ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

Development of Sulfonated Carbon Catalyst for Epoxidation of Vernonia Oil

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This is to certify that the thesis prepared by *Gebremedhn Tekeste*, entitled: *Development of sulfonated carbon Catalyst for Epoxidation of Vernonia Oil* and submitted in partial fulfilment of the requirement for the degree of Master of Science (Chemical and Bio Engineering) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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DECLARATION

I declare that this thesis entitled "*Development of sulfonated carbon Catalyst for Epoxidation of Vernonia Oil* " 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 Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given.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.Beteley.T (Assistant Professor)* instructor in Addis Ababa University, School of Chemical and Bio Engineering.

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ABSTRACT

A biochar-based catalyst was successfully prepared by sulfonation of pyrolysis char with high concentration (>96%) sulphuric acid. Three biochar-based catalysts with pyrolysis supports at three different temperatures (400, 450 and 500^{o}C) were prepared and compared for different characteristics of the catalyst. Further investigations on the biochar based catalyst were conducted to determine the effect of preparation protocol on the above properties of the catalyst. Two established preparation techniques (i.e. preparation protocol with ultrasound sonication and preparation protocol with magnetic stirring method) have been utilized to increase the acid density of sulfonic group (SO_3H) during sulfonation. The sulfonated catalysts were characterized using the following analyses: bulk density, elemental analysis, total acid density, Fourier Transform Infra-Red (FT-IR) spectroscopy, and X-Ray Diffraction (XRD) spectroscopy. The catalyst supported on biochar pyrolysis at 500^{o}C with ultrasound sonication (C-SO_3H-500^{u}) resulted the maximum, sulfur content and total acid density (4.10 mmol/g). Thus, from the prepared catalyst, catalyst prepared at 500^{o}C (C-SO_3H-500^{u}) was selected based on the above characterization and thus further evidence on the morphological structure (SEM) and stability (TGA) of the catalyst was performed.

The selected (C-SO_3H-500^{u}) catalyst was studied for its activity to catalyze Epoxidation of vernonia oil using peroxyformic acid. Design-Expert 7.0.0 three-level-three-factor BBD was applied for experimental design and statistical analysis of results. A total of 15 experiments were conducted at conditions of reaction temperature 65, 75 and 85^{o}C, molar ratio of hydrogen per oxide to oil 1.5, 2.5 and 3.5 and 2, 4 and 6 %wt of catalyst loading. From the analysis of experimental results the interaction effects were studied and the optimal epoxidation reaction process conditions, which will maximize the percentage of conversion, were found to be 65^{o}C reaction temperature, 2.36:1 molar ratio of hydrogen per oxide to oil and 6 %wt, catalyst loading which gave 51.45% percentage of conversion.

The yield of epoxidized vernonia oil were determined by identifying the structure and composition of vernonia oil, in comparison to epoxidized vernonia oil using NMR spectroscopy.

Keywords: *Bamboo; Sulfonated carbon catalyst; Vernonia* galamensis; *Epoxidation; Epoxidized vernonia oil*

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ACRONYMS

AAIT	Addis Ababa institute of technology
ANOVA	Analysis of Variance
AOAC	Association of Official Analytical Chemists
ASTM	American Society for Testing and Material
AV	Acid Value
BBD	Box -Bhenken Design
CBSCs	Carbon Based Solfonated Catalyst
CHNSa	Carbon Hydrogen Nitrogen Sulfur Analysis
EA	Elemental analysis
EN	European committee for standardization
EVO	Epoxidized Vernonia 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
LIDI	Leather Industry Development Institute
NMR	Nuclear Magnetic Resonance
ON	Oxirane Number
Ppm	Parts per million
PVC	Poly Vinyl Chloride
SEM	Scanning Electron Microscope
TAD	Total Acid Density
TGA	Thermogravimetric Analysis
VOAC	Vernolic acid
VO	Vernonia Oil
XRD	X-ray Diffraction

1. INTRODUCTION

1.1 Background

Epoxides, known as oxiranes, are cyclic ethers with a reactive three-membered ring and have been receiving growing commercial interest in recent years. The utilization of Epoxides will open a wide range of feasible reactions that can be carried out under moderate reaction conditions due to the high reactivity of the oxirane ring. Thus, they are highly reactive, versatile, poly functional intermediates that can be converted to a variety of products such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers and their demand is increasing day to day (Deshpande 2013).

Most of the Epoxides used industrially are derived from petroleum based chemicals. However, the depletion of the earth's limited petroleum reserves has heightened interest in using renewable resources as replacement materials for epoxidised vegetable oil. Also, increasing environmental concerns have made plant oils an attractive alternative for the production of epoxy-based materials, as plants are bio renewable resources that can be used to reduce the stress from synthetic chemical industries on the environment(PL et al. 2009).

Vegetable oils are promising feed stocks for epoxidised vegetable oil production since they are renewable in nature, and can be produced on a large scale and environmentally friendly. Most of the epoxidised vegetable oil production feed stocks come from edible oils since they are mainly produced in many regions and the properties of epoxidised vegetable oils produced from these oils are much suitable to be used as the epoxidised petroleum product substitute. However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and Epoxides and cause of deforestation. Furthermore, non-edible oil crops can be grown in waste lands that are not suitable for food crops and the cost of cultivation is much lower because these crops can still sustain reasonably high yield without intensive care.

Vernonia (*Vernonia galamensis*) is a potentially novel industrial oilseed crop. It plays a great role in oleochemical industries and as alternative cash crop. It is one of the only few plants that contain naturally occurring epoxydized oils in its seeds known as vernonia oil. It has the largest oil content, up to 42%; and the extracted oil can contain vernolic acid (78-80%), and Vernolic acid group serves as a key starting material for the synthesis of different important chemicals(Perdue et al. 1986).

Vernolic acid is a useful raw material for the manufacture of adhesives, varnishes, paints and coatings. Also degradable lubricants, lubricant additives, epoxy resins, plastic formulations for PVC, insecticides, insect repellants and reactive monomers in polymer synthesis (Grinberg et al. 1996). Vernonia oil has also been used as a source of hydroxyl alkoxy fatty esters and for the synthesis of epoxy secondary amides (Grinderg et al. 1994). Currently vernonia oil product on the market includes Vernola Super gloss; a car-care product used on tires, leather and rubber bumpers. In addition to this the triglyceride oil rich in vernolic acid, is environmentally friendly, less expensive and less viscous compared to other artificial epoxy oils (Shimelis and Gwata 2013).

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. The production of Epoxides from vegetable oil using epoxidation reaction is the subject of many studies. The catalysis is an important factor in the epoxidation reaction because the reaction is considerably slow without the use of a catalyst. The reaction is catalyzed by homogeneous catalysts such as H_2SO_4, *p*-toluene sulfonic acid, heterogeneous catalysts such as transition metals of variable valence, acidic ion exchange resin or enzymes (Uyama et al. 2003).

Epoxidation with percaboxylic acids (Prileschajew), the most widely used in industry which catalyzed by strong mineral acids such as sulfuric acids have several problems, it leads to many side reactions such as oxirane-ring opening to diols, hydroxyesters, estolides and other dimer formations. Furthermore it causes the equipment corrosion and must be neutralized and removed from the end product(Lathi, P.S. and Mattiasson 2006). In addition to this catalyst the heterogeneous catalyst also have several drawbacks associated with these traditional catalytic systems in connection with their application in biomass conversion such as low catalytic activity, poor reusability, high material costs (use of expensive precious metals and support materials) and so forth, thus making them less attractive for industrial scale applications (in short, poor activity for the price)(Rios et al. 2011).

In general chemical reactions that were carried out privileged the use of heterogeneous catalysts mainly because of environmental concerns, but also for technical and economic considerations.

In recent years, with the emerging concepts of green chemistry, the utilization of cheaper, green materials for chemical transformations has recently gained significant attention and several research groups have made efforts to develop a catalyst using inexpensive precursors such as biomass and waste materials. Among these, particularly the sulfonated carbons or –SO3H functionalized carbon catalysts have received considerable attention as a promising solid acid catalyst. These materials resemble H_2SO_4 in terms of acidity and catalytic activity, and also offer high operational stability (>240^{o}C and reusability), which make them versatile acid catalysts for the acid catalyzed reactions included in biomass transformation(K. Nakajima and M. Hara 2012).

1.2 Statement of the Problem

The depletion of world petroleum reserves and increased environmental concerns has stimulated the search for alternative renewable material that is capable of fulfilling increasing epoxides demand that serve as primary chemicals and intermediates in many industries. The problems related with petroleum product of epoxide is fluctuation of oil price, shifting toward higher value and natural fossil fuel depletion, instability of world political condition, high demand of the oil, as a whole, all over the world. In recent decades, research concerning and knowledge about the external benefits of renewable raw materials have intensified the efforts for sustainable epoxide fabrication sources. Epoxide that is obtained from plant oil plays a major role in this field because of the world-wide research, development, and exploitation activities of this sustainable raw material source.

From this point of view *vernonia galamensis*, which is originated in Ethiopia and can grow in all over the country, is a potentially novel industrial oilseed crop. It is a tropical, indeterminate annual plant. It requires a well-drained soil and can grow under low rainfall (up to 200 mm) and is most suitable for dry land farming. What makes interesting about the seed oil is that the oil (35 – 42% of the seed) contains as the major fatty acid vernolic acid (72 – 80%) of the oil(Rios et al. 2011). The vernolic fatty acid has unique characteristics for formulation of different products through different processes and has low viscosity.

Epoxidation reaction is affected by various parameters. Once of this parameter is catalyst which is homogeneous and heterogeneous catalyst. In industry, the epoxidation of plant oils has been already carried out homogeneously with a per carboxylic acid, such as per acetic acid and per formic acid, obtained by oxidation with hydrogen peroxide, using mineral acid, like sulfuric acid, as catalyst. However, soluble mineral acids (such as sulfuric acid) are essential for this process and these acidic components lead to several drawbacks: 1) side reactions because of acid-catalyzed epoxide ring opening; 2) separation of acidic by-products is difficult; 3) abundant neutralized salts which have to be disposed are produced; 4) corrosion problems due to the strong acids in the process. Additionally, the process does not fit to the green chemistry but also is dangerous to handle and generating a lot of wastes (Guidotti et al. 2007). Due to those disadvantages, several recent results have shown the way to large scale of new heterogeneous catalysis such as Al_2O_3, TiO_2 and ion exchange resin (AIER) have been used for epoxidation of unsaturated fatty acid derivatives.

From the heterogeneous catalyst which is used in epoxidation reaction carbon based sulphonated catalyst materials have lower production cost, renewable, abundant, and low-cost produced directly from biomass compared to other solid acid catalysts such as strong acidic cation-exchangeable resins, , i.e. nafion and metal oxides. Moreover all of the CBSCs own the carbon skeleton and $-SO_3H$ group, and the carbon skeleton is stable, high selectivity and insoluble in most acidic/basic conditions as well as organic solvents. In spite of this advantage the carbon based sulphonated catalyst is not widely used especially for epoxidation reactions.

1.3 Objective of the Research

1.3.1 General Objective

The main objective of this research is to prepare carbon based sulphonated catalyst with high catalytic activity, selectivity and good stability for production of epoxidized vernoia oil from locally available raw material, *Vernonia galamensis* seed oil, via epoxidation reaction.

1.3.2 Specific Objectives

The specific objectives are:-

- To prepare several sulphonated carbon catalyst with different synthesis protocol starting from bamboo sawdust and characterize their property
- To extract vernonia oil from vernonia seed and characterize the physicochemical properties (Moisture content, specific gravity, acid value, FFA and Iodine value).
- To study the catalytic performance (conversion) of prepared catalyst for epoxidation of Vernonia oil
- To investigate the main and interaction effect of Epoxidation reaction parameters (reaction temperature, molar ratio of hydrogen per oxide to oil, and catalyst loading) on the on production of Epoxidized vernonia oil using RSM.
- To generate model equation and determine the optimal operating condition aiming for maximum percentage conversion of double bond in vernonia oil
- To characterize the physicochemical properties of epoxidized vernonia oil (Oxirane ring formation and iodine value)

1.4 Significance of the Study

This research has benefits to many stakeholders in the economy and the final goal of this research project can be considered from different perspectives. Ethiopia is an importer of fossil fuel and products based on fossil fuels. The Ethiopian government spends a substantial amount of its foreign currency reserves on these fossil fuel based products. Hence by producing this product from locally available raw materials we can overcome this currency for our country.

Using this research private and public industry in Ethiopia such as plastic industries, rubber industries and others can significantly reduce their carbon footprint by employing bio based product. Secondary consumers of epoxy industries such as the construction industries can also make use of vegetable oil derived epoxides to cut their costs and make their production process sustainable. It will also help the scholarly interest of catalysis advances to the applications of biomaterial production.

In general the significance of this research can be seen from different perspectives.

- ✓ Provide a means to exploit and manage local resources.
- ✓ Provide a new potential industrial oilseed crop, *vernonia galamensis* seed oil, for production of epoxy oil.
- ✓ Provide a technically and economically feasible option to produce epoxy oil locally, which will play a major role to substitute the imported epoxide that saves foreign currency and create job opportunity.
- ✓ Serve as a starting material for further research studies on the application of *vernonia galamensis* oil for other potential purpose.

1.5 Scope of the Study

The thesis work generally covers carbon based sulphonated catalyst (CBSC) preparation, characterization, vernonia oil extraction and refining, vernonia oil characterization, synthesis of Epoxidized vernonia oil using sulfonated carbon catalyst and characterization of produced Epoxides. Extraction, refining, characterization of vernonia oil, preparation and characterization of CBSC and characterization of the produced Epoxides will be done using standard procedures and test methods.

2. LITERATURE REVIEW

Petroleum based products are ubiquitous in our everyday lives. We use them for our energy needs or as a source of material for manufacturing necessary products. But these petroleum products are non-biodegradable, unsustainable and have a volatile commodity market. This makes them undesirable for relying on them in a long term (James R. Pfafflin 2006). As such, researches in alternatives for petroleum derived materials have grown substantially. One potential area worth exploring in that regard is the research on vegetable oils as bio-material sources. Vegetable oils and fats, the important renewable resources, are biodegradable, are low in cost and readily available. A number of methods such as chemical and enzymatic modification of oils have been suggested for improving their properties. The modified oils serve as feedstock that can replace petroleum-derived materials in many applications(Biermann et al. 2000).

Epoxidation of vegetable oils using per acid is one of the most important and useful exploitations of double bonds since epoxides are reactive intermediates that are also readily converted to other functional groups through ring-opening reactions(A. Campanella and M. A. Baltanas 2005). The epoxidation of vegetable oils has been studied during the past few years owing to the commercial importance of these compounds as additives of polymers, lubricants and detergents. Epoxidation reactions are usually carried out using peracids formed *in-situ*, by reaction of carboxylic acid with concentrated hydrogen peroxide. The hydrogen peroxide serves as oxygen donor for the Oxirane ring formation. Since the by-product of oxidation with hydrogen peroxide is water, it is taken as an environmentally friendly and high oxygen content oxidant in comparison with similar oxidants such as N_2O and NaClO (Oyama 2008; Rios et al. 2011).

The epoxidation reaction of vegetable oils is a very slow reaction. To make the reaction rate high and achieve a substantial selection the choice of the catalyst for the epoxidation reaction is of at most importance(A. Goti and F. Cardona 2008). There are reports in literature on several routes to produce bio-materials(Moulijn et al. 1993). They include homogeneous catalysis using either inorganic acids and bases or metal complexes, as well as heterogeneous and phase-transfer catalysis procedures. It appears, thus, that the costs of the catalysts and of the utilities consumed (energy, chemicals) for the production of bio-material, constitute another important part of the final costs. Finally, the quality of final product and of the separated wastes represents another important component of the final cost.

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) (Oyama 2008). 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.

2.1 Raw materials for epoxide oil Production

Know a day's the conservation and management of resources is very important in various chemical industries. Traditionally the development of epoxide is based on mineral oil which is a fossil as a raw material. They consist mainly of hydrocarbons but also contain some sulfur and nitrogen compounds with very small mounts of a number of metals (Triantafyllidis et al. 2013). Due to the increasing of environmental issues like waste disposal problems, non-biodegradable resources, greenhouse effect, etc. and also the reduction of petroleum oil resources, renewable oils from vegetable origin have become an important issue (Moulijn et al. 1993) since many evidences prove that the substitution of renewable resources for petrochemical feedstock's can be a sustainable development. Now days, the epoxides from renewable-harvestable resources are a successful reality in many parts of the world.

In general, vegetable oils have many advantages such as high flash point, high viscosity index, high lubricity and low evaporative loss besides eco-compatible, renewability and non-toxicity. Vegetable oils are part of a larger family of chemical compounds known as fats and lipids. They are made up of triesters of glycerol with fatty acids and these are commonly called triglycerides. Fats of all types have been used in many fields, such as foods, fuels, lubricants and raw materials for other chemicals due to their unique chemical structures and physical properties(E. Poli et al. 2010). The vast majority of vegetable and animal fats consist of fatty acid molecules of more than 16 carbon atoms. Therefore, most of the chemical and physical properties of fats result from the effect of the various fatty acids because the portion of un saturated fatty acid in triglycerides is much larger (about 90%) than that of glycerol (E. Poli et al. 2010).

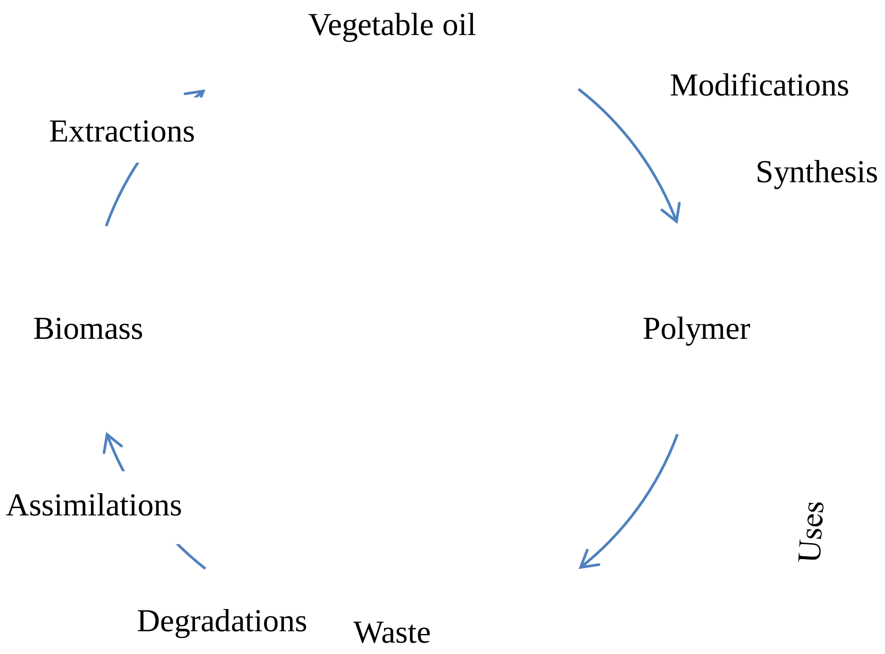


Figure 2-1: Life cycle of polymeric material based on vegetable oils.

Vernonia oil extracted from vernonia plant seed is one of the most vegetable oils which contain unsaturated vernolic acid. Typical fatty acid composition of the most widely traded commodity oils are shown in Appendix A.

But there are still some limitations that industries have not been able to overcome, such as low resistance to oxidative degradation at high temperature and poor low temperature properties(Wallace 1978). The reasons for the instability of vegetable oils are the structural unsaturation in the fatty acid part and the “β-CH group” of the alcoholic components (PL et al. 2009).

The physical and chemical properties of oils and fats can be modified through the use of diverse derivatization pathways. In fact, chemical modifications of vegetable oils constitute an important route to develop new efficient and environmentally friendly reaction pathways leading to new products or to find new applications for already existing oleo chemicals (Moser et al. 2008).This strategy can contribute to decrease our dependence on non-renewable, and therefore limited, natural resources such as mineral oil. For example, a high degree of multiple C=C unsaturation in the fatty acid (FA) chain (mainly linoleic $C_{18:2}$ and linolenic $C_{18:3}$ FA) of many vegetable oils (e.g. soybean/ linseed/ sunflower/ safflower etc.) causes poor thermal and oxidative stability and confines their use as lubricants to a modest range of temperature.

Vegetable oils also show poor corrosion protection and the presence of ester functionality renders these oils susceptible to hydrolytic breakdown. Although use of additives (antioxidants and pour point depressants) can overcome these shortcomings to some extent, the major way to improve these properties of vegetable oils is chemical modifications of fatty acid chains of triglycerides at the sites of double bonds and carboxyl groups. Thus the chemical modifications through application of various unit processes are essential for obtaining oleo chemicals with multi functionality, improved oxidative, thermal and photo stability and good low temperature properties for explorations in chemical industries(Petrovic, Zlatanic, et al. 2002).

2.1.1 Vernonia Seed Oil

Vernonia is a new potential industrial oilseed crop. The extracted oil is used for many applications. The company Ver-Tech International identified over seventy potential uses of vernonia oil. In this literature review description of the vernonia plant, its distribution, extraction, potential application and composition of vernonia oil is covered.

2.1.1.1 Description and Distribution of Vernonia Plant

Vernonia galamensis (V. galamensis) is a plant in the sunflower family of the genus vernonia (*asteraceae*), known for its use as an oilseed. This species, often called ironweed, is the largest source of vernonia oil (VO). It includes more than 1000 species distributed widely in tropical and subtropical regions of Africa, Asia and America and has two major centers of origin, South America and tropical Africa. About 200 species ranging from annual herbs and shrubs to perennial trees are found in Africa of which about 50 species of vernonia have been recorded in Ethiopia. According to the species, *galamensis* is recognized to include six subspecies including *galamensis, mutomoensis, nairobensis, afromomntana*, *gibbosa*, and *lushotoensis* (Addisu,A 2010). Subspecies *galamensis* grows in a wild form in Eritrea, Ethiopia, Malawi, Tanzania and Kenya (Tadesse et al.). It is highly diverse and has four botanical varieties, namely variety *galamensis, petitiana, australis, ethiopica,* which are limited in distribution primarily to eastern Africa(Addisu 2010).

V. galamensis subspecies *galamensis* variety *ethiopica* was first identified by Perdue in December 1964 in eastern Ethiopia near the old city Harar. Later south and south-eastern Ethiopia was described as a natural habitat of this botanical variety. A number of studies demonstrated the presence of considerable variability in oil and vernolic acid (VOAC) contents in this botanical variety(Perdue et al. 1986).

The subspecies *galamensis* is found in areas that receive as little as 200 mm rainfall per year. A porous, well-drained and sandy soil is best for its growth. Vernonia plant does not dowel on heavy clay. It tolerates high temperature and full sun as long as the soil moisture is adequate. A superior species of vernonia in terms of variability in composition of fatty acid and oil content was originally found in Ethiopia (Seganka 2006).

Figure 2-2: *Vernonia galamensis* var. *ethiopica* thriving at a semi-arid location at Syferkuil (Limpopo Province, South Africa)

Vernonia grows in many parts of Ethiopia, especially around the city of Harar, with an average seed yield of 2000 to 2500 kg per hectare. It is reported that the Ethiopian strains of vernonia have the highest oil content up to 41.9% with up to 80% vernolic acid content. In other review seed yield up to 4000 kg per hectare, equivalent to 1625 kg per hectare of oil with an oil content of 40% using unimproved local materials were obtained, which seem to be higher than those found elsewhere(Baye 1996; Belete 2006). Traditionally, farmers considered it to be an indigenous weed, so they tended to eradicate it in order to free their land for other crops. But due to the increased awareness of the importance of vernonia, however, it is now considered as a potential crop for inclusion in the agricultural system of the country.

2.1.1.2 Extraction of Oil

Extraction of vernonia oil can be done using different methods. Mechanical pressing and Solvent extraction using different solvents can be applied according to the desired output. The oil extracted from vernonia seeds by solvent extraction yield of up to 42% has been reported(Addisu 2010). In other review by (Mohammed et al. n.d.) it was found that Soxhlet extraction yielded somewhat more oil (38%) than cold extraction with hexane at room temperature (35%). The oil obtained at room temperature contained less free fatty acids. Mechanical pressing method can also be applied for vernonia oil extraction. The cake formed after oil extraction is high (43.75%) in crude protein and is suitable for animal feed (Perdue et al. 1986).

2.1.1.3 Composition and properties of vernonia seed oil

V. galamensis is potentially a useful industrial oil seed crop for the production of natural epoxy oil (Thompson 1994). The seeds of vernonia produce naturally exposidized oil consisting of vernolic acid (72-80%), palmitic acid (2-3%), linoleic acid (12-14%), oleic acid (4-6%), steraic acid (2-3%) and trace amount of arachidic acid (Thompson 1994). Vernolic acid is the dominant fatty acid. Because of the production of the naturally exposidized oil, the industrialized processing of this oil is inexpensive. It is also friendly to the environment largely because it does not emit volatile organic compounds. In addition, the oil can be stored at sub-zero temperatures. Preliminary investigations also showed that the seed oil extraction is a valuable source of crude protein (43.75 %); it also consists of crude fiber (10.90 %), ash (9.50 %) and the carbohydrate fraction (6.57 %) with sucrose (2.36 %), fructose (1.90 %) and glucose (0.77 %). The major mineral elements, calcium (11.08 mg/g), potassium (14.18 mg/g), magnesium (6.90 mg/g) and high phosphorus (644 mg/g), which are higher than in most other oilseeds(Carlson et al. 1981; Perdue et al. 1986).

Table 2-1: Physical and chemical properties of Vernonia oil

Property of Vernonia Oil	**Value**
Saponification value, mg KOH/g oil	165 – 210
Unsaponifiable, wt%	1.0 – 8.0

Iodine value, g I_2 /100 g oil	104 – 108
Refractive Index at 25$_0$C	1.4740 – 1.4860

(Source: Manuel des crops gras, AFCEG, Paris, 1992)

The natural, liquid epoxy oil from *V. galamensis* seed has properties, such as oxirane content (4.1 %), less viscous (110 cps) liquid compared to other artificial epoxy oils and molecular weight (926 g/mol), that relate to both commercial types. *V. galamensis* seed yields 40-42 % oil containing 72 - 78 % VOAC (cis-12, 13-epoxy-cis-9-octadecenoic). Furthermore, oleic (4 %) and linoleic (13 %) acid levels in *V. galamensis* oil represent additional epoxidizable unsaturation (110 % monoene equivalent), so that fully epoxidized VO could have an oxirane value near 10 % (Lligadas et al. 2006). The unique structure of the fatty acid contained within the trivernoline triglyceride (VO) enables a wide variety of reactions. Functional group present within the structure include an ester group, a double bond and an epoxy group as shown in Figure 2-3 below (Belete 2006).

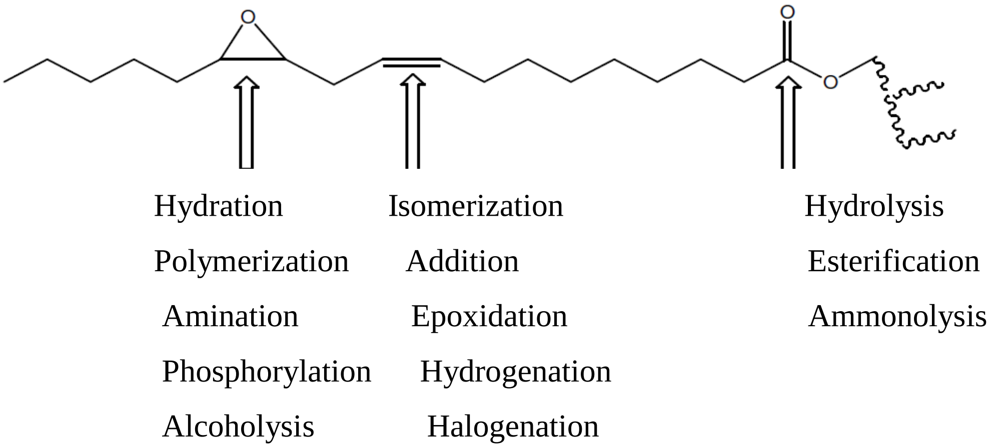


Figure 2-3 A wide variety of reaction characteristics of epoxy acid within the triglyceride

2.1.1.4 Application of Vernonia Oil

There has been a growing trend in utilizing epoxidized vegetable oils in various applications. In industry, epoxidized vegetable oil is currently used mainly as PVC stabilizers and plasticizers, in the painting and coating formulations preparation of polyols for polyurethane use. Moreover, epoxidized fatty acids are monomers suited for ring opening polymerizations and polyetherpolyols derived from epoxidized fatty acid compounds may substitute the petrochemical compounds in various applications (Ologunde et al. 1990). *Vernonia galamensis* is an enantiomerically unsaturated and naturally epoxidized plant oil with interesting applications as binder in coating and preferentially in photo curing coating. This plant oil represents excellent renewable resources, has low toxicity and inherent biodegradability (Metzger, J.O. and Bornscheuer 2006).

Vernolic acid which is obtained from vernonia oil is a useful raw material for the manufacture of adhesives, varnishes, paints and coatings. Using vernolic acid for paints and coating helps to avoid photochemical pollution. Also degradable lubricants and lubricant additives, epoxy resins, plastic formulations of polyvinyl chloride, adhesives, insecticides and insect repellants and reactive monomers in polymer synthesis (Lligadas et al. 2006). In addition, the oil used for the synthesis of the acrylate and methacrylate monomers by reacting VO with acrylic or methacrylic acid with high conversion of the epoxy group was used as solvent/reactive diluents in styrene–acrylate copolymerization's (Metzger, J.O. and Bornscheuer 2006). The oil can be used as a source of dibasic acid, these dibasic acids and their derivatives are used in the manufacture of polyurethanes, polyamides (nylons), alkyd resins, plasticizers, elastomers (synthetic rubber), lubricants and hydraulic fluids. VO can also be used by its own in the reformulation of oil-based (alkyd-resin) paints to reduce emission of volatile organic compounds in the animal feed industry and as a medicine to treat a variety of diseases (Casebolt et al. 2002). Moreover, recent investigation shows that VO reacted with carbohydrates such as glucose and starch to give carbohydrate esters of fatty acids, which has more application on cosmetic and pharmaceutical industries (Mohammed et al. n.d.).

2.2 Production of Epoxidized oil Via Epoxidation Reaction

The direct use of fatty oils for industrial purposes is limited to relatively small applications. The chemistry and technology of oils and fats derived industrial products i.e. oleochemicals run parallel to those of petrochemicals. Majority of the oleochemicals, being derived from oils and fats, are straight long chain, even numbered, primary functional compounds and their advantages including biodegradability and negligible sulfur, nitrogen and heavy metal content can be illustrated by several of the principles of green chemistry (Dandik et al. 1998; Salimon, J.and Salih 2010).

Oleochemicals derived from splitting (hydrolysis) or transesterification of natural fats and oils such as fatty acids (FA), mono-alkyl (mostly methyl) fatty esters (biodiesel-substitute for diesel fuel), and glycerol, are termed as basic oleochemicals. Further processing of these basic oleochemicals and their various fractions by different unit processes/ chemical modifications, such as transesterification and esterification (e.g. sucrose polyesters, monoglycerides), saponification and coprecipitation (metallic soaps) hydrogenation and hydrogenolysis (e.g. fatty alcohols), ethoxylation (e.g. alcohol ethers), sulphonation and sulphation (e.g. ester sulphonates, turkey red oil), ammonolysis and amidation (nitrogen derivatives), ozonolysis (azealic/ pelargonic acids), epoxidation and hydroxylation, dimerization and polymerisation, pyrolysis and alkali fusion produce secondary oleochemical or specialty chemical products for utilisation as surfactants, emulsifiers, lubricants, plasticizers, additives, bactericides, fungicides, etc.

Epoxidation is the reaction (Figure 2-4) 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 epoxides. The reaction is catalysed by homogeneous catalysts such as H_2SO_4, *p*-toluene sulfonic acid (Mungroo et al. 2008), heterogeneous catalysts such as transition metals of variable valence, acidic ion exchange resin (Mungroo et al. 2008) or enzymes (Uyama et al. 2003)

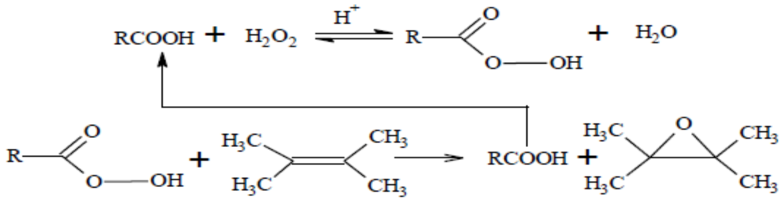


Figure 2-4 *in situ* peracid epoxidation reaction

The preparation or generation of peracid in epoxidation reaction can be performed either *in situ* or *ex situ* process. In *in situ* preparation of peracid first the acid (formic or acetic acid) is added in to the reactor which contains purified oil, then the required amount hydrogen per oxide will add drop wisely during the progress of the reaction. Where as in the case of *ex situ*, initially the mixture of the formic or acetic acid is stirred for some time to form per acid before adding to reactor that contains oil.

The *in situ* generation of peracids is mostly preferred because, when the organic peroxyacid is preformed, there are some safety issues associated with its storage since the concentrated peroxyacid is unstable and explosive(Okieimen et al. 2002; Salihi et al. 2011). Moreover the *in situ* process operates with a lower concentration of aliphatic acids. On the other hand, the presence of an acid during in situ epoxidation causes the opening of the oxirane ring with formation of undesirable secondary products.

In *ex situ* process, the acid is eliminated from preformed peracid by neutralizing it with a buffer or filtering. With preformed peroxyacetic acid, the conversions, yields and selectivity were higher than those with the *in situ* formed peroxyacetic acid.

The general process for the synthesis of the epoxide groups is known as an epoxidation reaction wherein an alkene is reacted with an organic peroxy acid.
Established methods of epoxidation based on the type of catalyst used are as follows:

2.2.1 Epoxidation Using Conventional Method

Epoxidized vegetable oils are commercially produced via the Prileschajew epoxidation by using peracids. Soluble mineral acids, most commonly sulphuric or phosphoric acid, are used as catalyst for this reaction. Industrially, various per oxyacids are possible, such as per formic, per acetic, per benzoic, m-cloroperbenzoic, from which per formic and per acetic are preferred due their easy availability, lower prices, high epoxidation efficiency and reasonable stability at ordinary temperature(R. A Sheldon 1973).
The use of mineral acid catalyst for epoxidation reaction is efficient due to high mass transfer contact between reagents or reactants. However, there are several drawbacks in the process: (i) high selectivity of epoxidation is not achieved due to acid-catalysed oxirane ring opening reaction; (ii) the separation of acidic by-products is difficult; (iii) the handling of concentrated hydrogen peroxide and strong acids is dangerous and causes corrosion problems and additionally, they are environmentally harmful(Rios et al. 2011). Thus, recently, a lot of interests of academia researchers and chemical companies have been made on the catalytic processes in order to overcome these disadvantages.

2.2.2 Epoxidation Using enzyme catalyst

Chemo-enzymatic epoxidation gained much interest because it does not show any undesired ring opening of the epoxide. Normally, the reaction mechanism is in two steps: first, the unsaturated fatty acid or ester is converted into an unsaturated peroxycarboxylic acid by the reaction of the enzyme with hydrogen peroxide. Then, it is epoxidized by an intermolecular pathway without the participation of the enzyme. In this reaction, both carboxyl group and the unsaturation are in the same molecule. The main advantage of this method is the immobilized enzymes can be easily separated by filtration and they are re-usable at least several times without loss of activity. However, as the disadvantage of such a system, the enzyme is very sensitive to the kind of substrate applied and thus it can be unsuitable and less versatile for some particular oleochemical applications (Guidotti et al. 2007).

2.2.3 Epoxidation Using Heterogeneous catalyst

Over the last decade, there has been a marked trend to develop more environmentally friendly and cost efficient routes of epoxidation processes (R. A Sheldon 1973). In this manner, the use of heterogeneous catalysts is one of the most attractive choices. The ideal catalyst for the process is not only excellent performance in the reaction but also: 1) stable, robust and re-usable, 2) cheap and easy to prepare, 3) versatile, or as to be used for many kinds of substrates, 4) environmentally friendly, etc. Typically, the catalyst used in the epoxidation is metal-catalysed material (R. A Sheldon 1973). Metals such as zeolites, silica and metal supported (Pt, Pd, Au, Ni) zeolites, silica etc. Nevertheless, there are several drawbacks associated with these traditional catalytic systems in connection with their application in epoxidation as well as transesterification of vegetable oils such as low catalytic activity, poor reusability, high material costs (use of expensive precious metals and support materials) and so forth, thus making them less attractive for industrial scale applications (in short, poor activity for the price) having low oxidation potentials, but high *Lewis* acidity in their highest oxidation states and acidic ion exchange resin are identified as superior catalysts(Konwar et al. 2014).

Cationic ion-exchange resins are versatile heterogeneous catalysts and offer several advantages over the homogeneous acid catalysts. Use of acidic ion exchange resin catalysts would reduce corrosion problem, avoid disposal of strong acids, and present better product recovery. The catalyst can be recycled, shows better selectivity, and avoids side reactions (R. A Sheldon 1973). However the rate of resin catalysed epoxidation slows down in comparison to that of homogeneous epoxidation. The heterogeneous method seems to be tedious due to the difficulty of separating the product from the resin.

In general chemical reactions that were carried out privileged the use of heterogeneous catalysts not only because of environmental concerns, but also for technical and economic considerations. Altogether, the use of a renewable feedstock, production of biodegradable materials and incorporation of heterogeneous catalysis place this research within the concept of green chemistry, and therefore, contribute to the sustainable development of our society. From those point of view carbon material has become a hot research area, and carbon-based sulfonated catalysts (CBSCs) are developing rapidly. All of the CBSCs own the carbon skeleton and -SO_3H group, and the carbon skeleton is stable and insoluble in most acidic/basic conditions as well as organic solvents.

2.3 Biochar-Based Solid Acid Catalyst

In recent years, with the emerging concepts of green chemistry, the utilization of cheaper, green materials for chemical transformations has recently gained significant attention and several research groups have made efforts to develop a catalyst using inexpensive precursors such as biomass and waste materials. Among these, particularly the sulfonated carbons or –SO_3H functionalized carbon catalysts have received considerable attention as a promising solid acid catalyst. These materials resemble H_2SO_4 in terms of acidity and catalytic activity, and also offer high operational stability (>240^{o}C and reusability), which make them versatile acid catalysts for the acid catalyzed reactions included in biomass transformation(K. Nakajima and M. Hara 2012). Functionalized carbon catalysts have been demonstrated to be amongst the most active and economically attractive catalysts for biodiesel production, as reviewed by(Konwar et al. 2014). Structurally they are comparable to active carbon and, like active carbon, they could also be prepared from any carbonaceous source, and their textural properties can easily be tuned by changing the carbonization/activation conditions. As a result, sulfonated carbons are much less expensive compared to traditional solids such as Amberlyst™, zeolites, sulfated zirconia etc. Besides, such activated carbon generated from inexpensive precursors could be a versatile support for the preparation of an inexpensive catalyst(Hara 2010).

Typically, activated carbons have a porous structure, usually with a relatively small amount of chemically bonded heteroatoms (mainly oxygen and hydrogen). Also, activated carbons have much higher specific surface area than other types of supports (>1000 m2/g). Although a high specific surface area is usually considered advantageous in catalysis, in some cases it may be detrimental if it is confined in narrow micropores that are not accessible to the reactant molecules. This is particularly important in processes where large biomass molecules, such as fatty acids, triglycerides and sugar oligomers are involved as in liquid phase reactions where diffusion of these reactants and their corresponding products may be hindered by the narrow porosity(Mo et al. 2008).

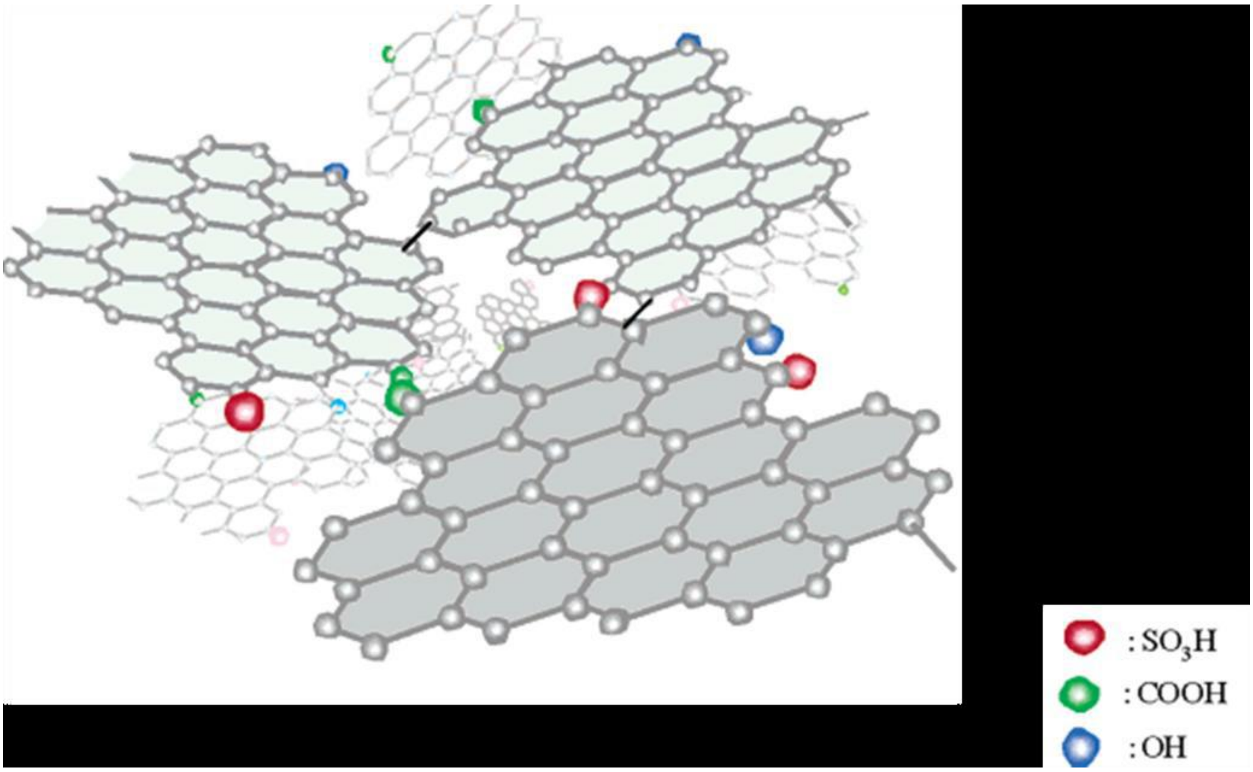


Figure 2-5 Structure of biochar-based catalyst (Okamura et al. 2006)

2.3.1 Factors that Affect the Performance of the Catalyst

2.3.1.1 Surface Area

Both catalyst surface area and total acid density are important parameters in the catalytic reactions. The Brunauer-Emmett-Teller (BET) area of the biochar produced by direct carbonization is often low (< $30m^2/g$), and sulfonation process seems having no effects on the improvement of BET area(Oyama 2008). In order to get high surface area of CBSC, the biochar can be activated to become porous carbon material followed by sulfonation to form activated carbon based sulfonated catalysts. (Dehkhoda et al. 2010a) have got high surface area carbon catalyst (BET area reach $207m^2/g$) through the carbonization, activation, and then sulfonation processes, and their results showed that the catalyst with the higher surface area has higher catalytic activity for the production of biodiesel.

However, the catalytic activity for some small molecule reactions (e.g. esterification of acetic acid with ethanol) was found to be independent of the specific surface area, but related to acid density of the carbon catalyst (Oyama 2008).

2.3.1.2 Degree of Sulfonation

Total acid density is one of the main parameter which affects the activity of solid acid catalyst (Kang, Ye and Chang 2013). This is due to, in the process of the hydrolysis of cellulose, once cellulose is adsorbed by COOH groups and phenolic OH groups and it will be readily hydrolyzed by SO_3H groups(Hu et al. 2015). Hence, in carbonaceous solid acid catalyst the activity of the catalyst is highly influenced by the concentration of SO_3H groups. Different researchers stated that increasing the sulfonation will increase the activity of the catalyst(Biermann et al. 2000). All in all when carbon based solid acid catalyst is prepared it is better to devise a way to increase the degree of sulfonation of the catalyst.

2.3.1.3 Morphology

The morphology of the catalyst related with the carbon source, when the carbon source changes the morphology is also changes. On top of this, (Pang et al. 2010)found that the types of carbon sources also have a large effect on the catalytic activities of carbonaceous solid acid catalysts. In order to illustrate this issue, six carbon sources including acetylene carbon black (ACB), multiwall carbon nanotube (MWCNT), cellulose carbon (CC), resin carbon (RC), coconut shell active carbon (CSAC) and ordered mesoporous carbon (CMK-3) were tested, and the results indicated that the sulfonated CMK-3 exhibited the highest catalytic activity for the hydrolysis of cellulose, resulting in 74.5% glucose yield in aqueous solution at 150°C for 24 h(Pang et al. 2010).

2.3.1.4 Temperature

The effect of temperature in the catalyst is too immense. This is due to the impact of temperature exists the catalyst properties starting from carbonization, activation, sulfonation and in the hydrolysis and esterification process. When the carbonization process runs at high temperature (>650°C) it will create rigid carbon material which is inert to react with H_2SO_4, hence the carbon material wouldn't carry any SO_3H ions. To avoid such rigidity and inertness of the carbon materials it is advised the carbonization temperature to be lies in the range of 350-400°C (Ormsby, Rick, James R. Kastner

2012).On the other hand, when it's come to sulfonation process (Pang, et al. 2010) showed high temperature sulfonation would increase the acid density (degree of sulfonation) in the carbon materials. Therefore sulfonation temperature which lies around 250˚C would be more preferable than lower ranges(Pang et al. 2010)

2.4 Parameters Affecting Epoxidation Reaction

There are different parameters which affects Epoxidation reaction. The main factors which highly affects include, agitation Speed, amount of hydrogen peroxide and molar ratio, reaction temperature, reaction time, catalyst loading and purity of reactants.

2.4.1 Agitation Speed

It is essential to operate the process at highest feasible speed to eliminate the effect of resistance to mass transfer of performic acid (PFA) from aqueous phase to organic phase and ensure that the reaction was kinetically controlled. In addition to this if the catalyst is heterogeneous higher agitation speed is required than that of homogeneous catalyst to eliminate the effect of mass transfer limitations.

(Dinda et al. 2008), investigates the effect of mass transfer resistance, the reaction was performed at different stirring speeds ranging from 800 to 2500 rpm. The oxirane formation rate was not substantially affected by stirring speeds beyond 1500 rpm, and hence it can be safely assumed that the reaction is free from mass transfer resistance beyond 1500 rpm under the given conditions of temperature and catalyst loading.

2.4.2 Amount of Hydrogen Peroxide molar ratio to formic acid and Time of Reaction

Hydrogen peroxide and Formic Acid (FoA) takes part in the overall reaction as a in the formation of oxirane ring and as a reactant in the hydrolysis of the oxirane ring.

(Dinda et al. 2008), have reported that the amount of hydrogen peroxide has the greatest influence on the rate of the reaction and the degree of epoxidation (conversion). An excess of hydrogen peroxide relative to the number of unsaturated bonds is necessary. This permits reaching full conversion of double bonds and compensation of hydrogen peroxide loss, caused by its decomposition at temperatures above 50 °C. The challenge is to shorten the reaction time. Too long a reaction time (6 to 12 h) and excess of hydrogen peroxide lead to increased level of carboxylic peracids in the final product. Peracids could be a potential problem for reasons of safety and contamination of the final product.

The reaction rate increased with increasing hydrogen peroxide concentration between 10–50 wt. %.

The optimal conditions (91% conversion, 5.99% epoxide content in product) for peracetic epoxidation of soybean oil were found to be: 0.5 mole of glacial acetic acid and 1.1 mole of hydrogen peroxide (30%) per mole of ethylenic unsaturation, 75^0C, 8 hrs, 5 wt% of the resin catalyst(Dinda et al. 2008).

2.4.3 Reaction Temperature

Increasing temperature shows a favorable effect on the formation of PFA. This resulted not only in more rapid epoxidation, but also in higher rate of hydrolysis of the product. Thus higher reaction temperature caused simultaneous rise in rate of epoxidation and oxirane ring opening reactions. Reaction at lower temperature shows lower rate but gave more stable oxirane ring.

Elevation of the temperature from 30 to 60^0C caused a decrease of the iodine number, while the value of the epoxy number rapidly decreased above 60^0C for the formation of epoxidised rapeseed oil(Dinda et al. 2008).

2.4.4 Purity of the reactants

Impurities present in vegetable oil also affect the epoxidation reaction significantly. The hydrolysis of glycerides resulting in free fatty acids affects the formation of epoxidized oil. For saturated and monounsaturated (C_{12}-C_{18}) free fatty acids (FFA), the epoxy oxygen content increased with increasing carbon chain length of FFA. For branched-chain unsaturated FFA, the epoxy oxygen group content decreased in the presence of hydroperoxide and hydroxyl group of FFA. The epoxy oxygen group content also decreased with increasing number of double bonds in FFA(Lu et al. 2010).

2.4.5 Catalyst loading

A catalyst is needed to improve the Epoxidation reaction and yield. The homogeneous catalysts such as sulfuric acid and heterogeneous catalysts like acid ion exchange Resin and metal catalyst are most widely used. Homogeneous catalysts increase the reaction rate several times faster than heterogeneous catalysts acid catalysts due to less mass transfer limitations. Even though homogeneous catalysts showed greater performance toward epoxidation reaction to obtain epoxidized oil. The problems associated with the homogeneous catalysts are the high consumption of energy, form unwanted soap byproduct by reaction of the FFA, expensive separation of the homogeneous catalyst from the reaction mixture and generation of large amount of wastewater during separation and cleaning of the catalyst and the products.

2.5 Analysis of epoxidation reaction mixtures

The progress of the epoxidation reaction or the quality of the epoxy product, as measured by the changes of the hydroxyl value, iodine number and epoxy number, is used to estimate the fractional conversion, yield, and the selectivity of transformation to epoxidized oil/ fatty acids/ ester. The structures of the products are confirmed by thin layer chromatography (TLC), Fourier transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) analysis.

2.5.1 Hydroxyl value (HV)

The HV characterization was used to monitor the extent of transesterification (or degree of substitution) of sucrose with FAME/ oil. It is determined by the titration of residual unreacted acetic anhydride left from the reaction of the free OH groups of the sample with an excess of acetic anhydride (DIN EN ISO 4629).

2.5.2 Iodine Number (IN)

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

2.5.3 Oxirane Number (ON)

The Oxirane Number defines the content of epoxy groups in epoxidized oil. The method involves the determination of oxirane oxygen by potentiometric titration. It is based on the reaction between perchloric acid and bromide, with the transformation of latter in the hydrogen bromid that by interaction with the oxirane group forms bromidrina. The equivalence point, determined by titration, is detected at an excess of perchloric acid (ASTM D 1652-97). The epoxidized vernonia oil was characterized by using Fourier transform infrared (FTIR) spectroscopy and NMR analysis.

3. MATERIALS AND METHODS

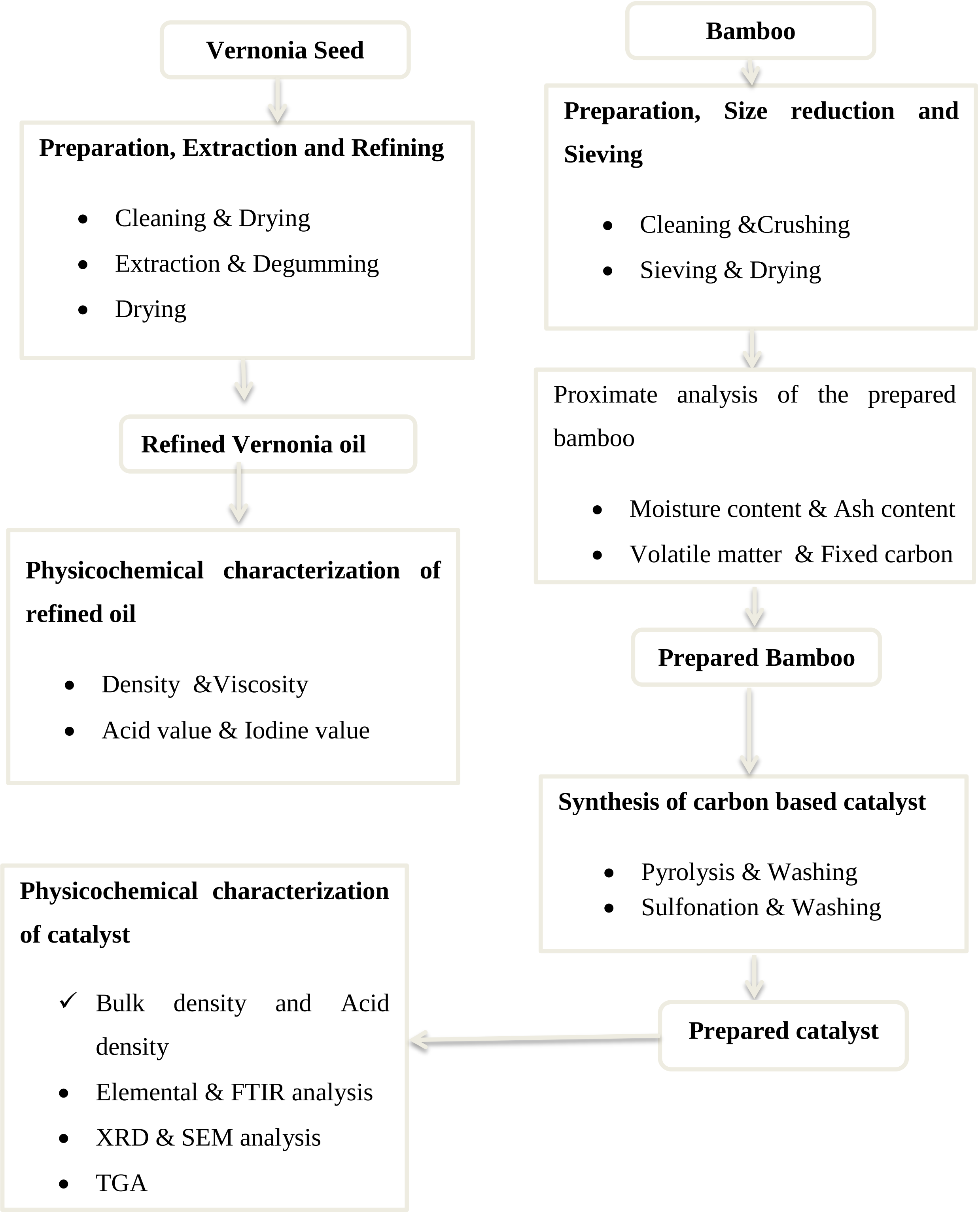
3.1 Materials

The major raw materials used during the experimental work were vernonia seed, bamboo, sodium thiosulphate, sodium hydroxide, hydrochloric acid, sodium chloride, sulfuric acid, formic acid, hydrogen per oxide, sodium chloride, Nitrogen gas, weij's solution, glacial acetic acid, cyclohexane, starch, potassium iodide, Potassium hydroxide, Hexane, ethanol and starch. Vernonia seed was acquired from Adet Agricultural Research Center, West Gojjam and the bamboo was bought from furniture houses, in Addis Ababa. All the other chemicals were analytical reagent grade and bought from different chemical stores in Addis Ababa.

3.2 Equipments

The equipment's used during the experimentations includes tubular Furnace with a stainless steel tubular reactor, soxhelet, a glass reactor equipped with a magnetic stirrer, water bath, condenser, crusher, separating funnel, vacuum pump, balance, oven, magnetic stirrer, Bunsen burner, Muffle furnace, different size conical and Erlenmeyer flasks, beakers, measuring cylinders, burette, micropipettes, GC/MS, FTIR, XRD, TGA and SEM.

The experimental work was started in December and end in April a total of six months was spent for the laboratory works. Preparation of the bamboo, pyrolysis of the bamboo, 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. Extraction of vernonia oil using soxhelet apparatus, Vernonia 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, XRD analysis, fatty acid composition of the refined oil (GC/MS) and NMR analysis of the epoxidized oil as well as vernonia oil were done at faculty of natural science department of chemistry, Arat Killo. SEM and TGA analysis of the catalyst was done at Leather industry development institute (LIDI). The overall structure of the experimental works is shown in Figure 3.1



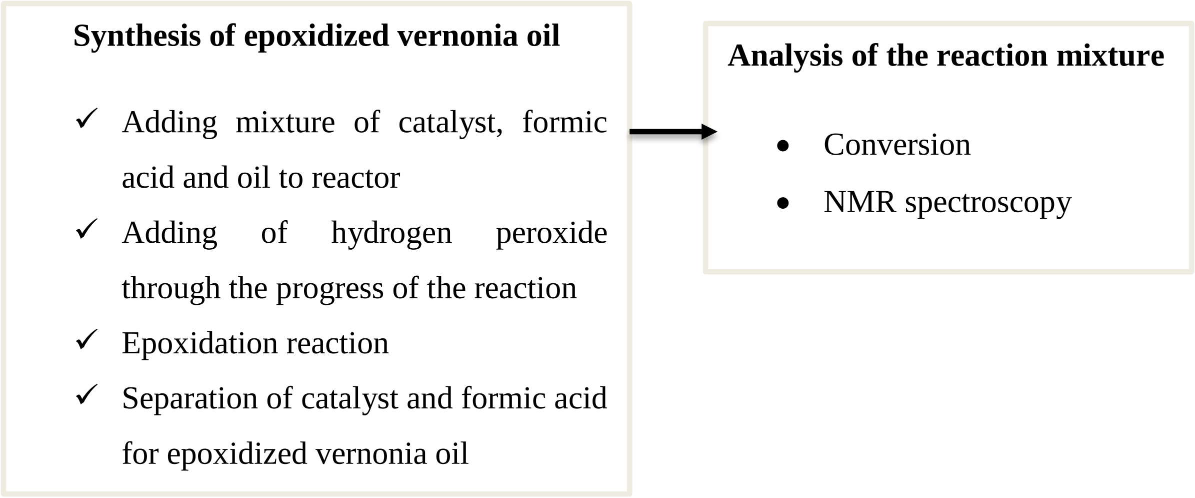


Figure 3-1 Frame work of the experiment

3.3 Experimental Method

3.3.1 Preparation of Carbon Catalyst Support

The bamboo collected from the local market was crushed using roller mill and sieved in order to obtain a desirable size fraction (0.5 -1.4mm). The bamboo was then dried in an oven for 12 hours at 105°C to reduce its moisture content (9.41-10.31%). The dried bamboo was then stored in air tight plastic bags and stored in clean space for further analysis.

After the bamboo was dry, the dried saw dust bamboo was pyrolysized in a Muffle furnace at different temperature ranges. The pyrolysis process was undergone at temperature 400, 450 and 500°C for constant time of two hours. Then, the char produced was discharged from the furnace and washed first by 0.1M solution of hydrochloric acid followed by hot distilled water (≥80°C) for several times to remove the ash content of the char until the pH of the washed water was neutral.

3.3.2 Functionalization of Chars via Sulfonation

The sulfonation method reported by (Fukuhara et al. 2011)was used. Two sets of experiments have been carried out: (1) experiments were carried out under magnetic stirrer and (2) same experiments were carried out under ultrasound sonication.

The sulfonation was conducted by sonication and stirring for all prepared chars. The bio-chars prepared at different temperature was then functionalized by heating in sulfuric acid (96 % of H_2SO_4; 102-153.125 ml of sulfuric acid for 10-15 g of char) at 150^oC under nitrogen flow for 15 hours. Then the final catalyst was washed with plenty of hot water (≥80^oC) to remove the homogeneous sulfuric acid until the pH of the washed water became neutral and no sulfate ions were detected. The samples were then dried at 105^oC for 4 hours to remove moistures from the samples using Oven. The bio-chars prepared at different temperatures and their sulfonated catalysts prepared with sonication and stirring can be designated as C-400, C-450, and C-500^oC for bio-chars; C-SO_3H-400^u, SO_3H- 450^u and SO_3H- 500^u ^oC for sulfonated carbon catalyst prepared by ultrasound sonication; SO_3H- 400^s, SO_3H- 450^s and SO_3H- 500^s ^oC and sulfonated carbon catalyst prepared by stirring.

3.4 Catalyst and Bamboo Characterization

3.4.1 Proximate analysis of the bamboo

The proximate analysis of the raw bamboo dust (moisture content, volatile matter, fixed carbon and ash content) was determined using ASTM D1762-84. The measurement was done three times and the average will be taken to increase the accuracy.

A. Moisture content

The raw bamboo crushed to desirable size was put into crucible. The crucible was weighed with and without the amount of bamboo dust. The crucible with bamboo dust was dried in an oven at 105°C for 8h. The sample was removed each 2 hour from the oven and placed in the desiccator for 30 minutes to cool and re-weighed till constant weight is obtained. Finally, the weight was taken and compared with the initially recorded weight. The percentage weight in the dust was calculated using the formula:

$$moisture\ content, \% = \frac{w_1 - w_2}{w_1} \times 100 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.1$$

Where W_1 is the original weight of the sample before drying and

W_2 is the weight of the sample after drying

B. Volatile matter

The muffle furnace was heated until it reaches to a temperature of 925℃. The crucible with its cover was preheated in furnace at 925℃ for around 10 minute to remove its moisture content and any physically adsorbed material with in the crucible and the crucible with its cover was put in to desiccator for 1 hours. Then, the crucible and its cover were weighed with and without the amount of bamboo dust. Then, the samples were heated at 925 °C in a closed crucible for 7 minutes and 30 seconds. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample. The percentage of volatile matter in the sample was calculated using the formula:

$$Volatile\ matter, \% = \frac{B-C}{B} \times 100 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.2$$

Where B grams of sample before drying and

C is grams of the sample after drying at 925^{o}C

C. Ash content

The muffle furnace was heated until it reaches to a temperature of 650℃. The crucible was preheated in furnace at 650℃ for around 10 minute to remove its moisture content and any physically adsorbed material with in the crucible and the crucible was put in to desiccator for 1 hours. Then, the crucible was weighed with and without the amount of bamboo 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:

$$Ash, \% = \frac{D}{B} \times 100 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.3$$

Where B grams of sample before drying and

D is grams of residue

D. Fixed Carbon Content

The fixed carbon content is determined by subtracting the sum of volatile matter content and ash content form 100. The value obtained 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 the formula:

$$fixed\ carbon\ content,\% = 100 - (B + C) \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.4$$

Where B - Percentage of volatile matter (%)

C - Percentage of ash (%)

3.4.2 Bulk Density of the Char

The bulk density of the material was obtained by weighting a certain grams 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:

$$Bulk\ density\ = \frac{weight\ of\ the\ samples\ (g)}{Volume\ of\ the\ sample\ (ml)} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.5$$

3.4.3 Bulk Density of the catalyst

The same procedure was used to determine the bulk density of the char as discussed above.

3.4.4 Acid Density of the Catalyst

The content of total acid density (TAD): 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 et al. 2014). The catalyst samples were pre-dried in the oven at 110°C for at least two hours prior to analysis. In a typical analysis, 0.05g 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 under ultrasonic vibration. 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, was 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:

$$TAD = \frac{(volume\ NaOH * Normality\ of\ NaOH - volume\ of\ HCl * Normality\ of\ HCl)}{Mass\ of\ the\ catalyst} \cdots\cdots 3.6$$

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:

$$AD_{\mathrm{SO3H}} = \frac{(volume\ of NaOH\ used\ for\ the\ titration * Normality\ of\ NaOH)}{Mass\ of\ catalyst} \cdots\cdots\cdots\cdots 3.7$$

3.4.5 Ultimate Analysis (CHNS) of Catalyst

The Ultimate Analysis of a sample determines 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 (T.C.D.), which gives an output signal proportional to the concentration of the individual components of the mixture. This determines the equivalent compositions of elements in the sample.

3.4.6 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-Transformed Infrared (FTIR) spectroscopy. The FTIR spectra were recorded on spectrum 65 FT-IR (perkinElmer) 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.

3.4.7 X-ray Diffraction (XRD)

Evaluation of the phase and morphology of sulfonated carbon catalyst was conducted using miniflex 300/600, Japan at 40 kV and a current of 15 mA with Cuk*a* radiation (1.54059-1.54441). The samples were placed on a sample holder made up of silicon wafer and the measurements were taken continuously from 10^{o} to 80^{o} angles. The resultant intensity data was processed by using in-built diffraction software Match! 3 to monitor the peak position.

3.4.8 Thermogravimetric Analysis (TGA)

Thermogravimetric analyzer (TA instrument, model: SDT Q600) was used to determine thermal stability characteristics of the sulfonated carbon catalyst (SO_3H- 500^{u} ^{o}C) composites using temperature programming from atmospheric temperature to $800^{o}C$ at the heating rate of $20^{o}C$/min. Testing was carried out under inert atmosphere (N_2) with a flow rate of 2 ml/min to remove all corrosive gases and avoid thermoxidative degradation. The thermal degradation onset temperature and the thermal degradation weight loss of composites were recorded and analyzed.

3.4.9 Scanning Electron Microscope (SEM)

Size and morphological analysis of sulfonated carbon catalyst (SO_3H- 500^{u} ^{o}C) were performed using low vacuum Scanning Electron Microscope (SEM, JSM-IT300 Model) capable of providing accelerating voltage of 0.5 to 20 kV and magnification of X10 to X1000.

3.5 Preparation, Purification and Characterization of Vernonia oil

3.5.1 Preparation of Vernonia Seed

Vernonia seeds were first cleaned from dirt, dust, sand, small stones and washed manually. Then the prepared Vernonia seeds were sun dried for two day. The clean seeds were weighted and 1.21 kg vernonia seeds were furtherr dried in an oven at $90^{o}C$ for an hour to remove the rest of their moisture content. Then the dried seed was crushed using a crushing mill with particle size of 0.5 – 1.0 mm for solvent extraction analysis.

3.5.2 Extraction of vernonia oil

Soxhlet extraction apparatus method was applied for vernonia oil extraction. For soxhlet extraction 105 g of grinded vernonia seed (packed in a filter paper) and 560 ml hexane solvent was placed in the soxhelt extraction unit. Then the solvent and crushed mixture was heated at constant temperature of 70°C for 5 hour to extract the oil. After extraction the solid suspension from the supernatant solution was separated using centrifuge at 4500 rpm for 30 minutes. Finally the solvent and oil was separated using rotary evaporator and the solvent was recovered using condenser. The yield of oil extracted will be calculated using the equation given below

$$yield\ of\ oil = \frac{mass\ of\ crude\ oil\ Extracted}{total\ mass\ of\ seed\ kernel} \times 100 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.8$$

3.5.3 Degumming

Degumming was done to avoid the interference of phosphatides, gums and other complex compounds during Epoxidation reaction and to avoid rancidity (increase in free fatty acid) of oil during storage. Distilled water 3 wt% of oil at 70°C was mixed with the oil. Then the mixture was stirred at speed of 350 rpm for 1 h heated at 70°C. Finally the mixture was separated using centrifuge at 3500 rpm for 30 minutes.

3.5.4 Determination of Moisture Content

The same procedure was used to determine the moisture content of the bamboo as discussed in section 3.4.1.

3.5.5 Determination of Density

The density of vernonia oil was determined using density meter. 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 15°C.

3.5.6 Determination of Kinematic Viscosity

Vibro viscometer was used to determine a viscosity of the oil. The sample was kept in the water bath heated by thermostat until it reaches the 40°C (equilibrium temperature). After maintaining the equilibrium temperature, the vibro viscometer tip was inserted in the sample and the reading was taken from the controller. This was done in triplicate and the average dynamic viscosity was recorded. The Kinematic viscosity was calculated using formula:

$$\text{Kinematic viscosity } (\frac{mm^2}{sec}) = \frac{dynamic\ viscosity\ (mpa.sec)}{density\ (\frac{Kg}{m^3})} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.9$$

3.5.7 Determination of Acid value

Standard alcoholic potassium hydroxide solution (0.1 N) was prepared by dissolving KOH (pellet) with 95 %ethanol. The solution was filtered and stored in brown bottle for five days. A phenolphthalein 1g per 100 ml of 95% v/v ethanol was used us an indicator. Furthermore, a mixture of 1 to 1 ratio (v/v) 95% ethanol and diethyl ether was prepared by mixing 250 ml diethyl ether and 250 ml of ethanol.

A weighed quantity of the oil sample was dissolved in 25 ml of 1 to 1 mixture of ethanol and diethyl ether. The solution was titrated with 0.1N ethanolic KOH solution in presence of 5 drops of phenolphthalein as indicator until the end point (colorless to pink) is recognized. The volume of 0.1 N ethanolic KOH (V) for the sample titration was noted. The total acidity (acid number) in mg KOH/ gm was calculated using the following equation:

$$Acid\ value\ = \frac{V \times N \times 56.1}{m} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.10$$

Where V is the volume expressed in milliliter of 0.1N solution of ethanolic KOH
m is mass in gram of the test portion
N is concentration of ethanolic KOH

3.5.8 Determination of Iodine value

The Iodine Number gives a measure of the average degree of unsaturation of oils and fats: the higher the iodine value, the greater the number of C=C double bonds. By definition, the Iodine Number is expressed in terms of centigrams of iodine per gram of sample (weight percent of absorbed iodine). For this research Wiji's method (AOAC 993.20) was applied to determine the iodine value of oil.

A standard Wiji's solution was obtained from JIJE analytical testing service laboratory and the solution was allowed to stand for three days before use.

To determine the iodine number, first a mixture of cyclohexane and glacial acetic acid (each 40 ml) was prepared. Then the oil was dissolved in 15ml cyclohexane and glacial acetic acid mixture in a ground in glass stopper conical flask and 25 ml standardized Wiji's solution was added. Then the stopper was replaced at once and the flask was allowed to stand for 1 hour at atmospheric temperature in the dark. When the reaction was completed, 20 ml of 10% KI solution and 150 ml water was added.

Finally the free iodine was titrated with 0.1N sodium thiosulphate until the color is pale yellow.

A few drops of starch solution (1ml) were added and the titration was continued until the blue color is discharged. The volume of 0.1N thiosulphate was recorded. Similarly a blank determination was done for the same length of time and at the same temperature. The result was calculated using equation:

$$Iodine\ Number\ = \frac{(V^{o} - V) \times C \times 12.69}{M} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 3.11$$

Where

V is titrant volume used for the sample

V^o is Titrant volume used for blank

C is titrant normality

M is weight of sample

3.5.9 Gas Chromatography Mass Spectroscopy (GC/MS)

GC analysis was performed with Agilent GC – 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^{o}C for a total run time of 38 minutes. The data, obtained using MS - Agilent Technologies EMS detector and processed using Chemstation software, were used to obtain fatty acid composition of oils.

3.6 Experimental Design for Epoxidized vernonia oil Production

In this work the epoxidized vernonia oil was produced using purified vernonia 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-three-factor Box-Behnken Design (BHD) and the response variable measured was the percentage of conversion. In addition analysis of physicochemical properties of epoxidized vernonia oil such as NMR spectroscopy was done at fecality of natural science department of chemistry, Addis Ababa University.

The three independent variables studied for the epoxidation reaction process were reaction temperature molar ratio of hydrogen per oxide to oil and catalyst loading. The independent variables interaction effect was analyzed to obtain maximum percentage of double bond in vernonia oil. In addition to achieve maximum conversion of double bond rotational speed was set at 1500 rpm, reaction time 3.5 hour and the molar ratio of formic acid to oil was fixed to the minimum amount of oil requirement (0.5 mole/mole).

Three-level-three-factor BHD was used in the optimization study which requires 15 experiments to be conducted. The fifteen experiments were done and the data was statistically analyzed using Design-Expert Software 7.0.0 to obtain a suitable model equation for the percentage conversion of double bond as a function of the independent variables.

Table 3-1 lists the range and levels of the three independent variables studied. The lower and higher levels are chosen by considering the operating limits of epoxidation reaction process conditions.

Table 3-1 Independent variables and levels used in the BHD for the epoxidized oil production

Variables	**Units**	**Levels**		
		-1	**0**	**+1**
Reaction temperature	^{o}C	65	75	85
Hydrogen per oxide to oil ratio	Mole/mole	1.50	2.50	3.50
Catalyst loading	Wt%	2	4	6

Below in Table 3-2 the complete experimental design matrix of BHD for the factorial design was shown. The order in which the runs were made was randomized to minimize systematic errors.

Table 3-2 the complete experimental design matrix

Run	**Actual Factors**		
	Temperature (^{o}C)	**H_2O_2 to oil ratio (mole/mole)**	**Catalyst loading (wt %)**
10	65.00	1.50	4.00
2	85.00	1.50	4.00
4	65.00	3.50	4.00
9	85.00	3.50	4.00
15	65.00	2.50	2.00
8	85.00	2.50	2.00

14	65.00	2.50	6.00
7	85.00	2.50	6.00
11	75.00	1.50	2.00
5	75.00	3.50	2.00
12	75.00	1.50	6.00
1	75.00	3.50	6.00
3	75.00	2.50	4.00
13	75.00	2.50	4.00
6	75.00	2.50	4.00

3.6.1 Experimental Setup

The epoxidation of feed material (mixture of Vernonia oil, peroxy acid and sulfonated carbon catalyst) was done on a 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 and rotational speed. The batch epoxidation reaction system was employed for epoxidized vernonia oil production as shown in the schematic diagram below.

Figure 3-2 Experimental set-up for epoxidized vernonia oil production through epoxidation

3.6.2 Feed Material Requirement

Fifteen ml of purified vernonia 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 1.5:1;

$$\frac{n\text{ Hydrogen peroxide}}{n\ oil} = 1.5$$

Substituting mass for mole;

$$\frac{\frac{\rho H_2O_2 \times VH_2O_2}{MH_2O_2}}{\frac{\rho oil \times Voil}{Moil}} = 1.5$$

$$\frac{\frac{1.11g/ml \times VH_2O_2}{34.01g/mol}}{\frac{0.92204g/ml \times 15ml}{292.69g/mol}} = 1.5$$

Solving for VH_2O_2 = 2.280 ml of hydrogen peroxide

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

$$\frac{n\text{ formic acid (FA)}}{n\ oil} = 0.5$$

Substituting mass for mole;

$$\frac{\frac{\rho FA \times VFA}{MFA}}{\frac{\rho oil \times Voil}{Moil}} = 0.5$$

$$\frac{\frac{1.22g/ml \times VFA}{46.03g/mol}}{\frac{0.92204g/ml \times 15ml}{292.69g/mol}} = 0.5$$

Solving for VFA = 0.9359 ml of formic acid

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

$$m\ oil = \rho oil \times Voil$$

$$m\ oil = 0.92204g/ml \times 15ml$$

$$m\ oil = 13.8306g$$

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

$$mass\ of\ catalyst = mass\ of\ oil\ \times 4\%$$

$$mass\ of\ catalyst = 0.553g$$

Similarly, the amount of hydrogen per oxide and catalyst is calculated for all experiments. The tabulated result for different processes parameter was given in appendix C.

3.6.3 Analysis of epoxidation reaction mixtures

The quality of the epoxy products is evaluated according to certain specifications such as iodine value and ^{1}HNMR spectroscopy. Such value was determined for each epoxidized products, obtained in this research work, according to the procedures described below.

To determine the iodine value of epoxy products the same procedure was used to determine the iodine value of the oil as discussed in section 3.5.8.

The conversion related to the double bonds reacted is calculated with the following

$$\text{Conversion (\%)} = \frac{(\text{Iodine N})_O - (\text{Iodine N})}{(\text{Iodine N})_O}$$

Where

$$(\text{Iodine N})_O = \text{Iodine value of the oil}$$

$$(\text{Iodine N}) = \text{Iodine value of the epoxy product}$$

3.6.4 NMR spectroscopy Analysis

The NMR spectra of epoxidized vernonia oil was recorded on Bruker Avance 400 spectrometer (Bruker, Rheinstetten, Germany) operated at 400 MHz using $CDCl_3$ as solvent. For this analysis only the epoxidized vernonia oil obtained at optimum process condition was analyzed.

4. RESULT AND DISCUSSIONS

4.1 Raw Bamboo Preparation and Catalyst Characterization

4.1.1 Proximate analysis of the raw bamboo

Figure 4-1 shows that the proximate analysis of the raw bamboo. Moisture content, volatile matter, fixed carbon content and ash content of the bamboo saw dust was 9.96, 80.97, 17.43 and 1.6% respectively. The bamboo sample was rich in volatiles (80.97%) and fixed carbon but low in ash content (1.6%). The bamboo supplied had a moisture content of about 9.96%, which is a well-tolerated value for production of bio-chars. The fixed carbon contents are well which is higher than various types of wood(Article 2013). Bio- mass with higher fixed carbon content has higher bio-char yield and higher surface area for attachment of the sulfonate group during sulfonation reaction.

The low ash content would result in minimal effects of inorganic impurities on pore development during activation process. Previous studies suggested that suitable activated carbon should be low in ash but rich in carbon and volatiles. The ash consists of mainly minerals such as silica, alumina, iron, magnesium and calcium. Ash in activated carbon is undesirable and taken as impurity. Ash may interfere with carbon adsorption through competitive adsorption and catalysis of adverse reactions. Usually materials with the lowest ash content produce the most active products(Journal et al. 2016).

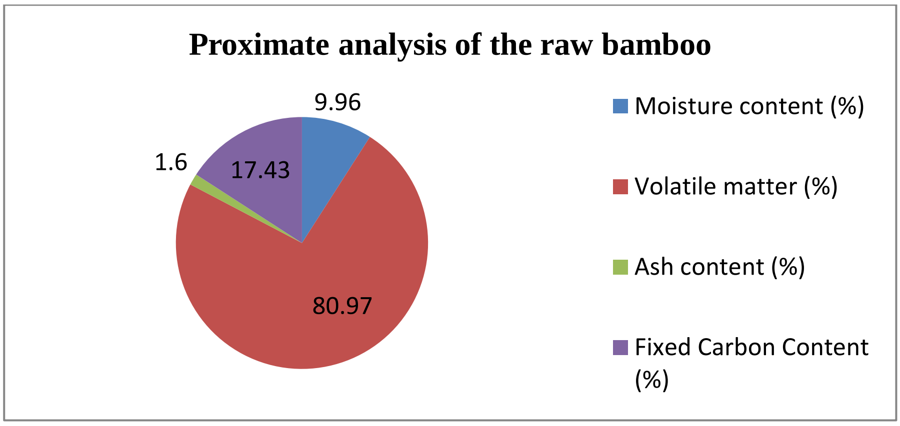


Figure 4-1 Proximate analysis of the Bamboo

4.1.2 Bulk density of Char and Catalyst

The bulk density of the bio-chars as well as catalysts was shown in Table 4-1. The bulk density of bio-chars for C-400, C-450 and C-500 was 0.284, 0.270 and 0.284 gm/ml respectively. The bulk density of catalysts prepared with ultrasound sonication i.e. C-SO_3H- 400^u, C-SO_3H- 450^u, and C-SO_3H- 500^u was 0.404, 0.350 and 0.365 gm/ml respectively and that of the catalyst prepared with stirring i.e. C-SO_3H- 400^s, C-SO_3H-450^s and C-SO_3H- 500^s ^{o}C was 0.376, 0.325 and 0.343gm/ml respectively.

Table 4-1 Bulk density of Bio-char and Catalyst

Sample type	Bulk density (g/ml)
C-400	0.284
C-450	0.276
C-500	0.284
C-SO_3H- 400^u	0.350
C-SO_3H- 450^u	0.365
C-SO_3H- 500^u	0.404
C-SO_3H- 400^s	0.325
C-SO_3H- 450^s	0.343
C-SO_3H- 500^s	0.376

The bulk density of the bio-chars is similar as shown in the above Table 4-1 but it is lower than that of catalyst prepared with ultrasound sonication as well as magnetic stirring. Hence, sulfonation reaction is sophisticated, many reactions may occur during sulfonation of bio-chars such as complete carbonization and thermal oxidative of the bio-chars. Since, 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.

However, the bulk density has shown significant difference between the catalyst prepared with ultrasound sonication and magnetic stirring as shown in Table 4-1. The ultrasound sonication preparation protocol shows a considerable enhancement in the reaction rate along with improved selectivity compared with reactions performed under magnetic stirrer(Qureshi et al. 2014). The carbonization temperature also shows significant effect on the bulk density of the catalysts. As carbonization temperature increases the bulk density of the catalyst also increases as long as the maximum temperature of carbonization is 500^{o}C i.e. for this specific case.

Such behavior could be attributed to the following reasons. Total pore volume increased with increasing activation 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(Dehkhoda et al. 2010b).

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 method and the results are shown in Table 4-2

Table 4-2 Total acid density and amount of SO_3H group of catalyst and bio-char

Sample type	Total acid density (mmol/g)	The amount of -SO_3H group (mmol/g)
C-400	1.8	………
C-450	1.9	………
C-500	1.96	………
C-SO_3H- 400^u	2.98	0.437
C-SO_3H- 450^u	3.71	0.447
C-SO_3H- 500^u	4.16	0.59
C-SO_3H- 400^s	2.91	0.398
C-SO_3H- 450^s	3.55	0.401
C-SO_3H- 500^s	4.00	0.528

The total acid density of the bio-chars was increased shown in as carbonization temperature increases the functional group such as carboxylic acid and phenolic may form mainly due to oxidization during the carbonization bamboo saw dust. Such principle was true only when the carbonization temperature is less than 600°C. If the carbonization temperature is greater than this temperature the total acid density of the catalysts decreases indicates a reduction in active acid sites available on the catalyst surface as a result of the decreasing amount of polycyclic aromatic carbons available to be functionalized as the carbonization temperature increases(Zhang et al. 2016).

The total acid density and amount of sulfonate group of the catalysts was higher than that of bio-chars which agrees with bulk density of those materials discussed above. In addition to this, the total acid density and amount of sulfonate group of the catalyst prepared with ultrasound sonication was also higher than that of the catalyst prepared with stirring protocol. This theory also supports the bulk density of the catalysts. The values of the total acid density as well as amount of sulfonate group are also in agreement with (Adrian et al. 2012).

4.1.4 Ultimate Analysis (CHNS) of Catalyst

Further investigation on ultimate or elemental analysis of the catalyst and bio-chars was also performed to analyze the composition of the materials and the results were shown in Table 4-3.

Table 4-3 Elemental analysis of catalyst

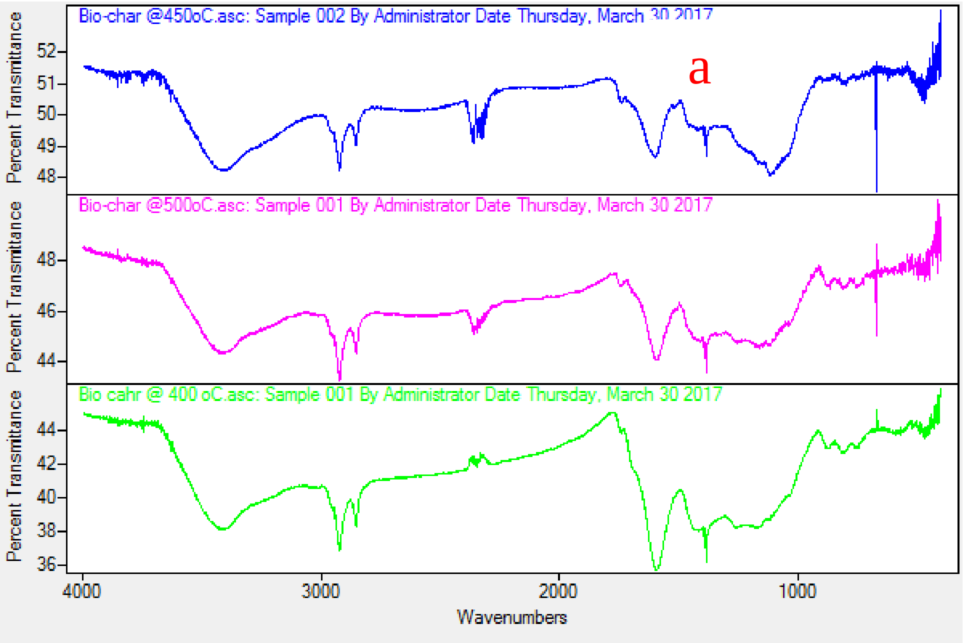
Samples	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Sulfur (%)
C-400	0.15	77.44	3.50	0.00
C-450	0.14	79.88	3.19	0.00
C-500	0.13	84.48	2.81	0.00
$C\text{-}SO_3H\text{- }400^u$	0.27	65.68	2.70	1.87
$C\text{-}SO_3H\text{- }450^u$	0.38	64.46	1.88	1.93
$C\text{-}SO_3H\text{- }500^u$	0.41	61.56	2.61	2.2
$C\text{-}SO_3H\text{- }400^s$	0.53	61.52	2.62	1.81
$C\text{-}SO_3H\text{- }450^s$	0.51	62.28	2.65	1.87
$C\text{-}SO_3H\text{- }500^s$	0.67	61.94	1.74	1.96

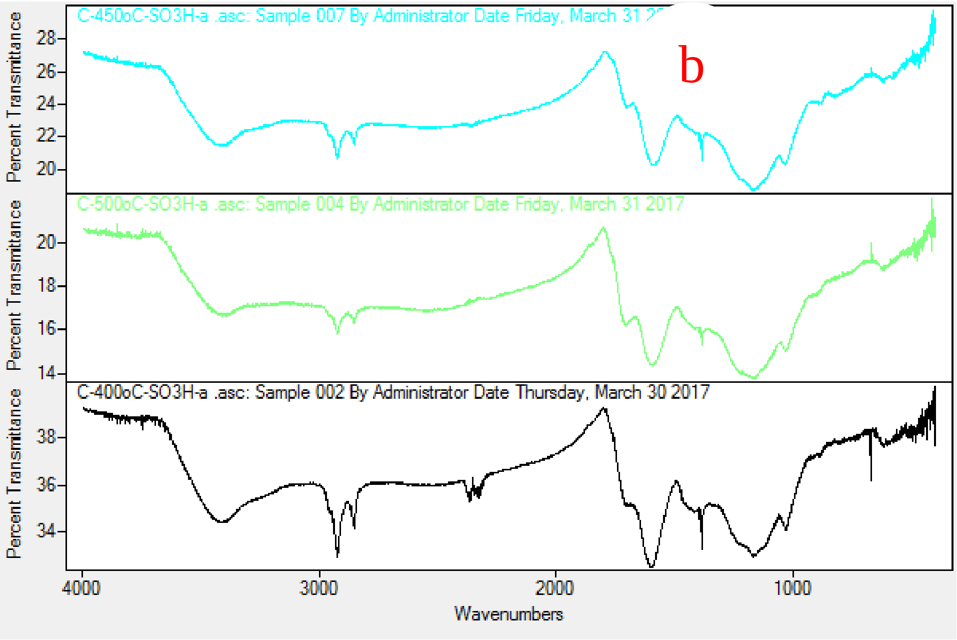
The results from the elemental analysis presented in Table 4-3 shows a increase in the percentage of carbon content of the bio-chars with increasing activation temperature, further supporting the hypothesis that the increasing temperatures cause the evaporation of an increasing number of heteroatoms from the carbon rings resulting in more graphite like structure and more ordering (Dehkoda 2010). Also, it confirms that by increasing the activation temperature more C-H bonds are ruptured through completing the carbonization of the support.

The elemental analysis also shows that, the catalyst prepared by ultrasound sonication has high sulfur content than the catalyst prepared by magnetic stirring which agrees with acid density and bulk density of the catalysts discussed above. In addition to this, the elemental analysis shows the increase in sulfur content with increasing carbonization temperature confirms increasing of active sites in the catalyst resulting in increasing total acid density and catalytic activity.

4.1.5 Fourier Transform Infra-Red (FTIR) spectroscopy

Further analysis on presence of functional groups on the surface of the bio-chars and catalysts was analyzed using Fourier transform infrared spectroscopy.





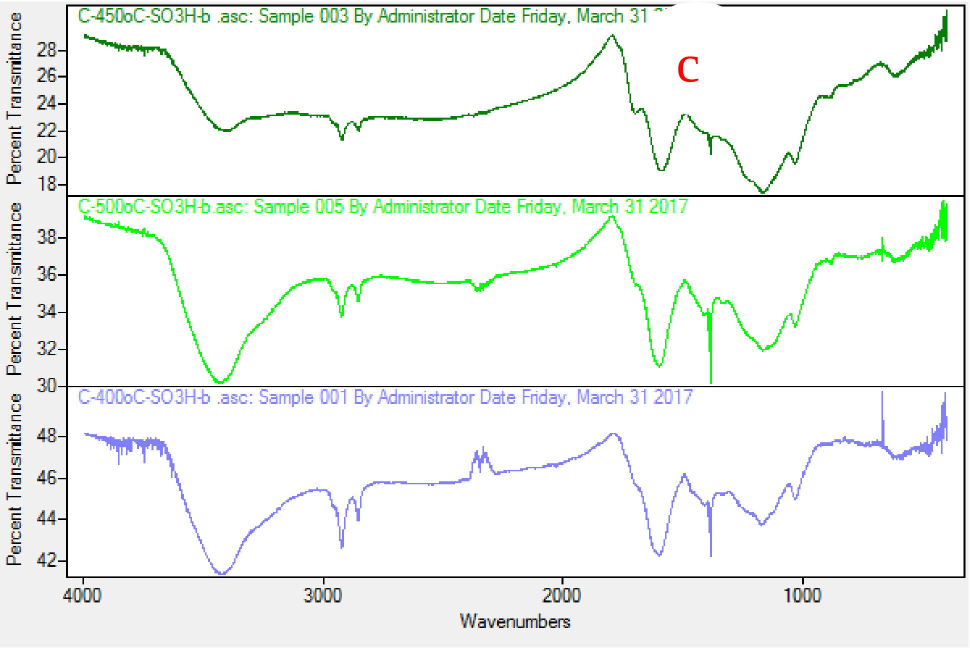


Figure 4-2 FT-IR spectra of (a) bio-chars (b) catalysts prepared by ultrasound sonication (c) catalysts prepared by stirring carbonized at temperature of 400,450 and 500°C.

Figure 4-2 (a) shows the IR spectrum of the char's carbonized at 400, 450 and 500°C before sulfonation. All spectra contains peaks attributable to aromatic ring modes in 1593.82 cm^{-1} – 1495.36 and peaks attributable to saturated C-H asymmetric stretching for bio-chars can be seen in 2924.33 – 2921.51 cm^{-1} which shows that the carbonization was incomplete(Sharma et al. 2004; Xing et al. 2007). The band shown in Figure 4-2 also exhibits additional peaks i.e. 1709 – 1700.01 cm^{-1} were C=O stretching vibration peak and 1171.88 – 1166.25 cm^{-1} (Xing et al. 2007) belonged to O-H stretching vibration peak.

The IR spectrum shown in Figure 4-2(b) and Figure 4-2(c) exhibit similar pecks with pecks shown in Figure 4-2(a) except another peck can be seen in 1056.55 – 1050.92 cm^{-1}, (Zong et al. 2007)which can be attributed to the symmetric S=O stretching, attributable to the presence of SO_3H groups, thereby confirming the incorporation of sulfonic groups onto the carbon matrix after sulfonation.

4.1.6 X-Ray diffraction (XRD) Spectrometer

Further evidence of the difference in carbon structures of the catalysts confirmed using X-ray diffraction (XRD).

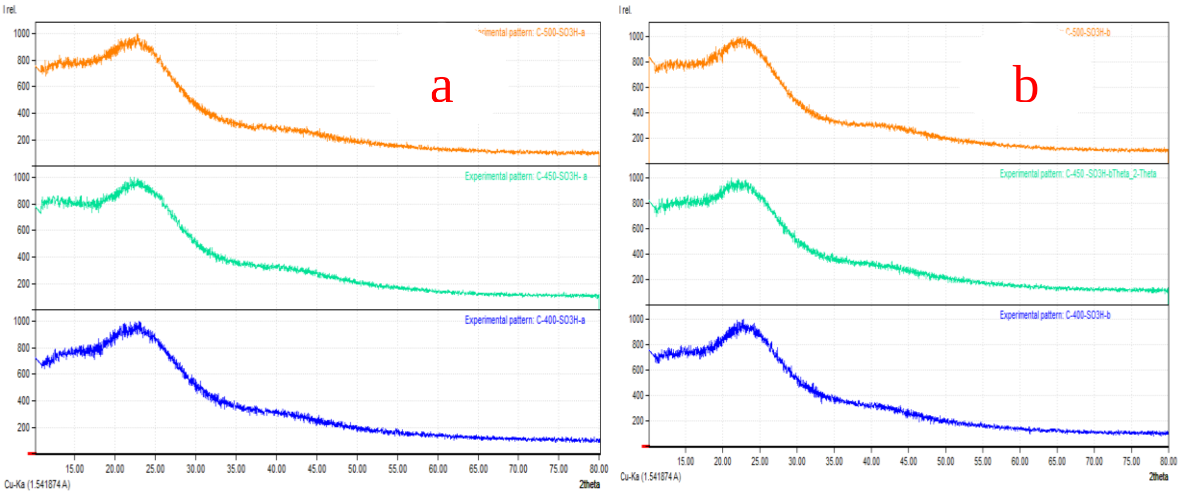


Figure 4-3 XRD pattern of (a)catalyst prepared by ultrasound sonication (b) catalyst prepared by stirring carbonized at temperature of 400, 450 and 500^{o}C

The XRD patterns shown in Figure 4-3(a) and Figure 4-3(b) exhibit similar patterns. Typical crystal diffraction peaks were not seen, and the width and weak diffraction peak around 23^{o} in all patterns implied the structures of both samples were amorphous. The process of carbonization of biomass is sophisticated, especially in the presence of sulfuric acid, and many reactions would occur. The cellulose and hemicellulose content of bamboo saw dust may dehydrate. Lignin may polymerize or rearrang. Crystal structure decomposed and amorphous hydrocarbon structure was detected.

Since, epoxidation reaction in the presence of homogenous catalyst such as sulfuric acid is very efficient relative to that of heterogeneous due to less mass transfer limitation between catalysts and reagents. Heterogeneous catalyst with amorphous structure resembles the homogeneous catalyst than heterogeneous catalyst with crystalline structure results the prepared catalyst was efficient for epoxidation reaction as long as the catalysts were amorphous structure.

Based on the above characterization (bulk density, acid density, elemental analysis, FTIR and XRD) of the catalyst the catalyst prepared at carbonization temperature of 500^{o}C with ultrasound sonication preparation protocol (C-SO$_3$H- 500^{u}) was selected for testing further performance (activity, stability and selectivity) of the catalyst.

4.1.7 Thermogravimetric Analysis (TGA)

Further investigation on the stability of the catalyst (C-SO$_3$H-500^{u}) with their respective bio-char (C-500) was performed and the thermal degradation weight loss of composites verses temperature were given in Figure 4-4.

As shown in Figure 4-4, both material started to lose weight from 50 °C. This can be attributed to the loss of water absorbed on the surface of the carbonaceous material. The second stage of the weight loss appeared around 435 °C for bio-chars (C-500). However, the second stage of the weight loss in the catalyst (C-SO_3H-500^u) appears lower than this temperature i.e. 230°C which can be interpreted as due to the decomposition of the SO_3H groups. This TGA result resembles that of the sulfonated carbon made by sulfonation of aromatic hydrocarbons such as naphthalene with concentrated sulfuric acid(Hara et al. 2004).

At a specified the same temperature let say 350°C for both materials quantitatively 16.25% of weight of the catalyst will be lost while that of bio-chars was only 3.14%. In addition, to the bulk density, acid density and elemental analysis TGA also shows the incorporation of sulfonic group to the carbon matrix.

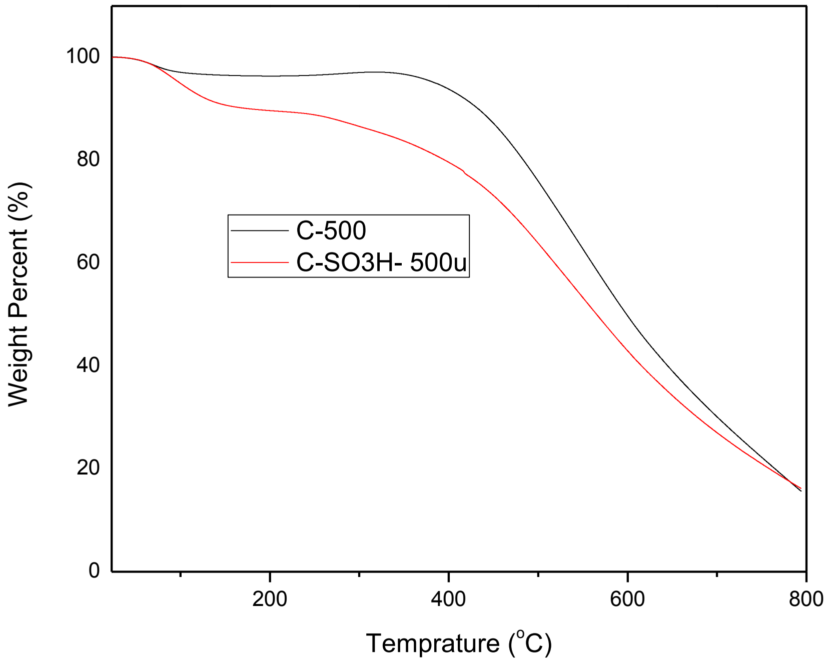


Figure 4-4 Thermo-gravimetric analysis (TGA) for catalyst from bio-char carbonized at 500°C before (C-500) and after sulfonation(C-SO_3H-500^u).

4.1.8 Scanning Electron Microscope

The morphology and surface structure of the carbonized bamboo dust before and after sulfonation are shown in Figure 4-5. The SEM images indicated that the surfaces of carbonized bamboo dust were modified with some occasional cracks, condensation and partial de-structure of porous structure during sulfonation.

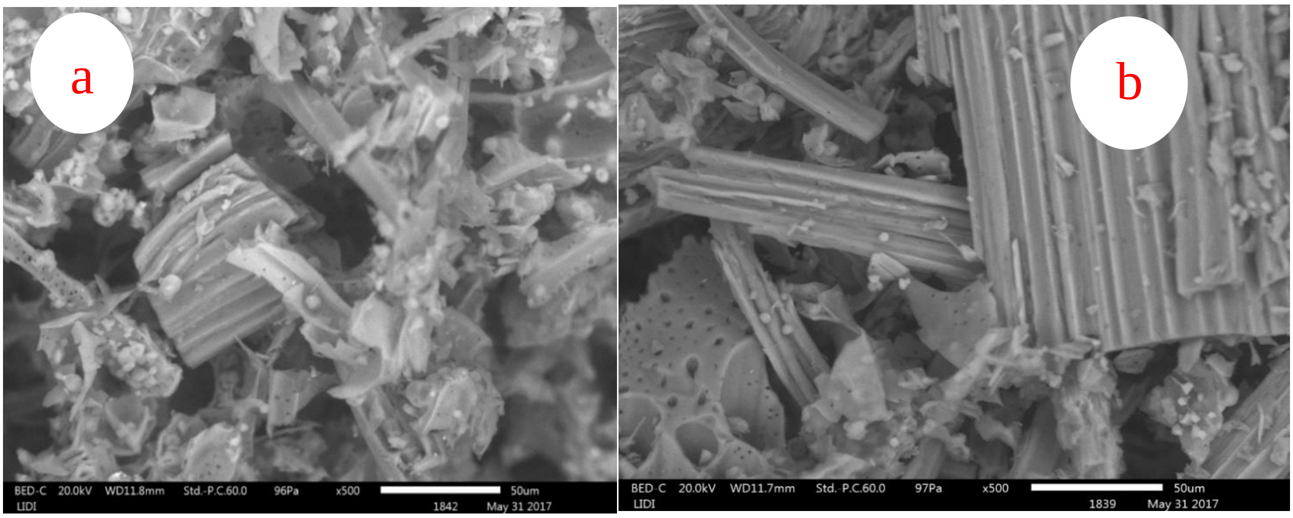


Figure 4-5 SEM image of (a) carbonized at 500^{o}C of bamboo saw dust and (b) and sulfonated carbon catalyst at 500^{o}C with sonication

4.2 Vernonia Seed Preparation, Oil Extraction, Purification and Characterization

About 1.37 kg of Vernonia seeds were taken for this research work. First it was cleaned from impurities thus, 2.55g wastes was removed. Therefore 1.34 kg cleaned Vernonia seeds were gained and the cleaned seeds was crushed using crushing mill with particle size of 0.5-1mm for solvent extraction analysis

Vernonia Oil Extraction

From 1.31 kg of the kernel, 0.544 liter of Vernonia crude oil was extracted using soxhlet solvent extraction method by using hexane as a solvent. The yield of oil (Oil Content of the seed) was 38.28%. The total amount of crude oil obtained from soxhlet solvent extraction was purified by using centrifuge to remove impurities from crude oil. Further purification of crude oil was performed to remove the amount of suspended solid using degumming.

4.2.1 Physicochemical Properties of Purified Vernonia Oil

The moisture content of vernonia seeds, density, acid value, viscosity and iodine value of Vernonia oil were determined. The A.O.A.C. official methods were followed for characterization.

The moisture content of the kernel seed, density of the oil, viscosity of oil and acid value of the oil was determined. The values of thus physicochemical was shown in Table 4-5.

The FFA composition of the purified Vernonia oil was less than two which is acceptable for epoxidation reaction which doesn’t need neutralization of crude vernonia 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 EVO and increase the shelf life.

4.2.1.1 Determination of Iodine value

The weight of oil taken for iodine value calculation was 0.319 and 0.354g according to the A.O.A.C. official method. The iodine value of the oil was 94.28gI_2/100goil.

The iodine number of Vernonia oil determined shows that the oil has higher degree of unsaturation bond than other vegetable oils next to soyabean and linseed can definitely be applied for epoxidized vernonia oil production. According to (Ayorinde et al. 1988) higher iodine value (which is higher than 85) indicates the ability to produce epoxides which are used for resins for paint and press-ink formulations.

4.2.1.2 Gas Chromatography Mass Spectroscopy (GC/MS)

The determination of fatty acid composition of vernonia oil by GC/MS was performed and the major component of the oil was shown in Figure 4-6.

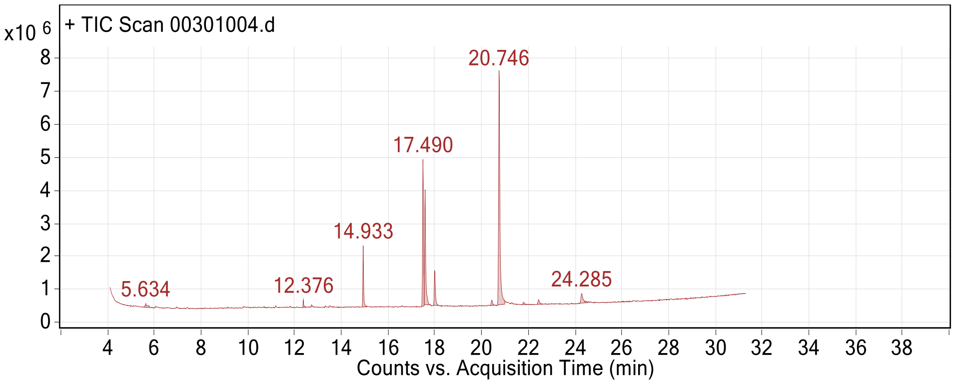


Figure 4-6 Total ion chromatogram of fatty acid profile of Vernonia oil

The fatty acid composition of vernonia oil was determined based on the possibility of the components which is given in library and percentage area of their respective peaks (appendix C).

Table 4-4 MS identification of major components of vernonia oil

Peak	**Area**	**Area (%)**	**Systematic Name of FA**	**Structure**
3	1798881.17	3.00	Hexadecanoic acid	16:0
4	8094965.264	13.50	9,12 – octadecadienoic acid methyl ester	18:2
5	3118060.69	5.20	9 – octadecenoic acid methyl ester	18:1
6	107932870.2	1.8	Octadecanoic	18:0
8	45331805.48	76.5	Cis-12, 13-epoxycis- 9-octadecenoic	18:1:1

The GC/MS identification of compounds from vernonia oil is presented in the Table 4-4. We can observe that the fatty acids that were identified by their time of retention from vernonia oil are in order of their retention time: palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid and vernolic acid. We can also observe that the higher percentage area is registered for the unsaturated fatty acid (vernolic acid, linolenic acid and linoleic acid), which is the most important fatty acid for production of epoxides. The GC/MS results also in agreement with iodine value of the vernonia oil where both indicates that vernonia oil had higher degree of unsaturation bond.

Table 4-5 Percentage of fatty acid (FA) composition and other characteristics of vernonia oil

Oil/fatty acid	**% FA composition by GC**					**Other Characteristics**			
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	Special FA	VI@15°C	IV	AV	ρ @15°C
Vernonia oil	3.0	1.8	5.2	13.5	[C18:1:1- 13-vernolic] 76.5	32.97	94.28	3.76	0.92204

VI: viscosity, IV: iodine value, AV: acid value ρ: density. $C_{16:0}$-palmitic acid, C_{18}- stearic acid, $C_{18:0}$- oleic acid, $C_{18:1}$- linoleic acid, $C_{18:2}$- linolenic acid, $C_{18:1:1}$- vernolic acid.

4.3 Performance of C-SO_3H-500 Catalyst for Epoxidized Vernonia oil Production

Further investigation on the activity of the catalyst was performed in epoxidation reaction for synthesis of epoxidized vernonia oil (EVO). The epoxidation reaction was carried out using a 100 ml capacity glass reactor which was equipped with a magnetic stirrer. The magnetic stirrer rotational speed, reaction time and temperature was adjusted to the desired conditions. The statistical analysis of the epoxidized vernonia oil synthesis is discussed in the following sections.

4.3.1 Statistical Analysis on Factors Affecting Degree of Epoxidation

The experimental design selected for this study is the Box-Behnken Design (BHD) and the response variable measured is the double bond conversion of vernonia oil. Box – Behnken design are the commonly used experimental design models for three level three factor experiments.

Box and Behnken proposed three level designs for fitting response surfaces. These designs are formed by combining 2^k factorials with incomplete block designs and 3 center points was employed in the optimization study, a total of 15 experiments were conducted, where K is three for three factors (independent variables) used in the analysis.he three epoxidation process variables are reaction temperature, amount of hydrogen per oxide to oil ratio and catalyst loading.

Box-Behnken designs (BHD) always have three levels for each factor and are purpose built to fit a quadratic model. The Box-Behnken design does not have runs at the extreme combinations of all the factors, but compensates by having better prediction precision in the center of the factor space. While a run or two can be botched in these designs the accuracy of the observations in the remaining runs is critical to the dependability of the model.

Design-Expert Software 7.0.0 was used in the least squares regression analysis of variance (ANOVA). The statistical software program is used to generate the model equation, interaction effects of the independent variables and surface plots using the fitted equation obtained from the regression analysis holding one of the independent variable constant. The BHD conditions and their respective responses and the ANOVA are given in Table 4-6 and Table 4-7 respectively.

The actual double bond conversion of vernonia oil of the epoxidized vernonia oil produced at different process parameters is determined by using the chemical characterization method of determination of iodine value Wiji’s method (AOAC 993.20). The detail calculations and results are discussed in sections below and in Appendix C.

Table 4-6 Experimental and predicted values

Run	Reaction temprature (^{o}C)	Hydrogen per oxide to oil ratio Mole/mole	Catalyst loading wt(%)	Expermental Conversion	Pridicted conversion	Residuals
1	65.00	1.50	4.00	43.5	43.13	0.37
2	85.00	1.50	4.00	40	40.83	-0.83
3	65.00	3.50	4.00	44	43.43	0.57
4	85.00	3.50	4.00	41	41.13	-0.13
5	65.00	2.50	2.00	40	40.60	-0.60
6	85.00	2.50	2.00	44	43.65	0.35
7	65.00	2.50	6.00	51.2	51.55	-0.35
8	85.00	2.50	6.00	44.5	43.90	0.60
9	75.00	1.50	2.00	38	37.65	0.35
10	75.00	3.50	2.00	43.5	43.60	-0.10
11	75.00	1.50	6.00	49	48.90	0.100
12	75.00	3.50	6.00	43.2	43.55	-0.35
13	75.00	2.50	4.00	50.4	50.10	0.30
14	75.00	2.50	4.00	49.3	50.10	-0.80
15	75.00	2.50	4.00	50.6	50.10	0.50

4.3.1.1 Development of Regression Model Equation

The model equation that correlates the response (conversion of double bond) to the epoxidation reaction process variables in terms of actual value after excluding the insignificant terms was given below. The predicted model for percentage of degree of conversion in terms of the coded factors is given in equation (4.1).

$$
\begin{aligned}
&Conversion\ of\ double\ bond\ (\%) = -220.96875 + 5.2762 \times A + 29.48750 * B \\
&+18.83750 \times C - 0.13375 \times A \times C - 1.41250 \times B \times C - 0.032375 \times A^{2} \\
&\qquad - 4.73750 \times B^{2} - 0.48437 \times C^{2} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots 4.1
\end{aligned}
$$

whre A = reaction temperature

B = molar ratio of hydrogen per oxide to oil

C = weight of catalyst amount

4.3.1.2 Model Adequacy Check

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, adjusted RSquared and predicted R-Squared having a value of 0.9869 0.9694 and 0.8970 respectively.

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 0.9869. It implies that 98.69% of the total variation in the percentage of conversion is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure 4-7. The results in Figure 4-7 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the three epoxidation reaction process variables to the percentage of conversion.

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table 4-7, based on a 95% confidence level, F – value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P – value less than 0.05. It is calculated by model mean square divided by residual mean square.

Here The Model F-value of 56.52 implies the model is significant. There is only a 0.01% chance that a "Model F Value" this large could occur due to personal error or disturbance.

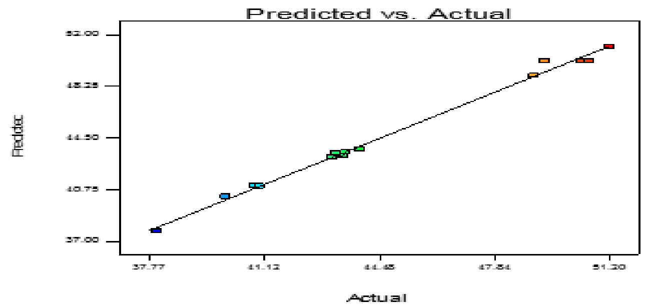


Figure 4-7 Predicted versus actual percentage conversion of the double bond in verrnonia oil

Table 4-7 ANOVA for the regression model equation and coefficients

Source	Sum of Squares	Df	Mean Square	F – value	P – value Prob > F	Remark
Model	254.54	8	31.82	56.52	< 0.0001	a
A – Reaction Temperature	10.58	1	10.58	18.79	0.0049	b
B –molar ratio of hydrogen per oxide to oil	0.18	1	0.18	0.32	0.5923	b
C – Catalyst loading	62.72	1	62.72	111.42	< 0.0001	a
AC	28.62	1	28.62	50.85	0.0004	b
BC	31.92	1	31.92	56.71	0.0003	b
A^2	38.70	1	38.70	68.75	0.0002	b
B^2	82.87	1	82.87	147.22	< 0.0001	a
C^2	13.86	1	13.86	24.62	0.0025	b
Residual	3.38	6	0.56			
Lack of Fit	2.40	4	0.60	1.22	0.4961	not significant
Pure Error	0.98	2	0.49			
Cor Total	257.92	14				

Note: [b] means significant and [a] means highly significant

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, C, AC, BC, A^2, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

This shows that the reaction temperature, amount of catalyst loading, interaction between reaction temperature and amount of catalyst loading, interaction between molar ratio of hydrogen per oxide to oil and amount of catalyst loading, square of the reaction temperature, square molar ratio of hydrogen per oxide to oil and square of amount of catalyst loading affects the percentage conversion of double bond in vernonia oil significantly.

The "Lack of Fit F-value" of 1.22 implies the Lack of Fit is not significant relative to the pure error. There is a 49.61% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good because we want the model to fit.

4.3.2 Effect of Epoxidation Reaction Process Variables

Based on the analysis of variance, epoxidation reaction was significantly affected by various interactions between the process variables. This result demonstrated that the advantage of using BHD surface response for experimental data analysis in capturing the interaction between variables that affects the epoxidation reaction. In addition to the interaction effect, significant individual process variables that affect the epoxidation reaction is reaction temperature, A and amount of catalyst loading, C.

4.3.3 Effect of Individual Process Variables

As shown in Figure 4-8 below the percentage of conversion is significantly affected by reaction temperature. It can be seen from the figure that with increasing reaction temperature until it reaches its center value would result increasing in the percentage of conversion, the percentage of conversion then starts to drop as the temperature tend to increase above the center limit. Such behavior could be attributed to the following reasons.

Increasing temperatures favored the formation of peroxyacetic acid. This resulted in a more rapid epoxidation rate, but also in higher rate of hydrolysis (oxirane cleavage) of the product which is reactions at lower temperatures had lower rates but gave a more stable oxirane ring.

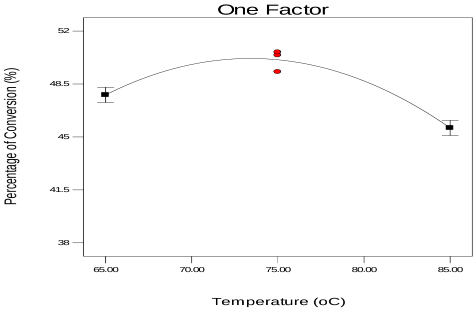


Figure 4-8 Percentage of conversion versus temperature at molar ratio of hydrogen per oxide to oil 2.5 and 4 % of catalyst amount.

According to (Goud & Pradhan, et al. 2006) results suggest that the optimal epoxidation level was obtained in a shorter time at moderate reaction temperature range (55 to 70°C), at which the hydrolysis rate was not high.

According to (Dinda et al. 2008) also elevation of the temperature from 50 to 70^{o}C caused a decrease of the iodine number, while the value of the epoxy number rapidly decreased above 60^{o}C for the formation of epoxidised rapeseed oil.

Epoxidation reaction is very slow without the use of catalyst and the reaction is catalyzed by homogeneous catalysts such as H_2SO_4. In general, increasing the catalyst concentration resulted in product with higher oxirane content in shorter reaction times. Higher sulphuric acid concentration reduces reaction time and results in higher relative conversion to oxirane owing to lesser cleavage of oxirane to glycol(Goud et al. 2006).

Figure 4-9 shows that the effect of catalyst loading on percentage of conversion. Increasing the amount of catalyst loading increases the percentage of conversion significantly. Hence, as the weight of the catalyst increases the acidic property (H^+) of the catalyst also increases so that the percentage of conversion increase significantly. The results obtained in this study are in agreement with this theory, as shown in Figure 4-8, where at higher amount of catalyst loading the percentage of conversion was increased.

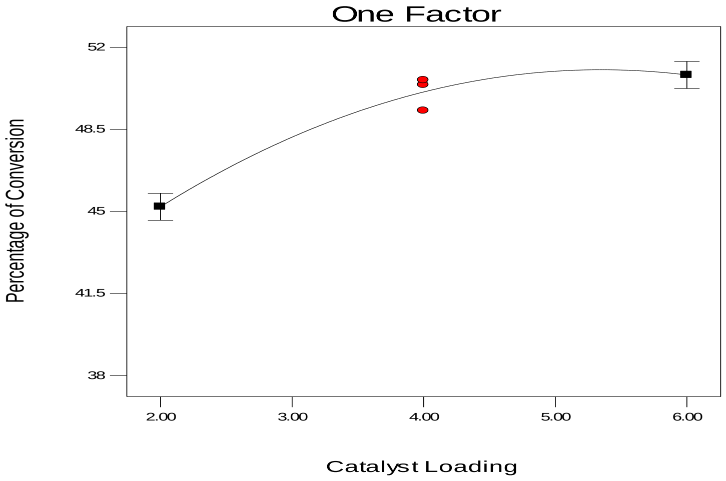


Figure 4-9 Percentage of conversion versus catalyst loading at molar ratio of hydrogen per oxide to oil 2.5 and at reaction temperature of 75^{o}C.

4.3.3 Effect of Interaction between Process Variables

The most common way to summarize the results of a central composite design experiment is in the form of a response surface plot and via response contours plot.

The process variables were found to have significant interaction effects except molar ratio of hydrogen per oxide to oil with temperature interaction. Figure 4-10 and Figure 4-12 shows the interaction between reaction temperature and amount of catalyst loading, and molar ratio of hydrogen per oxide to oil and amount of catalyst loading on percentage of conversion respectively.

Generally, an increase in amount of catalyst loading is found to increase the percentage of conversion. This similar explanation given in the previous section.

From the three interaction effects shown in the figures and contours at lower range of catalyst loading, reaction temperature at the center point and molar ratio of hydrogen per oxide to oil at center point, always resulted in the percentage of conversion higher than when using lower or higher reaction temperature and higher or lower molar ratio of hydrogen per oxide to oil.

The above observations can easily be explained as higher catalyst loading and medium reaction temperature will drive the reaction forward and medium molar ratio of hydrogen per oxide to oil will ensure the epoxidation reaction goes to maximum value which results in lower iodine value of the product.

Another notable observation is that at higher range of catalyst loading, the observations showed that using a combination of higher catalyst loading, higher amount of molar ratio of hydrogen per oxide to oil and higher reaction temperature is not beneficial in increasing the percentage of conversion.

This is because at this process conditions, higher amount of catalyst loading is already sufficient to push the reaction forward. This phenomena is further supported by the fact that catalyst loading is the most significant process variable that affect the percentage of conversion as indicated by the highest F – value in the ANOVA as shown in Table 4-7.

The Response Surface Methodology (RSM) was used to optimize the conditions of conversion for epoxidized vernonia oil and to understand the interaction of the factors affecting the epoxidized vernonia oil production. Figure 4-10 and Figure 4-12 show surface plots between the independent and dependent variable for fixed parameters.

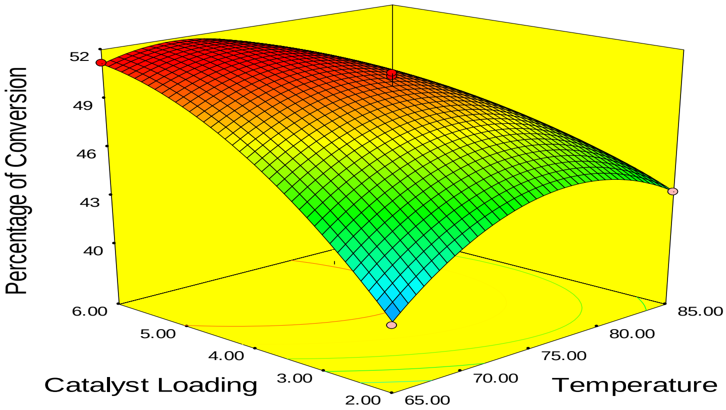


Figure 4-10 Surface plot of the interaction effect of reaction temperature and amount of catalyst loading versus percentage of conversion when the molar ratio of hydrogen per oxide to oil is 2.5.

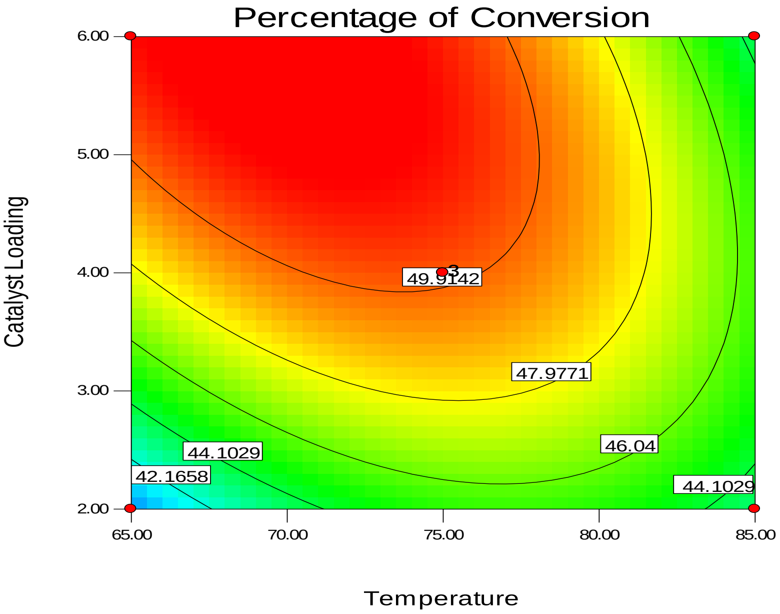


Figure 4-11 Contour plot of the interaction effect of reaction temperature and amount of catalyst loading versus percentage of conversion when the molar ratio of hydrogen per oxide to oil is 2.5.

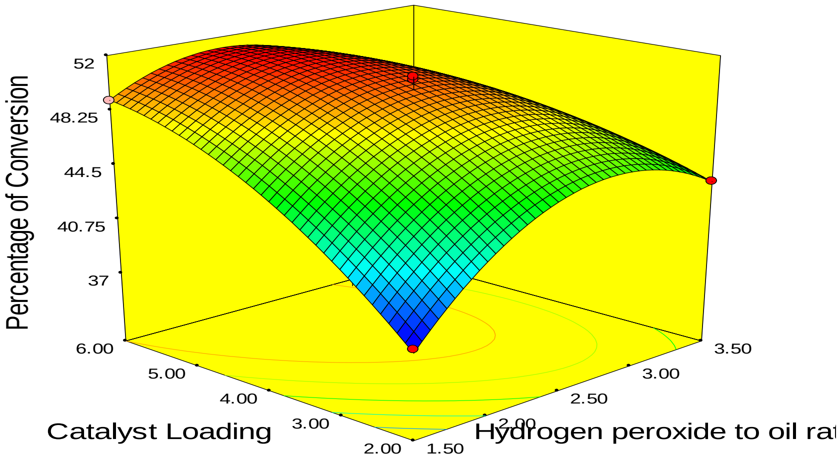


Figure 4-12 Surface plot of the interaction effect of molar ratio of hydrogen per oxide to oil and amount of catalyst loading versus percentage of conversion when the reaction temperature is 75.

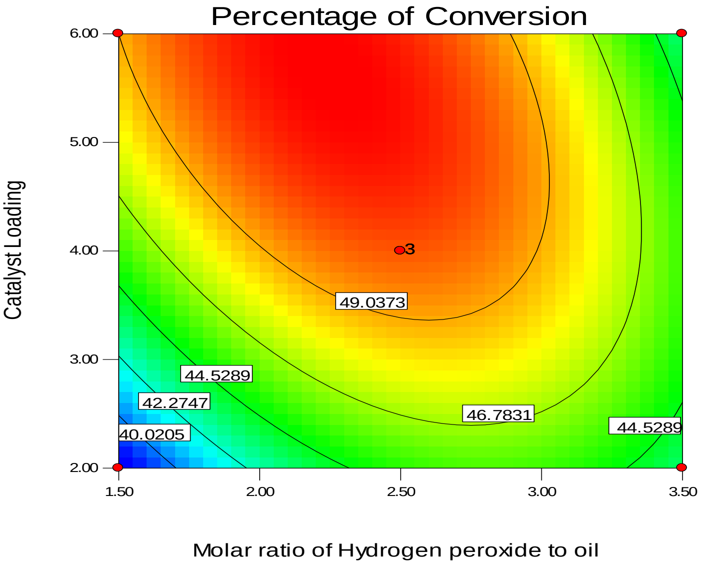


Figure 4-13 Contour plot of the interaction effect of molar ratio of hydrogen per oxide to oil and amount of catalyst loading versus percentage of conversion when the reaction temperature is 75.

Figure 4-12 shows the interaction of molar ratio of hydrogen per oxide to oil and amount of catalyst loading on the percentage of conversion. A relatively lower percentage of conversion at higher molar ratio of hydrogen per oxide to oil could also be due to decomposition of hydrogen per oxide in to water which adheres the formation of per formic acid which reduce its availability for epoxidation reaction.

From Figure 4-10, the percentage of conversion increased with increasing reaction temperature up to center point at optimal amount of catalyst loading. Also from Figure 4-12 the percentage of conversion gets higher at optimal amount of molar ratio of hydrogen per oxide to oil and higher amount of catalyst loading.

4.3.4 Optimization of Process Variables

The results above have shown that the two epoxidation process variables 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 using the model regression developed. So in order to obtain the maximum percentage of conversion, the predicted combination of parameters was as follows: temperature of 65 ^{o}C, molar ratio of hydrogen peroxide to oil 2.36:1 and catalyst loading of 6 (%wt). Under these conditions, the model predicted of 51.45% with a desirability value of 0.998.

To validate the optimum conditions predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized epoxidation process conditions and mean percentage conversion value of 50.6% was obtained and the results are closely related with the data obtained from optimization analysis using desirability functions.

Therefore, this study shows that vernonia oil can definitely be used for synthesis of epoxidized vernonia oil and optimum percentage of conversion can be obtained from the synthesis of vernonia oil using sulfonated carbon catalyst via epoxidation reaction.

4.4 NMR Spectrum Analysis of Epoxidized Vernonia oil

The comparison of H and C-NMR spectra between vernonia oil and epoxidized vernonia oil are shown in Figure 4-14 and Figure 4-15**.** In Figure 4-14**,** the signal at 5.48-5.25 ppm (-C**H**=C**H**-) is corresponding to double bond peak in vernonia oil. We can clearly see a decrease of the peak area at 5.46-5.30 ppm (double bond), whereas new peaks are arising at 3.76-3.65 ppm and 3.46-3.35 ppm correspond to CH protons attached to the oxygen atoms of both the epoxy group in Figure 4-14. This result indicate that double bond in vernonia oil acid has been converted to epoxy group during epoxidation reaction. The appearance of a multiple peak in 8.02-7.95 ppm region (HCOOC-) and disappearance peak at 3.13-3.02 ppm (–C**H**OC**H**–) is showing formation of new formate ester due to the ring cleavage by formic acid (Figure 4-14(b)).

As shown in Figure 4-15(a), the peaks at 133.24 – 132.41 ppm, 130.28-129.70 ppm and 128.51-127.32 ppm are representing the double bond in vernonia oil. Compared to that of vernonia oil, the epoxy peaks in epoxidized vernonia oil were assigned at 57.35-57.07 ppm and 54.99-54.38 ppm. Moreover, the short peak at 133.51-124.09 ppm (correspond to double bond) also indicate the conversion of double bond in epoxidized vernonia oil compare with the vernonia oil spectrum. All of the epoxide peaks observed are in agreement with(Shah et al. 2014) investigation. The peak at 163.64-162.76 ppm has been attributed to carbon of new ester.

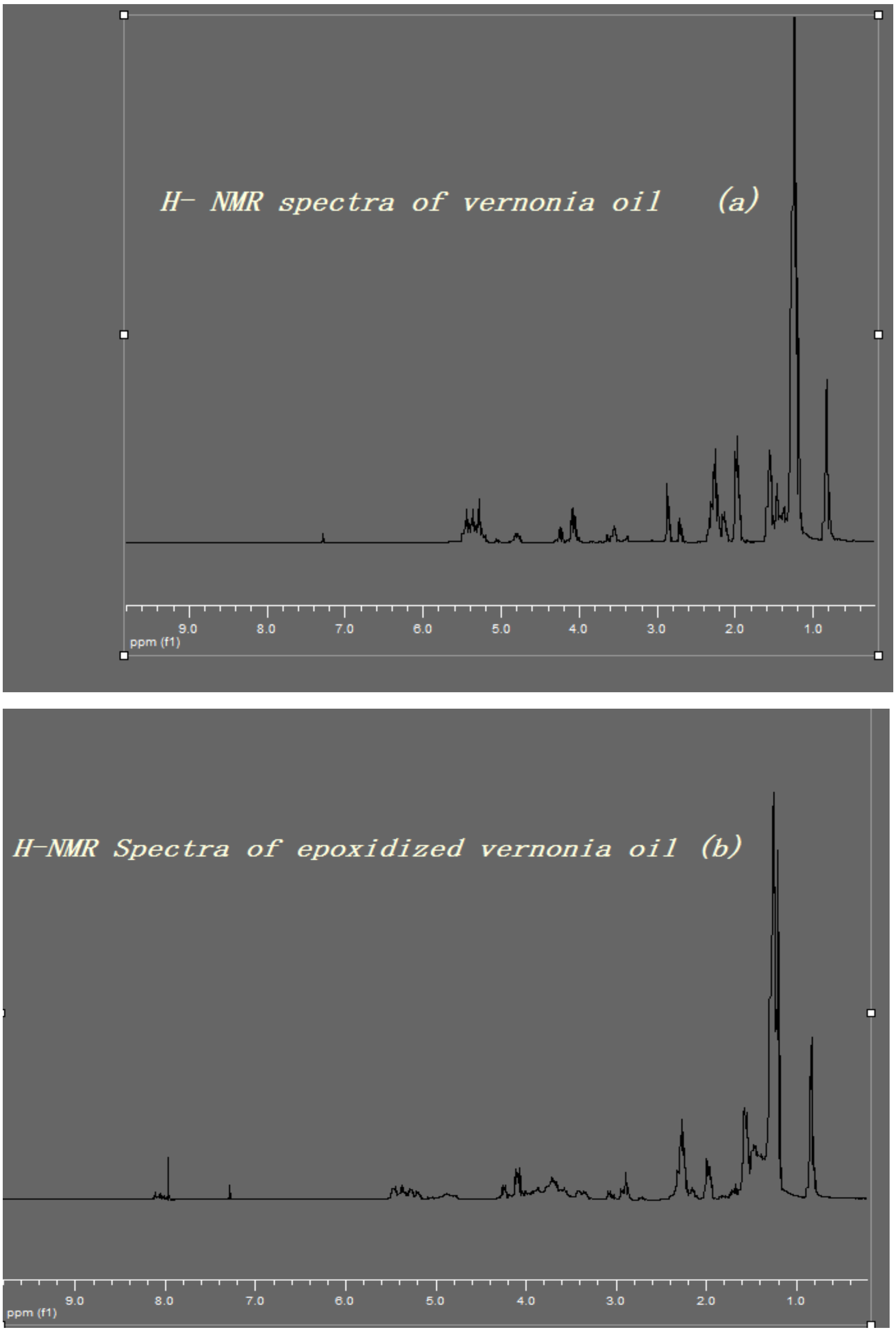
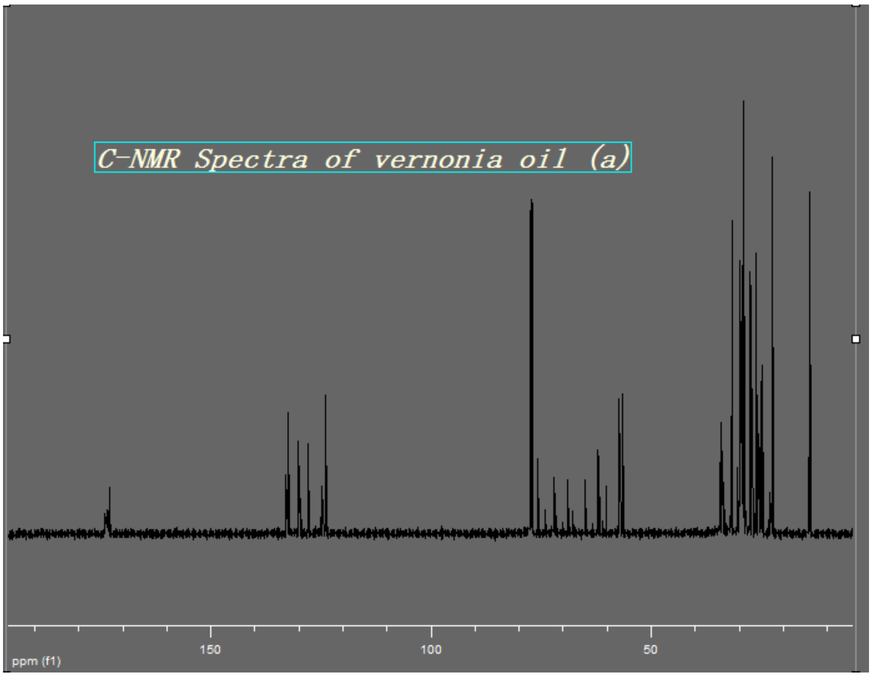


Figure 4-14 Spectrum H-NMR for (a) vernonia oil (b) Epoxidized vernonia oil



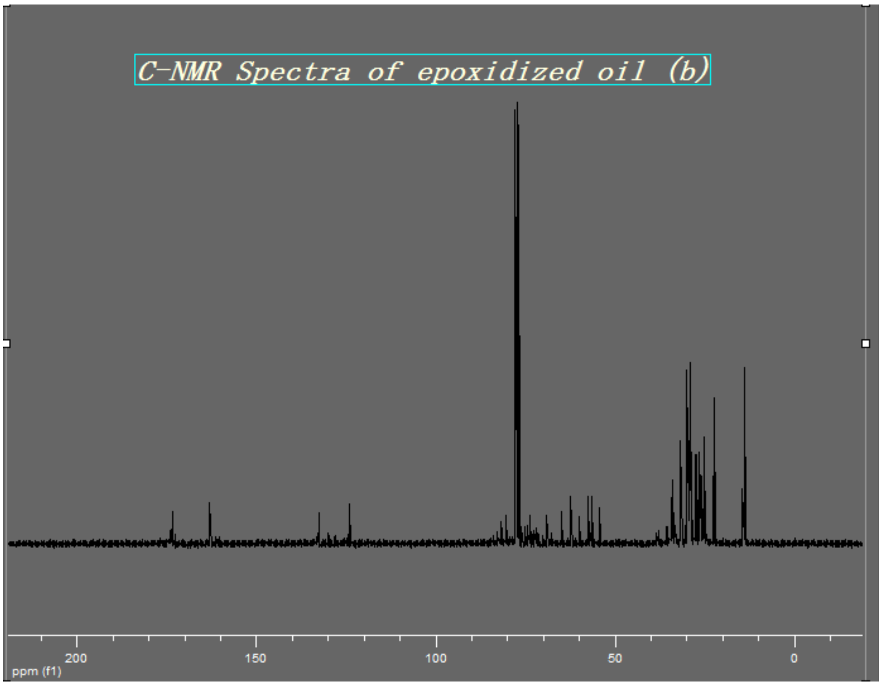


Figure 4-15 Spectrum C-NMR for (a) vernonia oil (b) Epoxidized vernonia oil

5. CONCLUSIONS AND RECCOMENDATIONS

5.1 Conclusions

Epoxidized oils, currently manufactured from animal fats or vegetable oils treated with per formicacid or from petrochemicals, are widely used in oleo chemical industry as plasticizers and stabilizers for thermoplastic products (*e.g.* PVC), in reformulation of oil based paints, in cosmetics, and for pharmaceutical applications.

The main objective of this research was to synthesize high surface area, porous, and high acidity carbon-based catalysts that have high activities on epoxidation reactions. All synthesized catalysts were physically and chemically characterized using bulk density, acid density, elemental analysis, Fourier transform-Infrared spectroscopy (FT-IR), X-Ray diffraction (XRD) spectrometer and further investigation for selected type of catalyst such as scanning electron microscopy (SEM) and thermo-gravimetric analysis (TGA) was performed. Structural study through Elemental Analysis and FT-IR spectroscopy suggests that biochar-based catalyst consists of polycyclic aromatic carbon sheets bearing three different acidic groups of phenolic, carboxylic, and sulfonic and the catalyst is stable up to temperature of 230^{o}C.

The first major contribution was the synthesis of porous and high acid density carbon based catalyst using a carbonization method. Bamboo was used as a carbon precursor to produce the catalyst support, while carbonization at different temperatures 400, 450 and 500^{o}C produced an incomplete carbonized of catalyst support. Sulfonation of the bamboo char in a high concentrated sulfuric acid with ultrasound sonication and magnetic stirring produced six different catalysts. In general, as carbonization temperature increases the total acid density of the catalyst also increases because total pore volume increased with increasing activation temperature, it was expected that the total acid 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. Sulfonation with ultrasound sonication produces a catalyst with a high acid density and sulfur content than the catalyst with stirring or without sonication. Based on the bulk density, acid density and elemental analysis of the prepared catalyst, catalyst prepared at

500^{o}C with ultrasound sonication (C-SO_3H-500^{u}) was selected for testing the activity of the catalyst.

The biochar-based catalysts supported on carbonization of bio-chars at temperature (i.e., 500°C with ultrasound sonication) were tested for epoxidation activity as one of the major factor that affects the reaction. The other reaction parameters affecting the percentage conversion of double bond in *Vernonia galamensis* oil were reaction temperature and molar ratio of hydrogen per oxide to vernonia oil has been studied.

The outputs of the experiment conducted have been analyzed by employing Design-Expert 7.0.0, surface response methodology, three-level-three-factor BBD, in which all samples were analyzed on iodine value of the product and the optimum value obtained from conversion of each samples were further analyzed by Nuclear Magnetic Resonance (NMR) to know the yield of epoxides.

Based on the analysis of experimental results, it is found that the two process variables exhibited significant interaction effect on the percentage of conversion. This shows that the capability of the design of experimental analysis in successfully capturing these effects. A reaction temperature of 65^{o}C, molar ratio of hydrogen per oxide to oil 2.36:1 and 6 %wt, catalyst loading results an optimal value of 51.45% percentage of conversion which is smaller than a similar work done by(Petkovic et al. 2002) with 58.9% percentage of conversion catalyzed by sulfuric acid.

In conclusion, carbon-based catalysts with high activity on epoxidation reactions were successfully synthesized. The carbon-based catalysts are promising catalysts for a more efficient epoxidized oils production.

5.2 Recommendations for future works

Further investigations are recommended to understand the behavior and to explore their commercial application of the carbon-based catalysts, such as:

- In this, research the selection of prepared catalyst were performed only based on elemental analysis and acid density of the catalyst but selection of the catalyst based on the surface area, pore size and the activity each catalyst in the reaction are very important concepts not covered in this research which needs further investigations.
- Study of reusability and regeneration of carbon-based catalysts. In addition, study of catalyst leaching due to the washing with solvents is also important.
- For more research works on the development of this catalyst, using stronger functionalizing reagents such as fuming acids with higher percentage of free SO_3 or super acids is suggested. Moreover, further investigations on the effect of pyrolysis process conditions and feedstock on the catalytic activity of biochar would be useful.
- 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 formicacid 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.

Further study on improvement of the epoxidation process parameters reaction time, molar ratio of formic acid to oil and speed of agitator on percentage of conversion is also suggested.

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APPENDICES

Appendix A: Composition of Vernonia Oil

Table A-1 Fatty acid composition of Vernonia oil

Fatty Acid	Systemic Name	Formula	Structure	Wt%
Vernolic	Cis-12, 13-epoxycis-9-octadecenoic	$CH_3(CH_2)_{12}(CH)_4OCOOH$	18:1:1	72 – 80
Linoleic	Cis-9,cis-12-octadecadienoic	$CH_3(CH_2)_{12}(CH)_4$ COOH	18:2	12 – 14
Oleic	Cis-9-Octadecenoic	$CH_3(CH_2)_{14}(CH)_2$ COOH	18:1	4 – 6
Palmitic	Hexadecanoic	CH_3 $(CH_2)_{14}$ COOH	16:0	2 – 3
Stearic	Octadecanoic	CH_3 $(CH_2)_{16}$ COOH	18:0	2 – 3

(Source: (Ayorinde et al. 1988)

Table A-2 Vernonia oil characteristics

Property of Oil	Value
Iodine value, gI_2 /100g oil	104 – 108
Saponification value, mg KOH/g oil	165 – 210
Unsaponifiable, wt%	1.0 – 8.0
Refractive Index at 25^0C	1.4740 – 1.4860
Relative Index at 25^0C	0.9050 – 0.9730
Boiling temperature, ^{0}C at 760 mmHg	183 – 190
Heat of vaporization, kJ/kmol	24.32
Calorific value, kJ/g	33.33 – 35.55

(Source: Manuel des crops gras, AFCEG, Paris, (1992))

Table A-3 Fatty acid composition of the major fatty oils and fats

Sr. No.	Name of the Oil	ρ	S.V.	I.V.	% Fatty Acid Composition					
					C14	**C16**	**C18**	**C18:1**	**C18:2**	**C18:3**
1	Castor	0.945-0.965/250 C	177-187	83-86	………	2	1	7	5	…….
2	Coconut	0.917-0.919/250 C	251-263	7.5-10.5	13.0-19.0	8.0-11.0	1.0-3.0	5.0-8.0	0-1.0	………
3	Groundnut	0.910-0.915/250 C	188-195	84-100	…….	6.0-9.0	3.0-6.0	52.0-60.0	13.0-27.0	……..
4	Mustard	0.906-0.910/250 C	169-176	98-110	…….	1.5	0.4	22	14.2	6.8
5	Soybean	0.916-0.922/250 C	189-195	128-143	tr.0.5	7.0-11.0	2.0-6.0	22.0-34.0	43.0-56.0	5.0-11.0
6	Sunflower	0.915-0.919/250 C	188-194	125-140	……	3.0-6.0	1.0-3.0	14.0-35.0	44.0-75.0	………
7	Cottonseed	0.915-0.926/150 C	191-196	103-115	0.4	20	2	35	42	………
8	Palm	0.921-0.925/150 C	196-205	48-58	0.5-2.0	32.0-45.0	2.0-7.0	38.0-52.0	5.0-11.0	………
9	Linseed	0.931-0.938/150 C	189-196	170-180	……	4.0-7.0	2.0-5.0	12.0-34.0	17.0-24.0	35.0-60.0

ρ: specific gravity, **I. V.:** Iodine value, **S.V.:** Saponification value,**:** Myristic acid , **C_{16} :** Palmitic acid, **C_{18}:** Stearic acid, **$C_{18:1}$:** Oleic acid , **$C_{18:2}$:** Linoleic acid , **$C_{18:3}$:** linolenic acid ,

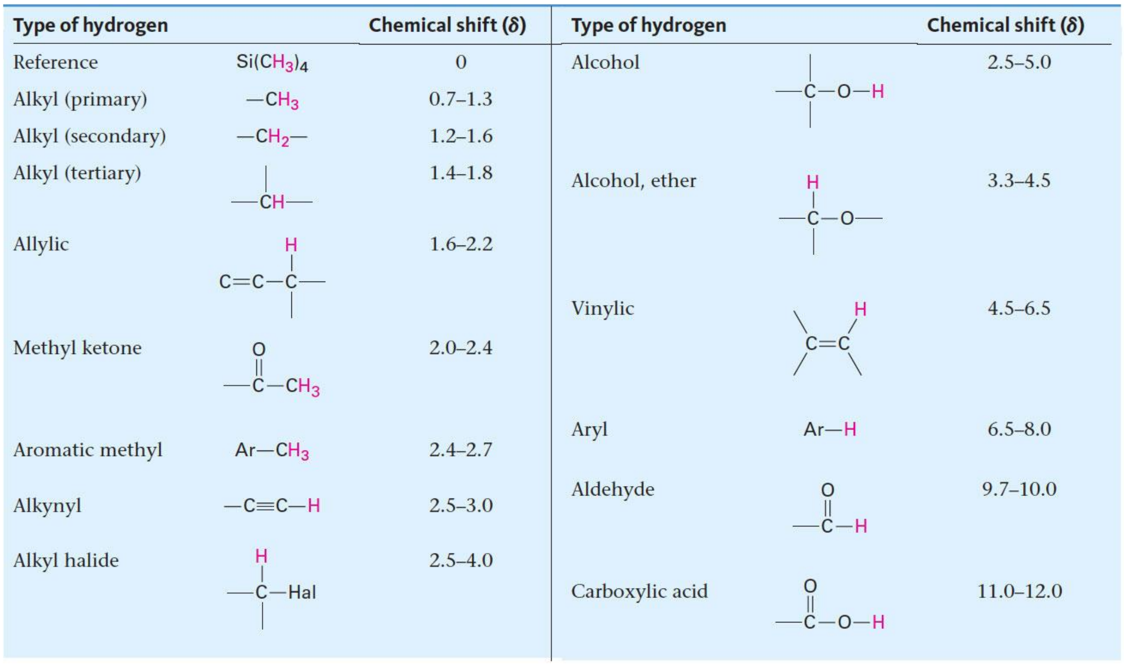
(Source: (Gunstone 2004)

Appendix B: Infrared Spectroscopy Correlation Table

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

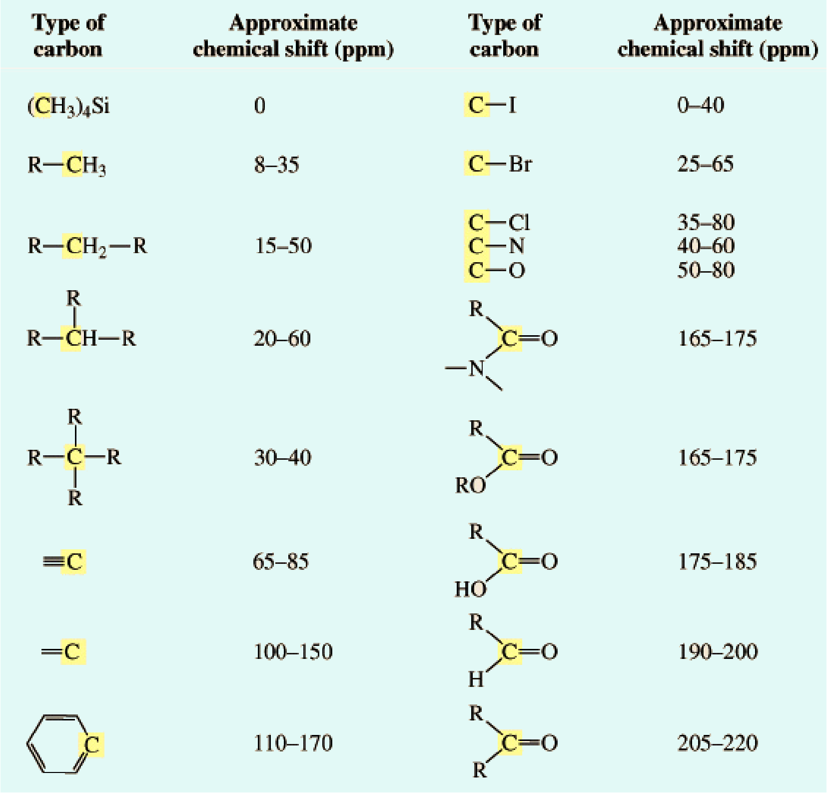
(Source: http://en.wikipedia.org/wiki/Infrared_spectroscopy_correlation_table**)**

Table B1: Proton (H) NMR structure-chemical shift Correlation Table



Type of hydrogen		Chemical shift (δ)
Reference	$Si(CH_3)_4$	0
Alkyl (primary)	$-CH_3$	0.7–1.3
Alkyl (secondary)	$-CH_2-$	1.2–1.6
Alkyl (tertiary)	$-\overset{\vert}{C}H-$	1.4–1.8
Allylic	$C{=}C{-}\overset{H}{\underset{\vert}{C}}{-}$	1.6–2.2
Methyl ketone	$-\overset{O}{\overset{\Vert}{C}}-CH_3$	2.0–2.4
Aromatic methyl	$Ar-CH_3$	2.4–2.7
Alkynyl	$-C{\equiv}C-H$	2.5–3.0
Alkyl halide	$-\overset{H}{\underset{\vert}{C}}-Hal$	2.5–4.0
Alcohol	$-\overset{\vert}{\underset{\vert}{C}}-O-H$	2.5–5.0
Alcohol, ether	$-\overset{H}{\underset{\vert}{C}}-O-$	3.3–4.5
Vinylic	$>C{=}C<^{H}$	4.5–6.5
Aryl	$Ar-H$	6.5–8.0
Aldehyde	$-\overset{O}{\overset{\Vert}{C}}-H$	9.7–10.0
Carboxylic acid	$-\overset{O}{\overset{\Vert}{C}}-O-H$	11.0–12.0

Table B2: Carbon (C) NMR structure-chemical shift Correlation Table



Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$C-I$	0–40
$R-CH_3$	8–35	$C-Br$	25–65
$R-CH_2-R$	15–50	$C-Cl$ $C-N$ $C-O$	35–80 40–60 50–80
$R-\overset{R}{\overset{\vert}{C}}H-R$	20–60	$R(-N<)C{=}O$	165–175
$R-\overset{R}{\underset{R}{C}}-R$	30–40	$R(RO)C{=}O$	165–175
$\equiv C$	65–85	$R(HO)C{=}O$	175–185
$=C$	100–150	$R(H)C{=}O$	190–200
C (benzene ring)	110–170	$R(R)C{=}O$	205–220

Source: https://www.ucl.ac.uk/nmr/NMR_lecture_notes/L2_3_web.pdf

Appendix C: Experimental Result

Table C-1 Moisture content of bamboo saw dust

Run	Sample weight (g)			Moisture Content (%)	Average Moisture Content (%)
	W_1	**W_2**	**$(W_1 - W_2)$**		
1	1.00	0.8969	0.0935	10.31	9.96
2	1.00	0.8982	0.0924	10.18	
3	1.00	0.9058	0.0861	9.42	

Table C-2 Volatile matter of bamboo saw dust

Run	Sample weight (g)			Volatile matter (%)	Average Volatile matter (%)
	$W1$	**$W2$**	**$(W1 - W2)$**		
1	1.0008	0.1866	0.8142	80.4	80.97
2	1.0002	0.1846	0.8156	81.5	
3	1.0011	0.1998	0.8013	80.04	

Table C-3 Ash content of bamboo saw dust

Run	Sample weight (g)		Ash Content (%)	Average Ash content (%)
	$W1$	$W2$		
1	1.0007	0.0156	1.56	1.6
2	1.0008	0.0151	1.51	
3	1.0010	0.0173	1.73	

Table C-4 Bulk density of the Bio-chars and catalyst prepared at pyrolysis temperature of 400°C

Run	Mass (g)	Bulk volume (ml)	Stirring	Sonication	Catalyst density (g/ml	Bio-char Density (g/ml)	Average density (g/ml)
1	0.4314	1.6	……	…….	……..	0.2696	0.284
2	0.7558	2.6	……	……	……..	0.2907	
3	1.163	4	……	……	………	0.2907	
1	0.5912	1.4	✓	…….	0.4222	……	0.325
2	1.5369	4.5		…….	0.3415	…….	
3	2.1156	5.8		………	0.3647	……	
1	0.679	1.6	……	✓	0.4243	……	0.350
2	1.5531	3.9	……		0.3982	……	
3	2.3955	6	……		0.3992	……	

Table C-5 Bulk density of the Bio-chars and catalyst prepared at pyrolysis temperature of 450°C

Run	Mass (g)	Bulk volume (ml)	Stirring	Sonication	Catalyst density (g/ml	Bio-char Density (g/ml)	Average density (g/ml)
1	0.4531	1.7	……	…….	……..	0.2665	0.276
2	1.0239	3.8	……	……	……..	0.2694	
3	1.7236	6.3	……	……	………	0.235	
1	0.4665	1.4	✓	…….	0.3332	……	0.343
2	0.8626	2.8		…….	0.308	…….	
3	1.2819	3.84		………	0.3338	……	
1	0.5082	1.4	……	✓	0.363	……	0.365
2	0.8415	2.5	……		0.3366	……	
3	1.4628	4.2	……		0.3483	……	

TableC-6 Bulk density of the Bio-chars and catalyst prepared at pyrolysis temperature of 500°C

Run	Mass (g)	Bulk volume (ml)	Stirring	Sonication	Catalyst density (g/ml	Bio-char Density (g/ml)	Average density (g/ml)
1	0.5338	1.9	……	…….	……..	0.2809	

2	1.1906	4.2	……	……	……..	0.2835	0.284
3	1.8094	6.3	……	……	………	0.2872	
1	0.5017	1.4	✓	…….	0.3584	……	0.376
2	1.0011	3		…….	0.3337	…….	
3	1.6831	5		………	0.3366	……	
1	0.6331	1.6	……	✓	0.3957	……	0.404
2	1.3228	3.8	……		0.3481	……	
3	1.8266	5.2	……		0.3512	……	

Table C-7 Acid Value of *Vernonia galamensis* oil

Run	**Titration , ml**	**Color Change**
1	1.72	Gray to Pink
2	1.69	Gray to Pink
3	1.72	Gray to Pink
Average value	**1.71**	

Table C-8 Moisture content determination for Vernonia seed

Run	Sample weight (g)				
	W_1	W_2	$W_1 - W_2$	Moisture Content (%w)	Average (%w)
1	3.156	3.011	0.145	4.59	**4.69**
2	3.304	3.152	0.152	4.60	
3	3.421	3.246	0.174	5.10	
4	3.285	3.135	0.149	4.55	
5	3.114	2.954	0.160	5.13	
6	3.853	3.692	0.161	4.18	

Table C-9 Iodine value of *Vernonia galamensis* oil

Run	**Titration Volume,**	**Colour Change**
Blank		
1	39.9	Blue to colorless
2	40.4	Blue to colorless

3	40	Blue to colorless
Average value	**40.1**	
Oil		
1	15.4	Blue to colorless
2	15.1	Blue to colorless
3	14.8	Blue to colorless
Average value	**15.1**	

Table C-10 Experimental processes conditions for epoxidized oil production

Run	Reaction temperature (^{o}C)	Hydrogen peroxide(ml)	Amount of Catalyst(g)	Reaction Time(hrs)	Speed (rpm)	Formic acid(ml)
1	65	2.28	0.58	3.5	1500	0.94
2	85	2.28	0.58	3.5	1500	0.94
3	65	5.32	0.58	3.5	1500	0.94
4	85	5.32	0.58	3.5	1500	0.94
5	65	3.8	0.29	3.5	1500	0.94
6	85	3.8	0.29	3.5	1500	0.94
7	65	3.8	0.87	3.5	1500	0.94
8	85	3.8	0.87	3.5	1500	0.94
9	75	2.28	0.29	3.5	1500	0.94
10	75	5.32	0.29	3.5	1500	0.94
11	75	2.28	0.58	3.5	1500	0.94
12	75	5.32	0.58	3.5	1500	0.94
13	75	3.8	0.58	3.5	1500	0.94
14	75	3.8	0.58	3.5	1500	0.94
15	75	3.8	0.58	3.5	1500	0.94

Table C-10 Iodine value of the epoxidized oil

Run	Mass(g)	Titration volume(ml)	Iodine Value
Blank	……..	40.1	
1	0.3636	24.8	53.27
2	0.3635	23.9	56.57
3	0.3584	25.2	52.8
4	0.388	23.1	55.63
5	0.4056	22	56.57
6	0.3652	24.9	52.8
7	0.3481	27.5	46
8	0.3574	25.1	53.33
9	0.338	24.5	58.45
10	0.3133	26.9	53.27
11	0.3445	27	48.08

12	0.3366	25.9	53.55
13	0.358	26.9	46.76
14	0.348	27	47.8
15	0.3456	27.4	46.57

Appendix D: Calculation Part

D1: Proximate Analysis of Bamboo

- **Moisture content**

A. Wt of empty crucible : 37.5546g

B. Wt of bamboo dust : 1.0000gm

C. Wt of bamboo dust and crucible after drying : 37.6242gm

$$moisture\ content, \% = \frac{C-A}{B} \times 100 = \frac{37.6542 - 37.5246}{1.000} = 9.96\%$$

- **Volatile matter**

A. Mass of crucible, cover, and sample, g: 23.23gm

B. Mass of crucible and cover, g: 22.23gm

C. mass of crucible, cover, and de-volatilized sample, g: 22.42gm

$$Volatile\ matter, \% = \frac{A-C}{A-B} \times 100 = \frac{23.23 - 22.42}{23.23 - 22.23} = 80.97\%$$

- **Ash content**

A. Mass of crucible before burning: 17.09gm

B. Mass of sample : 1.0008g

C. Mass of sample + Crucible after burning: 17.016

$$Ash, \% = \frac{C-A}{B} \times 100 = \frac{17.106 - 17.09}{1.0008} = 1.6\%$$

- **Fixed carbon content**

$$fixed\ carbon\ content, \% = 100 - (\text{Volatile matter} + ash\ content)$$

$$= 100 - (+80.97 + 1.6) = 17.43\%$$

D2: Bulk Density of Bio-chars and catalyst

Sample calculation for the determination of bulk density of the catalyst and bio-char

- **Bulk density of bio-chars prepared at 400°C**
  A. Mass of bio-char: 0.7834gm
  B. Volume of bio-chars: 2.733ml

$$Bulk\ density\ = \frac{weight\ of\ the\ samples\ (g)}{Volume\ of\ the\ sample\ (ml)} = \frac{A}{B} = \frac{0.7834}{2.733} = 0.2867 gm/ml$$

- **Bulk density of catalyst prepared at 400°C**

A. Mass of bio-char: 1.4145gm
B. Volume of bio-chars: 3.6ml

$$Bulk\ density\ = \frac{weight\ of\ the\ samples\ (g)}{Volume\ of\ the\ sample\ (ml)} = \frac{A}{B} = \frac{1.4145}{3.6} = 0.363 gm/ml.$$

The measurement was repeated three times, with the average reported as the bulk density.

D3: Determination of Acid density of the catalyst

- **Determination of total acid density**

Total acidity was determined using a back-titration method. In a typical analysis, 0.05g of sample was put in a beaker containing 20 mL of 0.01 M NaOH, and stirred for 60 min at room temperature. The NaOH solution (containing the sample), as the analyte, was then titrated using 0.01 M HCl as the titrant.

Sample calculation for the determination of total acidity

Number of moles of 20 mL 0.01 M NaOH (titrator)

$$= 0.01 \frac{mol}{litre} \times 20ml \times \frac{1l}{1000ml} = 2 \times 10^{-4} moles\ NaOH$$

Number of moles of 2.1 mL 0.01 M HCl (titrant) (data obtained from the titrator analysis)

$$= 0.01 \frac{mol}{litre} \times 2.1ml \times \frac{1l}{1000ml} = 2.1 \times 10^{-5} moles\ HCl$$

In a back titration analysis, the acid functional groups on the sample were neutralized with an excessive 20 mL 0.01 M NaOH to ensure a complete neutralization. Therefore, the total acidity of the sample can be calculated as:

$$= 2 \times 10^{-4} mol - 2.1 \times 10^{-5} mol = 0.179 mmol$$

The total acidity per gram of catalyst

$$= \frac{0.179 mmol}{0.05 gm} = 3.58 mmol/gm$$

The measurement was repeated three times, with the average reported as the total acidity.

Sample calculation of SO_3H acid density

Volume of 0.01 M NaOH (titrant) (data obtained from the titrator analysis): 2.7ml

SO_3H acidity per gram of the catalyst

$$= \frac{(volume\ of NaOH\ used\ for\ the\ titration * Normality\ of\ NaOH)}{Mass\ of\ catalyst} = \frac{2.7 \times 0.01}{0.05}$$

$$= 0.54 mmol/gm$$

The measurement was repeated three times, with the average reported as the SO_3H acidity.

D4: Purification of Crude Vernonia Oil

The total amount of crude Vernonia oil obtained from mechanical extraction is 0.544 liter out of 1.31 kg of Vernonia seed.

- **Oil content of the vernonia seed**

The density of the crude oil = 922.04 kg/m^3

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

$$m = \rho \times V$$

$$922.04 \frac{kg}{m^3} \times 0.544\ liter \times \frac{1m^3}{1000 liter} = 0.502 kg$$

$$yield\ of\ oil = \frac{0.502 kg}{1.31\ \text{kg}} \times 100 = 38.28\%$$

- **Degumming**

It is the removal of phosphatides, gums and other complex compounds the extracted crude Vernonia oil. Hence, based on the method discussed in previous chapter 3 wt% of distilled water is required for degumming process of crude oil.

Amount of distilled water required = amount of Vernonia oil× 3%

$$0.502kg \times 0.03 = 0.0154litre = 15.1ml$$

- **Molecular weight of Vernonia oil**

Table D11: Molecular Weight of Fatty Acids

Fatty Acids	Elementary Formula	Constitutional Formula	Corresponding Fatty acid composition (%)	Molecular weight
Vernolic	$C_{18}H_{32}O_3$	$CH_3(CH_2)_{12}(CH)_4$ OCOOH	76.5	296
Linoleic	$C_{18}H_{32}O_2$	$CH_3(CH_2)_{12}$	13.5	280
Oleic	$C_{16}H_{34}O_2$	$CH_3(CH_2)_{14}$	5.2	282
Palmitic	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}$	3	256
Stearic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{16}$	1.8	286

Molecular mass of Triglyceride = Molecular mass of Vernolic acid
+ Molecular mass Linoleic Acid
+ Molecular mass Oleic Acid
+ Molecular mass Palmitic Acid
+ Molecular mass Stearic Acid

Molecular mass of Triglyceride = $(296 \times 0.765) + (280 \times 0.135) + (282 \times 0.052) +$

$(256 \times 0.03 + (286 \times 0.018) = 292.26 g/mole$

Appendix E: Laboratory Equipment's and Samples Photo

D1: Horizontal tubular furnace (Carbolite)

D2: Sonicator

D3: Bio-chars and Catalyst

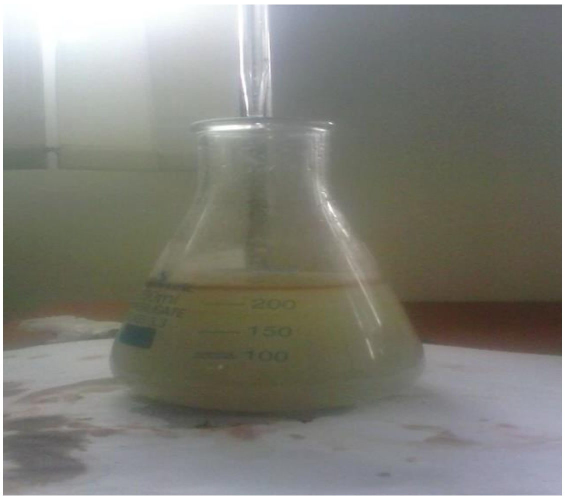
D4: FT-IR instrument

D5: GC/MS instrument

D6: Elemental analysis instrument

D7: SEM insrument

D8: TGA instrument



D9: EVO sample before Titration

D10: EVO sample after Titration

> ***"Humanity needs practical men, who get the most out of their work, and, without forgetting the general good, safeguard their own interests. But humanity also needs dreamers, for whom the disinterested development of an enterprise is so captivating that it becomes impossible for them to devote their care to their own material profit."***
>
> **Marie Curie**
> ***(1867-1932, physicist and chemist)***