratio of H_2O_2. On the other hand, at low concentrations of H_2O_2, oxirane ring was quite stable.

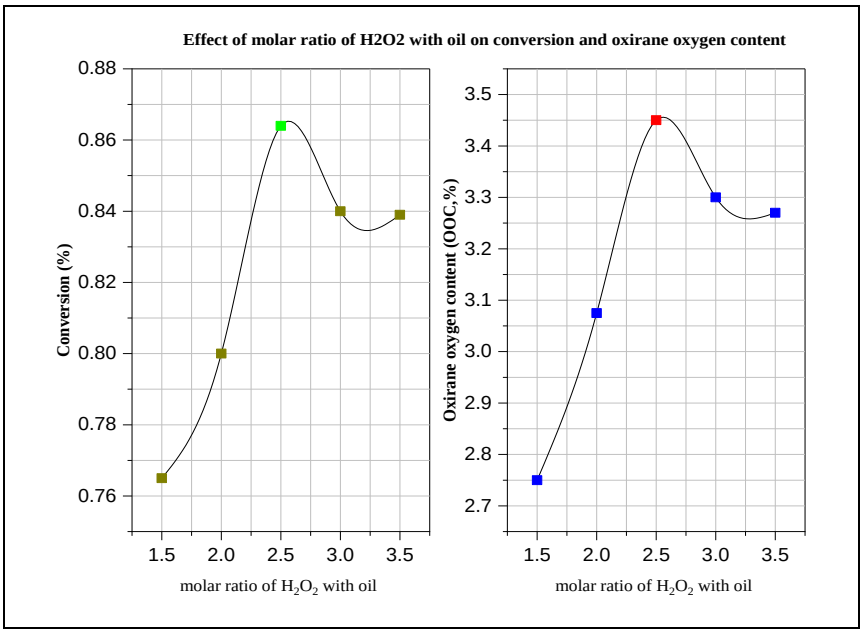


Figure 4-13. Effect of hydrogen peroxide on conversion and oxirane content

The effect of H_2O_2 to mole ratio of podo carpus falcatus seed oil on the conversion to oxirane and ratio was studied in the ratio range 1.5–3.5 Figure 4.14 shows that the epoxidation rate increased as the concentration of H_2O_2 in the system increased. Although the maximum conversion to oxirane was obtained for a mole ratio of 2.5, the stability of the oxirane ring was very poor at this high mole ratio. On the other hand, at low concentrations of H_2O_2, oxirane ring was quite stable. It was also observed that the formation of oxirane oxygen content increased as this ratio increased until it reaches 2.5 and this figure clearly show the conversion and oxirane oxygen content became high when the molar ratio 2.5 of hydrogen peroxide with podo carpus falcatus seed oil.

4.6. Interaction effect Between Process Variables

To achieve a high OOC value of epoxide, there were some parameters that we have to consider such as concentration of peroxy acid (epoxidation agent), reaction temperature, reaction time and Catalyst loading. An increasing in the peroxy acid content of the reaction mixture is accompanied by an increase of oxirane oxygen content (OOC) value. For a

reaction mixture containing a fixed amount of vegetable oil (double bonds), there may be a concentration of acid (oxygen carrier) required for optimum epoxidation, beyond which oxirane cleavage (epoxide degradation) may become important

The most usual way to describe the results of an interaction effect of process variable is using central composite design experiment is in the form of a response surface plot additional to this it's possible to show response contours plot. The process variables were found to have significant parameter have direct relationship for conversion and oxirane oxygen content of epoxidized podo carpus falcatus seed oil and their interaction effects describe in the Figure 4-15 to 4- 16 shows the interaction effect of reaction time and temperature toward conversion and oxirane oxygen content ,interaction effect of reaction time and Catalyst loading toward Conversion and oxirane oxygen Content and their effect is describe by using surface response plot and contours plot

4.6.1. Effect of time and temperature on conversion and oxirane content

the effect of time and temperature on conversion as well as oxirane oxygen content and when Reaction at lower temperatures gave lower epoxidation rate but led to lesser ring opening the time required for attainment of the maximum OOC value at different temperatures (65, 75, 85℃) is shown in Figure 4-16.and figure 4-17 Reaction at lower temperature (65℃) showed lower OOC value in the beginning of reaction but gave more stable oxirane ring after 4 hours of reaction. Meanwhile, others showed a decreasing trend of their OOC value after 1hours minutes of reaction. These results suggest that optimum levels of epoxidation could be attained at moderate (75℃) reaction temperatures at which epoxide degradation would be minimal. when the reaction time increase from 2 hour to 4 hour it's favors the conversion of double bond to epoxy ring but when the time and temperature increase the conversion decrease as well as the formation of oxirane content. because when temperature above 75℃ and when the reaction time exceed 4 hour the oxirane ring cleavage Will occur and the conversion will decrease and this result agree with (Nugrahani, 2017)

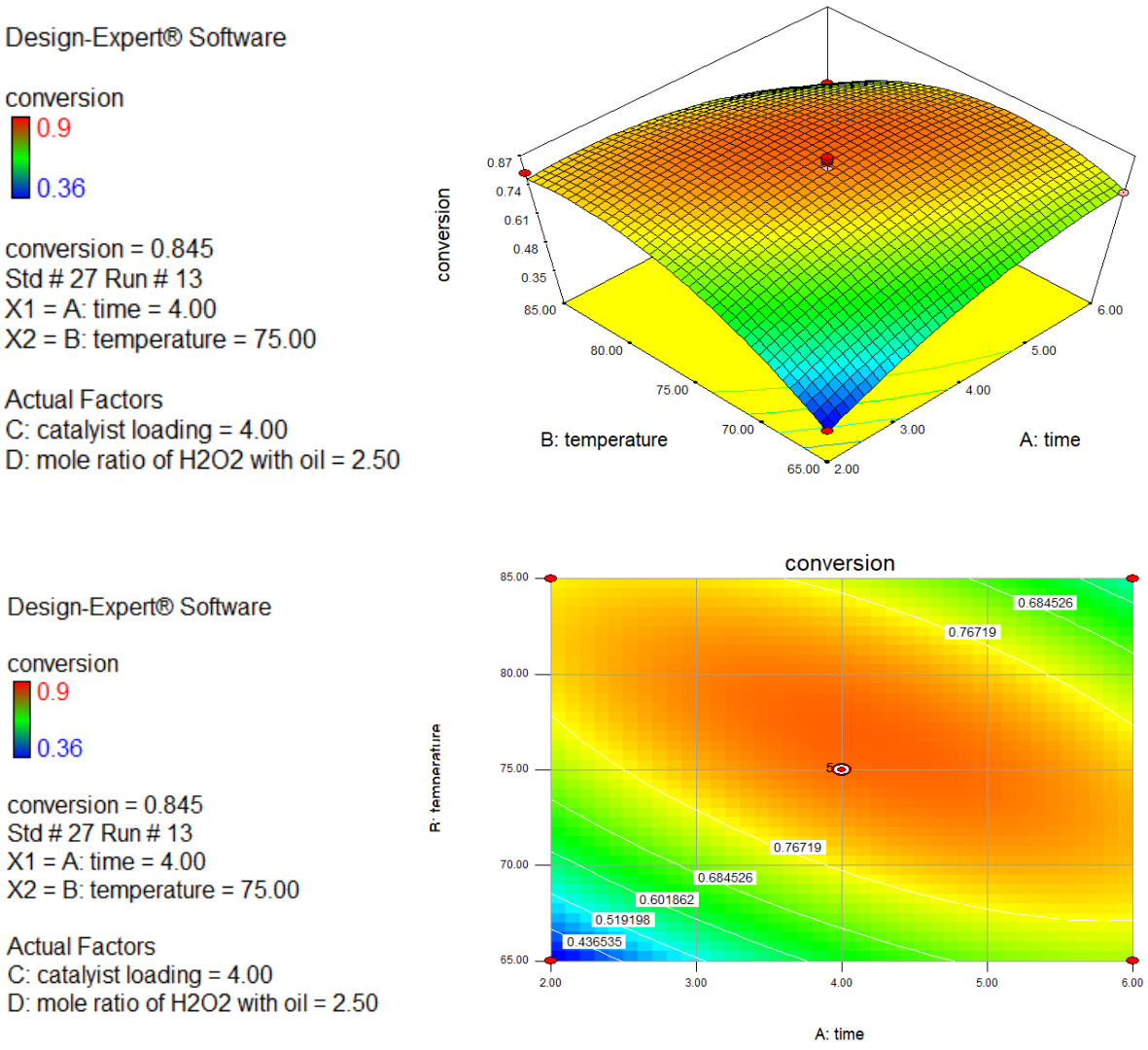
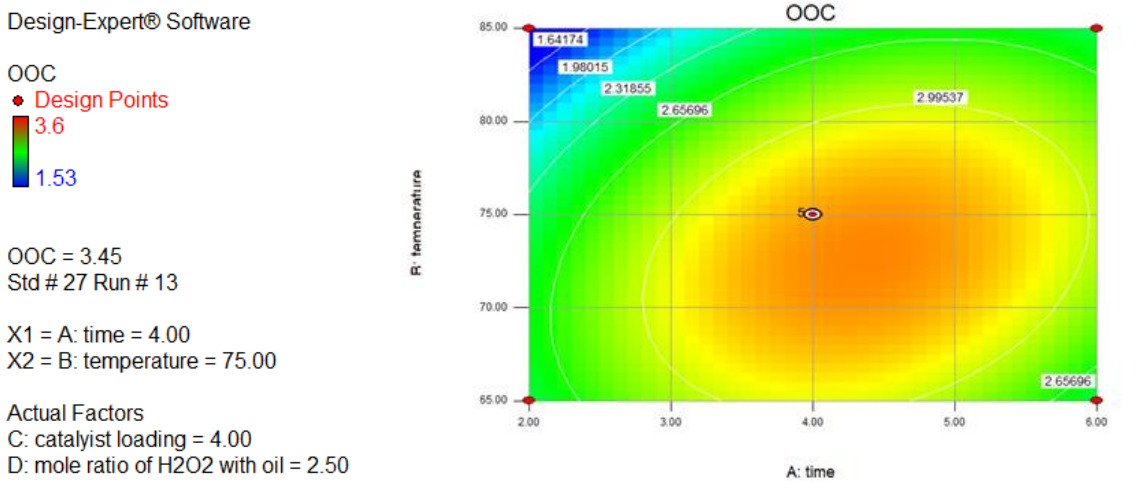


Figure 4-14 Effect of time and temperature on conversion



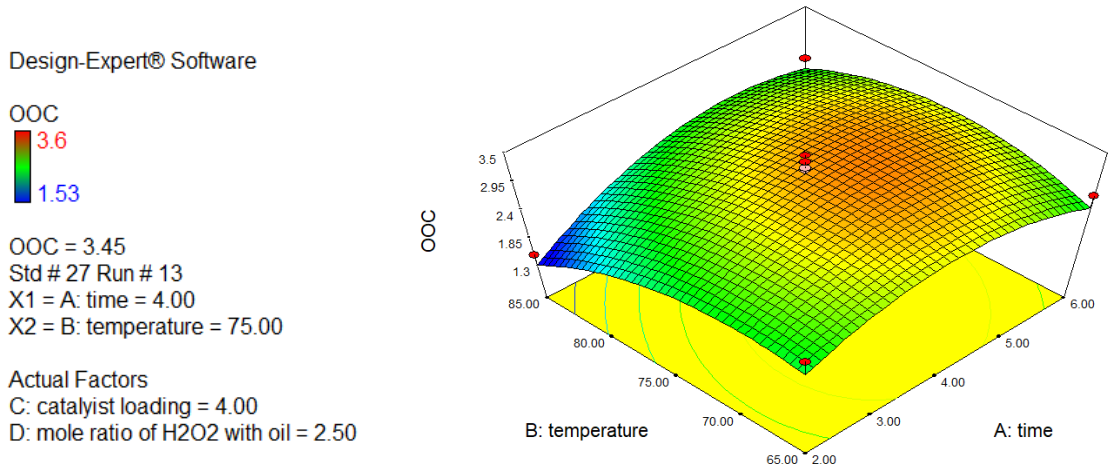
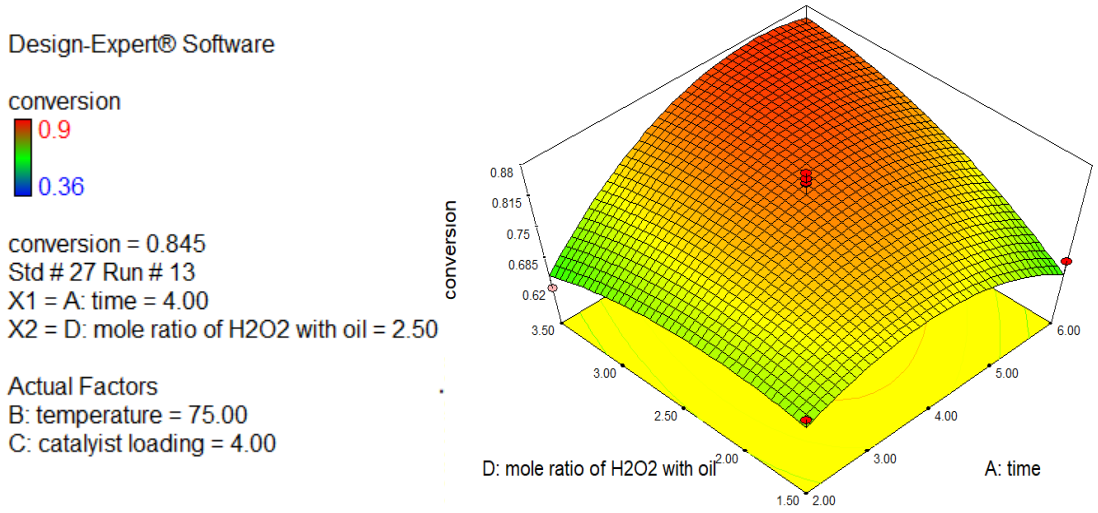


Figure 4-15 Effect of time and temperature on oxirane oxygen content

4.6.2 Effect of Reaction Time and molar ratio of hydrogen peroxide with oil on Conversion and Oxirane Oxygen Content (OOC)

To achieve a high OOC value of epoxide and conversion of double bond to epoxide, there were some parameters that we have to consider such as concentration of peroxy acid (epoxidation agent), reaction temperature, reaction time and Catalyst loading. An increasing in the peroxy acid content of the reaction mixture is accompanied by an increase of oxirane oxygen content (OOC) value. For a reaction mixture containing a fixed amount of vegetable oil (double bonds), there may be a concentration of acid (oxygen carrier) required for optimum epoxidation beyond which oxirane cleavage (epoxide degradation) may become important. The epoxidation rate increased as the concentration of H_2O_2 in the system increased. But, the stability of the oxirane ring was very poor at this high mole ratio of H_2O_2. On the other hand, at low concentrations of H_2O_2, oxirane ring was quite stable Reaction time played a role as the variable in order to obtain the optimum condition of a reaction by integrating with other parameters. Beyond the optimum reaction time of a parameter, the OOC value of epoxide decreased rapidly and the figure 4.17 shows the interaction effect of time and hydrogen peroxide and the conversion and oxirane oxygen content gives maximum yield when the hydrogen peroxide reach 2.5 molar ratio with oil and the time to reach this point 4 hours.



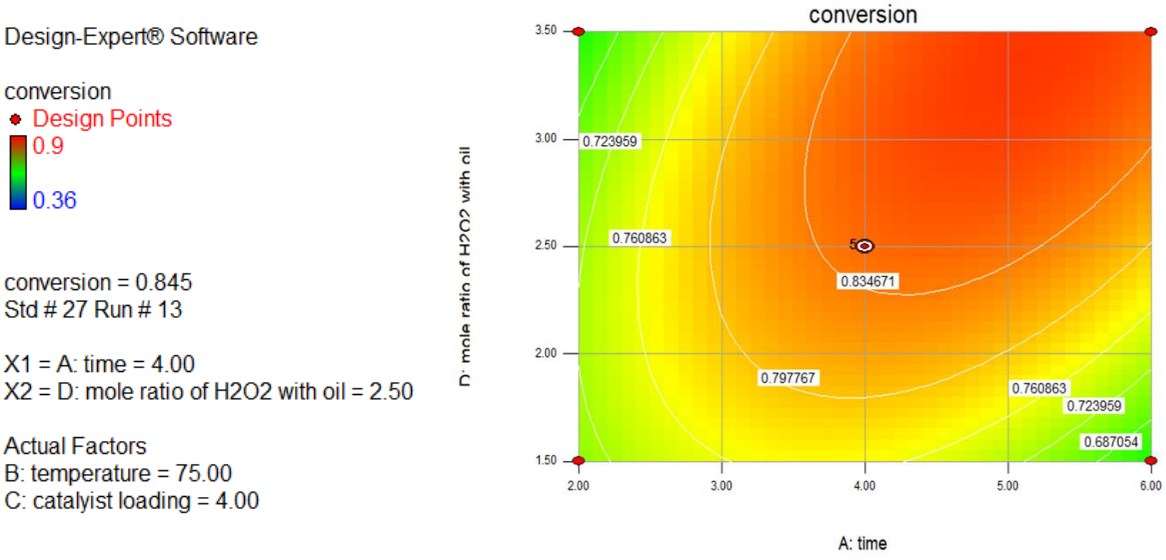


Figure 4-16 Effect of time and temperature on conversion

4.7 Optimization of Process Variables

The results above have shown that the four epoxidation process variables (time, Temperature Catalyst loading, molar ratio of hydrogen peroxide with oil) and the interaction among the variables affect the percentage of conversion. Therefore, the next step is to optimize the process variables in order to obtain the highest percentage of conversion and maximum oxirane oxygen content using the model regression developed. So, in order to obtain the maximum percentage of conversion and maximum oxirane content the setup on the optimization criteria will be range for epoxidation variable except for the two response such as conversion and oxirane oxygen content

and set to maximum .because our aim is to find the optimum value .this means the design software help us to identify individual effect as well as interaction effect of epoxidation process variable . the predicted combination of parameters was as follows: temperature of 71.38℃, molar ratio of hydrogen peroxide to oil 2.36:1 and catalyst loading of 2.94 (%wt). Under these conditions, the model predicted of 93.60% conversion and 3.952 OOC, % with a desirability 1.

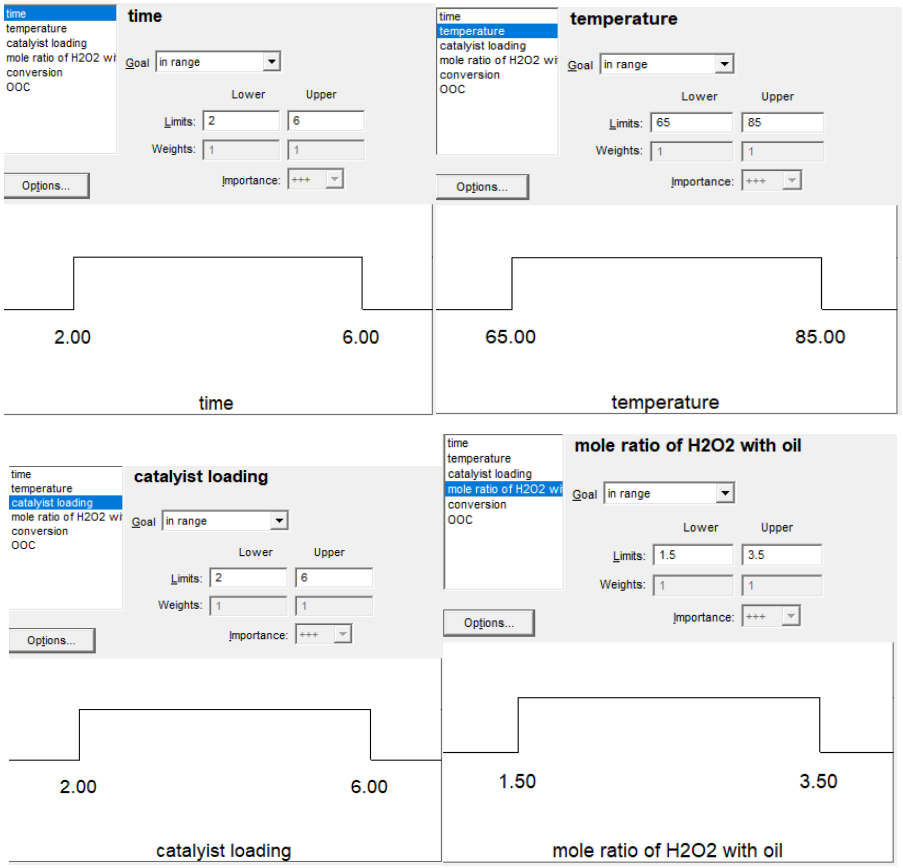


Figure 4-17 Optimization process variables

To validate the optimum conditions predicted by the model using desirability ramp experiments were conducted using the optimized epoxidation process conditions and mean percentage conversion value of 93.60 % was obtained and the results are closely related with the data obtained from optimization analysis using desirability functions.

Therefore, this study shows that podo carpus falcatus seed oil can definitely be used for synthesis of epoxidized podo carpus falcatus seed oil and optimum percentage of conversion can be obtained from the synthesis of podo carpus falcatus seed oil using sulfonated carbon catalyst via epoxidation reaction by using activated rice husk as support for sulfonic acid.

4.9. FTIR Analysis for Podo Carpus Falcatus Seed Oil and Epoxidized Podo Carpus Falcatus Seed Oil

FTIR analysis of podo carpus falcatus seed oil and epoxidized podo carpus falcatus seed oil is investigated by using FTIR by observing the existence of new peaks and this study show ,The presence of new peak in the FTIR spectra of Epoxidized podo carpus falcatus seed oil at 824.3 cm-1, attributed to epoxy group, corroborated the conclusion that the success of the epoxidation reaction of podo carpus falcatus seed oil .the epoxy groups were found in epoxidized podo carpus falcatus seed oil (doublet at 823 cm-1 and 843 cm-1) indicating that all of the carbon double bonds were turn into epoxy groups. (Vlček & Petrović, 2006) reported the presence of epoxy groups at 822–833 cm−1, which agrees well with this study

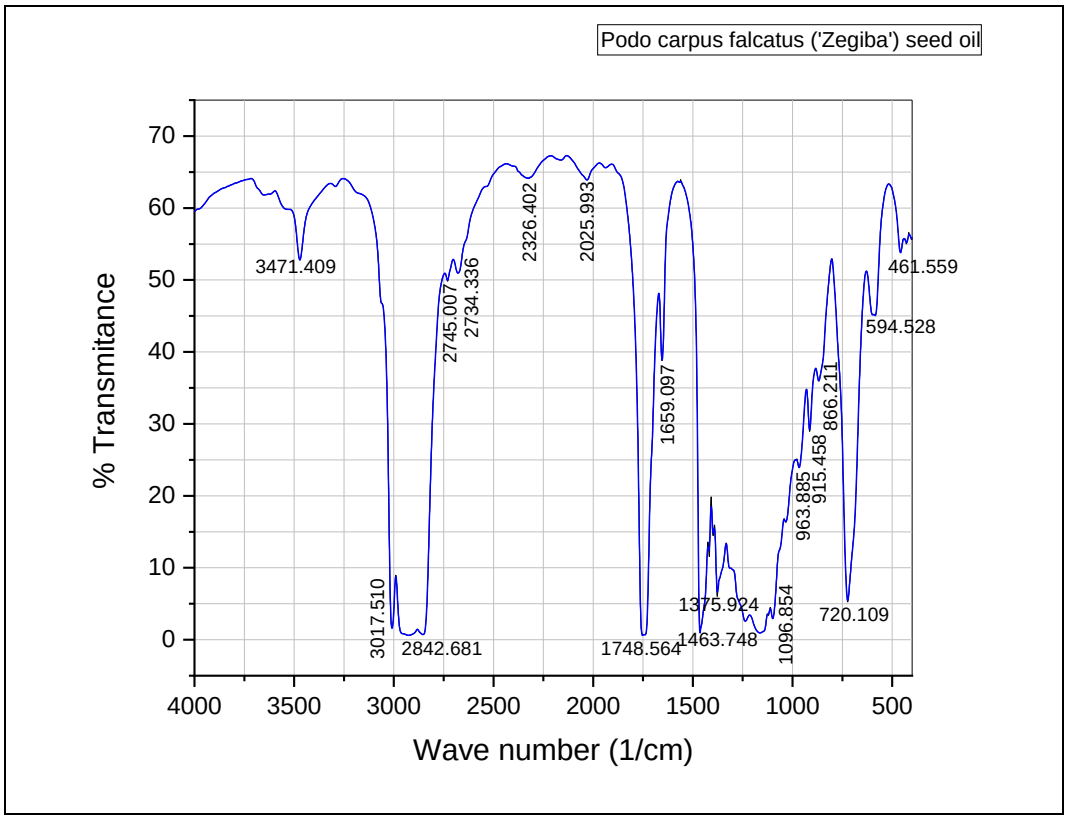


Figure 4-18 FTIR spectrum of podo carpus falcatus seed oil

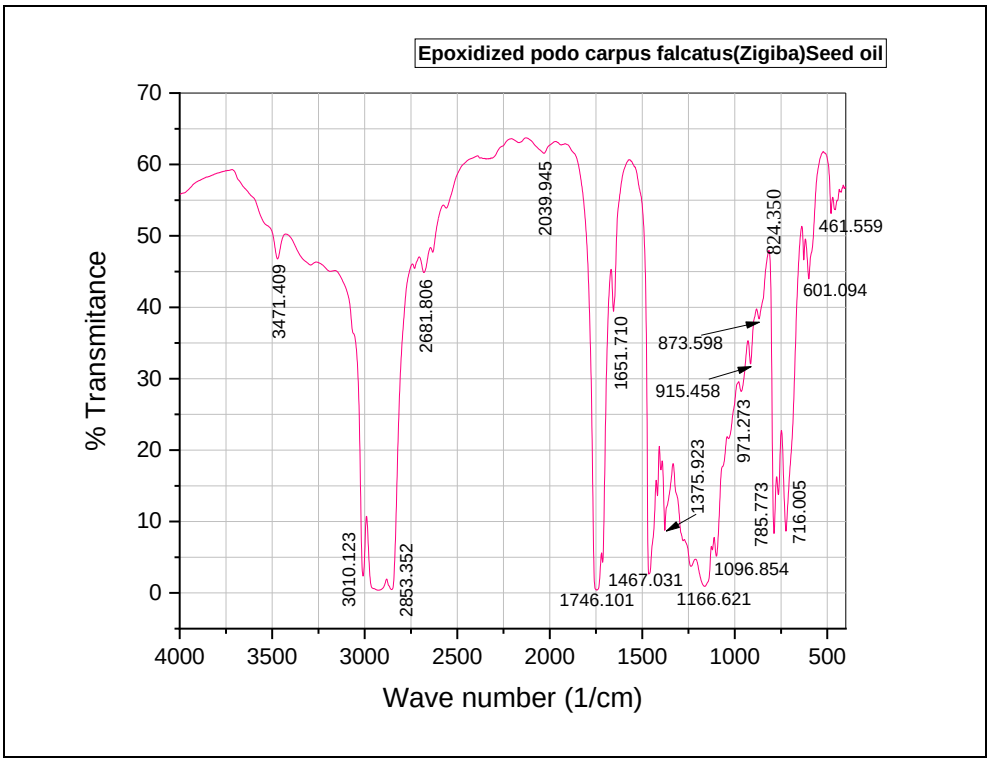


Figure 4-19 FTIR spectrum of Epoxidized podo carpus falcatus seed oil

The characteristic band at about 3000–3020 cm−1 is attributed to the C—H stretching of the oil attached to a double bond. This band disappeared or decreased in intensity following the epoxidation reaction. The strong absorption bands at 1030–1050 cm−1 confirmed the presence of alkyl–aryl ether groups in the structure. Similarly, a strong absorption band at 1240–1250 cm−1 confirms the presence of aryl–aryl ether linkage in the structure of the resins. The band at 3410–3450 cm−1 is due to the O—H stretching, which is formed by hydroxylation of the epoxy group during Conversion of C=O stretching vibration band at 1720–1750 cm–1 remained unchanged after the epoxidation reaction. (N.Karak, 2012) and this study confirms the existence of epoxy group in the product.

4.10. NMR Spectrum Analysis of Epoxidized podo carpus falcatus seed oil

Figure 4.22 and figure 4.23 shows H NMR and C NMR was used to characterize the epoxides synthesized from Podo carpus falcatus seed oils and epoxidized podo carpus falcatus seed oil by reaction with formic acid and hydrogen peroxide with sulfonated carbon catalyst. for epoxides derived from Podo carpus falcatus seed oil were between 1.45–1.60 ppm and 1.70–1.85 ppm, distinct from other chemical groups in these oils and in the first range it's has mono epoxide and in the second range have diepoxide and this study shows there is epoxy formation around on

1.584ppm. Chemical shifts of epoxy groups moved downfield with an increasing number of epoxy groups in the fatty acid chain. Results also suggested that epoxide was formed during the epoxidation process under the conditions of this study

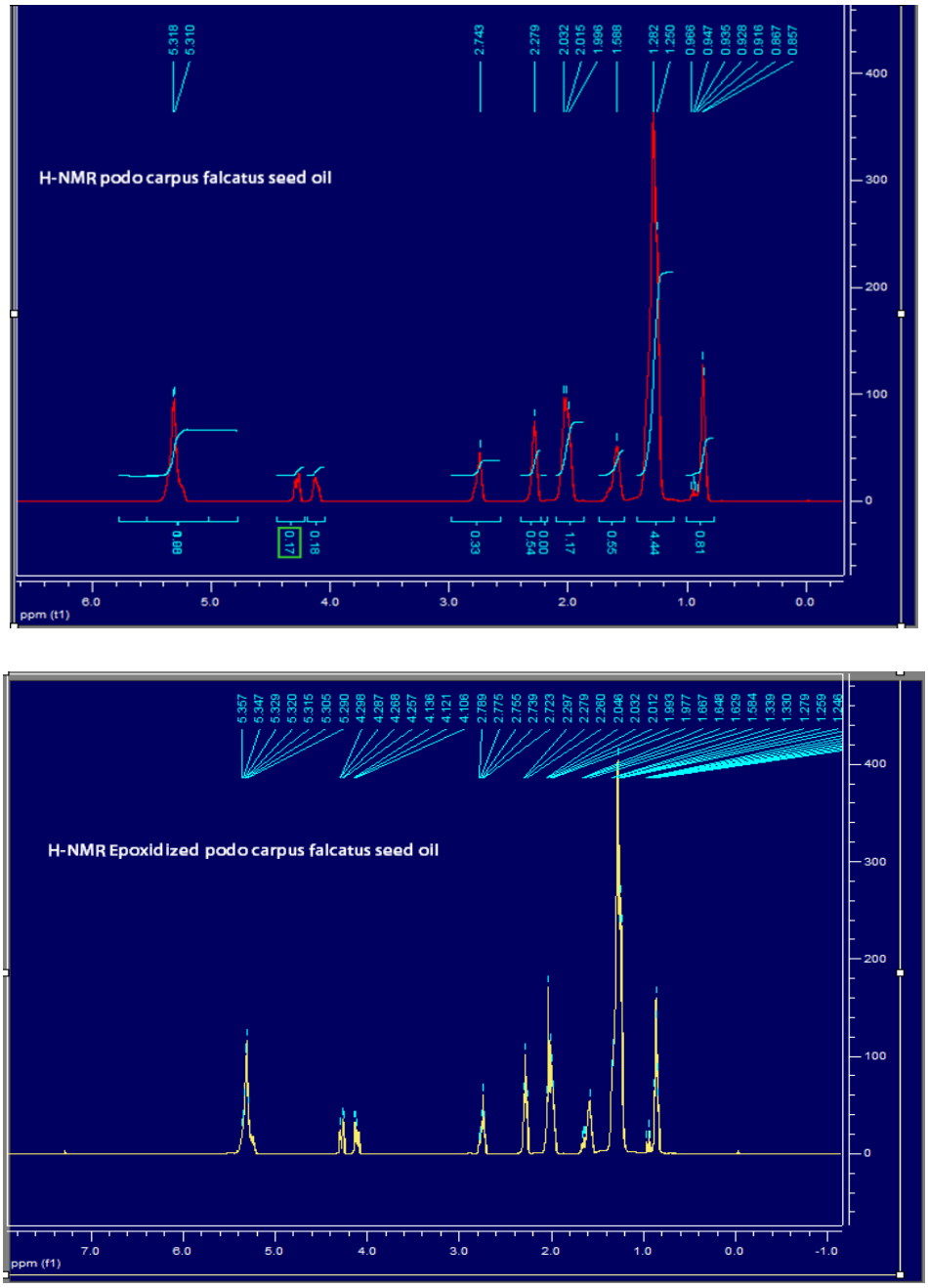


Figure 4-20 . H-NMR analysis of podo carpus falcatus seed oil and epoxidized oil

H NMR spectra of vegetable oils indicate the presence of peaks at δ = 0.80–0.90 ppm are for the terminal methyl group of the fatty acid chains, δ = 1.50–1.60 ppm are due to protons of -CH2 group attached to the terminal methyl group, peaks at δ = 1.10–1.30 ppm are for protons of all the internal -CH2 groups present in the fatty acid chains, peaks for protons of unsaturated carbons

appear at δ = 5.30–5.40 ppm and the methylene protons (-CH2) of glycerol moiety appear at δ = 3.50–4.90 ppm. The -CH proton of the same (glycerol) moiety appears at δ = 5.30–5.90 ppm.

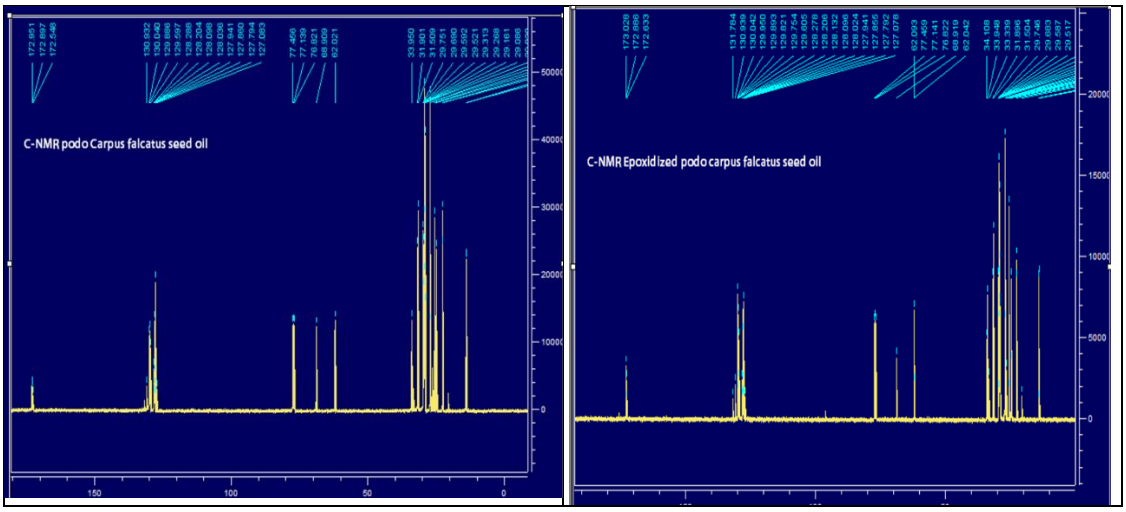


Figure 4-21 C-NMR analysis of podo carpus falcatus seed oil and epoxidized oil

CHAPTER FIVE

5. CONCLUSIONS AND RECOMENDATIONS

5.1 Conclusions

Epoxidation of fatty acids is a reaction of a carbon – carbon double bond with active oxygen, which results in the addition of an oxygen atom, converting the original double bond into a three membered epoxide (oxirane) ring. epoxidation increases the polarity and the stability of vegetable oils by improving their compatibility with polymers such as polyvinyl chloride (PVC), and The potential utility of epoxidized vegetable oil has begun to be realized in industrial applications with increasing the concern of research in aspirants to develop value added products from the local available plant oils.

The main objective of this research was to produce epoxidized podo carpus falcatus seed oil by new synthesized high acidity carbon-based catalysts from rice husk that have high activities on epoxidation. Synthesized catalysts were physically and chemically characterized considering bulk density, acid density, elemental analysis, absorbance of carbonized and activated rice husk using Fourier transform-Infrared spectroscopy (FTIR). among prepared bio-char at different carbonization temperature (400 ,500, 600 ℃); and further confirmed by using FTIR analysis. The results from carbonized rice at 600℃ give improved results therefore carbonized and sulfonated rice husk catalyst confirmed that the catalyst can be used for epoxidation of podo carpus falcatus seed oil. The results of this study suggest that epoxidation can be successfully performed by using novel material.

Podo carpus falcatus seed oil was epoxidized successfully by peroxyacetic with hydrogen peroxide at the temperature range 65-85℃. The epoxidation of podo carpus falcatus seed oil was tested by conversion (%), oxirane oxygen content (OOC, %) and further confirmed by FTIR analysis and NMR analysis. It was found that the optimal value of oxirane oxygen content was obtained (3.78%) at 71.89 °C reaction temperature, in 5.1 hours reaction time, and 1.94:1 hydrogen peroxide to oil molar ratio with desirability of 100 %. The relative conversion achieved of double bond was 90.89%. and this study showed that podo carpus falcatus seed oil had the potential to be used as epoxidized vegetable oil after a chemical reaction takes place.

Epoxidized oil can be successfully produced from locally available raw material 'zigba' (podo carpus falcatus) seed oil. And by introducing novel carbon based sulfonated heterogeneous catalyst used in this experiment. The carbon-based catalysts prepared from rice husk are promising

catalysts for a more efficient epoxidized oils production. Carbon based catalysts with high activity on epoxidation reactions were successfully prepared from rice husk. There are several drawbacks associated with using sulfuric acid as a catalyst, (or even all of the homogeneous catalysts), such as equipment corrosion, the release of toxic residues causing environmental issues, purification and separation of desired product and recovery of the catalyst. This heterogeneous carbon-based catalyst does not have these disadvantages and can be easily separated from epoxidized podo carpus falcatus seed oil and works successfully for epoxidation reaction of vegetables oil.

5.2 Recommendations

The following recommendations are made based on a holistic review of the subject area for production of epoxidized podo carpus falcatus seed oil from podo carpus seed and by using novel Carbon-based sulfonated Catalyst from rice husk.

- Further investigations must be conducted to understand the behavior and to explore their commercial application of the carbon-based catalysts from rice husk for epoxidation reaction studying the kinetics of adsorption process. (attachment of sulfonic acid to active site of the carbon catalyst
- Further investigation must be conducted to control the effect of process variable at a time by fixing other process variable and understand the effect of single variable must be conducted to control and optimum conversion and oxirane oxygen content
- To increase the conversion as well as oxirane oxygen content of epoxidized oil, there should be proper reactor should be available. when we think of pilot Scale.
- The kinetics of epoxidation reaction and also finding the optimal temperature which favor's both the two consecutive reactions of epoxidation (i.e., reaction of hydrogen peroxide and acetic acid in the presence of catalyst to form per-formic acid and reaction of per-formic acid with oil to produce epoxidized oils) would be another interesting aspect of catalyst development.
- In Ethiopia, there is a huge suitable land, weather, climate condition, which helps production of podo carpus falcatus tree. podo carpus falcatus seed oil have a potential of producing epoxidized oil having commercial values can be extracted. For these, the government should give due emphasis to exploit and devise ways to properly utilize the bio resources. agricultural sector should also give more emphasis for podo carpus falcatus tree.

REFERENCES

Access, O. (2015). *We are IntechOpen , the world ' s leading publisher of Open Access books Built by scientists , for scientists TOP 1 %*.

Adrian, J., & Janaun, B. (2012). *Development of sulfonated carbon catalysts for integrated biodiesel production by*. (August).

Ahiduzzaman, M., & Sadrul Islam, A. K. M. (2016). Preparation of porous bio-char and activated carbon from rice husk by leaching ash and chemical activation. *SpringerPlus*, *5*(1), 1248. https://doi.org/10.1186/s40064-016-2932-8

Ahmad, A., Abbas, A., Rasheed, T., Bilal, M., Iqbal, M. N., & Wang, S. (2019). *Science of the Total Environment Development , in fl uencing parameters and interactions of bioplasticizers : An environmentally friendlier alternative to petro industry-based sources*. *682*, 394–404. https://doi.org/10.1016/j.scitotenv.2019.05.140

Alemu, A. (2019). *CHARACTERISTICS OF SEED KERNEL OIL FROM PODOCARPUS FALCATUS Author (s): S Feleke , F Haile , A Alemu and S Abebe Source : Journal of Tropical Forest Science , Vol . 24 , No . 4 (October 2012), pp . 512-516 Published by : Forest Research Institute Mala*. *24*(4), 512–516.

Alemu, D. (2015). *EFFECT OFPARTICLE SIZE AND TEMPERATURE ON YIELD AND*.

Aller, D., Bakshi, S., & Laird, D. A. (2017). Modified method for proximate analysis of biochars. *Journal of Analytical and Applied Pyrolysis*, *124*(January), 335–342. https://doi.org/10.1016/j.jaap.2017.01.012

Alsaiari, R. (2017). *Effects of reaction conditions on the conversion of epoxides to cyclic carbonates through CO 2 inclusion University of Cardiff for the degree of*.

An, B. K., Kim, K. E., Jeon, J. Y., & Lee, K. W. (2016). Effect of dried Chlorella vulgaris and Chlorella growth factor on growth performance, meat qualities and humoral immune responses in broiler chickens. *SpringerPlus*, *5*(1). https://doi.org/10.1186/s40064-016-2373-4

ASTM. (2013). Standard test method for bulk density of densified particulate biomass fuels," American Society for Testing and Materials, 2013. *Retrieved Online at Http://Www.Astm.Org/Standards/E873.Htm*, *15 January 2015*, *82*(Reapproved), 1–2. https://doi.org/10.1520/E0873-82R13.4.

Beltrán, A. A., & Boyacá, L. A. (2011). Preparation of oleochemical polyols derived from soybean oil. *Latin American Applied Research*, *41*(1), 69–74.

Biermann, F., & Boas, I. (2010). Preparing for a warmer world: Towards a global governance system to protect climate refugees. *Global Environmental Politics*, *10*(1), 60–88. https://doi.org/10.1162/glep.2010.10.1.60

Brewer, C. E., Brown, R. C., & Laird, D. A. (2012). Biochar characterization and engineering. *Graduate Teses and Dissertations*, 12284. https://doi.org/12284

Brittany holt. (2016). *No Title*. *1*(1).

Chappell, L. (1998). *Vegetable Oil Production : Vegetable Oil Production : Prepared for*. (68).

Cheng, F., & Li, X. (2018). Preparation and Application of Biochar-Based Catalysts for Biofuel Production. *Catalysts*, *8*(9), 346. https://doi.org/10.3390/catal8090346

Coud, V. V., Pradhan, N. C., & Patwardhan, A. V. (2006). Epoxidation of karanja (Pongamia glabra) oil by H2O2. *JAOCS, Journal of the American Oil Chemists' Society*, *83*(7), 635–640. https://doi.org/10.1007/s11746-006-1250-7

Dewandono, G. L., Gabriel, D., Nurcahyo, R., & Prasetiyo, K. (2018). *VALUE UPGRADING OF RICE HUSK WASTE WITH BAMBOO*. (June), 10–14.

Dinda, S., Patwardhan, A. V., Goud, V. V., & Pradhan, N. C. (2008). Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids. *Bioresource Technology*, *99*(9), 3737–3744. https://doi.org/10.1016/j.biortech.2007.07.015

Ding, F., Rosén, A., & Bolton, K. (2012). *Molecular Dynamics Study of the Catalyst Particle Size Dependence on Carbon Nanotube Growth I . Introduction*.

Eider, A. (2017). North Dakota State University. *Dissertation*, (March).

Erhan, S. Z. (2005). *Industrial Uses of Editor*.

Feleke, S. T., Kilmer, R. L., & Gladwin, C. H. (2005). Determinants of Food Security in Southern Ethiopia. *American Agricultural Economics Association*, *33*(November), 351–363. https://doi.org/10.1007/s13398-014-0173-7.2

Gamage, P. K., O'Brien, M., & Karunanayake, L. (2009). Epoxidation of some vegetable oils and their hydrolysed products with peroxyformic acid - Optimised to industrial scale. *Journal of the National Science Foundation of Sri Lanka*, *37*(4), 229–240. https://doi.org/10.4038/jnsfsr.v37i4.1469

Ganesan, K., Sukalingam, K., & Xu, B. (2018). Impact of consumption and cooking manners of vegetable oils on cardiovascular diseases- A critical review. *Trends in Food Science and Technology*, *71*(November), 132–154. https://doi.org/10.1016/j.tifs.2017.11.003

Gawrilow, I. (2004). Vegetable oil usage in lubricants. *INFORM - International News on Fats, Oils and Related Materials*, *15*(11), 702–705.

Gebremedhin, T. (2017). Development of carbon-based sulfonated catalyst for epoxidation of g. vernonia oil. *Unpeplished*, (June).

Geng, Y., Zhang, H., Song, H., Zhang, L., Xu, J., Liu, M., … Han, L. (2015). *PREVENTING EFFECT ON DIET-INDUCED OBESITY OF WATER-EXTRACT FROM MASSON PINE POLLEN ON MICE*. *12*, 14–21.

Gerbase, A. E., Gregório, J. R., Martinelli, M., Brasil, M. C., & Mendes, A. N. F. (2002). Epoxidation of soybean oil by the methyltrioxorhenium-CH2CL2/H2O2 catalytic biphasic system. *JAOCS, Journal of the American Oil Chemists' Society*, *79*(2), 179–181. https://doi.org/10.1007/s11746-002-0455-0

Gîtin, L., Habulin, M., Knez, Ž., & Hopulele, T. (2006). Some Parameters Optimization for Enzymatic Epoxidation Reaction of Sunflower Seed Oil at Atmospheric Pressure and 40 ° C. *Romania*, (February), 0–5.

Glass, E. M., & Meyer, F. (2011). The Metagenomics RAST Server: A Public Resource for the Automatic Phylogenetic and Functional Analysis of Metagenomes. *Handbook of Molecular Microbial Ecology I: Metagenomics and Complementary Approaches*, *8*, 325–331. https://doi.org/10.1002/9781118010518.ch37

Gordon, M. H. (2005). Chemistry of oils and fats – sources, composition, properties and uses. *Food Chemistry*, *94*(3), 464. https://doi.org/10.1016/j.foodchem.2004.12.002

Goud, V. V., Patwardhan, A. V., & Pradhan, N. C. (2006). Studies on the epoxidation of mahua oil (Madhumica indica) by hydrogen peroxide. *Bioresource Technology*, *97*(12), 1365–1371. https://doi.org/10.1016/j.biortech.2005.07.004

Hara, M., Yoshida, T., Takagaki, A., Takata, T., Kondo, J. N., Hayashi, S., & Domen, K. (2004). A carbon material as a strong protonic acid. *Angewandte Chemie - International Edition*, *43*(22), 2955–2958. https://doi.org/10.1002/anie.200453947

Homrich, M. S., Wiebke-strohm, B., Luís, R., Weber, M., & Bodanese-zanettini, M. H. (2012). Soybean genetic transformation: A valuable tool for the functional study of genes and the production of agronomically improved plants. *Genetics and Molecular Biology*, *35*(4 SUPPL.), 998–1010. https://doi.org/10.1590/S1415-47572012000600015

Hu, L., Lin, L., Wu, Z., Zhou, S., & Liu, S. (2015). Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts. *Applied Catalysis B: Environmental*, *174–175*, 225–243. https://doi.org/10.1016/j.apcatb.2015.03.003

J. D. Espinoza Pérez, D. M. Haagenson, S. W. Pryor, C. A. Ulven, & D. P. Wiesenborn. (2013). Production and Characterization of Epoxidized Canola Oil. *Transactions of the ASABE*, *52*(4), 1289–1297. https://doi.org/10.13031/2013.27772

Jia, L. K., Gong, L. X., Ji, W. J., & Kan, C. Y. (2011). Synthesis of vegetable oil based polyol with cottonseed oil and sorbitol derived from natural source. *Chinese Chemical Letters*, *22*(11), 1289–1292. https://doi.org/10.1016/j.cclet.2011.05.043

Kane, S. N., Mishra, A., & Dutta, A. K. (2016). Preface: International Conference on Recent Trends in Physics (ICRTP 2016). *Journal of Physics: Conference Series*, *755*(1). https://doi.org/10.1088/1742-6596/755/1/011001

Kitano, M., Arai, K., Kodama, A., Kousaka, T., Nakajima, K., Hayashi, S., & Hara, M. (2009). Preparation of a sulfonated porous carbon catalyst with high specific surface area. *Catalysis Letters*, *131*(1–2), 242–249. https://doi.org/10.1007/s10562-009-0062-4

Kudzin, Z. H., & Waśkowski, B. (2004). Outline of {CHN} Elementary and {CN} Environmental Analysis. *Acta Universitatis Lodziensis. Folia Chimica*, *Acta Unive*(13), 27–133.

Land-, B. O. Der, & Er-, F.-. (1997). *I Rezensionen / Book Reviews*. 922528.

Li, H., Lu, J., & Mo, J. (2012). Physiochemical lignocellulose modification by the formosan subterranean termite. *BioResources*, *7*, 675–685.

Liu, C., Chen, W., Hong, S., Pan, M., Jiang, M., Wu, Q., & Mei, C. (2019). Fast Microwave Synthesis of Hierarchical Porous Carbons from Waste Palm Boosted by Activated Carbons for Supercapacitors. *Nanomaterials*, *9*(3), 405. https://doi.org/10.3390/nano9030405

Liu, X. Y., Huang, M., Ma, H. L., Zhang, Z. Q., Gao, J. M., Zhu, Y. L., … Guo, X. Y. (2010). Preparation of a carbon-based solid acid catalyst by sulfonating activated carbon in a chemical reduction process. *Molecules*, *15*(10), 7188–7196. https://doi.org/10.3390/molecules15107188

Lu, E. T., & Love, S. G. (2005). Gravitational tractor for towing asteroids. *Nature*, *438*(7065), 177–178. https://doi.org/10.1038/438177a

Ludueña, L., Fasce, D., Alvarez, V. A., & Stefani, P. M. (2011). Nanocellulose from rice husk following alkaline treatment to remove silica. *BioResources*, *6*(2), 1440–1453.

Manley, G. (2013). *Public Access NIH Public Access*. *71*(2), 233–236. https://doi.org/10.1038/mp.2011.182.doi

Martin, cary J. (2010). *4-Epoxy-Resins.pdf*.

Mo, X., López, D. E., Suwannakarn, K., Liu, Y., Lotero, E., Goodwin, J. G., & Lu, C. (2008). Activation and deactivation characteristics of sulfonated carbon catalysts. *Journal of Catalysis*, *254*(2), 332–338. https://doi.org/10.1016/j.jcat.2008.01.011

Mohanta, K., Kumar, D., & Parkash, O. (2012). *Properties and Industrial Applications of Rice husk : A review*. *2*(10), 86–90.

Mungroo, R., Pradhan, N. C., Goud, V. V., & Dalai, A. K. (2008). Epoxidation of canola oil with hydrogen peroxide catalyzed by acidic ion exchange resin. *JAOCS, Journal of the American Oil Chemists' Society*, *85*(9), 887–896. https://doi.org/10.1007/s11746-008-1277-z

N.Karak, W. P. (2012). *Vegetable oil-based polymers*.

Nugrahani, R. A., Redjeki, A. S., Mentari, Y., Jannah, M., & Wibowo, T. Y. (2017). *STUDY EFFECT OF TEMPERATURE AND REACTION KINETICS MODEL SELECTION EPOXIDATION AGAINST RICE BRAN OIL METHYL ESTER WITH CATALYST AMBERLITE IR-120*. *12*(13), 3947–3952.

O., K., & M.B., K. (2006). The elimination of trans fats from spreads: How science helped to turn an industry around. *Nutrition Reviews*, *64*(6), 275–279. https://doi.org/10.1301/nr.2006.jun.275-279

Onda, D., Benico, G., Sulit, A., & Lorenzo, P. (2013). Morphological and molecular characterization of some HAB-forming dinoflagellates from Philippine waters. *Philippine Science Letters*, *6*(1), 97–106. Retrieved from http://www.philsciletters.org/pdf/2013n1.11.pdf

Ouyang, S., Kuang, X., Xu, Q., & Yin, D. (2014). Preparation of a Carbon-Based Solid Acid with High Acid Density via a Novel Method. *Journal of Materials Science and Chemical Engineering*, *02*(06), 4–8. https://doi.org/10.4236/msce.2014.26002

Paquot, C. (1978). *COMMISSION ON OILS , FATS AND DERIVATIVES STANDARD METHODS FOR THE ANALYSIS OF OILS , FATS AND DERIVATIVES*. *1*.

Peng, F., Zhang, L., Wang, H., Lv, P., & Yu, H. (2005). Sulfonated carbon nanotubes as a strong protonic acid catalyst. *Carbon*, *43*(11), 2405–2408. https://doi.org/10.1016/j.carbon.2005.04.004

Perdue, R. E., Carlson, K. D., & Gilbert, M. G. (1986). *Vernonia galamensis,*. *40*(1), 54–68.

PerkinElmer, & Inc. (n.d.). *PerkinElmer Frontier FT-IR, NIR and FIR Spectroscopy IR READY FOR ANY CHALLENGE*. Retrieved from https://www.perkinelmer.com/lab-solutions/resources/docs/BRO_FrontierFTIR.pdf

Piazza, G. J., Nuñez, A., & Foglia, T. A. (2003). *Hydrolysis of Mono- and Diepoxyoctadecanoates by Alumina*. *80*(9), 10–13.

Piazza, G. J., Nuñez, A., & Foglia, T. A. (2017). *Hydrolysis of Mono- and Diepoxyoctadecanoates by Alumina Hydrolysis of Mono- and Diepoxyoctadecanoates by Alumina*. *80*(September 2003), 901–902. https://doi.org/10.1007/s11746-003-0792-z

Rios, S. D. A., Cristina, M., Paes, D., & Schaffert, R. E. (2015). *Adaptability and stability of carotenoids in maize cultivars*. (March).

Sani, Y. M., Raji, A. O., Alaba, P. A., Abdul Aziz, A. R., & Wan Daud, W. M. A. (2015). Palm frond and spikelet as environmentally benign alternative solid acid catalysts for biodiesel production. *BioResources*, *10*(2), 3393–3408. https://doi.org/10.15376/biores.10.2.3393-3408

Sasaki, S. (2012). Gas Chromatography and Mass Spectroscopy. *Journal of the Mass Spectrometry Society of Japan*, *1958*(10), 10–22. https://doi.org/10.5702/massspec1953.1958.10

Saurabh, T., Patnaik, M., Bhagt, S. L., & Renge, V. C. (2011). *EPOXIDATION OF VEGETABLE OILS : A REVIEW*. (Iv).

Schneider, R. de C. S., Lara, L. R. S., Bitencourt, T. B., da Graça Nascimento, M., & dos Santos Nunes, M. R. (2009). Chemo-enzymatic epoxidation of sunflower oil methyl esters. *Journal of the Brazilian Chemical Society*, *20*(8), 1473–1477. https://doi.org/10.1590/S0103-50532009000800013

Section, I., Products, S., Products, N. M., Methods, M. T., & Procedures, A. (n.d.). Astm toc. *Marine Technology*, *01*(I).

Silviana, S., Anggoro, D. D., & Kumoro, A. C. (2017). *Waste Cooking Oil Utilisation as Bio-plasticiser through Epoxidation using Inorganic Acids as Homogeneous Catalysts*. *56*, 1861–1866. https://doi.org/10.3303/CET1756311

Sinadinović-Fišer, S., Janković, M., & Petrović, Z. S. (2001). Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. *JAOCS, Journal of the American Oil Chemists' Society*, *78*(7), 725–731. https://doi.org/10.1007/s11746-001-0333-9

Tan, I. A. W., Hameed, B. H., & Ahmad, A. L. (2007). *Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon*. *127*, 111–119. https://doi.org/10.1016/j.cej.2006.09.010

Tayde, S., M., D. P., Bhagat, S. L., & Prof.Renge V.C. (2012). Studies on Synthesis of Biobased Epoxide Using. *International Journal of Advanced Engineering Research and Studies*, *1*, 279–284.

Teketay, D. (2005). Seed ecology and regeneration in dry Afromontane forests of Ethiopia. *Acta*

Universitatis Agriculturae Sueciae. Silvestria (Sweden), *46*(1), 29–44. https://doi.org/10.1016/j.foreco.2012.09.025

Touhami, D., Zhu, Z., Balan, W. S., Janaun, J., Haywood, S., & Zein, S. (2017). Characterization of rice husk-based catalyst prepared via conventional and microwave carbonisation. *Journal of Environmental Chemical Engineering*, *5*(3), 2388–2394. https://doi.org/10.1016/j.jece.2017.04.020

Tzialla, A. A., Pavlidis, I. V., Felicissimo, M. P., Rudolf, P., Gournis, D., & Stamatis, H. (2010). Lipase immobilization on smectite nanoclays: Characterization and application to the epoxidation of α-pinene. *Bioresource Technology*, *101*(6), 1587–1594. https://doi.org/10.1016/j.biortech.2009.10.023

Uses, F. (2007). Sucrose Esters of Fatty Acids. *Food Additives Data Book*, *4*, 382–383. https://doi.org/10.1002/9780470995327.ch107

Vlček, T., & Petrović, Z. S. (2006). Optimization of the chemoenzymatic epoxidation of soybean oil. *JAOCS, Journal of the American Oil Chemists' Society*, *83*(3), 247–252. https://doi.org/10.1007/s11746-006-1200-4

Wade, D. T. (2002). Recent advances: Recent advances in rehabilitation. *Bmj*, *320*(7246), 1385–1388. https://doi.org/10.1136/bmj.320.7246.1385

Zein, S. H. (2018). *No Title*.

Zong, T., Kharismadewi, D., Ra, C.-S., & Shim, J.-J. (2012). Effect of Temperature and Reaction Time on the Synthesis of Butadiene Monoepoxide Using Iron Complex as an Efficient Catalyst. *Clean Technology*, *18*(1), 51–56. https://doi.org/10.7464/ksct.2012.18.1.051

Appendixes

Appendix A: Proximate Analysis

Table A-1 Moisture Content of rice husk

Run	Sample Wight(g)			Moisture content (%)	Average Moisture content (%)
	W_1(gram)	W_2(gram)	W_1-W_2		
1	16	14.72	1.28	8	8.33
2	16.5	15.11	1.39	8.4	
3	16.3	14.89	1.41	8.6	

Table A-2 Ash content of rice husk

Run	Sample Weight (g)		Ash content (%)		Average Ash Content (%)
	W_1	W_2			
1	16	2.51		15.7	15.967
2	16	2.60		16.3	
3	16	2.55		15.9	

Table A-3 volatile matter of rice husk

Run	Sample weight (g)			Volatile matter (%)	Average volatile matter (%)
	W_1	W_2	W_1-W_2		
1	1.986	0.811	1.175	59.6	59.75
2	2.0295	0.8285	1.201	59.17	
3	1.997	0.789	1.208	60.49	

The fixed carbon content of rice husk saw dust

Carbon content (%) = 100 − volatile content − Ash content

= 100 − (59.75 + 15.967)

= 24.27

Table A-4 Bulk density of bio-chars and catalyst prepared at pyrolysis temperature 400 ℃

Run	Mass (g)	Bulk Volume (ml)	Bio-char density (g/ml)	Catalyst Density (g/ml)
1	0.673	3.22	0.209	----------
2	0.536	2.56		----------
3	0.890	4.25		----------
1	1.132	4.49	----------	0.252
2	1.032	4.09	--------	
3	1.367	5.42	----------	

Table A-5 Bulk density of bio-chars and catalyst prepared at pyrolysis temperature 500 ℃

Run	Mass (g)	Bulk Volume (ml)	Bio-char density (g/ml)	Catalyst Density (g/ml)
1	0.567	2.64	0.214	----------
2	0.673	3.14		----------
3	1.654	7.72		----------
1	1.321	5.02	----------	0.263
2	1.476	5.61	----------	
3	1.45	5.51	----------	

Table A-6 Bulk density of bio-chars and catalyst prepared at pyrolysis temperature 600 ℃

Run	Mass (g)	Bulk Volume (ml)	Bio-char density (g/ml)	Catalyst Density (g/ml)
1	0.3451	1.6	0.214	----------
2	0.6534	3.05		----------
3	1.1671	5.453		----------
1	0.6056	2.07	----------	0.292
2	2.113	7.23	----------	
3	1.02	3.14	----------	

Table A-7 Acid value of podo carpus falcatus seed oil

Run	**Titration (ml)**	**Color change**
1	3.9	Gray to pink
2	4.0	Gray to pink
3	4.2	Gray to pink
Average Value	4.0	

Table A-8 Moisture content determination of podo carpus falcatus seed oil

Run	**Sample Wight(g)**			**Moisture content (%)**	**Average Moisture content (%)**
	W_1	**W_2**	**(W_1 -- W_2)**		
1	1.19	0.4879	0.7021	0.59	0.6
2	1.08	0.4212	0.6588	0.61	
3	1.04	0.416	0.624	0.60	

Appendix B: Iodine value and conversion and oxirane oxygen content

Table B-1 weight of the oil which to be taken for iodine value calculation

Iodine Value Expected	Weight to Be Taken for Test (gram)
< 5	3.00
5 To 20	1.00
21 To 50	0.40
51 To 100	0.20
101 To 150	0.13
151 To 200	0.10

Source: (Paquot, 1978)

Table B-2 Iodine value of Blank Sample

Run	Titration Volume (ml) **Blank sample**	Color change
1	49	Blue to Colorless
2	48	Blue to Colorless
3	46	Blue to Colorless
Average	47	

Table B-3 Iodine value of podo carpus falcatus seed oil

Run	Titration Volume (ml) **oil sample**	Color change
1	16	Blue to Colorless
2	19	Blue to Colorless
3	18	Blue to Colorless
Average	17.67	

Appendix C Actual experimental process condition for epoxidized

Table C-1 Actual Experimental processes conditions for epoxidized oil production

Std	Run	Time(hr.)	Temperature (℃)	Catalyst loading (%, Wt.)	Volume of H_2O_2	Glacial acetic acid (ml)	Speed (rpm)
1	12	2.00	65.00	0.7296	1.68	1.24	1500
2	9	6.00	65.00	0.7296	1.68	1.24	1500
3	24	2.00	85.00	0.7296	1.68	1.24	1500
4	26	6.00	85.00	0.7296	1.68	1.24	1500
5	25	4.00	75.00	0.3648	1.50	1.24	1500
6	29	4.00	75.00	1.0944	1.50	1.24	1500
7	6	4.00	75.00	0.3648	3.50	1.24	1500
8	15	4.00	75.00	1.0944	3.50	1.24	1500
9	21	2.00	75.00	0.7296	1.50	1.24	1500
10	10	6.00	75.00	0.7296	1.50	1.24	1500
11	4	2.00	75.00	0.7296	3.50	1.24	1500
12	7	6.00	75.00	0.7296	3.50	1.24	1500
13	11	4.00	65.00	0.3648	1.68	1.24	1500
14	27	4.00	85.00	0.3648	1.68	1.24	1500
15	20	4.00	65.00	1.0944	1.68	1.24	1500
16	8	4.00	85.00	1.0944	1.68	1.24	1500
17	3	2.00	75.00	0.3648	1.68	1.24	1500

18	5	6.00	75.00	0.3648	1.68	1.24	1500
19	2	2.00	75.00	1.0944	1.68	1.24	1500
20	16	6.00	75.00	1.0944	1.68	1.24	1500
21	17	4.00	65.00	0.7296	1.50	1.24	1500
22	19	4.00	85.00	0.7296	1.50	1.24	1500
23	22	4.00	65.00	0.7296	3.50	1.24	1500
24	14	4.00	85.00	0.7296	3.50	1.24	1500
25	23	4.00	75.00	0.7296	1.68	1.24	1500
26	18	4.00	75.00	0.7296	1.68	1.24	1500
27	13	4.00	75.00	0.7296	1.68	1.24	1500
28	1	4.00	75.00	0.7296	1.68	1.24	1500
29	28	4.00	75.00	0.7296	1.68	1.24	1500

Table C-2 Iodine value of epoxidized podo carpus falcatus seed oil

Run No.	*Mass of oil taken (gram)*	*Volume of titrant (ml)*	*Iodine value*	*Conversion (%)*
Blank	---------	47	------	-------
Oil	0.3136	17	121.396	-------
1	0.4053	36.4	33.18	0.853
2	0.4077	32.5	45.13	0.709
3	0.4033	35	37.75	0.628
4	0.4043	45	6.277	0.62

5	0.4000	31.3	49.80	0.89
6	0.4014	34.6	39.20	0.9
7	0.4042	39.2	24.48	0.84
8	0.4056	38.1	27.84	0.662
9	0.4049	40	21.93	0.714
10	0.4011	36.1	34.48	0.6821
11	0.4023	35.8	35.32	0.55
12	0.4045	28	59.60	0.36
13	0.4071	29.5	54.55	0.845
14	0.4063	34.6	38.72	0.632
15	0.4004	22.5	77.64	0.74
16	0.4026	27	63.04	0.61
17	0.4056	40	21.90	0.451
18	0.4001	26	66.60	0.843
19	0.4020	37	31.56	0.74
20	0.4065	32.7	44.64	0.602
21	0.4066	39	24.968	0.727
22	0.4046	31	50.18	0.739
23	0.4021	36	34.71	0.812
24	0.3996	44.7	7.03	0.798
25	0.4077	31.8	47.3	0.7
26	0.4046	31	50.18	0.56

27	0.4034	43	12.58	0.765
28	0.4072	32	46.74	0.864
29	0.4058	37.9	28.45	0.73

Determination of Epoxy-Group Oxygen (Oxirane Oxygen Content, OOC %)

Oxirane Oxygen Content (OOC, %) = $\frac{1.6*V*N}{Wm}$

Where: V: consumed titrated solution

N: normalized value = 0.1 eq/mol

Wm: used amount of epoxidized oil Sample calculation step to generate the OOC value in Table C-3

For #std 1 OOC, % = $(5.4 * 0.1 * 1.6)/0.402$

= 2.4

Table C-3. Actual value of Oxirane oxygen content

STD NO.	WEIGHT OF EPOXIDIZED OIL (GRAM)	VOLUME OF TITRANT (HBR) (ML)	OOC%
Pure Oil	0.4046	3.0	1.60
1	0.4023	5.4	3.23
2	0.4013	6.1	2.43
3	0.4026	4.3	1.7
4	0.4011	4.5	1.79
5	0.4017	5.5	3.2
6	0.4033	7.3	3.52
7	0.4000	9.8	3.6
8	0.4075	5.4	2.12
9	0.4034	6.7	2.71

10	0.4033	4.3	1.7
11	0.4082	8.4	3.29
12	0.4056	7.4	2.74
13	0.4068	7.6	3.45
14	0.4022	4.5	1.92
15	0.4028	2.9	2.84
16	0.4021	5.1	2.02
17	0.4035	6.9	2.05
18	0.4068	4.8	3.13
19	0.4016	5.6	2.23
20	0.4055	3.5	2.1
21	0.4052	5.6	2.21
22	0.4000	10.43	3.34
23	0.4025	6.4	3.21
24	0.4073	3.9	1.53
25	0.4079	3.6	2.78
26	0.4047	6.5	2.61
27	0.4055	6.4	2.18
28	0.4025	7.3	3.33
29	0.4011	5.4	2.93

Appendix D: NMR analysis reference

Supplementary Table 1. *The integrals of the relevant signals in* ***Fig.1*** *by taking the sn-1,3 glycerol protons as the internal standard (4.00), where overlapped peaks are deconvolved with lorentzian line shapes.*

chemical shift (δ, ppm)	protons	spectrum[a]				
		a	b	c	d	e
1.45-1.60	CH_2-CH(O)CH	nd[b]	1.74	6.32	10.23	11.21
1.70-1.85	CH(O)CH-CH_2-CH(O)CH	nd	0.09	0.61	1.77	3.24
2.00-2.10	CH_2-CH_2-CH=CH	9.60	8.21	5.13	2.44	0.65
2.80-2.85	CH=CH-CH_2-CH=CH	3.86	2.94	1.22	0.29	nd
2.90-2.95[c]	CH(O)CH / CH(O)CH-CH_2-CH=CH	nd	1.07	2.43	2.86	1.99
3.00	CH(O)CH-CH_2-CH(O)CH	nd	0.02	0.61	1.46	2.68
3.06-3.24	CH(O)CH-CH_2-CH(O)CH	nd	0.04	0.48	1.49	2.92
5.35-5.45	CH=CH	7.83	6.33	1.94	0.42	0.02
5.40-5.50	CH(O)CH-CH_2-CH=CH	nd	nd	1.55	0.92	0.30
5.50-5.60	CH(O)CH-CH_2-CH=CH	nd	0.46	1.09	0.82	0.27
5.60-5.65	CH(O)CH-CH_2-CH=CH-CH_2-CH(O)CH	nd	nd	0.06	0.10	0.10

a. *The sequence of the spectra corresponds to Fig.1 in the manuscript.*
b. *nd = 'not detected'.*
c. *The signals due to the epoxy protons in saturated monoepoxides completely coincide with those of the epoxy groups β to the double bond.*

Appendix E Infrared Spectroscopy Correlation Table

Simplified Infrared Correlation Chart			
	Type of Vibration	Frequency (cm^{-1})	Intensity
C-H	Alkanes (stretch)	3000-2850	s
	-CH_3 (bend)	1450 and 1375	m
	-CH_2- (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-NO_2)	1550 and 1350	s
S-H	Mercaptans	2550	w
S=O	Sulfoxides	1050	s
	Sulfones, Sulfonyl Chlorides, Sulfates, Sulfonamides	1375-1300 and 1200-1140	s

Appendix F: Laboratory Equipment's and Sample Photo

Figure D-1 Measuring Balance of crashed seed for Soxhlet and extraction unit with water bath

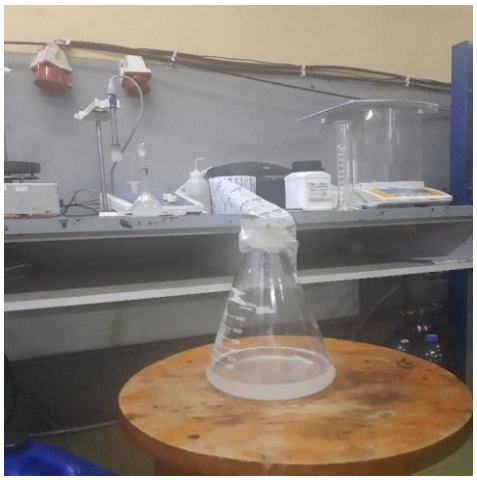


Figure D-2 Iodine value analysis of sample and final titration of iodine value of the sample

Figure D-3 Epoxidized oil and carbonized Rice husk