ADDIS ABABA UNIVERSITY

Addis Ababa Institute of Technology
School of Chemical and Bio Engineering

Production of Epoxy Cottonseed Oil using Carbon Based Sulfonated Acid Catalyst

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A Thesis

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DECLARATION

I declare that this thesis entitled "*Production of Epoxy Cottonseed Oil using Carbon Based Sulfonated Acid Catalyst*" has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. 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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This is to certify that the thesis prepared by ***Alemshet Dessalegn***, entitled: Production of Epoxy Cottonseed Oil using Carbon Based Sulfonated Acid Catalyst 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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Abstract

Epoxidation process is a method by which triglyceride (fatty acids) are converted to a three-membered epoxide (oxirane) ring as the carbon-carbon double bond reacts with active oxygen. This work is on the production of epoxy oil via epoxidation reaction using sulfonated solid acid catalyst from cottonseed oil. A sulfonated carbon catalyst was synthesized by carbonization of bamboo (at 500^{o}C temperature and 3hr pyrolysis time) followed by sulfonation (with concentration of 98% sulfuric acid and for 15hr at 150 ^{o}C) and the performance of this catalyst was tested on the epoxidation of cottonseed oil. Investigations on the sulfonated carbon catalyst were conducted to determine the effect of reaction time, reaction temperature, and hydrogen peroxide to oil molar ratio. The sulfonated solid acid catalysts were characterized using analysis: elemental analysis (CNHS), bulk density, total acid density, FT-IR, and TGA.

The cottonseed oil was characterized by acid value (3.03 mmol KOH/l), iodine value (81.66 g/100 g of I_2), GC/MS, FT-IR and including other physical properties (density, specific gravity, and kinematic viscosity). The epoxidation reaction experiment was performed at reaction temperature of 45^{o}C, 60^{o}C and 75^{o}C, hydrogen peroxide to the cottonseed oil molar ratio 1:1, 1.75:1 and 2.5:1, acetic acid to cottonseed oil molar ratio 0.5:1 and reaction time of 2, 4, and 6h and physicochemical property of epoxidized oil was characterized. The optimal value of oxirane oxygen content was obtained (3.03%) at 62.4°C reaction temperature, in 4.2h reaction time, and 1.94:1 hydrogen peroxide to oil molar ratio with desirability of 87%. The relative conversion to oxirane oxygen content was 61.8% and the rate constant for epoxidation reaction kinetics were $8.025 * 10^{-2} \mathrm{l}^2 \mathrm{mol}^{-2}. s^{-1}$ and $8.01 * 10\ \mathrm{l}^2 \mathrm{mol}^{-3}. s^{-1}$at 60 ^{o}C for pseudo-first and pseudo-second order with activation energy of 16.8kJ/mol and 23.2 kJ/mol respectively.

Key words: *Epoxidation reaction, biomass, cottonseed oil, sulfonated solid acid catalyst, oxirane oxygen content, and epoxidized oil*

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Acronyms

AAiT	Addis Ababa institute of technology
AC	Activated Carbon
AOCS	American Oil Chemists' Society
ANOVA	Analysis of Variance
AOAC	Association of Official Analytical Chemists
ASTM	American Society for Testing and Material
AV	Acid Value
BC	Biochar
CHNS	Carbon Hydrogen Nitrogen and Sulfur element
CSO	Cottonseed Oil
EA	Elemental Analysis
ECSO	Epoxidized Cottonseed Oil
EN	European Committee for Standardization
FA	Fatty Acid
FFA	Free Fatty Acid
FT-IR	Fourier Transform Infrared Spectroscopy
GCMS	Gas Chromatography Mass Spectroscopy
ISO	International Standards Organization
IV	Iodine Value
LIDI	Leather Industry Development Institute
ON	Oxirane Number
OOC	Oxirane oxygen content
PVC	Poly Vinyl Chloride
RSM	Response Surface Methodology
SCBAC	Sulfonated Carbon-Based Acid Catalyst
Std	Standard Run Order
TAD	Total Acid Density
TGA	Thermogravimetric Analysis

1. Introduction

Epoxides, known as oxiranes, are cyclic ethers with a reactive three-membered ring. Epoxidation process is a new method by which fatty acids are converted to a three-membered epoxide (oxirane) ring as the carbon-carbon double bond reacts with active oxygen. The cyclical structure of oxirane rings has a bond angle of 60º, making them highly strained and highly reactive (Silva et al., 2017). Typically, the method to promote epoxidation of double bonds uses hydrogen peroxide and acetic acid as oxygen carriers in acid media (by mineral acid). The reaction causes the formation of proxy carboxylic acid, a compound that promotes oxirane formation. Due to high reactivity, the oxirane group can be converted into other groups with interesting properties, making it one of the best organic groups for organic synthesis. Epoxides can also act as raw materials for the synthesis of a variety of chemicals, such as alcohols (polyol), glycols, alkanol amines, carbonyl compounds, olefinic compounds, and polymers like polyesters, polyurethanes, and epoxy resin (Rios, et. al., 2005). Another advantage of conversion of a double bond to oxirane group is an enhancement of oxidation stability of materials that have high unsaturation content. Materials like vegetable oils, biodiesel, and some rubber compounds belong in this class (Silva et al., 2017).

Epoxidized oils are also used as effective plasticizers, lubricants, and stabilizers for thermoplastics. Epoxidized oil-based polyols are currently used as alternatives to petrochemical raw materials for the synthesis of polyurethane pre-polymers, foams and elastomers. These polyols are also used in the production of multilayer materials, adhesives, joints and polyester resins. Epoxidized oils exhibit the ability to reduce the viscosity of epoxy resins, independently of the viscosity of the resin and to a degree comparable to those of commercial reactive diluents (Dinda et al., 2008)

The epoxidation of alkenes and other unsaturated hydrocarbon chains constitutes one of the most useful reactions in organic synthesis, as the epoxide group is an active intermediate, which can be readily transformed to the required functionality. Epoxidation of long-chain olefins and unsaturated fatty acid derivatives such as soybean oil and other plant oils is carried out on an industrial scale for the synthesis of commercially valuable plasticizers and polymer stabilizers (Dinda et al., 2008; Biermann et al., 2008)

Fats and oils are renewable resources that can be treated chemically or enzymatically to produce materials like epoxy, that can often act as a replacement for materials derived from petroleum (Gan et al., 1995). However, the depletion of the earth's limited petroleum reserves has heightened interest in using renewable resources as replacement materials for epoxidized 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 (Chua, et al., 2012).

Vegetable oils are promising feedstocks for epoxidation and vegetable oil production since they are renewable in nature, can be produced on a large scale, biodegradable, low cost, readily available, and environmentally friendly (Coud, et al., 2006). Cottonseed oil is one of the vegetable oils produced from cottonseed. Cottonseed is a byproduct of cotton fiber production and as such is dependent upon the supply of and the demand for the cotton fiber surrounding the oilseed. The fatty acid profile of cottonseed oil is typical of the oleic-linoleic group of vegetable oils since these two-unsaturated fatty acids make up almost 75% of the total fatty acids. (O'brien, 2002).

Vegetable oils rich in oleic, linoleic, and linolenic acyl groups may be used to introduce functional groups such as epoxides. The process of Epoxidation is affected by the mode of reaction, agitation Speed, reactant concentration and molar ratio, temperature, purity of reactant and reaction time. Various studies have been carried out using different oils as the raw material and different carboxylic acid i.e. CH_3COOH and HCOOH, as well as different catalysts, notably homogeneous ones such as liquid inorganic acids i.e. HCl, H_2SO_4, HNO_3, and H_3PO4 (Dinda et al., 2008) and enzymes such as lipases. Recent research has focused on the application of heterogeneous catalysts like Al_2O_3, TiO_2, and ion exchange resin to produce epoxides, because of their environmental and economic advantages.

Classic methods employed for the oxidation of vegetable oils use homogeneous catalytic processes that generate a lot of waste, corrode equipment and require large amounts of reagents. Heterogeneous catalysts have the advantage of easy separation and recycling of the catalyst. For this reason, ion exchange resin has been studied to promote epoxidation of vegetal oils (Mungroo, et al., 2008,Turco et al., 2013). Catalysts based on biomass have advantages such as low cost and surface chemical properties that can be tailored appropriately. Among the desirable characteristics of the catalyst support is stability, inertness, reusability, high surface area, porosity and appropriate chemical structure (Mavrogiorgou, et al., 2014). The process usually produces sulfonated carbon with high surface area and high acid site content (Geng, et al., 2011). Environmentally benign sulfonic acid modified solid acid catalysts have been successfully applied for various organic transformations such as etherification, dehydration, oxidation, acetylation, acetylation and sialylation reactions etc. Due to its higher acid strength, higher surface area, large pore space and increased thermal stability, which makes it an efficient catalyst for organic reactions (Rios et al., 2005).

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes in which a response of interest is influenced by several variables, and the objective is to optimize this response. Analyzing the effects of the independent variables, this experimental methodology generates a mathematical model which describes the chemical processes within the experimental range (Montgomery, 2001).

Thus, the goals of this study were to produce a sulfonated catalyst from biomass using pyrolysis (synthesis of catalyst support) and chemical modification (sulfonation). This bio-based catalyst was used for epoxidation reactions of cottonseed oil. Conversion and Oxirane oxygen content were evaluated under typical synthesis conditions.

1.1. Statement of the Problem

Now a day the depletion of world natural petroleum reserves and increased environmental concerns is the main element and this stimulates the search for alternative renewable material that is capable of fulfilling increasing epoxides demand that serve as primary chemicals and intermediates in many industries. Epoxy oil is used widely for rubber, polymer, cosmetic and lather factory in Ethiopia. The problems related with petroleum product of epoxide is non-degradability of petroleum epoxy product, 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 and vegetable oil plays a major role in this field because of the worldwide research, development, and exploitation activities of this sustainable raw material source.

Based on this point of view cottonseed, which is growing in the most country including Ethiopia and it has a potential to be industrial oilseed crop. What makes interesting about the seed oil is that the oil contains as the major unsaturated fatty acid (around 75% Oleic, linoleic and linolenic) of the oil. On the other hand, the cottonseed oil has gossypol chemical. Due to this chemical, cottonseed oil is going out from the edible oil market. So, to handle this sustained production and market of cottonseed oil, it must be used for another production purpose. One of the product from this vegetable oil is epoxy oil which uses for many industrial applications.

Currently, for epoxidation reaction most homogeneous catalysts are used. In industry, the epoxidation of plant oils has been already carried out using a homogeneous catalyst with a per carboxylic acid, such as peracetic acid and performic acid, obtained by oxidation with hydrogen peroxide, using mineral acid, like sulfuric acid, as a catalyst. However, several drawbacks are associated with using sulfuric acid (Or all of the homogeneous catalyst) as a catalyst, such as equipment corrosion, the release of toxic residues causing environmental issues, purification and separation of desired product and recovery of the catalyst. Therefore, in recent years' continuous efforts have been made by investigators around the world to replace the conventional homogeneous acid catalysts by environmentally friendly and efficient heterogeneous catalyst (Corma, 1995).

Even if scholars work on the replacement of the homogeneous catalyst by the heterogeneous catalyst; But this catalyst is not widely applicable for epoxidation reaction of vegetable oil still now. Strong acidic cation-exchangeable resins and metal oxides of heterogeneous catalysts have high production cost, small specific surface area, less effective and non-bio-based product. To solve such types of problem among heterogeneous catalyst which is sulfonated carbon-based acid catalyst material has lower production cost, renewable, abundant, and low-cost produced directly from biomass compared to other solid acid catalysts and all of the SCBACs 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 (Silva et al., 2017). In spite of this advantage, the carbon-based sulfonated catalyst is not widely used especially for epoxidation reactions. In this work, Sulfonated Carbon-based acid catalyst (SCBAC) was used for epoxidation reaction of cottonseed oil.

1.2. The Objective of the Research

1.2.1. General Objective

The main objective of this research is to produce epoxidized cottonseed oil using sulfonated carbon-based acid (acidic) catalyst with high catalytic activity, selectivity, and good stability.

1.2.2. Specific Objectives

The specific objectives are: -

- ✓ To synthesize and characterization of a synthesized sulfonated carbon-based catalyst.
- ✓ To characterize the physicochemical properties of cottonseed oil and epoxidized cottonseed oil (by measuring physicochemical properties, GC/MS and FT-IR).
- ✓ To study the catalytic performance of prepared catalyst for epoxidation of cottonseed oil (by determining of oxirane oxygen content, iodine value, and conversion).
- ✓ To investigate the main and interaction effect of epoxidation reaction parameters (reaction temperature, reaction time, and the molar ratio of hydrogen peroxide to cottonseed oil) on the production of epoxidized cottonseed oil using RSM.
- ✓ To determine kinetics of epoxidation reaction.

1.3. Significance

The significance of this research work is used for economical stakeholders' and for our environmental safety. Especially this research is very important for countries like Ethiopia which has not source of petroleum and accumulation. So, this epoxidized cottonseed oil (locally available raw materials) can substitute petroleum product of epoxy oils which is imported by the huge amount of money from the foreign country.

By using this research product private and public industry in Ethiopia such as plastic industries, rubber industries, and others can significantly reduce environmental load. It was also help to the scholarly interest on catalysis advancement to the applications of biomaterial production. Other further process epoxide oil users like cosmetics factory, soap factory and other can get their raw material at low cost and in short time in our country.

The significance of this research can be seen in the following perspectives

- ✓ For reduction of environmental loads through the production of sulfonated carbon-based acid catalyst and save foreign currency for epoxy oil consumers and creation of job opportunity for the community.
- ✓ Provide a way for researchers for further study on epoxidation of cottonseed (Ethiopian cottonseed) oil
- ✓ Providing to handle the sustained production of cottonseed oil because now a day's cottonseed oil is going out from the edible oil market
- ✓ Provide a means to exploit and manage local resources.

2. Literature Review

2.1. Epoxy Oil

Petroleum-based products are abundant in our everyday lives. We use it for our energy needs or as a source of material for manufacturing necessary products including epoxy oil and polymer. 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. As such, researchers 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 a feedstock that can replace petroleum-derived materials in many applications (Rios, et. al., 2005).

The epoxidation of alkenes and other unsaturated hydrocarbon chains constitutes one of the most useful reactions in organic synthesis, as the epoxide group is an active intermediate, which can be readily transformed to the required functionality. Epoxidation of long-chain olefins and unsaturated fatty acid derivatives such as soybean oil and other plant oils is carried out on an industrial scale (Rios, et. al., 2005; Dinda et al., 2008). 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 (Saurabh et al., 2011).

Epoxides, known as oxiranes, are cyclic ethers with a reactive three-membered ring. Epoxidation process is a new method by which fatty acids are converted to a three-membered epoxide (oxirane) ring as the carbon-carbon double bond reacts with active oxygen. The cyclical structure of oxirane rings has a bond angle of 60^o, making them highly strained and highly reactive (Silva et al., 2017).

2.2. Epoxidized Vegetable Oil

Vegetable oil is an oil that is extracted from a plant, usually from the fruits or seeds. Some of the most common vegetable oils include canola, coconut, corn, cottonseed, olive, palm, peanut, rapeseed, safflower, sesame, soybean, and sunflower oil. All of these oils are edible but can also be used as fuel oils. Vegetable oils are a sustainable and renewable raw material resource. The unsaturation present in vegetable oils can be chemically modified to a value-added product like epoxy oil. Epoxidation of vegetable oils on an industrial scale is most frequently carried out with peroxyacetic and peroxyformic acids, Fatty acid epoxides can be used directly as plasticizers and stabilizers for PVC resins to improve flexibility, elasticity, and toughness and to impart stability to the polymer towards heat and UV radiation. Due to the high reactivity of the oxirane ring, epoxides also act as a raw material for a variety of chemicals, such as alcohols, glycols, alkanol amines, carbonyl compounds, olefinic compounds, and polymers like polyesters, polyurethanes, and epoxy resins (Vijay, et.al., 2015). Typical conversions of double bonds to epoxy groups are about 90% and Epoxidation may be carried out to reach a maximum conversion (epoxy yield), especially if the product is to be used for further chemical transformations. On the other hand, epoxidation may be employed to obtain a product in the most economical way, e.g. aiming at the highest conversion rate but not necessarily at the highest conversion. The kinetics for each individual set of conditions differ (Petrovic, et. al). Epoxidation is a commercially important method of functionalizing vegetable oils and other natural materials. The epoxide derivatives produced from these renewable raw materials have been used for various applications, e.g., as additives in lubricants, as components in polyurethane foams, and in synthetic detergents (Yang & Zhang, 2016)

However, the cost-effectiveness of the route greatly depends upon the local and cheap availability of the raw material. It is possible that few agricultural belts may not be suitable for its cultivation but may be favorable for some other vegetable oils. Hence, a large number of such oil systems have to be studied for the cost-effectiveness and easy availability of raw materials like cottonseed, sesame, sunflower, Niger, and others (Zhang, 2016). Epoxidized vegetable oils (EVO) are a frequently studied polymer precursor in recent years. Epoxidized soybean oil (ESO) and epoxidized linseed oil (ELO) are currently the only bio-renewable epoxies that reach industrial scale production.

2.2.1. Cottonseed Oil

The cotton plant (*Gossypium hirsutum* or *G. barbadenseis*) is grown for its fiber. The oil is a by-product with about 12 percent of the gross value of the total product. Cottonseed oil was once the major vegetable oil competing with the more widely-used animal fats. The whole cottonseed contains 15-20% oil and about 30 - 38% of the kernel, depending on the quality of seed and the species (Sekhar & Rao, 2011). Today, it occupies ninth place in production tables after five vegetable oils (soybean, palm, rape/canola, sunflower, and groundnut) and three land animal fats (tallow, lard, and butter) (Gunstote, 2004).

Figure 2-1 cotton plant

:

Figure 2-2 cottonseed

2.2.2. Composition and Property of Cottonseed Oil

Most vegetable oils contain fatty acids that vary from 14 to 22 carbon atoms in length, with 0 to 3 double bonds per fatty acid (Isaac, et.al., 2015) and cottonseed oil is one of this class. Cottonseed is a byproduct of cotton production and as such is dependent upon the supply of and the demand for the cotton fiber surrounding the oilseed. The fatty acid profile of cottonseed oil is typical of the oleic-linoleic group of vegetable oils since these two-unsaturated fatty acids make up almost 75% of the total fatty acids. Oleic makes up about 22%, linoleic about 52% and linolenic acid is usually less than 1%. Palmitic acid a saturated fatty acid usually associated with β crystals make up around 24% of the total and only minor amounts of other saturated fatty acids, stearic and myristic, are detected in typical cottonseed oils (O’brien, 2002).

Cottonseed oil is unique among the commercially important fats and oils in the presence of a relatively complex system of pigments. Most of the pigments are of the gossypol. Gossypol is one of natural toxin in cottonseed oil, according to “Institutional Food Management,” by Mohini Seth (2006) in people, gossypol inhibits sperm production as well as motility.

Gossypol is a toxic phenolic C40 compound present in cotton boll cavities. When the seed is extracted, the gossypol adheres to the protein meal and only a small proportion remains in the crude oil giving it a red-brown colour. This is largely removed during refining – especially through caustic refining and bleaching when it falls to safe levels, not exceeding 1–5 ppm (Gunstote, 2004).

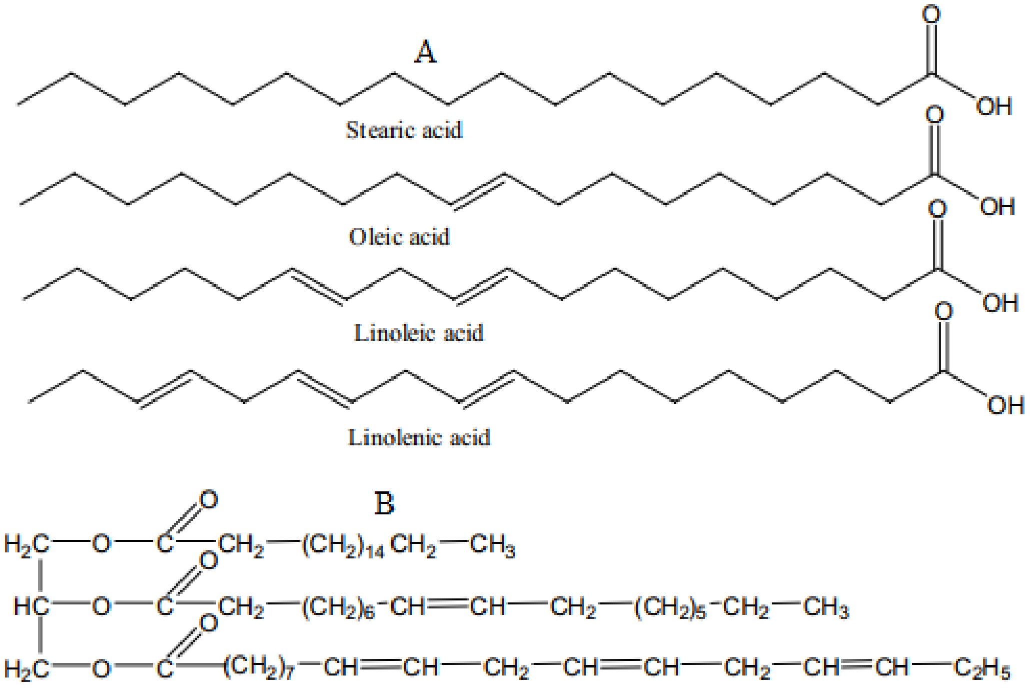


Figure 2-3 A) Chemical structures of stearic, Oleic, Linoleic and Linolenic acids and B) is a structure of a possible triglyceride

The characteristics of a particular cottonseed oil sample are dependent upon the variety of cotton grown and on growing conditions such as temperature, soil conditions, fertilizers, and rainfall, as well as the handling and storage conditions after harvesting. Factors that contribute to variations in the properties of cottonseed oil before it is crushed or extracted from the seed are geographic regions, climate, fertilizers, seed handling, and storage conditions (Tharp, 1948; Stansbury et al., 1953; Jones et al., 1996).

Both the chemical and physical properties of fats and oils are largely determined by the fatty acids that they contain and their position within the triacylglycerol molecule. Chemically, all fats and oils are esters of glycerol and fatty acids. Nevertheless, the physical properties of natural fats and oils vary widely. This is because (1) the proportion of the fatty acids vary over wide ranges, and (2) the triacylglycerol structures vary for each individual oil and fat. Fats and oils are commonly referred to as triacylglycerols (triglycerides) because the glycerol molecule has three hydroxyl groups where a fatty acid can be attached (Stansbury et al., 1953).

Table 2-1 Typical refined cottonseed oil analytical characteristics

Characteristics	Typical	Range
Specific gravity, g/cc at 25/25◦C		0.916 – 0.918
Refractive index at 25◦C		1.468 – 1.472
Iodine value	110.7	90 -117
Saponification number		189 – 198
Unsaponifiable matter (%)		0.5 – 0.7
Titer (◦C)		30.0 – 37.0
Melting point (◦C)		10.0 – 16.0
Cloud point (◦C)		-1.1 – 3.3
Pour point (◦C)		-3.9 – 0

Source: (O’brien, 2002)

Table 2-2 Fatty acid composition (wt. %) of cottonseed Oil

Fatty acid	Carbon atom: Double bond	Range (%)
Myristic	14:0	0.5 – 2
Palmitic	16:0	17.0 – 29.0
Palmitoleic	16:1	0.5 – 1.5
Stearic	18:0	1.0 – 4.0
Oleic	18:1	13.0 – 44.0
Linoleic	18:2	33.0 – 58.0
Linolenic	18:3	0.1 – 2.1

Source: (O’brien, 2002)

All triacylglycerols have the same glycerol unit, so it is the fatty acids which contribute the different properties. The fatty acid components are distinguished in three ways: - (i) chain length, (ii) the number and position of the double bonds, and (iii) the position of the fatty acids within the glycerol molecule. Variations in these characteristics are responsible for the chemical and physical differences experienced with edible fats and oils. (O'brien, 2002).

2.2.3. Epoxy Oil Production via Epoxidation Reaction

The epoxidized oil contains epoxide groups or oxirane rings. The term epoxide can be defined as cyclic ethers which consist of three elements in the epoxide ring. 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 are as follows:

- ✓ Epoxidation by Conventional Method/chemical treatment
- ✓ Epoxidation using acid ion exchange resin(AIER)
- ✓ Epoxidation using enzymes
- ✓ Epoxidation using a metal catalyst
- ✓ Other Systems

2.2.4. Epoxidation by Conventional Method

The conventional chemical treatment method is the most widely used process of epoxidation. For safety point of view, these epoxidations are usually carried out using peracids formed in-situ, by reacting a carboxylic acid with concentrated hydrogen peroxide. This process performs industrially on large scale. In 2008, Dinda et al; worked on the epoxidation kinetics of cottonseed oil using a hydrogen peroxide catalyzed by liquid inorganic acids i.e. HCl, H_2SO_4, HNO_3, and H_3PO_4. They used carboxylic acid i.e. CH_3COOH and HCOOH as oxygen carrier but they found that acetic acid is more effective oxygen carrier than formic acid. Out of all liquid inorganic acid studied as a catalyst, H_2SO_4 was found to be most efficient and effective(Dinda et al., 2008).

In the same year Meyer et al. (2008), worked on the epoxidation of the soybean oil and jatropha oil by a conventional method. They carried out the epoxidation reaction at 50 ^{0}C and atmospheric pressure for about 10 hours. The maximum reaction conversion was 83.3% for epoxidation of soybean oil as catalyst.

Similarly, Cai et al. (2008), worked on the kinetics of in-situ epoxidation of soybean oil, sunflower oil and corn oil by peroxyacetic acid catalyzed H_2SO_4. In this work, they found that soybean oil has greatest conversion rate and lowest activation energy for epoxidation using peroxyacetic acid (Cai et al., 2008).

2.2.5. Acid Ion Exchange Resin (AIER) Method

Acidic Ion Exchange Resin (AIER) is an insoluble gel type catalyst in the form of small yellowish organic polymer beads. Peroxy acid is obtained by reaction of H_2O_2 with carboxylic acid ($HCOOH/CH_3COOH$). The peroxy acid interacts with the catalyst by way of entering the pores of the catalyst. Thus, when AIER loaded into the reactor its pores get filled with peroxy acid. It leads to low oxirane degradation as triglyceride couldn't enter into the gel type structure of AIER(Campanella & Baltanás, 2005).

It is investigated that the conversion of unsaturated fatty acids to oxirane ring using peroxy acid either peroxyformic acid or peroxyacetic acid in the presence of AIER shows different conversion for different vegetable oil. Petrovic et al. worked on the epoxidation kinetics and side reactions of soybean oil in toluene with peroxyacetic acid and peroxy formic acid in the presence of AIER as a catalyst. They found that peroxyacetic acid is less efficient than peroxy formic acid. Acidic ion exchange resin can be used as a catalyst to synthesize peroxy acids followed by in-situ epoxidation of vegetable oils. While studying the kinetics of in-situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin, they find that AIER has prominent advantages over the conventional chemical method of epoxidation of vegetable oil is that by improving the selectivity and undesirable side reactions can be reduced to a certain level (Petrovic, et al., 2002). Goud et al. in 2006 worked on in-situ epoxidation of Karanja oil with aqueous hydrogen peroxide and acetic acid in presence of Amberlite IR-120 acidic ion exchange resin as catalyst. The variables studied were stirring speed, hydrogen peroxide to ethylenic unsaturation molar ratio, acetic acid to ethylenic unsaturation molar ratio, temperature and catalyst loading. The effects of this parameter on the conversion to epoxidized oil were studied at the optimum condition for the maximum oxirane content was established. They reported that the intermediate temperature in the range of 55^0C to 65^0C gives a maximum conversion of double bonds to oxirane groups and the reaction time was minimized. Further, they added that molar ratio of acetic acid to Karanja oil is 0.5 mole and a mole ratio of 1.5 for hydrogen peroxide to oil was the optimal concentration for the epoxidation reaction (Goud, et al., 2007).

Mungroo et al. worked on the epoxidation of canola oil with H_2O_2 as oxygen donor, acetic acid as an oxygen carrier and AIER (22 % loading) as a catalyst. The heterogeneous catalyst, AIER, was found to be reusable and exhibited a negligible loss of activity. The formation of an epoxy adduct of canola oil was confirmed by FTIR and 1H NMR spectral analysis (Mungroo, et al., 2008).

2.2.6. Enzymatic Method

To avoid side reactions and to make the process more environmentally friendly, enzyme catalyst is preferred. Immobilized Candida Antarctica lipase was used as the catalyst. The epoxidation reaction can be improved by adding the lipase step wisely. The enzymatic catalyst for epoxidation is a good alternative to chemical treatment. The main limitation, however, is the low stability of the lipase under the reaction conditions. The parameters affecting the lipase activity and operational lifetime during chemoenzymatic epoxidation of fatty acids were investigated (Tzialla et al., 2010).

2.2.7. Metal Catalyst Method

Researchers and scientist are always in search of some new method and techniques to improve the existing technology. In the same line, many workers and co-workers have given their contribution to increase the oxirane content and improve the efficiency of epoxidation reaction. Various metal catalysts such as titanium, molybdenum, tungsten.

Mohamed et al worked on the epoxidation kinetics of sunflower oil using tungsten as a catalyst. But in this case, they got less conversion as compared to proxy acid system (Mohamed, et al., 2007).

2.3. The Reaction Mechanism for Epoxidation of Vegetable Oil

In situ epoxidation of vegetable oil with a carboxylic acid in the presence of a suitable catalyst in which peracetic acid formation is an acid-catalyzed reaction (Saurabh et al., 2011). Epoxidation reaction mechanism of vegetable oil follows two-step reactions. These reactions are the formation of peracid and oxirane ring formation reaction.

$$RCOOH + H_2O_2 \xrightleftharpoons{H^+} RCOOOH + H_2O \text{ .... Eq. 2-1}$$

Whereas the main reaction involving the epoxy group formation is an uncatalyzed reaction:

$$R_1\text{-CH=CH-}R_2 + RCOOOH \Longrightarrow R\text{-}\overset{O}{CH\text{-}CH}\text{-}R2 + RCOOH \text{ .... Eq. 2-2}$$

Precisely it can be represented as

.....................................Eq. 2-3

Eq. Epoxidation reaction mechanism

2.3.1. Epoxidation Reaction Kinetics

There are two major reactions involved in the epoxidation reaction as mentioned above. During the first stage, peroxy acid is formed from the reaction of acetic acid and hydrogen peroxide while in second stage epoxidized oil is produced from the reaction between peracetic acid and double bond in the oil (Gan, et al., 1992).

Considering hydrogen peroxide as oxygen donor and acetic acid as oxygen carrier, we can write following steps (Purwanto, 2010).

Step I: Formation of Peroxyacetic acid

$\mathrm{AA} + \mathrm{H_2O_2} \rightleftharpoons \mathrm{PAA}$ ....Eq. 2-4

Step II: Epoxidation Reaction

$\mathrm{DB} + \mathrm{PAA} \longrightarrow \mathrm{EO} + \mathrm{AA}$..Eq. 2-5

Where: $\mathrm{AA} = \text{Acetic Acid}$

$\mathrm{PAA} = \text{Peracetic Acid}; \mathrm{DB} = \text{Double Bonds}; \mathrm{EO} = \text{Epoxidized Oil}$

$\mathrm{K1}, \mathrm{K2}(\text{forward and reverse}), \mathrm{K3} = \text{Reaction Rate Constant}$

The reaction was found to be overall second order and a one-step mechanism (Step 2) has been proposed (J. March, 1992).

If the first step is considered rate determining and the concentration of peroxy acetic acid is assumed constant throughout the reaction then following rate laws can be applied:

$-\frac{d[DB]}{dt} = K3[DB]^{n1}[PAA]^{n2}$ …………………………………………………………… Eq. 2-6

Where: $[\mathrm{DB}] = $ Molar Concentration of Double Bond

$[\mathrm{PAA}] = $ Molar Concentration of Peroxyacetic Acid

$\mathrm{K3} = $ Reaction rate constant

$\mathrm{n1} = $ Reaction order with respect to double bonds concentration.

$\mathrm{n2} = $ Reaction order with respect to Peroxyacetic Acid concentration.

2.4. Factors Affecting Epoxidation Reaction

There are many factors which affect Epoxidation reaction. The most common factors are agitation Speed, amount of hydrogen peroxide and acetic acid/formic acid molar ratio, reaction temperature, reaction time, catalyst loading, type and purity of reactants/oil.

According to Tayde & Thorat work, the epoxidized cottonseed oil (ECO) was synthesized by reaction of cottonseed oil with glacial acetic acid and 30 % aqueous hydrogen peroxide using sulfuric acid as a catalyst. The optimum conditions obtained from the their study include reaction time of 4 hours and temperature of 60^{o}C, hydrogen peroxide to ethylenic unsaturation ratio of 2:1, acetic acid to ethylenic unsaturation ratio of 0.5:1 and the sulfuric acid loading was 2% by weight of the total weight of hydrogen peroxide and acetic acid at stirring speed of 850 rpm (Tayde & Thorat, 2015).

The factors and the kinetics of epoxidation of cottonseed oil by a peroxyacetic acid generated in situ from hydrogen peroxide and glacial acetic acid in the presence of liquid inorganic acid catalysts were studied by (Dinda et al., 2008). It was possible to obtain up to 78% relative conversion to oxirane with very less oxirane cleavage by in situ technique

2.4.1. Reaction Temperature

The reaction temperature is the temperature at which the reaction takes places. Some researchers studied the effect of temperature on epoxidation reaction.

According to Dinda et al.; 2008 they were found that as temperature increased, the epoxidation rate increased. At lower temperatures (30 and 45 ^{0}C), the relative percentage conversion to oxirane continuously increased within the experimental time limit. However, at a higher temperature (60 ^{0}C), the relative percentage conversion to oxirane attained a maximum, after which it gradually decreased. The relative percentage conversion to oxirane showed a continuous decrease at 75 ^{0}C, after some increase during the initial phase of the reaction. This indicates that an increase in temperature not only increased the epoxidation rate but also increased the rate of hydrolysis (oxirane cleavage) of the product. These results suggested that an optimum level of epoxidation could be obtained within a shorter time at a moderate reaction temperature of about 60 ^{0}C (Dinda et al., 2008).

2.4.2. Agitational Speed

It is essential to operate the process at highest feasible speed to eliminate the effect of resistance to mass transfer of peracetic acid from the aqueous phase to the 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 stirring speed that the oxirane formation rate was not substantially affected by stirring speeds beyond 1800 rev/min, and hence, it was assumed that the reaction was free from mass transfer resistance beyond 1800 rev/min under the given conditions to ensure that the reaction was kinetically controlled (Dinda et al., 2008).

2.4.3. Reaction Time

Time is one of main and important factors for any reactions. The epoxidation reaction was take place by using heterogeneous catalyst and the heterogeneous catalyst also needs enough time for mixing with other mixture component and to contact the active site of the catalyst to acetic acid and hydrogen peroxide to form peracetic acid. The effect of reaction time toward the conversion of double bond always increased and oxirane rings produced in the reaction were not considered stable in the presence of acidity for longer time. The maximum %OOC value and percentage conversion of oxirane obtained within an optimal reaction time. With an increased reaction time, from small to higher gradual increase in OOC was observed; however, further increased in reaction time, OOC value became decrease.

2.4.4. Effect of Hydrogen Peroxide (H_2O_2)

The epoxidation rate increased as the concentration of H_2O_2 in the system increased. Although the maximum conversion to oxirane was obtained for a mole ratio of 2.5, the stability of the oxirane ring was very poor at this high mole ratio. On the other hand, at low concentrations of H_2O_2, oxirane ring was quite stable. It was also observed that the formation of a-glycol increased as this ratio increased (Dinda et al., 2008).

2.4.5. Effect of Acetic Acid (CH_3COOH)

The epoxidation rate increased as the concentration of CH_3COOH in the system increased. It has been observed that at a high mole ratio of CH_3COOH, the stability of the oxirane ring was very poor. It was also observed that the formation of a-glycol increased as the CH_3COOH mole ratio increased. Therefore, to obtain the maximum oxirane, the optimum level of concentration of CH_3COOH should be used where both the effects are optimized. Hence, within the experimental conditions, the most favorable concentration of CH_3COOH appeared to be 0.5-mole ratio (Dinda et al., 2008).

2.4.6. Unsaturation of Vegetable Oil

The unsaturated double bonds of vegetable oils rich in oleic, linoleic and linolenic acyl groups may be used to introduce functional groups like epoxides. Generally, oil consists basically of triacylglycerols with different degrees of unsaturation and different distribution and proportions of fatty acid acyl chains. The high content of unsaturated fatty acids of about 77% a suitable starting material for epoxidation (Okieimen, et al., 2005).

2.4.7. Catalyst Load

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate without undergoing a net chemical change itself. The order of effectiveness of catalysts was found to be sulfuric acid > phosphoric acid > nitric acid > hydrochloric acid for epoxidation reaction. Acetic acid was found to be superior to formic acid for the in-situ cottonseed oil epoxidation. The epoxidation of cottonseed oil in situ generated peroxy acid could be carried out at a moderate temperature of about 60^oC. Out of all liquid inorganic acid studied as a catalyst, H_2SO_4 was found to be most efficient and effective. Higher temperature and higher acid concentration reduced the reaction time needed to reach the maximum conversion to oxirane value; however, it simultaneously increased the extent of oxirane ring cleavage to glycols. The reaction was kinetically controlled beyond a stirring speed of about 1800 rpm (especially for heterogeneous solid acid catalyst requires higher agitational speed than the homogenous one) (Dinda et al., 2008).

Maximum yield of oxirane with a negligible amount of oxirane cleavage could be obtained if the epoxidation of cottonseed oil, using in situ generated peroxyacetic acid, is carried out at optimum conditions. These optimum conditions include a temperature range of 50-60^oC, H_2O_2-to-unsaturated mole ratio range 1.5-2.0, CH3COOH-to- unsaturated mole ratio of about 0.5 and H_2SO_4 loading of about 2% (by weight) of the aqueous phase.

Silva et al.; 2017 studied on the production of catalyst to vegetable oil epoxidation from toxic biomass residue and they reported the optimum heterogenous carbon-based sulfonated catalyst is from 10 up to 22% (Silva et al., 2017).

2.5. Characteristic Element for Epoxy Oil

The conversion of the raw material to the product by epoxidation reaction or the quality of the epoxy product, is measured by the changes of the hydroxyl value, iodine number and epoxy number or oxirane oxygen content, 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 transforms infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) analysis.

2.5.1. Iodine Value

The iodine value (or iodine number) is a measure of the degree of unsaturation, that is, the number of carbon-carbon double bonds in relation to the amount of fat or oil. iodine value is defined as the gram of iodine absorbed per 100 g sample (Silva et al., 2015). The higher the amount of unsaturation, the more iodine absorbed; therefore, the higher the iodine value, the greater the degree of unsaturation (Nieisen, 2003).

Common practice is to determine calculated iodine value from the fatty add composition using AOCS Recommended Practice Cd lc-85. The calculated iodine value is not meant to be a rapid method. but instead gives two results (iodine value of triacylglycerols and free fatty acids) from one analysis (fatty acid composition).

A quantity of fat or oil dissolved in a solvent is reacted with a measured amount of iodine or some other halogen. Halogen addition to double bonds takes place (Eq. 2-7) A solution of potassium iodide is added to reduce excess ICl to free iodine (Eq. 2-8). The liberated iodine is then titrated with a standardized solution of sodium thiosulfate using a starch indicator (Eq. 2-9).

$\mathrm{ICl} + \mathrm{R-CH=CH-R} \rightarrow \mathrm{R-CHI-CHCl-R} + \mathrm{ICl}$……………………………...Eq. 2-7
(excess) (remaining)

$\mathrm{ICI} + 2\mathrm{KI} = \mathrm{KCl} + \mathrm{KI} + \mathrm{I_2}$ ………………………………………………………… Eq. 2-8

$\mathrm{I_2} + \mathrm{starch} + 2\mathrm{Na_2S_2O_3} \rightarrow 2\mathrm{NaI} + \mathrm{starch} + \mathrm{Na_2S_4O_6}$………………………….... Eq. 2-9
(blue) (colorless)

The iodine value is calculated using (Eq. 2-10): -

$\mathrm{Iodine\ value} = \frac{(B-S)*N*12.69}{w}$………………………………………………………… Eq. 2-10

Where: $B = \text{blank titration, ml}$

$S = \text{volume used for titration, ml}$

$N = \text{normality of } \mathrm{Na_2S_2O_3}$ solution

12.69 is used to convert from mEq thiosulfate to g iodine; molecular weight of iodine is 126.9.

Iodine value is used to characterize oils, to follow the hydrogenation process in refining, and as an indication of lipid oxidation. since there is a decline in unsaturation during oxidation.

2.5.2. Oxirane Oxygen Content

The Oxirane oxygen content 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 bromide that by interaction with the oxirane group forms bromide ring. The equivalence point, determined by titration, is detected at an excess of perchloric acid (ASTM D 1652-97).

The percentage of the oxirane oxygen was determined by the direct method established by (Paquot & A. Hautfenne, 1987) using hydrobromic acid solution in glacial acetic acid. The content oxirane oxygen (OO) was calculated according to the consumed amount of the halogen atom. To determine the oxirane oxygen content for the epoxidized oil use direct titration with hydrogen bromide in acetic acid.

2.5.3. Selectivity

Experimental values of IV and IV_0 can be used for calculate the reaction selectivity (S) value, which is a measurement for estimate the non-occurrence of secondary reactions during the synthesis steps. The search for greater selectivity was calculated according to the equation below (Silva et al., 2015).

$$S = \frac{\mathrm{OOC_{exp}}}{\mathrm{OOC_{the}}} \Big/ \frac{[\mathrm{IV_o} - \mathrm{IV}]}{\mathrm{IV_o}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq. 2-11}$$

Where: -

$\mathrm{OOC_{exp}}$ = the experimentally determined content of epoxy(oxirane) oxigen in 100 g

IV = iodine value of the sample;

$\mathrm{IV0}$ = initial iodine value;

$\mathrm{OOC_{the}}$ = the theoretical oxygen content of the epoxide formation.

2.6. Carbon-Based Solid Acid Catalyst

The catalyst is a substance that causes or accelerates a chemical reaction without itself being affected. Various studies have been carried out for epoxidation using different oils as the raw material and different carboxylic acid i.e. CH_3COOH and $HCOOH$, as well as different catalysts, notably homogeneous ones such as liquid inorganic acids i.e. HCl, H_2SO_4, HNO_3 and H_3PO_4 and enzymes such as lipases. Recent research has focused on the application of heterogeneous catalysts to produce Epoxides, because of their environmental and economic advantages (Guidotti, et al., 2007). Catalysts based on biomass have advantages such as low cost and surface chemical properties that can be tailored appropriately.

2.6.1. Heterogeneous Catalyst

Catalysts are generally classified into homogeneous, biocatalyst and heterogeneous catalyst (Ramachandran, et al.; 2013) and their subclassification also listed in the flowchart below.

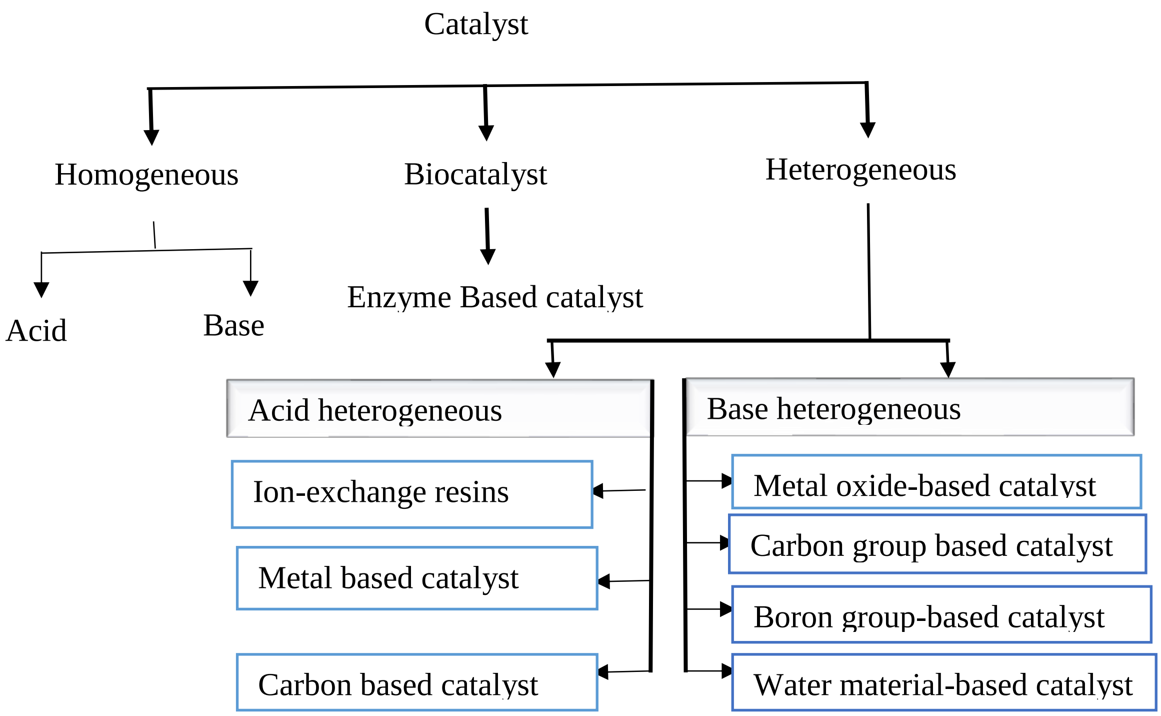


Figure 2-4 Classification of catalyst

2.6.2. Carbon Based Catalyst

Porous carbon materials constitute a very flexible set of supports for the preparation of heterogeneous catalysts. Their physical and chemical surface properties can easily be tailored to develop a large surface area to disperse the active phases, the proper pore size distribution to facilitate the diffusion of reactants and products to and from the surface, and the acid-base character needed for obtaining the best performance.

More recently, Rodr´ıguez-Reinoso (Geoffrey S. Simate et al., 2010) has reviewed various aspects of the use of carbon materials as catalysts and catalyst supports.

A large variety of carbon materials can and have been used as catalyst supports. The most important are granular and powdered activated carbons and carbon blacks, but there is increasing interest in related materials, such as activated carbon fibers and cloths, nanotubes, and nanofibers(Duong-viet et al., 2016). A comprehensive review of the use of these materials as catalysts and catalyst supports has been published (Serp, et al., 2003). Although carbon materials cannot be used in reactions that are carried out under certain conditions (hydrogenation at temperatures higher than 700 to 800 K or oxidation above 500 K), they show some advantages over other traditional catalyst supports (Marsh & Rodriguez-reinoso, 2006):

- The carbon surface is resistant to both acidic and basic media.
- The structure is stable at high temperatures.
- The pore structure can be tailored to obtain the pore size distribution needed for a given application.
- Porous carbons can be prepared with a variety of macroscopic shapes (e.g., granules, powder, fibers, cloths, pellets, monoliths, disks).
- The chemical properties of the surface can be modified to control the polarity and hydrophobicity.
- The active phase can be recovered easily from spent catalysts by burning away from the carbon support.
- Carbon supports are usually cheaper than another conventional catalyst supports.

These properties can be exploited in a great number of catalytic reactions. The main properties of carbon materials involved in their role as a catalyst support, and some of the processes that employ carbon materials as a catalyst support, are presented below.

2.6.2.1. Properties Affecting Carbon’s Role as Catalyst Support

i. Surface Area and Porosity

High surface area and a well-developed porosity are very important for achieving a high dispersion of the active phase in the catalyst (dispersion is the fraction of metal atoms that are on the surface of the support in relation to the total metal loading).

ii. Surface Chemical Properties

The carbon surface contains a given number of heteroatoms (O, N, H) in the form of functional groups, similar to the way that heteroatoms appear in organic compounds. The presence of these groups can affect the preparation of carbon-supported catalysts, as they confer the carbon surface acid-base and hydrophilic character.

2.7. Source of Carbon for Catalyst-Support

Biomass is the main source of carbon. Biomass used for carbon support production must have high fixed carbon and high density. Based on this bamboo was selected. Bamboo is a giant grass, belonging to the same family as sorghum, wheat, Teff, other cereals and sugar cane. It is an integral part of forestry, but it is also widely spread outside forests, including farmlands, riverbanks, roadsides and urban areas. The growth vigor of bamboos is unmatched by any other plant in nature; some species reach 40 meters in height and only in a few months' time (Directorate, 2013).

Given its fast growth, high soil conservation potential, multiple uses, and adaptability to low-quality sites, bamboo has the capacity to redress most of the deforestation-related problems. Bamboo forest is a material source for furniture, building, pulp, particleboard, bioenergy, food, forage, and medicine. It plays a vital role in environmental amelioration, bio-diversity preservation and soil and water conservation and has waste purification potential (Embaye et al., 2003).

3. Materials and Methods

Various equipment, chemicals, and materials were used for the successful completion of the experimental work.

3.1. Raw Material

Bamboo was collected from Addis Ababa local market and used for the synthesis of the activated carbon support. Cottonseed oil was procured from Mojo oil factory and used for the production of epoxy cottonseed oil.

3.2. Equipment

The following equipment were used during the research work. Glass reactor, mechanical stirrer, magnetic stirrer, burette, oil bath, crusher, pH meter, tong, analytical balance, pipette, horizontal tubular electrical furnace(pyrolizer), graduated cylinder, density meter, thermometer, glass beakers, drying oven all were found in AAiT laboratory, Fourier transform infrared (FT-IR) and Ultimate analysis (CHNS elemental analyzer) were found in natural science college of AAU at Chemistry department. GC/MS (gas chromatograph-mass spectroscopy) was found in leather technology institute. Supportive appliance: - Stopwatch, Glove, Masks, Safety cloth and others were procured from local market.

3.3. Chemicals

Sodium hydroxide, hydrogen peroxide (30 wt.%), acetic acid (99-100 wt.%), Nitrogen gas, Sulfuric Acid (98 wt.%), Hydrogen bromide acid, Potassium hydroxide, Hydrochloric acid (HCl), Sodium Thiosulphate, potassium iodide, Benzene, Cristal violet indicator, Starch indicator, and phenolphthalein indicator were collected from Addis Ababa chemical importing plc.

3.4. Experimental Method

3.4.1. Synthetization of the Activated Carbon Support

The collected bamboo was cut into pieces manually and crushed using the crushing machine and sieved mechanically to get a uniform size distribution (between 1mm- 2mm), then after washed with distilled water and dried at 105 °C for 8 h. These bamboo precursors were immersed in a sodium hydroxide(NaOH) solution (with 0.1 M) for one day. Next, the mixture was dehydrated in a drying oven for 16 h at 105 °C and then put on a metal mesh inside a stainless-steel chamber. After drying the mixture was placed in an electrical furnace connected with Nitrogen gas (1.1 up to 1.2 ATM pressure reading hose) and the chamber was heated, to initiate carbonization process. The heating rate was 15.71^{o}C/min and continued until the final temperature of 500 ^{o}C±10^{o}C. The pyrolysis (carbonization) process was maintained at 500 ^{o}C ±10^{o}C for 3 h and then carbon char product was cooled down to room temperature under nitrogen atmosphere.

After pyrolysis process to remove some impurities such as ash, phosphate etc. the synthesized biochar was washed with a hydrochloric (HCl) solution (0.1M), followed by washing with distilled water several times until the pH of the washing solution was neutral. Then the biochar was dried at 105 °C for 14 h and grounded into 100-250 μm and stored in clean space prior to characterization of char and sulfonation process.

3.4.2. Synthesizing of Sulfonated Solid Acid Catalyst through Sulfonation

The prepared biochar (sized between 100μm up to 250μm) was weighted and added into sulfuric acid having 98% concentration (with ratio 1:10 for weight of biochar to volume of acid), then the sulfonation process take place for 15 hours at 150^{o}C temperature (Silva et al., 2017). After sulfonation, the catalyst was washed by hot distilled water (>80 ^{o}C) for several times until the pH of catalyst was the same as the pH of distilled water (Ouyang, et al., 2014).

Sulfonation was carried out by 1:10 ratio of the pyrolyzed biochar materials to concentrated sulfuric acid (H_2SO_4) and heated at 150^{0}C for 15 h (Silva et al., 2017). The sulfonated sample was washed rigorously with hot distilled water (> 80 ^{0}C) to remove any physically adsorbed element and sulfate ions. The sample was then dried by drying oven at 105^{0}C for 8hr. Then the sulfonated catalyst was ready.

Once the carbon-based sulfonated catalyst produced, some of the physical and chemical properties such as acid density, elemental analysis and amount of sulfur content in the sulfonated carbon catalyst etc. of the product was analyzed using the analytical method.

3.4.3. Characterization of Precursor and Sulfonated Solid Acid Catalyst

3.4.3.1. Proximity Analysis for Raw Material

As defined by ASTM; D1762-84 (Reapproved 2007), proximate analysis of carbon- based biomass, separates the component into four groups: (1) moisture, (2) volatile matter, consisting of gases and vapors driven off during pyrolysis, (3) fixed carbon, the nonvolatile fraction of biomass, and (4) ash, and the inorganic residue remaining after combustion.

(i) Moisture Content

The raw bamboo crushed to desirable size (1-2 mm) was put into the ceramic crucible. The crucible was weighed with and without the amount of bamboo sawdust. The crucible with bamboo dust was dried in a drying oven at 105°C for 8h. The sample was removed every 2 hours from the oven and placed in the desiccator for 10 minutes to cool and re-weighed until constant weight is obtained. Finally, the weight was taken and compared with the initially recorded weight. The percentage weight of moisture in the sawdust was calculated using the formula:

$$\text{moisture content}(\%) = \frac{W_b - W_a}{W_b} * 100 \quad \ldots\ldots\text{Eq. 3-1}$$

Where: W_b = the original weight of the sample before drying and

W_a = the weight of the sample after drying.

(ii) Volatile Matter

The sample was measured and placed in a closed metal crucible (crucible with head cover) and heated at 950°C for exactly 5 min in a furnace. The crucible was then cooled in a desiccator and weighed. The weight of the sample between before heating and after heating was used to determine the amount of volatile matter present in the sample using the following equation.

$$\text{volatility matter }(\%) = \frac{W_a - W_c}{W_a} * 100 \quad \ldots\ldots\text{Eq. 3-2}$$

Where: W_a = an Average mass of bamboo sawdust after drying

W_c = an average mass of bamboo sawdust after burned@950°C

(iii) Ash Content

The dried sample was measured and put into an open ceramic crucible. Then the dried sample was heated by 550 °C muffle furnace for 4hr. After the required heating, the crucible was cooled in a desiccator and then weighed. The amount of residual substance is equal to the ash present in the sample.

$\text{Ash content } (\%) = \frac{W_d}{W_c} * 100$ ……………………………………..……………………Eq. 3-3

$W_d = \text{a gram of res}idue$

(iv) Fixed Carbon Content

The fixed carbon content is determined by subtracting the sum of volatile matter content and ash content form 100 by assuming the negligible content of other elements(Vijayanand, et al., 2016). 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:

$\text{Fixed carbon content } (\%) = 100 - (V_m + A_c)$ ……………………………………...Eq. 3-4

Where: $V_m = \text{Volatile matter}$

$A_c = \text{Ash content}$

3.4.3.2. Bulk Density of Biochar and Sulphonated Carbon Catalyst

The bulk density of the biochar prepared for sulfonation process and the sulfonated catalyst was measured by using graduate measuring cylinder and density meter with in triplicate measurement and taken an average. For determination of bulk density method described by ASTM Test Methods (D 2854 – 96 (Reapproved 2000) was used with a slight modification.

$BD_{bc} = M_{bc}/V_{bc}$ ………………………………………………………………….……Eq. 3-5

Where: $BD_{bc} = \text{Bulk Density of biochar}$

$M_{bc} = \text{Mass of biochar}$

$V_{bc} = \text{volume of biochar}$

The bulk density of the sulfonated carbon catalyst prepared from biochar was measured by using graduate measuring cylinder and density meter.

$BD_{sc} = M_{sc}/V_{SC}$ ....Eq. 3-6

Where: $BD_{sc} = \text{Bulk Density of sulfonated carbon catalyst}$

$M_{sc} = \text{Mass of sulfonated carbon catalyst}$

$V_{SC} = \text{the volume of the sulfonated carbon catalyst}$

3.4.3.3. Determination of Acidity

Total acid density and sulfonic acid density of carbon-based solid acid catalyst and biochar were tested by acid-base titration following the reference(Wu et al., 2010).

Total acid density for sulfonated carbon-based catalyst and biochar was carried out in back titration method. The method was done by dissolving biochar and sulfonated solid catalyst by NaOH solution (0.01M) and sonicate the dissolved for one hour, then titrate by HCl solution(0.01M) in the presence of 5 drop phenolphthalein indicator.

The content of $–SO_3H$ (sulfate) groups on the sulfonated solid acid catalyst was determined by direct titration with sodium hydroxide solution. The sulfonated solid acid catalyst was weighted (0.02g) and added into an aqueous sodium chloride solution (0.01 M, 20 mL). The dissolved sample was shacked for 60 min at room temperature under ultrasonic vibration with water. After that, the supernatant was titrated with sodium hydroxide solution (0.01 M) until there was no color change of phenolphthalein(Silva et al., 2017). The density of $-SO_3H$ group (N mmol/g) was calculated as follows:

$\mathrm{N\_}SO3 \ = \mathrm{V_{NaOH}} \times \mathrm{N_{NaOH}}$……………………….………………………………...…Eq. 3-7

Where: $\mathrm{N_{SO3}} = \text{density of } \mathrm{SO_3} \text{ group}$

$\mathrm{V_{NaOH}} = \text{The volume of NaOH used(mL) per gram of the sulfonated carbon}$

$\mathrm{N_{NaOH}} = 0.01\ \mathrm{N}\text{(the normality of the NaOH solution)}$

The total acidity of the sulfonated carbons is expressed as a sum of the contributions from all of the acidic groups such as SO_3H, OH, CO_2H, etc. (Lee, 2013). The total acid density of sulfonated carbon catalyst was measured by back acid-base titration method using the mole of the titrator NaOH and the mole of titrant HCl.

$\mathrm{TAD_{sc}} = \mathrm{N_{NaOH}} - \mathrm{N_{HCl}}$ ……….…………..…………………………………………… Eq. 3-8

Where: $\mathrm{TAD_{sc}} = \text{The total acid density of sulfonated carbon catalyst}$

$\mathrm{N_{NaOH}} = \text{mole of titrator NaOH}$

$\mathrm{N_{HCl}} = \text{mole of titrant HCl}$

$\mathrm{TAD\_(sc/gram) = TAD\_sc/w\_sample}$ ……………………………………………….………. Eq. 3-9

Where: $\mathrm{TAD_{\_sc/gram}} = \text{total acid density of catalyst per gram of catalyst}$

$\mathrm{w_{\_sample}} = \text{a gram of catalyst sample}$

3.4.3.4. Fourier Transform Infrared Spectroscopy (FT-IR) for Catalyst

FT-IR spectroscopy is an important method to determine the presence and absence of particular bands of functional groups. FT-IR is most useful for identifying chemicals that are either organic or inorganic. Samples were recorded in the range 400 - 4000 cm-1 on a Perkin Elmer FT-IR spectrometer using KBr powder mixed with the sample and milled by mortal, then pressed the mixed sample (sample and KBr) up to 10 MPa for 10 min to form a pellet. The functional group analysis of the pyrolysis biochar and the sulfonated carbon catalyst was analyzed using Fourier-Transformed Infrared (FTIR) spectroscopy. 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 recorded data was processed using essential FT-IR software origin pro 8. FT-IR Analysis conducted in Addis Ababa University, college of natural science at chemistry department.

3.4.3.5. Elemental Analysis (CHNS) for Sulfonated Carbon Catalyst

The ultimate analysis for sulfonated carbon catalyst was done by using a device “EA 1112 Flash CHNS/O- analyzer” under these conditions: Carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 900 °C and oven temperature of 75 °C. The sample was feed into an analyzer for combustions process. The combustion products are separated by a chromatographic column and are detected by the thermal conductivity detector (TCD), which gives an output signal proportional to the concentration of the individual components of the mixture. The sample was run in duplicate and the average values are to be taken. Before preforming the experiment Calibration of the equipment was done. Six calibration points were taken for every component.

3.4.3.6. Thermogravimetric Analysis (TGA)

The thermal stability of raw material was tested using TGA by measuring the mass loss during a heating ramp rate 10^{o}C. Thermal stability of the sulfonated biochar catalyst was determined by a thermogravimetric analyzer (TA instrument, SDT Q600 V20.9 Build 20 module DSC-TGA Standard) using temperature programming from 25^{o}C to 800^{o}C at the heating rate of 10^{o}C/min to which the sample was heated. For the thermogravimetric analysis to be carried out, a small amount of the sample (22-30mg) was placed in a vial, which was present in the TGA analyzer. This vial is connected to sensors which detect the weight of the sample at all times. Testing was carried out under inert atmosphere (N_2) with a flow rate of 100 ml/min to remove all corrosive gases and avoid thermoxidative degradation and the retention time of the sample at the maximum temperature

(Vuthaluru, 2004). These values were used as the basis for the analysis. TGA was performed in Leather Industry Development Institute (LIDI) laboratory. The thermal degradation onset temperature and the thermal degradation weight loss of composites were recorded and analyzed using origin pro 8.0 software.

3.5. Pretreatment and Characterization of the Cottonseed Oil

The raw cottonseed oil was pretreated to decrease FFA (free fatty acid), solid matters and water content to acceptable level to enhance the epoxidation yield. Characterization of oil was conducted by measuring moisture content (ASTM D-3277-95e1), specific gravity (ASTM D-445), acid value, and Iodine value (Wiji method) of the oil. If the FFA and water contents of the cottonseed oil are above the required (max.1-1.5% water) values, pretreatment of this oil was conduct to decrease the FFA (degumming to remove FFA) and water content (heating in an oven) to the accepted level and this enhance the epoxide yield.

A) Degumming

Degumming was done to avoid the interference of phosphatides, gums, FAA, and other complex compounds which affect the epoxidation reaction and to avoid rancidity (increase in free fatty acid) of oil during storage. A 3 wt.% distilled water to oil at 70°C was mixed with the oil. Then the mixture was stirred by an overhead stirrer for 1 h at 70°C hot water bath. The degummed sample was put on a drying oven with a temperature of 105 for 1:30 hour and then the FAA and other impurity was separated by separating funnel.

B) Moisture Content of Oil

The moisture content of the oil was determined according to ASTM D-3277 and A.O.A.C. the moisture content of oil was determined by content analyzer and weight measure procedure. The weight measuring procedure follows; the Petri dish was weighed with and without cottonseed oil. The Petri dish with cottonseed oil was dried in an oven at 105°C until the weight measurement become constant. Finally, the weight was taken and compared with the initially recorded weight and the percentage weight in the oil was calculated using the formula:

$$\text{moisture content}(\%) = \frac{W_i - W_f}{W_i} * 100 \quad \text{……………………………………………………. Eq. 3-10}$$

Where: W_i = the original weight of the sample before drying and

W_f = the weight of the sample after drying.

C) Specific Gravity of Oil (SP)

The specific gravity of the oil was determined using ASTM D-445. The oil was injected using a syringe to the density meter and the density meter automatically recorded the density and specific gravity of treated oil at 20^{o}C.

$\mathrm{SP} = \rho_{\mathrm{oil}}/\rho_{\mathrm{water}}$ ……………………..Eq. 3-11

ρ_{oil} = density of cottonseed oil @20℃

ρ_{water} = density of water

D) Kinematic Viscosity of Cottonseed Oil

The kinematic viscosity of cottonseed oil was determined by using ASTM D-445 by measuring dynamic viscosity. Kinematic viscosity is important to compare the initial property to the final property of the product. The kinematic viscosity was determined from dynamic viscosity and density of the oil using Eq. 3-12.

$\nu_{\mathrm{oil}} = \mu_{\mathrm{oil}}/\rho_{\mathrm{oil}}$ ……………………………………………………………………………. Eq. 3-12

Where: ν_{oil} = Kinematic viscosity

μ_{oil} = Dynamic viscosity

ρ_{oil} = density

E) Acid Value of Cottonseed Oil

The sample (0.1 g) was placed in a reaction flask and dissolved in 1:1 (v/v) mixture of 95% ethanol (15 ml, 0.26 mmol) and diethyl ether (15 mL, 0.16 mmol). The solution was titrated with standard 0.1 M ethanolic potassium hydroxide solution, using phenolphthalein indicator (4-6 drops). The determinations were duplicated for each batch of purified cottonseed oil. The acid value, AV was calculated using the formula (Eq. 3-13) (Mukasa-Tebandeke et al., 2014);

$\text{Acid value}(\mathrm{AV}) = \frac{56.1*V*C}{m}$ ……………………………………………………………Eq. 3-13

Where: V is the consumption of titrant KOH solution volume, mL

C = the concentration of KOH solution, $\frac{\mathrm{mol}}{\mathrm{L}}$

m = the weight of the oil g

56.1 = potassium hydroxide molar mass, $\frac{\mathrm{g}}{\mathrm{mol}}$

All experiments were measured three times in parallel and then take an average.

F) Iodine Value of Oil

Iodine value was determined according to Wiji's method (Siggia & Hanna, 1979; Weiss, 1970). A standard Wiji's solution (iodine chloride) was prepared by dissolving a known amount of iodine trichloride in a known volume of carbon tetrachloride and the known volume of acetic acid. To determined iodine value, the oil was dissolved in a known volume tetrachloride in a glass stopper conical flask and known the volume of standardized Wiji's solution was added. Then the stopper was replaced at once and the flask was allowed to stand for 60 minutes at an atmospheric temperature in the dark. After the reaction was completed, 15 ml 15 % KI solution and 50 ml water were added. Finally, the free iodine was titrated with 0.1N sodium thiosulphate until the color is pale yellow. A few drops of starch solution 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 the equation 3-14:

$$\text{Iodine number} = \frac{12.69(V^0 - V)}{W} * N \qquad \text{Eq. 3-14}$$

Where: - V^0 = the ml of 0.1N thiosulphate required for the blank determination

V = the ml of 0.1N thiosulphate required for the titration

W = the weight of oil used in the test.

3.5.1. Gas Chromatography-Mass Spectroscopy (GC/MS)

Gas chromatography (GC) analysis was performed with Agilent GC – system – 7820A. Sample analysis was carried out on the 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°C for a total run time of 38 minutes. The data, obtained using MS - Agilent Technologies EMS detector and processed using Che station software, were used to obtain a fatty acid composition of oils.

3.5.2. FT-IR Analysis of Cottonseed Oil

The FT-IR of cottonseed oil was done by following the same procedure described on section 3.4.3.4 the only difference in the procedure was the solid KBr replaced by liquid sample holder made of NaCl. The FT-IR analysis was done at Natural science college of Addis Ababa University in the department of chemistry.

3.6. Epoxidation of the Cottonseed Oil

Epoxidized cottonseed oil was done in the present research works. The epoxidation work was performed within different factors and levels of those factors with the present of sulfonated solid acid catalyst.

3.6.1. Experimental Design for Epoxidation of the Cottonseed Oil

The laboratory experiment was carried out on a three-level full factorial design where the different treatment factors (combination of factor and level) was analyzed for the different combinations of their test levels.

The experimental design selected for this study was response surface methodology, three-level full factorial and the response variables were measured the percentage of conversion and oxirane oxygen content (Oxirane ring). In addition, analysis of physicochemical properties of epoxidized cottonseed oil was determined and characterization by using analytical method.

Response surface methodology (RSM) is method for performing process optimization using mathematics and statistics to construct a model of the process to determine the optimal process conditions (Montgomery, 2001). The relationship between independent variables (factors) and dependent (response) variables is usually unknown and complex and RSM is applied to determine an estimation equation that represents closely the relationship between factors and response variables. For ease of application, a low-order polynomial model is normally employed to represent estimation function.

The next step is to perform an experimental design and then this step is followed by data analysis. Following this, the range and level of variables is determined to indicate scope of variables includes the experimental design to determine the model parameters. The fitted surface is then employed to analyze the response surface. If the resulting response surface is statistically a good fit then the response surface will be a close approximation of the real system.

Three-level-full factorial was used in the optimization study which requires 32 experiments to be conducted. The thirty-two 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 and oxirane oxygen content as a function of the independent variables. Using response surface method, the optimum combination of the operational factors was determined.

Application of RSM for process optimization is a commonly used strategy. The developed model can be easily maximized or minimized to determine the best response variables. Thus, in process optimization of a particular chemical process, RSM can determine the optimal operating condition and offer benefits such as reduced experimental time, a less complexity, and highly efficient process.

Randomization of the experimental runs (to minimize systematic error), as well as appropriate analysis technique, was ensured through proper utilization of software Design-Expert 7.0.0. Results from analyses were the bases to conclude this research. Experimental factors and levels are given in table 3.1.

Table 3-1 Experimental factors and levels for epoxidation reaction

Factors	Levels		
	lower	Middle	Higher
Temperature (^oC)	45	60	75
Hydrogen per oxide/cotton seed oil molar ratio (mole/mole)	1	1.75	2.5
Time (hr.)	2	4	6

Note: - in many reviews, the range of acetic acid to oil ratio is 0.25-0.75. By taking the average of 0.5 mole/mole is necessary to this work. The three-level-full factorial the complete experimental data was shown below in Table 3.2.

Table 3-2 Experimental factors and levels for epoxidation reaction

Std	Run	Temperature (^oC)	Time (hr.)	The molar ratio of H_2O_2 /oil (mol/mol)
17	1	60	6	1.75
25	2	45	6	2.50
2	3	60	2	1.00
12	4	75	2	1.75
5	5	60	4	1.00
21	6	75	2	2.50
14	7	60	4	1.75
28	8	60	4	1.75
1	9	45	2	1.00
27	10	75	6	2.50

15	11	75	4	1.75
32	12	60	4	1.75
8	13	60	6	1.00
26	14	60	6	2.50
22	15	45	4	2.50
9	16	75	6	1.00
19	17	45	2	2.50
18	18	75	6	1.75
13	19	45	4	1.75
31	20	60	4	1.75
3	21	75	2	1.00
30	22	60	4	1.75
10	23	45	2	1.75
6	24	75	4	1.00
16	25	45	6	1.75
29	26	60	4	1.75
4	27	45	4	1.00
7	28	45	6	1.00
23	29	60	4	2.50
11	30	60	2	1.75
24	31	75	4	2.50
20	32	60	2	2.50

3.6.2. Experimental Setup for Epoxidation Reaction

The epoxidation reaction was carried out in a 100 ml three neck flask. 15 ml of cottonseed oil was taken in the reactor and with respect to this calculated amount of CH_3COOH (acetic acid) and sulfonated solid acid catalyst was added to the three-neck glass reactor. The three-neck reactor glass was immersed in oil bath equipped with hotplate having magnetic stirrer, temperature, and time controller and the mixture stirred for 20 minutes before hydrogen peroxide was added. The glass reactor was fixed by a metal clamp in an oil bath with required oil temperature, time and stirring speed of 1200 rpm for different experimental run.

To start the epoxidation, Hydrogen Peroxide solution was gradually charged into the mixture with in thirty minutes. Epoxidation of the purified cottonseed oil was carried out by using carbon-based sulfonated solid catalyst at atmospheric pressure. The reaction was stirred at a constant stirring speed of 1200 rpm for all test runs. The experiments were planned to investigate the optimum conditions and to study the effects of the variables on the reactions, such as hydrogen peroxide to oil ratios, reaction temperature, and reaction time. The reaction set-up given in Appendix E, Figure E-1.

Samples were collected with the desired experimental time duration. The collected samples were put in separatory funnel (Appendix figure E-2) and then washed with cold and slightly hot water successively to remove free acid then after centrifuging of the sample was carried out to remove the sulfonated solid acid catalyst.

The final product pH was checked to have a value above 5 and then analyzed for iodine value, oxirane content and other properties.

3.6.3. Characterization of Epoxy Oil

3.6.3.1. Physical and Chemical Property of Epoxy Oil

The quality and the quantity of epoxy oil was determined based on its property. The physical and chemical properties of epoxidized cottonseed oil was determined during analysis time. The property like moisture content, specific gravity, acid value, iodine value/ number, conversion of carbon-carbon bonds, and oxirane oxygen content were determined. The moisture content, specific gravity, acid value, and iodine value of epoxidized cottonseed oil were determined like cottonseed oil property determinations at section 3.6.2., 3.6.3., 3.6.4., and 3.6.5. respectively.

3.6.4. Conversion of Unsaturated Cottonseed Oil

After performed the experiment, the conversion of the double bond was calculated by using iodine value. The iodine value is used to quantify unsaturation/double bond of oil. The conversion was determined using Eq. 3-15.

$$Cco = \frac{INo - IN}{INo} * 100\% \quad \text{.......... Eq. 3-15}$$

Where: - Cco = conversion of unsaturated cottonseed oil

INo = Iodine number before epoxidation

IN = Iodine number after epoxidation

3.6.5. Oxirane Oxygen Ring Determination for Epoxidized Cottonseed Oil

The percentage of the oxirane oxygen was determined by the direct method established by (Paquot & A. Hautfenne, 1987) using hydrobromic acid solution in glacial acetic acid. The content oxirane oxygen (OO) was calculated according to the consumed amount of the halogen atom. By using direct titration with hydrogen bromide in acetic acid was determined. The procedure was shown to be free from interference by many impurities (including water, at a concentration of 1-1.5%).

The method was as follows: The sample (generally about 0.4 g) was dissolved in chlorobenzene or benzene, 5 drops of 0.1% crystal violet indicator solution are added, and the sample was stirred and titrated with the HBr/acetic acid solution to a blue-green end-point which persists for at least 30 sec. (Dobinson et al., 1969).

The following equation was used to calculate the epoxy functionalities of ECO (Saremi et al., 2012).

$\mathrm{Oxirane\ Oxygen\ Content}(OO_{exp}) = \frac{\mathrm{V*n*1.6}}{\mathrm{w_m}}$ ……………………………………….. Eq. 3-16

$\mathrm{V} = \mathrm{consumed\ titrated\ solution}$

$\mathrm{n} = \mathrm{normalized\ value}$

$\mathrm{w_m} = \mathrm{used\ amount\ of\ epoxidized\ oil}$

Dry epoxidized samples was analyzed for their percent's (by weight) of epoxy functional groups by an official method AOCS Cd 9-57 (Oxirane Oxygen in Epoxidized Materials). From the oxirane content values, the relative percentage conversion to oxirane was calculated using the following expression:

$\mathrm{Relative\ percentage\ conversion\ to\ oxirane} = \frac{OO_{exp}}{OO_{the}} * 100$ ……………………... Eq. 3-17

where $OO_{\ exp}$(g/100 g sample) is the experimentally obtained oxirane oxygen and OO_{the} is the theoretically obtainable maximum oxirane oxygen, which was determined from the following expression:

$OO_{the} = \frac{\left(\frac{VI_o}{2*Ai}\right)}{100+\left(\frac{VI_o}{2*Ai}\right)*Ao} * Ao * 100$ ……………………………………………………Eq. 3-18

where $A_{\ i}$(126.9) and $A_{\ o}$(16.0) are the atomic weights of iodine and oxygen respectively and IV_o is the initial iodine value of oil sample.

3.6.6. FT-IR for Epoxidized Cottonseed Oil

The conversion of double bonds to oxirane rings were observed under FT-IR spectra. The procedure was the same in section 3.4.3.5. except KBr changed by NaCl liquid sample carrier (spread sample on NaCl) and no need of making pellet.

4. Result and Discussion

This section summarizes the result obtained from the experiments performed in the laboratory. Specifically, it will discuss synthesis and characterization of sulfonated solid acid catalyst and epoxy oil production on cottonseed oil.

4.1. Proximate Analysis

The proximate analysis of bamboo was done to determine the distribution of component, before pyrolysis in order to know the amount of moisture content, volatile matter, ash content, and the fixed carbon content of the bamboo. Knowing the amount of component in the raw material is important to determine whether the raw material used for catalyst purpose or not. proximate analysis was carried out using moisture analyzer, drying oven, and muffle furnace by using ASTM D1762 – 84 (reapproved 2007) standard and the result recorded was shown in figure 4.1. The detailed calculation part is also included under Appendix-A. (The analysis was Based on average values of three replicates, errors less than 1.5% with consideration of instrumental error in all components, the weight percent were on dry basis).

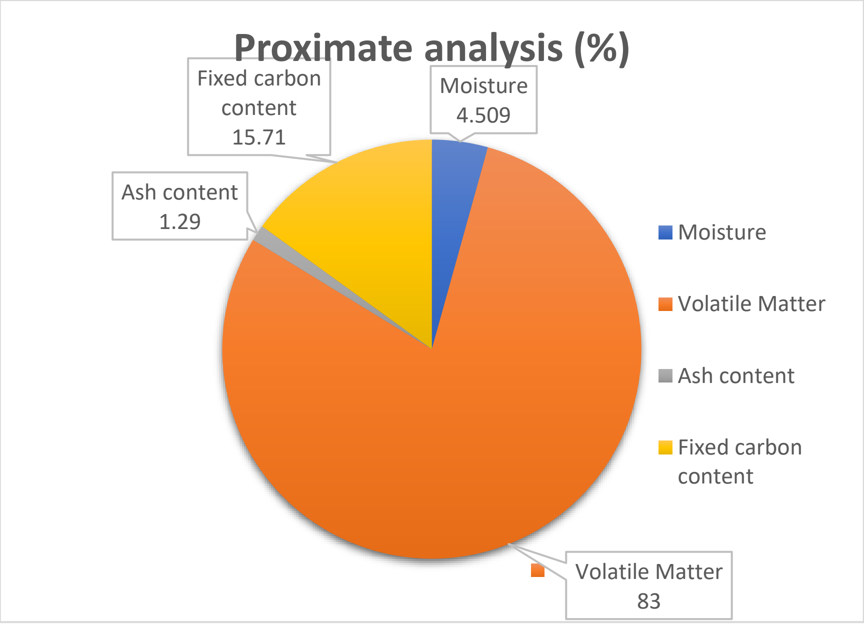


Figure 4-1 Proximate analysis for bamboo saw dust

As shown on the Figure 4-1 the total amount of moisture content, volatile matter, ash content, and fixed carbon content were 4.5%, 83%, 1.3%, and 15.7% respectively. This proximate analysis was match closer to value the study reported by (Gebremedhin, 2017). The bamboo sample was rich in high volatiles matter and low in ash content. The low ash content would result in minimal effects of inorganic impurities on pore development during pyrolysis process. Bio- mass with higher fixed carbon content and high volatile has higher bio-char yield and higher surface area for attachment of the sulfonate group during sulfonation reaction (Kang, et al., 2013).

Previous studies suggested that suitable activated carbon support should be low in ash but rich in carbon and volatiles. Because ash may interfere with carbon adsorption through competitive adsorption and catalysis of adverse reactions. Mostly materials with the lowest ash content produce, high volatile matter, and high fixed carbon content are good catalyst support product. Those properties are comparable with the raw material used for the present work.

4.2. Characterization of Biochar and Sulphonated Carbon Catalyst

4.2.1. Yield of Biochar and Sulphonated Carbon Catalyst

Biochar production from bamboo sawdust was conducted at 500^{o}C pyrolyzing for 3hrs and at this condition production yield of biochar (carbon-char) was recorded averagely 22.89% and the detail calculation was done in Appendix-A (Table A-2) in dry weight basis. According to Mašek et al.,(2013) the yield of bamboo biochar was recorded from 28 up to 30 % (Ondřej, Peter, Andrew, & Saran, 2013).

Sulphonated solid acid catalyst production from carbon-char in sulfuric acid was impregnated at 150^{o}C for 15hr. After that, the yield of carbon catalyst was recorded and averagely 99% in dry weight basis.

4.2.2. Bulk Density of Carbon Char and Sulphonated Carbon Catalyst

Bulk density is used to characterize the particles of carbon-char and sulfonated carbon catalyst by measuring the density for both of the biochar and the catalyst. Bulk density is also useful for the estimation of tank or packing volume of catalyst during reaction. Bulk density, or packing density, includes all pores and voids (inter-particle spaces in its composition). The bulk density of the carbon char and the catalyst are given in Table 4-1.

The bulk density determination was done detail in Appendix A and the determination was in dry weight basis with triplicate of sample measurement for both carbon-char and catalyst.

Table 4-1 Bulk density of biochar and sulphonated catalyst

Component	Bulk density (gram/litter)
Carbon-char	264.4
Sulfonated catalyst	358.0

As shown in the Table 4-1 the bulk density of sulfonated catalyst is higher than its carbon-char (biochar). This was due to the impregnation of carbon-char in sulfuric acid and other incomplete reactions. In sulfonation process, many reactions may occur during sulfonation of carbon-char such as complete carbonization and thermal oxidative of the biochar. Since, as long as the bulk density of the carbon-chars is less than that of the catalysts due to sulfonation reaction. This reaction was a dominant reaction than other possible reactions occur in sulfonation process. The other reason to dominate sulfonation reaction was the reaction take place under inert condition due to the continuous supply of nitrogen gas. This indicates the sulfonated catalyst has -SO_3H functional group on the surface of the carbon char. Thus, increment of sulfonated catalyst bulk density is due sulphate (-SO_3H) functional group presented on surface of carbon-char and this result is similar with Ouyang, et al. (Ouyang, et al., 2014). Heterogeneous catalysts having high density are more favorable catalytic activity than low density catalyst (Ouyang, et al., 2014).

4.2.3. The Acidity of Carbon-char and Sulphonated Carbon-Based acid Catalyst

In table 4-2 the total acid density and sulphate acid density are shown. The total acidity of the sulfonated carbons catalyst and carbon-char/biochar are expressed as a sum of the contributions from all of the acidic groups such as SO_3H (except in biochar), OH, CO_2H, etc. (Lee, 2013). The total acid density of sulfonated carbon catalyst and carbon-char/biochar was measured by acid-base back titration method discussed at section 3.4.3.3. Based on this method the mole of the titrator was $2.5 \times 10\hat{} - 4$ and 2.5×10^{-4}moles of NaOH and the mole of titrant was $5.6 \times 10\hat{} - 5$ and 1.89×10^{-4}moles of HCl for the catalyst and carbon-char respectively (the detail calculation was given in Appendix A).

-SO_3H acid density was determined using direct titration of catalyst in sodium chloride solution by sodium hydroxide solution given at section 3.4.3.3.

Table 4-2 Acid density of sulfonated catalyst and carbon-char/biochar

Catalyst	Total acid density (mmol/g)	-SO_3H acid density (mmol/g)
Carbon-char	0.82	…..
Sulfonated catalyst	3.8	2.8

The contents of –SO3H, -OH, -COOH groups on BC-SO_3H are usually among 0.1-4.9, 0-0.9, 0-7.8 mmol/g, respectively (R. Benak, et al., 2002;Nakajima & Hara, 2012; Takagaki et al., 2006; Onda, et al.; 2008). Though -SO_3H groups are considered as the key active acidic site, the existence of -OH and -COOH groups would provide hydrophilic reactants accessing to the -SO_3H groups, which would be in favor of effective catalytic performance.

The data from acid base titration showed that biochar (0.82 mmol/g) have lower number of acid sites than sulfonated biochar (3.8 mmol/g) (Table 4-2). Thus, shows good and same result with elemental (ultimate) analysis and bulk density analysis done in this work. All the data recorded in the laboratory is included in the range listed above paragraph.

4.2.4. Elemental Analysis (CHNS) for Sulfonated Carbon-Base Acid Catalyst

The elemental (ultimate) analysis of sulfonated carbon catalyst is given in Table 4-3. Based on the Table 4-3 result shown, the total average of each element is N = 0.725%, C = 74.01%, H = 1.74% and S = 3.27% and the average content of oxygen form this result is $\approx 20.255\%$. The sample was run in duplicate and the average values are to be taken.

The elemental analysis shows the catalyst has high sulfur element (average 3.27%), and by assuming that all Sulfur atom was present as sulfate (–SO_3H) form on the surface like the study report by Ngaosuwan, et al. (Ngaosuwan, et al., 2016).

Table 4-3 elemental analysis result of sulfonated carbon catalyst

Name	Sample Code	N (%)	C (%)	H (%)	S (%)
Sulfonated catalyst	S20	0.65	74.35	1.78	3.02
	S20a	0.80	73.67	1.70	3.52
Average		0.725	74.01	1.74	3.27

Where: N= nitrogen, C= Carbon, H= Hydrogen, and S= Sulfur.

4.2.5. FT-IR Analysis for Biochar and Sulphonated Catalyst

FT-IR used for the identification of the functional groups on the surface of particles. FT-IR result of biochar and the sulfonated carbon catalyst is shown in Figure 4-2 below. The peaks at 1604 cm−1 and at 1112 cm−1 are due to the presence of CO_2H and C-O functional groups, respectively (Ouyang, et al., 2014). The peaks due to the $-SO_3H$ group are seen at 1032 cm−1 and at 582 cm−1. The peaks attributable to aliphatic C-H bond, aromatic C-H bond, O-H bond in a carboxylic acid group, and O-H bond in a phenol group are seen as abroad peak between 3600 cm−1 and 2400 cm−1. This result is agree with research's done by (Ouyang et al., 2014) and (Mar & Somsook, 2012)

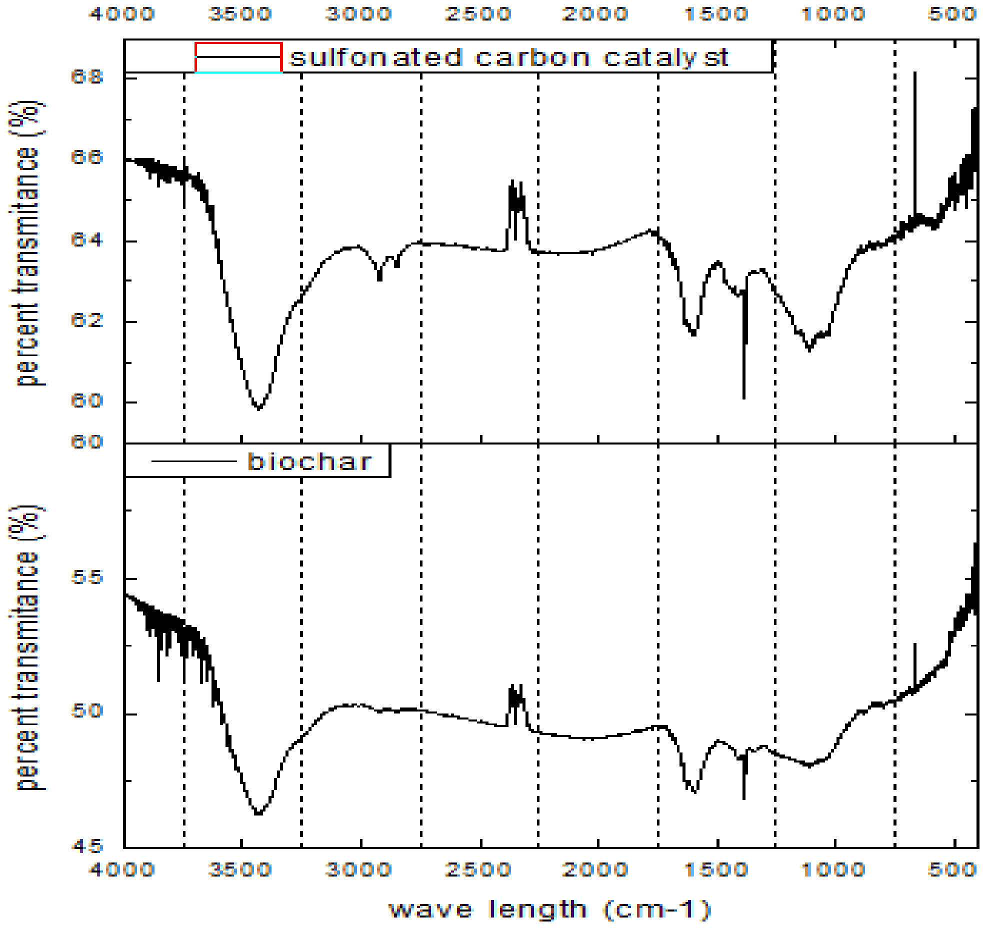


Figure 4-2 FTIR graph for sulfonated carbon-based catalyst and Biochar of bamboo saw dust.

4.2.6. Thermogravimetric Analysis (TGA)

Thermogravimetric (TG) analysis was accomplished on SDT Q600 V20.9 Build 20 TGA instrument from 25 °C to 800 °C at a heating ramp of 10 °C, under a constant flow (100 ml/min) of nitrogen gas and the TGA result of sulfonated catalyst was shown in figure 4-3.

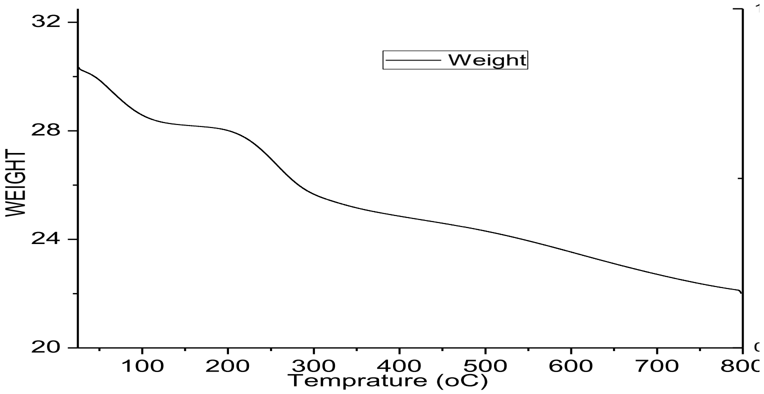


Figure 4-3 Thermogravimetric analysis of sulfonated catalyst

The graph shows weight loss of sulfonated catalyst with respect to temperature. The weight loss at beginning was 1.83665 mg due to moisture up to 105.08 ^{o}C and after 105.08 ^{o}C up to 201.5^{o}C, the weight loss is negligible. Above 250^{o}C of temperature, the weight loss of the catalyst was almost uniform within slight decrement. As shown on the graph the total loss of weight for the catalyst in percent is 27.75% at end temperature. So, this result shows that the catalyst is highly stable starting low temperature up to high temperature (800 ^{o}C). Based on the thermogravimetric analysis the catalyst that was synthesized in this work is thermally stable for high temperature. The epoxidation reaction was performed at low temperature (maximum 75 ^{o}C). Therefore, the catalyst is thermally stable for this work.

4.3. Characterization of Cottonseed Oil

4.3.1. Physicochemical Property of Cottonseed Oil

The physicochemical property of cottonseed oil was shown in Table 4-4.

Table 4-4 Physicochemical Property of cottonseed oil

Property	Value
Moisture content	0.33 %
Density	918.9 kg/m^3 @19.8 ^{o}C

Specific gravity	0.9189
Dynamic viscosity	61.6 mPa s
Kinematic viscosity	$6.7 * 10^4\ \mathrm{m}^2/s$
Acid value	3.086 mol/gram
Iodine value	81.66 gI_2/100gram oil

The moisture content, acid value, and iodine value of cottonseed oil are 0.33 %, 3.086 mol/gram and 81.66 respectively. These values are good character for the oil used in epoxidation reaction process according to (Saurabh, et al., 2012) and the other properties given in Table 4-4 are also similar to refined cottonseed oil studied by O'BRIEN, (2002). According to (Biermann et al., 2008) the moisture content of oil must be below 1.5 % and higher iodine value (>78) of the oil is better for epoxy oil production. All of the properties shown in the Table 4-4 are under the required value range for epoxy oil raw material (specially for vegetable oil) and the detail calculation is given in Appendix B.

4.3.2. Gas Chromatograph – Mass Spectroscopy Analysis of Cottonseed Oil

The gas chromatography/mass spectroscopy of cottonseed oil was conducted in Leather Industry Development Institute and the result is shown in Table 4-5.

Table 4-5. gas chromatograph mass spectroscopy value of cottonseed oil

fatty acid composition for cottonseed oil				
	C: double bond	$Mwt.$	Area %	$Area\ (\%) * Mwt.$
linoleic	C18:2	280	55.8	156.24
Oleic	C18:1	282	17.5	49.35
Palmitic	C16:0	256	23	58.88
Linolenic	C18:3	278	0.3	0.834
Stearic	C18:0	284	2.1	5.68
Myristic	C14:0	228	0.8	1.824
Palmitoleic	C16:1	254	0.7	1.778
Average $Mwt.$				**274.68**

Where: $\mathrm{Mwt.} = \mathrm{molecular\ weight}\ \mathrm{C} = \mathrm{Carbon}$

Table 4-6 retention time, scientific Name and reference number of GC/MS result

Retention time	C: double bond	Scientific Name	Reference number
42.175	C16:1	9-hexadecenoic acid	117507
42.995	C16:0	hexadecenoic acid	119400
47.916	C18:1	9-octadecenoic acid	141306

48.395	C18:0	Methyl Stearate	143131
49.810	C18:2	10,13-octadecadienoic acid	139716
62.007	C18:3	Cis-13-octadecenoic acid	416531

As shown Table 4-5 fatty acid composition for cottonseed oil and area percentage of each component was recorded based on the method mention in section 3.5.1. This result is closely related with cottonseed oil composition mention in literature review section 2.2.2 at Table 2-2 and the report by Gunston, (2004) and (Milchert, et al., 2016), Cottonseed oil is unusual among commodity vegetable oils and contains a relatively high level of palmitic acid (typically 23%) along with oleic acid (17%) and linoleic acid (56%) (Gunstote, 2004).

According to Bland, et al., (1991), calculations from the areas of both the GC and the HPLC chromatograms gives palmitic, oleic and linoleic acid percentages of 24, 19 and 57 respectively (Bland, et al., 1991). According to (Ouedraogo & J.A. Bezard, 1982) percentage of palmitic acid, oleic acid, and linoleic acid was 25, 20, and 52 % reported for cottonseed oil. The results given in Table 4-5 are match closely with the result mentioned by Gunston, (2004), Bland, et al., (1991) and Ouedraogo & J.A. Bezard, (1982).

4.4. Performance of Sulfonated Catalyst on Epoxidation of Cottonseed Oil

The epoxidation of cottonseed oil was performed under different factor (three-level-factor) and two responses in the present of sulfonated solid acid catalyst. The performance of the catalyst was studied by analyzing the epoxidized cottonseed oil through statistical and analytical method. The result of epoxidation for the two responses were given in Appendix C Table C-3.

4.4.1. Statistical Analysis on Factors Affecting Epoxidation

The statistical analysis was done based on experimental method described in the methodology part at section 3.6.1. and the Design Expert 7.0.0 software was used.

The actual experimental data at different epoxidation condition was recorded and given in Appendix C, at Table C-1 and C-2. The mathematical models were developed to correlate the epoxidation factors with the response conversion and oxirane oxygen content (see Appendix C). The diagnostics case statistics report (the actual experimental data and the predicted experimental data) has been given in Appendix C at Table C-4 and Table C-5 for conversion and oxirane oxygen content respectively.

4.4.2. Model Adequacy Checking

The model adequacy checking is essential to confirm whether the fitted model provides an adequate approximation of actual values or not. The model was tested for adequacy by analysis of variance.

For each reaction time, reaction temperature, and corresponding hydrogen peroxide to oil ratio, the conversion, and oxirane oxygen content were determined for the epoxidation process. The correlation of responses conversion and oxirane oxygen content to the coded value of variables were estimated using non-linear regression in the help of design expert software. The estimated regression coefficients were presented in Table 4-6 and the analysis of variance (ANOVA) was provided at Table 4-7 and Table 4-8 for conversion and oxirane oxygen content respectively.

Table 4-7 Regression statistics for conversion and oxirane oxygen content of cottonseed oil

Regression statistics	Conversion	Oxirane oxygen content
R-Squared	0.85	0.9
Adj R-Squared	0.79	0.87
Pred R-Squared	0.67	0.8
Adeq Precision	13.7	17.1
Observation	32	32

For conversion and oxirane oxygen content the "Pred R-Squared" of 0.67 and 0.8 are in reasonable agreement with the "Adj R-Squared" of 0.79 and 0.87 respectively. Because the difference is less than 0.2, then the model is fitting the data and can reliably be used to interpolate. "Adeq Precision" measures the signal to noise ratio and a ratio greater than 4 is desirable. The ratio of signal to noise is 13.7 for conversion and 17.1 for oxirane oxygen content. So, the result indicate an adequate signal for the model can be used to navigate the design space.

Table 4-8: Analysis of variance (ANOVA) for conversion of epoxidized cottonseed oil

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2950.99	9	327.89	14.05	< 0.0001	***
A-temperatur	800.93	1	800.93	34.31	< 0.0001	***
B-time	455.62	1	455.62	19.52	0.0002	**

C-Hydrogen peroxide/Oil	450.90	1	450.90	19.32	0.0002	**
AB	78.75	1	78.75	3.37	0.0798	
AC	43.82	1	43.82	1.88	0.1845	
BC	214.04	1	214.04	9.17	0.0062	**
A^2	399.04	1	399.04	17.09	0.0004	**
B^2	35.16	1	35.16	1.51	0.2327	
C^2	171.66	1	171.66	7.35	0.0127	
Residual	513.58	22	23.34			
Lack of Fit	461.17	17	27.13	2.59	0.1487	*
Pure Error	52.40	5	10.48			
Cor Total	3464.56	31				

Where: *** highly significant ** significant * not significant

Table 4-9: Analysis of variance for oxirane oxygen content of epoxidized cottonseed oil

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	2.56	9	0.28	24.14	< 0.0001	***
A-temperatur	0.092	1	0.092	7.84	0.0105	*
B-time	0.076	1	0.076	6.45	0.0187	*
C-Hydrogen peroxide/Oil	0.28	1	0.28	23.63	< 0.0001	***
AB	0.23	1	0.23	19.46	0.0002	
AC	0.025	1	0.025	2.14	0.1580	
BC	4.083E-004	1	4.083E-004	0.035	0.8541	
A^2	0.35	1	0.35	29.35	< 0.0001	***
B^2	0.33	1	0.33	27.59	< 0.0001	***
C^2	0.48	1	0.48	40.46	< 0.0001	***
Residual	0.26	22	0.012			
Lack of Fit	0.23	17	0.014	2.29	0.1833	*
Pure Error	0.030	5	5.910E-003			
Cor Total	2.82	31				

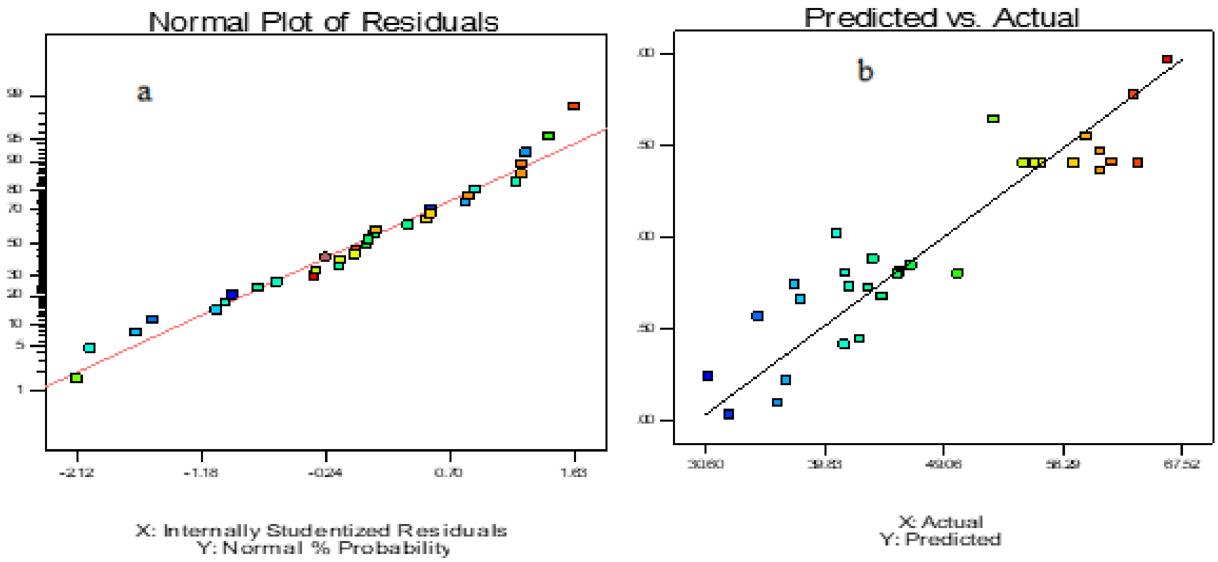
Where: *** highly significant ** significant * not significant

As shown in Table 4-8 and Table 4-9, the model F-value for conversion and oxirane oxygen content are 14.05 and 24.14 respectively and the results implie the model are significant. There is only a 0.01% chance that a "Model F-Value" is large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In case of conversion A, B, C, BC, A^2,

C^2 and in cas of oxirane oxygen content A, B, C, AB, A^2, B^2, C^2 are significant model terms respectively.

The "Lack of Fit F-value" of conversion and OOC are 2.59 and 2.29 respectively and that implie the Lack of Fit is not significant relative to the pure error. There are 14.87% and 18.3% chance that a "Lack of fit F-value" large could occur due to noise for conversion and OOC respectively. Non-significant lack of fit is good and this want the model to fit.

The model is a good fit of the experimental data as indicated by high values of the correlation coefficient for the responses and models having significant limit. To check the validity of the model, the model validation technique was used. The primary method of model validation checking is graphical residual analysis; and that is, through an assortment of plots of the differences between the observed data and the predicted value from the model. Figure 4-4 and figure 4-5 shows that the graphical residual analysis for conversion and oxirane oxygen content respectively.



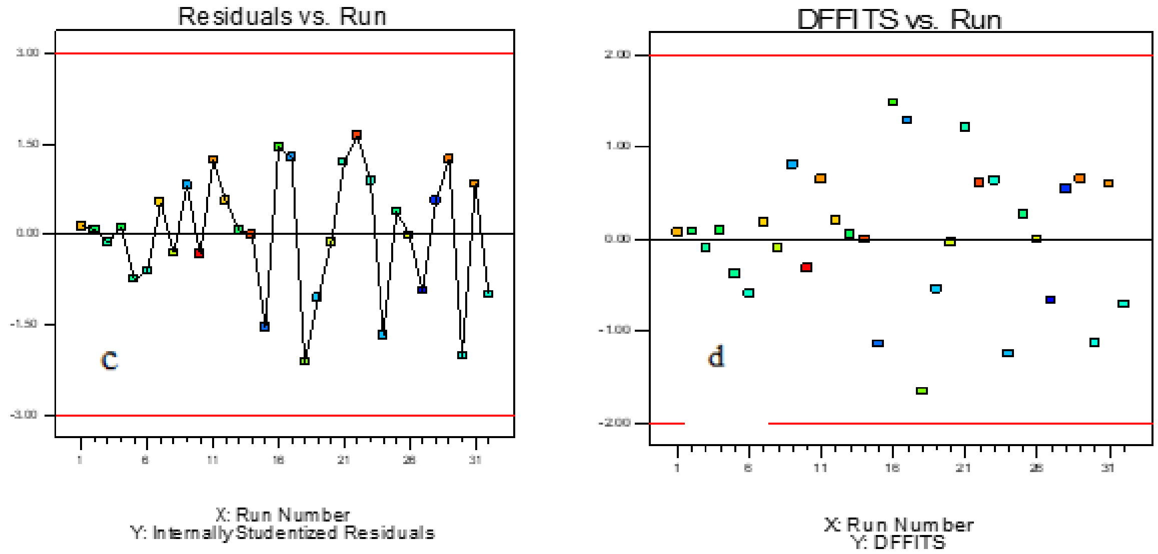
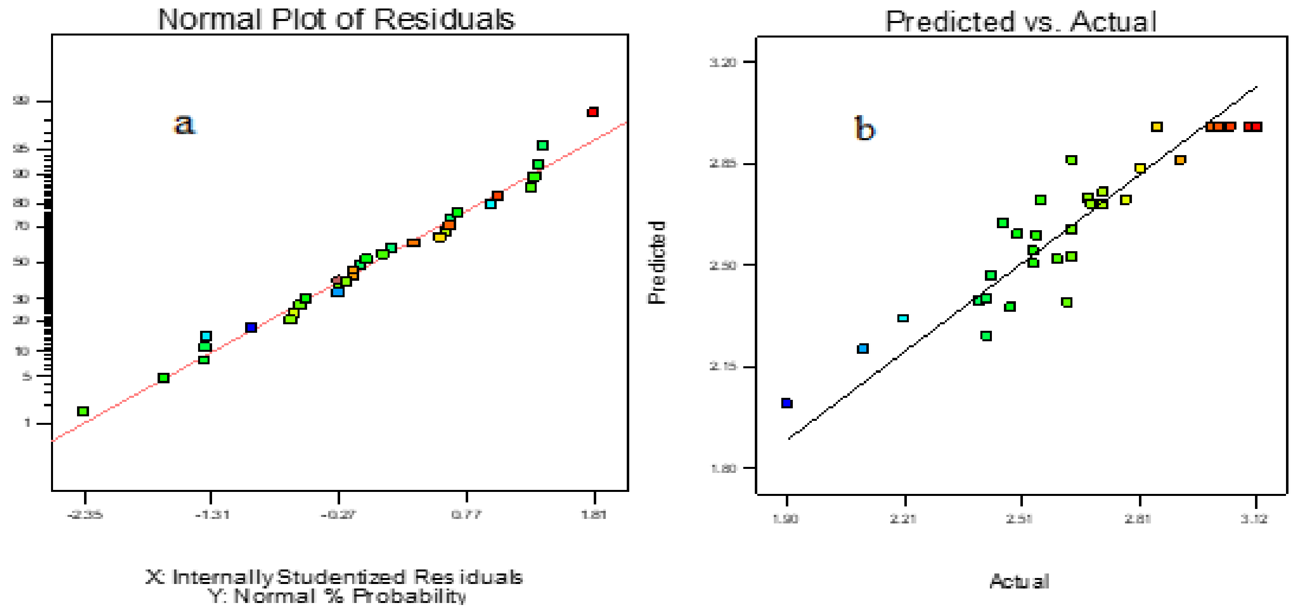


Figure 4-4 Diagnostic graph of conversion for proposed model



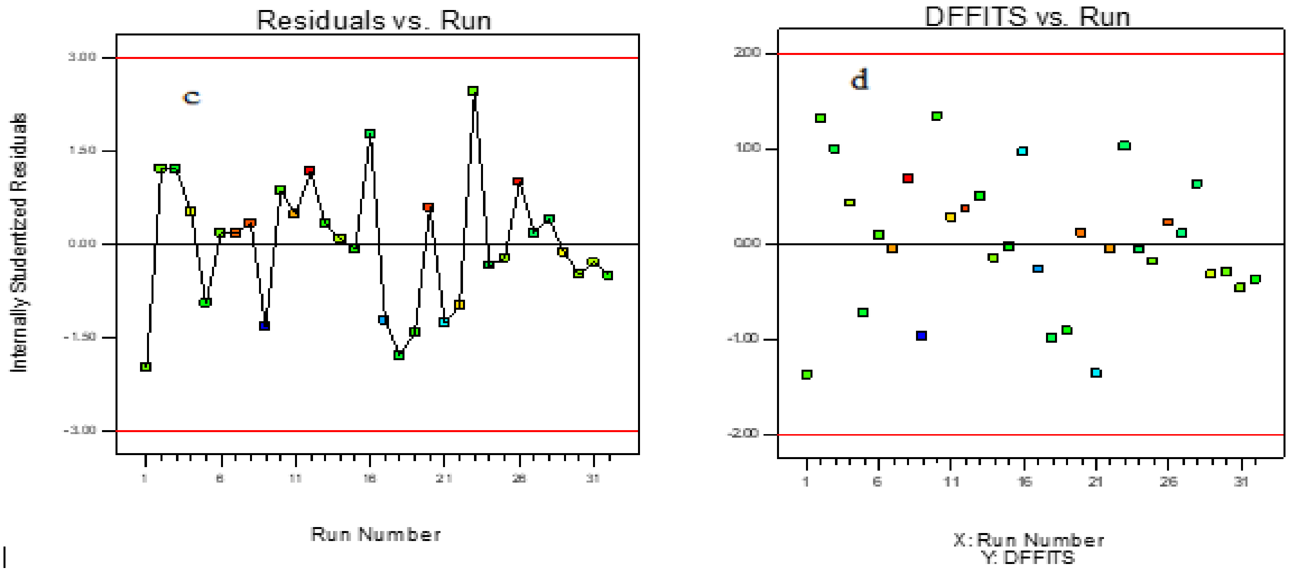


Figure 4-5 Diagnostic graph of conversion for proposed model

The Normal probability plot assumption of regression models, an error was normally distributed with a mean of zero. In figure 4-4 (a) and 4-5 (a), the normal probability plot of residual shows the data are distributed normally along center as they lie reasonably close to the straight line and shows no deviation of the variance for conversion and oxirane oxygen content.

As shown in Figure 4-4 (b) and 4-5 (b) the predicted values obtained from the developed model were quite close to the experimental data and lie reasonably close to the straight line and indicated the adequate agreement with actual data.

Internally studentized residuals plot (predicted vs run number) was plotted to justify the satisfactory fit of the developed model and the plot (Figure 4-4 c, 4-5 c) shows that all the data points lie within the limits (±3). The internally studentized residuals plot have no structured shape for both conversion and oxirane oxygen content. This shows the experimental data are reasonable fitted with the empirical model and conducted arbitrarily.

As shown in figure 4-4 (d) and 4-5 (d), there is no data out of the range in both graph for conversion and oxirane oxygen content respectively. The data are out of the outlier means bad experiments and it should be done again, if it is within the outlier/range the data are good, it is not necessary to repeat again. So, the statistics analysis of the model based on normal probability plot predicted versus actual plot, Outlier, and residual graph shape the model is satisfy the requirement to check model adequacy.

4.4.3. Effect of Variables on Conversion

The epoxidation reaction of cottonseed oil catalyzed by sulfonated solid acid catalyst was examined in different reaction temperature, time, and hydrogen peroxide to oil molar ratio. The effect of variables to the conversion response is given in figure 4-6 up to figure 4-10.

A) Effect of Temperature

As shown in figure 4-6 at constant reaction time and hydrogen peroxide to oil ratio the effect of different reaction temperature on epoxidation reaction of cottonseed oil in terms of conversion is increased as the temperature increased. The graph shows as the temperature increased from 45 ^{o}C to 75 ^{o}C the conversion also increased from 45 % to 67 %. As temperature increased from 45 ^{o}C to 60 ^{o}C and 60 ^{o}C to 75 ^{o}C the conversion increase by 27 % and 7.5 % respectively. In theoretical as temperature increased the conversion of double bond mostly increased. According Cai et al., Petrovic et al., and Vijay, et al. studies result, as the temperature increased conversion of double bond also increased (Cai et al., 2008; Petrovic et al., 2002 andVijay, et al., 2015). The rate of conversion is higher at lower temperature (45 to 60 ^{o}C) but following that temperature (60 to 75 ^{o}C) the rate of conversion was decreased. Because at lower temperature rate of conversion increased rapidly to consume the reactant and then it becomes slow due to completion of reactant. From the result, temperature has a highly significant effect on the conversion of double bond and to facilitate reaction rate.

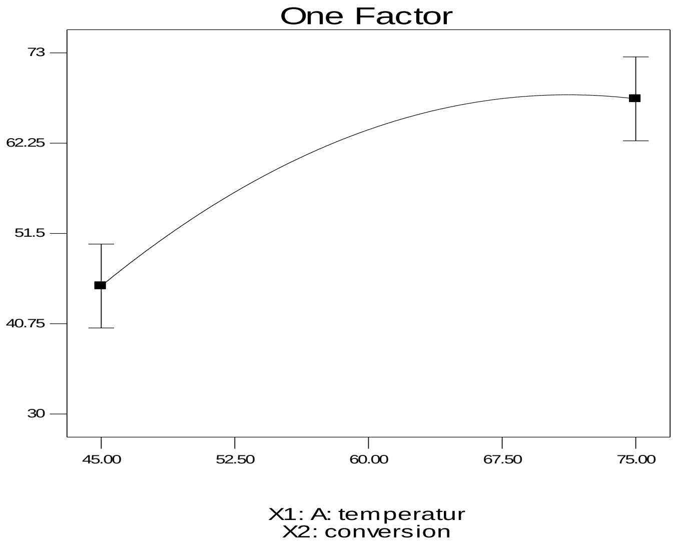


Figure 4-6 The effect of temperature for conversion

B) Effect of Time

Figure 4-7 shows that at certain reaction temperature and hydrogen peroxide to oil ratio the effect of different reaction time on epoxidation reaction of cottonseed oil in terms of conversion was increased linearly, and shows the time has a positive effect on conversion. As time increase the conversion also increased but the rate of the reaction has not visible change. This implies in epoxidation reaction using heterogeneous catalyst needs more time to complete the reaction. According to (Milchert, et al., 2016) study on "Technological aspects of vegetable oils epoxidation in the presence of ion exchange resins" as time increased the conversion also increased. From the graph, time has a significant effect on the conversion of double bond during the reaction.

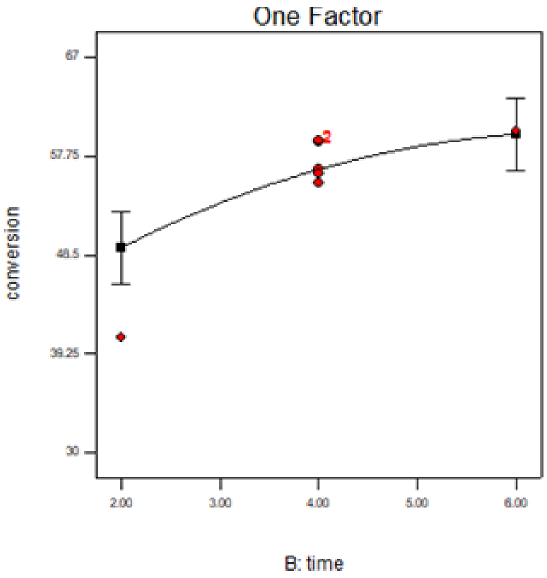


Figure 4-7 The effect of reaction time for conversion

C) Effect of Hydrogen Peroxide to Oil Ratio

The effect of hydrogen peroxide to oil ratio on conversion is depicted in figure 4-8. The graph shows at given reaction temperature and reaction time, the effect of different hydrogen peroxide to oil molar ratio on epoxidation reaction of cottonseed oil, the conversion was increased as the hydrogen peroxide to oil ratio increased linearly. The graph shows H_2O_2/oil molar ratio increased from 1:1 to 2.5:1 and the conversion increased from 44 to 62 %. As H_2O_2/oil molar ratio increased from 1:1 to 2:1 mol/mol and 2:1 to 2.5:1 mol/mol the conversion increase by 18% and 6% respectively. Mostly the graph shows conversion increased as increaseing of H_2O_2/oil molar ratio and the result was related with researchers finding by Dinda et al., Mungroo et al., and Mohamed et al., (Dinda et al., 2008; Mungroo et al., 2008 and Mohamed et al., 2007).

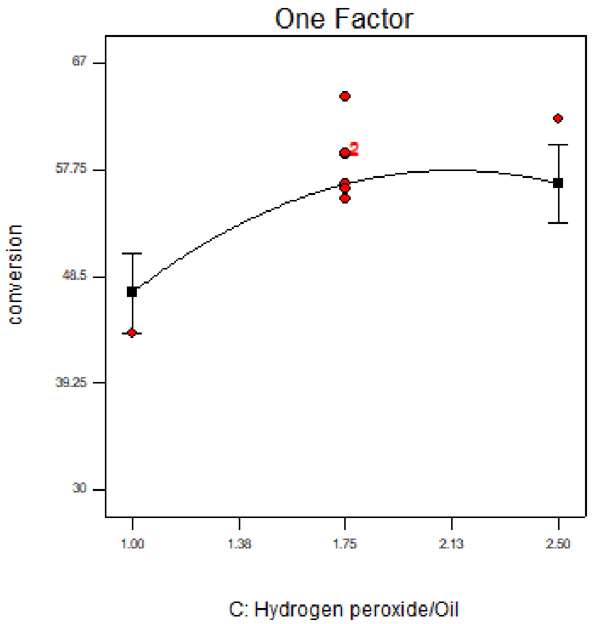


Figure 4-8 Effect of hydrogen peroxide to oil ratio for conversion

D) Effect of Time and Hydrogen Peroxide to Oil Ratio

The interaction effect of all variables was presented in the response model of conversion and they affects the conversion response positively. Among these interacting variables, the interaction between time and hydrogen peroxide to oil ratio has a significant effect on response model of conversion (see Table 4-7).

The result indicates that the conversion of double bond in cottonseed oil (CSO) increases linearly with the rise of reaction time and hydrogen peroxide to oil ratio, and at a faster rate with H_2O_2/oil ratio than with reaction time (see figure 4-10). As shown in figure 4-10, the conversion was increased with increasing of time and hydrogen peroxide to oil ratio. For more justification, see 3D model of this interaction on figure 4-10.

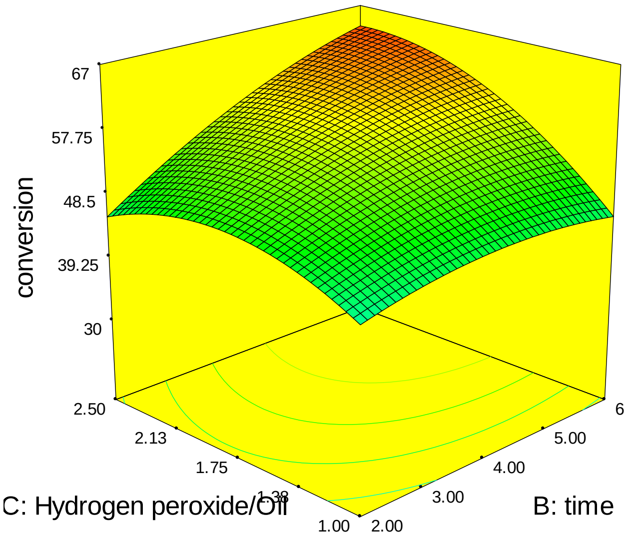


Figure 4-9: The interaction effect between time and hydrogen peroxide to oil ratio

Unsaturated double bonds present in the oil are converted through the epoxidation reaction as indicated the decreasing in the iodine value. This value in the CSO represents the concentration of double bonds and it decreases with reaction time (Mungroo et al., 2008). Therefore, the conversion increases with reaction time, temperature, and H_2O_2/oil molar ratio. The present research work result is also consistent for epoxidation of cottonseed oil using homogeneous catalyst with Dinda et al. (2008) who also reported a similar result.

4.4.4. Effect of Variables on Oxirane Oxygen Content

The epoxidation reaction of cottonseed oil catalyzed by sulfonated solid acid catalyst was examined in different reaction temperature, time, and hydrogen peroxide to oil ratio in terms of OOC. The effect of these variables to the Oxirane oxygen content are given in figure 4-10 up to figure 4-14.

A) Effect of Temperature

At constant reaction time and hydrogen peroxide to oil ratio, the effect of different reaction temperature on epoxidation of cottonseed oil in terms of oxirane oxygen content was shown in figure 4-10, the OOC is increase smoothly up to 67.5 ^{o}C temperature and after following the temperature OOC becomes decreasing almost parabolically. The graph shows that the stability of oxirane oxygen content was decreased as temperature further increased above 67.5 ^{o}C. According to Dinda, et al., (2008) and Goud, et al., (2006) were studied on “epoxidation of cottonseed oil” and “epoxidation of mahua oil” respectively using homogeneous catalyst and they report the OOC was stably up to 60 ^{o}C temperature. According to Silva et al., (2017) was studied on “Production of Catalyst to Vegetable Oil Epoxidation from Toxic Biomass Residue” and report the stability of OOC was up to 70 ^{o}C (Silva et al., 2017). This indicates that an increase in temperature not only increased the epoxidation rate but also increased the rate of oxirane cleavage of the product. Reaction at lower temperatures gave lower epoxidation rate but directed to minor ring opening.

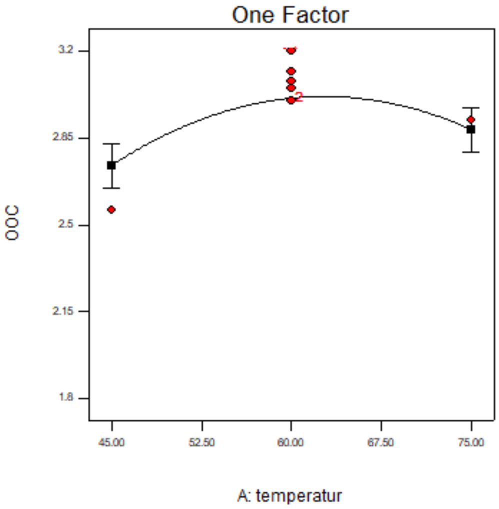


Figure 4-10 effect of temperature on Oxirane oxygen content

B) Effect of Time

Figure 4.11 shows that at given reaction temperature and hydrogen peroxide to oil molar ratio, the effect of different time on epoxidation reaction of cottonseed oil in terms of oxirane oxygen content was increased as the time increased, and after some time higher than 4:30hr the OOC become decreased. This was happened basically due to oxirane ring cleavage of further reaction forming other product like glycol, polyol, and other side reaction. Many researchers report that at optimal temperature, H_2O_2/oil molar ratio, and other parameter the time of epoxidation reaction must be less than 4hr using homogenous catalyst (Zhenyu et al., 2017). From the result shown in figure 4-11, time has a significant effect on the formation of oxirane oxygen content and stability of OOC.

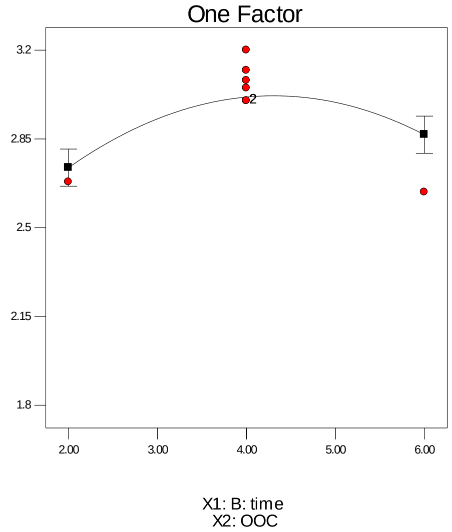


Figure 4-11 Effect of reaction time for oxirane oxygen content

C) Effect of Hydrogen Peroxide to Oil Ratio

In figure 4-12 the effect of H_2O_2/Oil ratio for OOC was given. The graph shows as the H_2O_2/oil molar ratio increased from 1:1 to 2.5:1 the OOC also increased from 2.6 % to 2.8%. As H_2O_2/oil molar ratio increased from 1:1 to 2.2:1 and 2.2:1 to 2.5:1 the OOC increase by 13.3% and -6.6% respectively. H_2O_2/Oil molar ratio has positive effect for OOC formation up to 2:1 and following that the OOC become decreased from 3% to 2.8%. In theoretical aspect as ratio increased above 2:1 the stability of OOC was decreased and the formation of other products ahead of OOC may happened. The idea was tested by many researchers and report the same result with the graph shown in figure 4-12. Among the researchers the studies by Saurabh et al., (2012) and the studies by Dinda et al., (2008) the optimal stability of OOC was below 2:1 H_2O_2/oil molar ratio in the present of homogeneous catalyst.

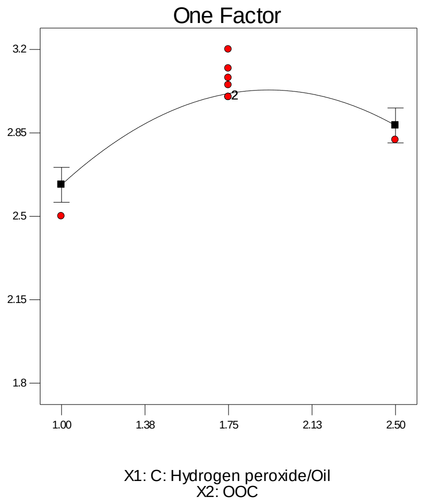


Figure 4-12 Effect of hydrogen peroxide to oil ratio

D) Effect of Reaction Temperature and Time

The interaction effect of all variables was presented in the response model of oxirane oxygen content (OOC). Among these interacting variables, the interaction between reaction time and temperature has a significant effect on oxirane oxygen content response (see Table 4-8). The graph in figure 4-13 has a shape of concaved downward (means maximum at the center and minimum at the end). As shown in figure 4-13 the amount of oxirane oxygen content (OOC) increased as reaction time and temperature increased and then that value reaches the maximal level. Following the maximal level, the oxirane oxygen content decreases with reaction time and temperature increase.

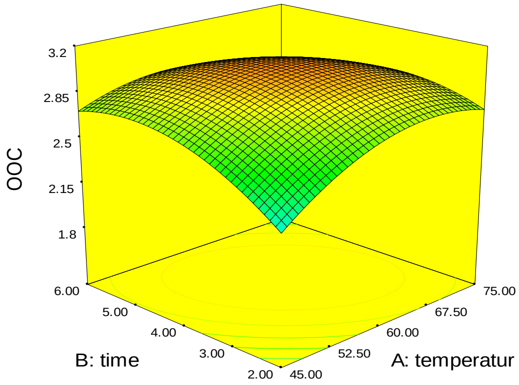


Figure 4-13 3D interaction effect of reaction time and temperature for OOC

4.5. Optimum Value for Oxirane Oxygen Content

The results in previous section shows that the three epoxidation process variables (the reaction temperature, reaction time, hydrogen peroxide to oil ratio) and one interaction among the variables affect the oxirane oxygen content (OOC). Therefore, the next step is to optimize the process variables (interaction between reaction temperature and reaction time) in order to obtain the optimal oxirane oxygen content using the model regression developed at Eq.C-2. This function searches for combination of independent parameter levels that simultaneously satisfy the requirement for response in the design. The optimal value of oxirane oxygen content was determined by using design expert software, in the software, there are many options of optimization choices. Among the optimization choices option using Numerical optimization by setting goals for each response then click on the solution to generate optimal condition. Based on this procedure the predicted value of the three factors are reaction temperature 62.46 ^{o}C, reaction time 4.23 hr, and hydrogen peroxide to oil ratio 1.91:1 with disirability 87% (Table C-8 and figure4-14). Standing on this result the software gives 3.03 % of oxirane oxygen content with 59.08 % of conversion.

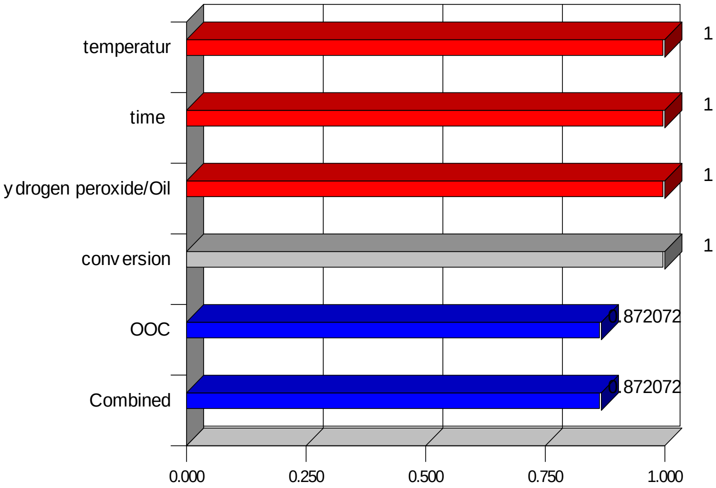


Figure 4-14 Desirability bar graph

To validate (see Appendix C Table C-9) the optimum conditions predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized epoxidation process conditions and mean percentage oxirane oxygen content value of 2.9 % was obtained and the results are closely related with the data obtained from optimization analysis using desirability functions. The results are closely related with the data obtained from optimization analysis using desirability functions (within the error less than 5%), indicated by optimization choices incorporate with desirability function could be effectively used to optimize the parameters that affect oxirane oxygen content. At higher reaction time, temperature and H_2O_2/oil, the results in lower oxirane oxygen content. This is a result of a higher temperature of epoxidation reaction favoring a high rate of oxirane ring opening thereby producing a product with reduced oxirane content (Dinda et al., 2008). Therefore, higher side reaction products may be formed above the optimal temperature such as reaction between oxirane rings and acetic acid or water and a dimerization reaction may occur (Purwanto, 2010, Milchert, et al., 2016). These findings are also consistent with those of Dinda et al. (2008) who found at higher temperature (higher than 60^oC) the relative conversion to oxirane increased to an optimal operating point and then declined gradually in the epoxidation of cottonseed oil using homogeneous catalyst.

4.6. Physicochemical Property of Epoxidized Cottonseed Oil

The physicochemical property of epoxidized oil was determined using the procedure mentioned on section 3.6.3.1 and the result is given (Table 4-9).

Table 4-10 Physicochemical property of epoxidized oil at optimal condition

Characteristics	Value
Density	920.7 kg/m3
Specific gravity	0.922
Kinematic viscosity	$1.23*10^5$ m2/s
Iodine value	32.4 gram/100 gram of I_2
Conversion	59.1 %
Oxirane oxygen content	2.9 %

Note: - For the detail see Appendix B.

The result given at Table 4-9 was agree with the study conducted by Tayde et al., (2015) and Dinda et al., (2008).

4.6.1. FT-IR for Epoxidized Cottonseed Oil

Based on the method mentioned on section 3.5.2 and section 3.6.6 for cottonseed oil and epoxy oil the FT-IR result was recorded respectively. The FT-IR spectra of cottonseed oil and epoxidized cottonseed oil are shown in following figure 4-15 and 4-16. From these figures, it is clear that the peak related to carbon-carbon double bonds from cottonseed oil at 3010 cm-1 disappeared on epoxidation and the epoxy groups were found in epoxidized cottonseed oil indicating that all of the carbon-carbon double bonds were turn into epoxy groups. Vleck and Petrovic (Vlček & Petrović, 2006) reported the presence of epoxy groups at 822-833 cm^{-1}, which agrees well with this study. Following Figure 4-15 and figure 4-16 shows the FTIR spectra of cottonseed oil & epoxidized cottonseed oil given respectively.

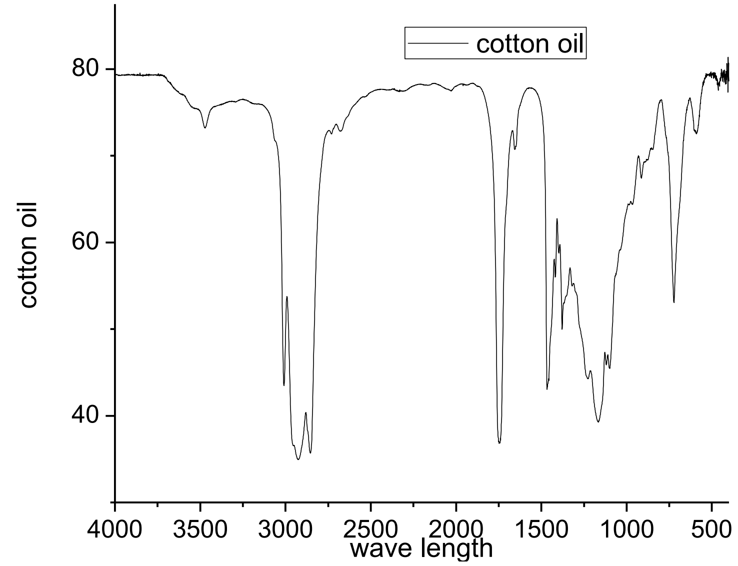


Figure 4-15 FT-IR result of cottonseed oil

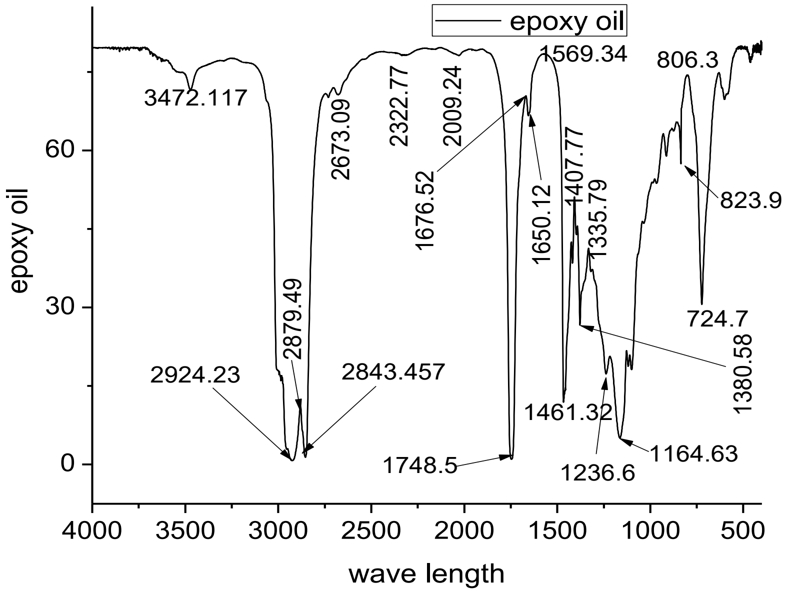


Figure 4-16 FT-IR result of epoxidized cottonseed oil

4.7. Epoxidation Reaction Kinetic

4.7.1. Pseudo-First Order kinetics

The epoxidation reaction kinetics were mentioned in the literature review at section 2.3.1. If it is assumed that the reaction is pseudo-first order with respect to double bonds, the rate equation for the pseudo-first order can be expressed as:

$-\frac{d[DB]}{dt} = K[DB]$………………………………………………………………………. Eq. 4-1

Where: $K = K3[PAA]^{n2}$

According to reaction engineering concept: the double bond of oil can be expressed by using conversion (X_{DB}) (Levenspiel, 1999). That is:

$[DB] = [DB_0](1 - X_{DB})$……………………………………………………………...Eq. 4-2

Where: $[\mathrm{DB_0}] = \text{initial concentration of double bond}$

$\mathrm{X_{DB}} = \text{conversion of double bond}$

The integrated value of Eq. 4-1 was expressed as the following pseudo-first order equation given in Eq. 4-3

$\ln(1 - \mathrm{X_{DB}}) = -\mathrm{K}[\mathrm{DB_0}] * \mathrm{t}$…………………………………………………………Eq. 4-3

Using Eq. 4-3, and the data given in Appendix D at Table: D-1; The Plots of time versus $\ln(1 - \mathrm{X_{DB}})$ for in situ epoxidation of cottonseed oil at different temperatures are shown in Figure 4-17. The rate constants values obtained for the reactions were $5.09 * 10^{-2}\mathrm{l^2 mol^{-2}. s^{-1}}$, $8.025 * 10^{-2}\mathrm{l^2 mol^{-2}}. s^{-1}$, and $8.753 * 10^{-2}\mathrm{l^2 mol^{-2}}. s^{-1}$ at 45 ºC, 60 ºC, and 75 ºC of the respectively temperature for pseudo-first order reaction. As shown in figure 4-17, and Table 4-11 the rate constant was increased as temperature increased and this shows that the conversion of cottonseed oil is increased as temperature increased. This phenomena is agree with the values reported for cottonseed oil (Dinda et al., 2008) and mahua oil (Goud et al., 2006). Table 4-11 also shows fitting statues of linear fitting line to the first order curve (drawn by experimental data) with Adjusted R-square value 81.7 %, 84.6%, and 85.7% for pseudo-first order at 45 ºC, 60 ºC, and 75 ºC respectively. The adj. R square value indicates how much the linear line represent the experimental reaction curve.

Table 4-11 Statistical analysis summary for pseudo first order kinetics data

Temperature (ºC)	Slope	Adj. R-Square	K ($\frac{l}{mol.s}$)	K3 ($l^2 mol^{-2}. s^{-1}$)

45	-0.10133	0.81661	$5.19 * 10^{-2}$	$5.09 * 10^{-2}$
60	-0.15973	0.8464	$8.191 * 10^{-2}$	$8.025 * 10^{-2}$
75	-0.17422	0.85665	$8.934 * 10^{-2}$	$8.753 * 10^{-2}$

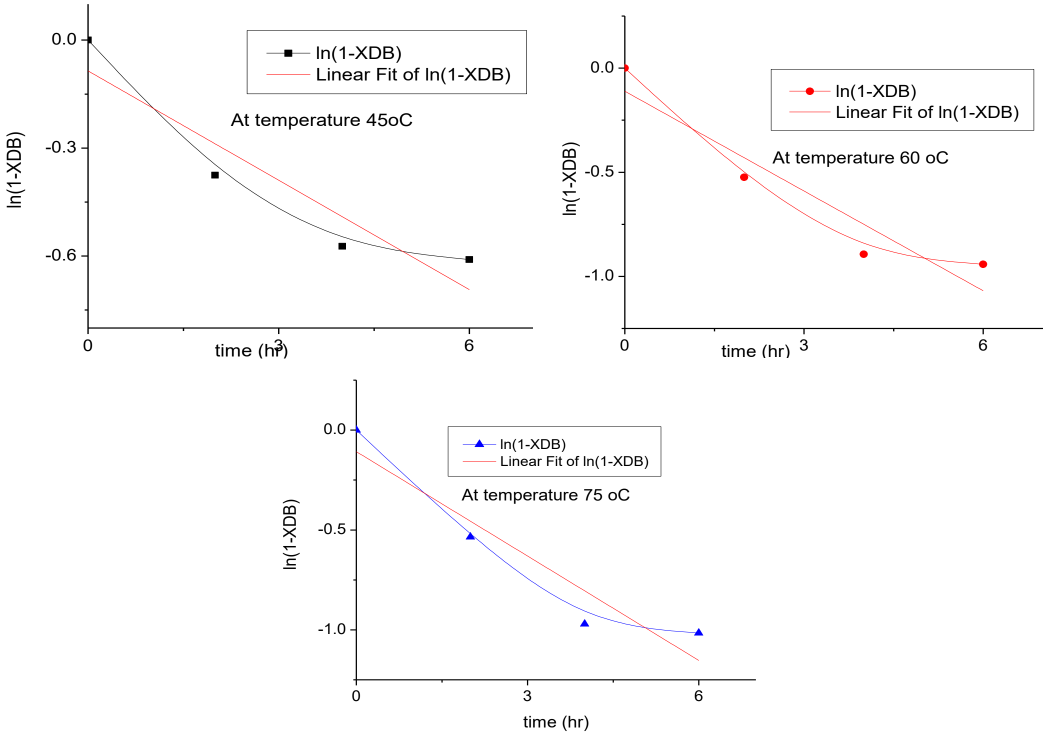


Figure 4-17 Kinetics graph (Time vs ln(1-XBD)) at different temperature

Activation energy for the in-situ epoxidation of cottonseed oil was calculated from the slope of the Arrhenius plot. The Arrhenius plot shown in Figure 4-18 gives an activation energy 16.8 kJ mol^{-1} (a slope -2020.63 and intercept 30.82) for cottonseed epoxidation over sulfonated solid acid catalyst. This apparent activation energy is close to that reported by Coud et al. (Coud et al., 2006) and Goud, et al. (Goud et al., 2006).

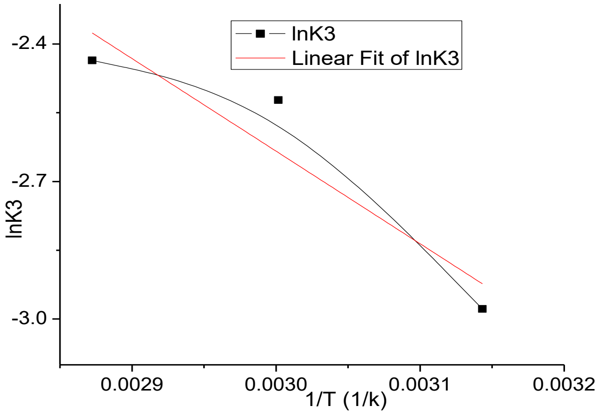


Figure 4-18 Arrhenius plot for epoxidation of cottonseed oil for pseudo-first order kinetics

4.7.2. Pseudo-Second Order Kinetics

If it is assumed that the reaction is pseudo-second order with respect to double bonds, the rate equation for the pseudo-first order can be expressed as:

$-\frac{d[DB]}{dt} = K[DB]^2$………………………………………………………………… Eq. 4-4

Where: $K = K3[PAA]^{n2}, n2 = 1$

$-\frac{d[DB]}{dt} = K[DB_0]\hat{}2(1 - X_{DB})\hat{}2$ ……………………………………………….......Eq. 4-5

The integrated value of Eq. 4-5 pseudo-second order was expressed as the following equation given in Eq. 4-6

$\frac{X_{DB}}{1-X_{DB}} = K[DB_0]\hat{}2 * t$………………………………………………………………… Eq. 4-6

Using Eq. 4-6, and the data given in Appendix D at Table: D-1; The Plots of time versus $X\_DB/(1 - X\_DB\ )$ for in situ epoxidation of cottonseed oil at different temperatures are shown in Figure 4-19. For pseudo-second order reaction, the rate constant was $3.79 * 10^{-2}$, $7.00 * 10^{-2}$ and $8.01 * 10^{-2} l^2 mol^{-3}.s^{-1}$ at 45, 60, and 75°C of temperature respectively. As shown in figure 4-19, and Table 4-12 the rate constant was increased as temperature increased and this shows that the conversion of cottonseed oil is increased as temperature increased. This phenomenon was agreed with the values reported in pseudo-first order kinetics. Table 4-12 also shows fitting statues of linear fitting line to the second order curve (drawn by experimental data) with Adjusted R-square value 89.9 %, 90.01%, and 89.99% for pseudo-second order at 45 °C, 60 °C, and 75 °C respectively. The adj. R square value indicates how much the linear line represent the experimental reaction curve.

Table 4-12 Statistical analysis summary for kinetics data on second order

Temperature (°C)	Slope	Adj. R-Square	K $(1/(mol^2.s))$	K3 $(l^2mol^{-3}.s^{-1})$
45	0.147	0.89974	$3.86 * 10^{-2}$	$3.79 * 10^{-2}$
60	0.272	0.90003	$7.15 * 10^{-2}$	$7.00 * 10^{-2}$
75	0.311	0.89938	$8.18 * 10^{-2}$	$8.01 * 10^{-2}$

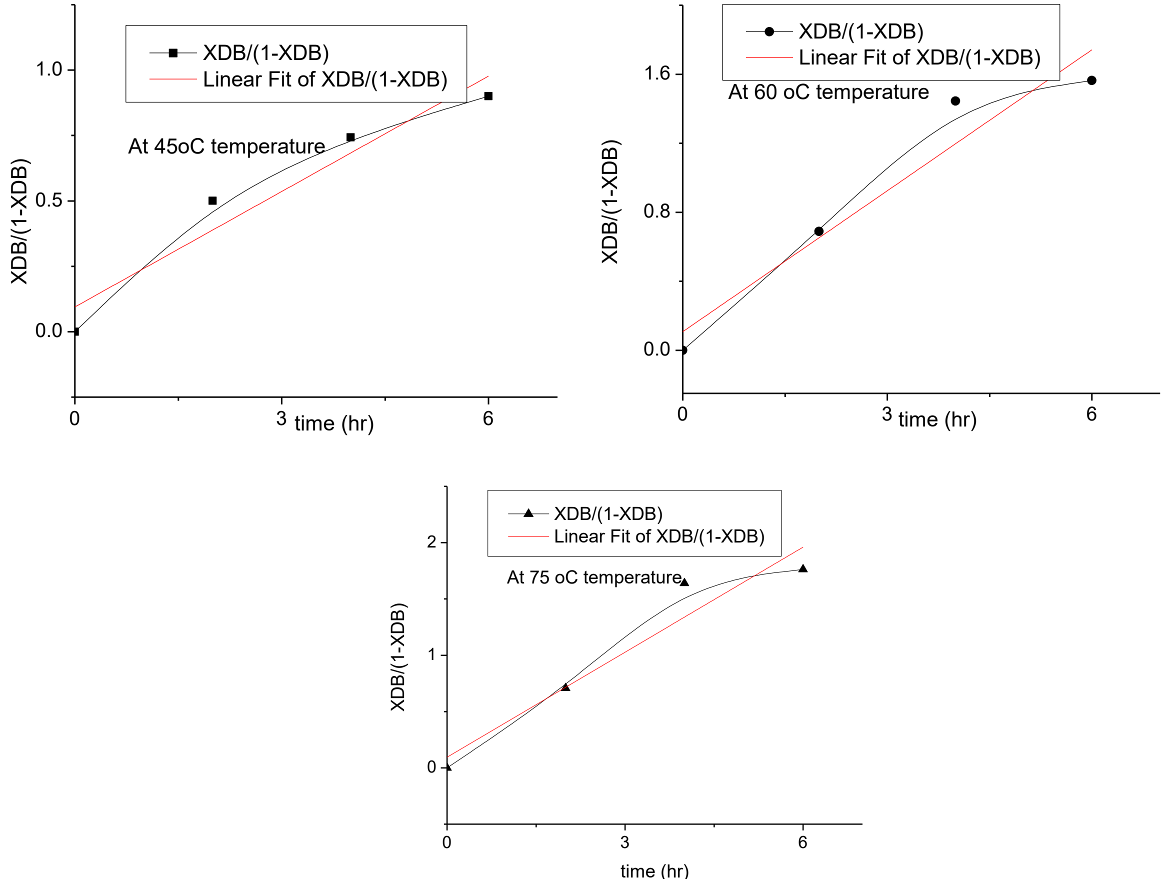


Figure 4-19 pseudo-second order kinetics graph at different temperature

The Arrhenius plot shown in Figure 4-20 gives an activation energy 23.209 kJ mol^{-1} (a slope -2791.526 and intercept 6.24) with Adj R-square 0.79101 for cottonseed epoxidation over sulfonated solid acid catalyst. This apparent activation energy is close to that reported in pseudo-first order kinetics.

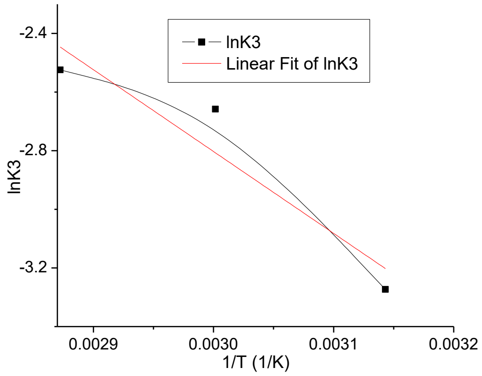


Figure 4-20 Arrhenius plot for epoxidation of cottonseed oil for second order kinetics

Based on the value of Adj. R-square rate constants the pseudo-second order kinetics fitting line is better than the pseudo-first order kinetics. The rate constant of the two reaction kinetics are almost similar but the activation energy of those are different.

5. Conclusion and Recommendation

5.1. Conclusion

In this research work, synthesization of sulphonated solid acid catalyst was carried out at 500 ^oC pyrolysis temperature for 3hr followed by Sulfonation process. The synthesized catalyst was characterized physically and chemically using bulk density (358.0 gram/litter), acid value (total acid = 3.8 mmol/g and -SO3 = 2.8 mmol/g), elemental analysis (NCHS = 0.725, 74.01, 1.74, and 3.27 %respectively), FT-IR, and TGA. This character was excellent property for heterogeneous catalyst and more comparable with commercialized ion exchange and metal catalyst heterogeneous catalysts. The cottonseed oil physicochemical property was characterized using acid value, iodine value, kinematic viscosity, specific gravity, FT-IR, and GC/MS.

The epoxidation of cottonseed oil using *in situ* generated peroxyacid could be carried out in the presents of sulfonated solid acid catalyst. Acetic acid (CH3COOH) and hydrogen peroxide was used as oxygen carrier and oxygen donor in this work respectively. Higher temperature and higher hydrogen peroxide molar ratio reduced the reaction time needed to reach the maximum conversion to oxirane value. however, it simultaneously increased the extent of oxirane ring cleavage to other product. The rate constants obtained for the reaction were in the range of $5.09 - 8.753 * 10^{-2}\ l^2/mol^2 s$ and $3.79 * 10^{-2} - 8.01 * 10^{-2} l^2/mol^3 s$; the activation energy also $16.8\ kJ/mol$ and 23.2 kJ/mol for pseudo first order and pseudo second order respectively. It could be concluded that it is possible to develop value–added products from a locally available renewable natural resource such as cottonseed oil and environmental friendly heterogeneous catalyst. Maximum value of oxirane oxygen content could be obtained if the epoxidation of cottonseed oil, using *in situ* generated peroxyacetic acid, is carried out at optimum conditions. These optimum conditions include a temperature range of 60-70 ^oC, H_2O_2 to-unsaturation mole ratio range 1.75–2.0, CH3COOH to unsaturation mole ratio of about 0.5 and sulfonated solid acid catalyst loading of about 10% (weight by weight) of the cottonseed oil.

This sulfonated catalyst was good for epoxidation reaction having 3.03% optimal oxirane oxygen content and also it was easy to separate from the product using centrifugal separation. So, the catalyst can be used as green chemistry approaches to produce epoxy oil from vegetable oils. 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. Recommendation

The work is recommended that further research be undertaken in the following areas:

- ✓ Production of carbonized material at different temperature and time from different biomass by using efficient and effective pyrolizer.
- ✓ Different chemicals may be used for sulfonation process other than sulfuric acid like Oleum.
- ✓ The specific surface area and morphology of sulfonated solid acid catalyst further analysis should be required.
- ✓ Studying of epoxidation reaction kinetic including mass transfer parameters in the reaction kinetics.
- ✓ Investigate other factors that influence in the epoxidation reaction such as mole ratio of acetic acid to oil (oxygen carrier to oil), stirring speed, catalyst loading to achieve a high content of epoxy groups in the epoxidized oil.
- ✓ Investigate the performance of the catalyst, use different vegetable oil for production of epoxidized oil.

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Appendix A Proximity Analysis

The Proximate Analysis of the bamboo was done by the average measurement (triplicate) of each analysis.

a) Moisture content

Table A-1 data recorded for moisture content of bamboo sawdust

Drying condition	weight of sample (gram)		
	W1	W2	W3
Before drying	1.994	2.004	2.014
After drying	1.9107	1.903	1.928

$$\text{Moisture content (\%)} = \frac{\mathrm{W_{before}} - \mathrm{W_{after}}}{\mathrm{W_{before}}}$$

Where: $\mathrm{W_{before}}$ = mass of bamboo sawdust before drying

$\mathrm{W_{after}}$ = mass of bamboo sawdust after drying

$$\text{The average mass of bamboo sawdust before drying} = \frac{1.994 + 2.004 + 2.014}{3}$$

$$= 2.0046 \text{ gram}$$

$$\text{Average mass of bamboo saw dust after drying} = \frac{1.9107 + 1.9039 + 1.928}{3}$$

$$= 1.9142 \text{ gram}$$

$$\text{Moisture content (\%)} = \frac{2.0046 - 1.9142}{2.0046} * 100$$

$$= 4.509\%$$

Volatile matter of bamboo

The volatility of bio-mass be determined by using ASTM D1762 – 84 (2007) at 950 ^{O}C for five minutes.

$$\text{volatility of bamboo saw dust} = \frac{\mathrm{W_{after}} - \mathrm{W_{burned}}}{\mathrm{W_{after}}}$$

Where: $\mathrm{W_{after}}$ = Average mass of bamboo saw dust after drying

$\mathrm{W_{burned}}$ = average mass of bamboo saw dust after burned@950^{o}C

$$= \frac{1.91 - 0.313}{1.91} = 0.83$$

$$\text{volatility } (\%) = 83\ \%$$

Ash content determination using ASTM D1762 – 84 (2007) at a temperature of 550°C for 6 hr.

$$\text{Ash content}(\%) = \frac{(1.35 + 1.46 + 1.07)}{3}$$

$$= 1.29\%$$

The fixed carbon content of bamboo saw dust

$$\text{Carbon content}(\%) = 100 - \text{volatile content} - \text{Ash content}$$

$$= 100 - 83 - 1.29$$

$$= 15.71\%$$

A-2 Yield of Biochar Calculation

To calculate yield, use this equation. $\text{yield} = \frac{\text{final value}}{\text{initial value}}$ based on this equation the Table below was complete.

Table **A-2** yield of biochar and recorded value for to determine biochar

Sample Weight			
Before pyrolysis	After pyrolysis	Difference	Percent
40 g	9.3 g	30.7	23.25
40 g	7.8 g	32.2	19.5
50 g	12.4 g	37.6	24.8
50 g	12 g	38	24
Average	10.375	34.625	<u>22.89</u>

A-3 Bulk Density of Biochar and Sulphonated carbon catalyst

$$\text{Bulk Density of biochar} = \frac{\text{Mass of biochar}}{\text{volume of biochar}}$$

$$= \frac{0.661\text{gram}}{2.5\text{ml}}$$

$$= 264.4\text{gram/litter}$$

The bulk density of the sulfonated carbon catalyst prepared from biochar was measured by using graduate measuring cylinder and density meter.

$$\text{Bulk Density of sulphonated carbon catalyst} = \frac{\text{Mass of sulphonated carbon catalyst}}{\text{volume of sulphonated carbon catalyst}}$$

$$= \frac{0.895\text{gram}}{2.5\text{ml}} = 358.0\ \text{gram/litter}$$

Table **A-2**. Data used for total acid density determination

	Solution	Amount
Sulfonated carbon catalyst	NaOH	25 ml
	HCl	5.9 ml
		5.6 ml
		5.3 ml
	Average HCl	5.6 ml
	Mass of catalyst	0.05 g
Carbon-char/Biochar	NaOH	25 ml
	HCl (Average)	20.9 ml
	Mass of biochar	0.05 g
Indicator colour change	Pink to colour less	

$$\text{Total acid density of carbon char} = (2.5 \times 10^{-4} - 2.09 \times 10^{-4})\text{mole}$$

$$= 0.41 \times 10^{-4}\text{mole or } 0.041\ \text{mmole}$$

$$\text{total acid density of biochar per gram of char} = \frac{0.041\ \text{mmole}}{0.05\ \text{gram}}$$

$$= \frac{0.82\ \text{mmole}}{\text{gram of biochar}}$$

$$\text{Total acid density of sulphonated carbon catalyst} = (2.5 \times 10^{-4} - 5.6 \times 10^{-5})\text{mole}$$

$$= 1.94 \times 10^{-4}\text{mole or } 0.194\text{mmole}$$

$$\text{total acid density of catalyst per gram of catalyst} = \frac{0.194\ \text{mmole}}{0.05\ \text{gram}}$$

$$= \frac{3.8\ \text{mmole}}{\text{gram of catalyst}}$$

Appendix-B Calculation for Characterization of cottonseed oil and Epoxy oil

Moisture content of oil

Table B-1 Weight value for moisture content of oil

Weight of oil	Weight at 0 hr. (W_o)	Weight at 2 hr.	Weight at 4 hr.	Weight at 8 hr.
Sample 1	3.04	3.03	3.03	3.03
Sample 2	3.02	3.01	3.01	3.01
Sample 3	3.15	3.14	3.14	3.14
Average	3.07	3.06	3.06	3.06

$$\text{Moisture content of oil}(\%) = \frac{W_{oavg} - W_{8\ avg}}{W_{oavg}} * 100$$

$$= \frac{3.07 - 3.06}{3.07} * 100$$

$$= 0.33\ \%$$

Specific gravity of cottonseed oil

$$\text{specific gravity} = \frac{\text{density of the oil}}{\text{density of water}}$$

Note: - The density of water @20°C was 998.4 kg/m3 when it measured using density meter DMA4100M**.**

Density of cottonseed oil is 918.9 kg/m^3 at 19.98 °C by using density meter DMA4100M. Then specific gravity@19.98 oC $= \frac{918.9}{998.4} = 0.92$

Specific gravity of epoxidized cottonseed oil

Density of epoxidized cottonseed oil is 920.7 kg/m^3 at 20.01 °C by using density meter DMA4100M.

$$\text{specific gravity} = \frac{\text{density of the epoxy oil}}{\text{density of water}}$$

$$= \frac{920.1}{998.4} = 0.922$$

Dynamic viscosity of cottonseed oil is 61.6 mPa s at temperature of 21.6 °C

$$\text{kinematic viscosity} = \frac{\text{dynamic viscosity}}{\text{density}}$$

$$= \frac{61.6\text{Mpa.s}}{918.9\text{kg/m3}} = 6.7 * 10^4 \frac{\text{m}^2}{\text{s}}$$

Dynamic viscosity of epoxidized cottonseed oil is 113.2 mPa s at temperature of 20.6 ^{o}C

$$\text{kinematic viscosity} = \frac{\text{dynamic viscosity}}{\text{density}}$$

$$= \frac{113.2\text{ mPa s}}{920.7\text{kg/m3}} = 1.23 * 10^5 \frac{\text{m}^2}{\text{s}}$$

Acid Value for Cottonseed Oil

$$\text{Acid value(AV)} = \frac{56.1 * \text{V} * \text{C}}{\text{m}}$$

$$\text{Acid value}_{\text{oil}} = 3.086\text{ mol/gram}$$

Table **B-2** Iodine value of cottonseed oil is given in section 3.6.5.

Sample type	Volume of titrant (average value)	Volume of Wiji's (ICl) solution	KI solution (15%)	Mass of sample	Color change
Blank	40.8 ml	25 ml	20 ml	0	Dark blue to colorless
Cottonseed oil in Wiji solution	26 ml	25 ml	20ml	0.230 g	Dark blue to colorless

Iodine number determination for the cottonseed oil

Table **B-3** Data used to determine iodine value for cottonseed oil

Solution type	Weight (g)	Volume (ml)	Indicator	Colour change
Without sample (Blank)	0	40.8	Starch	Dark pink to colorless
With sample	0.23	26.0	Starch	Dark pink to colorless

$\text{Iodine number} = \frac{12.69(\text{V}^0 - \text{V})}{\text{W}} * \text{N}$ ……………………………………………………...Eq. 3-13

Where: - V^0 = the ml of 0.1N thiosulphate required for the blank determination

V = the ml of 0.1N thiosulphate required for the titration

N = normality sodium thiosulphate

W = the weight of oil used in the test.

$$= \frac{(40.8 - 26.0) * 0.1 * 12.69}{0.23} = 81.66$$

Appendix C Experimental Data and Statistical Result

The iodine value for each run was determined by using the data in Table C-1 and equation 3-13

Table C-1 weight of sample and consumed volume for determination of iodine value

std	Weight of oil (g)	titrant volume (ml)	iodine value (g/100 g I_2)
1	0.20	32.7	51.5
2	0.21	33.1	46.4
3	0.24	31.9	46.9
4	0.20	31.9	56.5
5	0.19	33.9	46.1
6	0.22	31.9	51.0
7	0.20	32.1	55.1
8	0.23	32.8	44.4
9	0.21	34.0	40.7
10	0.24	31.7	47.9
11	0.20	33.2	48.3
12	0.20	33.9	43.6
13	0.21	32.4	50.6
14	0.20	35.5	33.4
15	0.23	35.1	31.7
16	0.20	33.6	45.5
17	0.19	35.9	32.6
18	0.22	34.1	38.4
19	0.20	32.6	52.1
20	0.21	32.9	47.8
21	0.23	32.2	47.5
22	0.26	29.9	53.3
23	0.24	34.9	30.9
24	0.25	34.6	31.7
25	0.18	34.5	44.5
26	0.19	36.4	29.6
27	0.22	36.0	27.4
28	0.21	34.8	36.5
29	0.20	35.2	35.4
30	0.18	36.6	29.3
31	0.20	35.2	35.8
32	0.22	35.0	33.3

Oxirane oxygen content of epoxidized cottonseed oil was determined using equation 3-15 and the recorded data in Table C-2.

$$\text{Oxirane Oxygen Content}(\text{OO}_{\text{exp}} \text{ or OOC}) = \frac{\text{V} * \text{n} * 1.6}{\text{w}_{\text{m}}}$$

V: consumed titrated solution

$\text{n: normalized value} = 0.1\ \text{eq/mol}$

w_{m}: used amount of epoxidized oil

Sample calculation step to generate the OOC value in Table C-3

$$\text{For \#std 1 OOC} = (4.5 * 0.1 * 1.6)/0.38$$

$$= 1.90$$

Based on this sample calculation all the other be calculated.

Table C-2 weight of sample and consumed volume for determination of OOC

Std	Weight of epoxy oil (g)	Volume (ml)	OOC (%)
1	0.38	4.5	1.90
2	0.40	6.2	2.48
3	0.42	5.8	2.20
4	0.41	6.2	2.40
5	0.42	6.6	2.50
6	0.39	5.9	2.43
7	0.37	5.6	2.42
8	0.40	6.4	2.54
9	0.43	6.0	2.22
10	0.44	6.7	2.43
11	0.38	6.4	2.68
12	0.41	7.1	2.78
13	0.45	7.2	2.56
14	0.40	7.5	3.00
15	0.43	7.8	2.92
16	0.39	6.6	2.69
17	0.39	6.4	2.64
18	0.42	6.5	2.46
19	0.43	5.6	2.10
20	0.41	6.5	2.55
21	0.43	7.1	2.64
22	0.44	7.0	2.54
23	0.41	7.2	2.82
24	0.40	6.8	2.72
25	0.42	6.9	2.64
26	0.39	6.6	2.72

27	0.45	7.3	2.60
28	0.43	8.6	3.20
29	0.41	7.9	3.08
30	0.38	7.1	3.00
31	0.37	7.1	3.05
32	0.39	7.6	3.12

Table C-3 Experimental result of epoxidation of cottonseed oil

Std	Run	Temperature (oC)	Time (hr.)	H2O2/Oil (mol/mol)	Conversion (%)	OCC (%)
17	1	60	6	1.75	60.10	2.64
25	2	45	6	2.50	45.52	2.64
2	3	60	2	1.00	43.23	2.48
12	4	75	2	1.75	46.56	2.78
5	5	60	4	1.00	43.60	2.50
21	6	75	2	2.50	41.80	2.64
14	7	60	4	1.75	59.10	3.00
28	8	60	4	1.75	55.27	3.20
1	9	45	2	1.00	36.90	1.90
27	10	75	6	2.50	66.40	2.60
15	11	75	4	1.75	61.20	2.92
32	12	60	4	1.75	59.20	3.12
8	13	60	6	1.00	45.65	2.54
26	14	60	6	2.50	63.80	2.72
22	15	45	4	2.50	34.70	2.54
9	16	75	6	1.00	50.20	2.22
19	17	45	2	2.50	36.20	2.10
18	18	75	6	1.75	52.96	2.46
13	19	45	4	1.75	38.00	2.56
31	20	60	4	1.75	56.10	3.05
3	21	75	2	1.00	42.60	2.20
30	22	60	4	1.75	64.14	3.00
10	23	45	2	1.75	41.37	2.43
6	24	75	4	1.00	37.52	2.43
16	25	45	6	1.75	44.31	2.69
29	26	60	4	1.75	56.60	3.08
4	27	45	4	1.00	30.87	2.40
7	28	45	6	1.00	32.50	2.42
23	29	60	4	2.50	62.12	2.82
11	30	60	2	1.75	40.80	2.68
24	31	75	4	2.50	61.20	2.72

20	32	60	2	2.50	41.42	2.55

Table C-4 Actual experimental data and predicted experimental data for conversion

Standard Order	Actual Value	Predicted Value	Residual
1	36.9	34.1068	2.793199
2	43.2	43.77341	-0.54341
3	42.6	38.50291	4.097088
4	30.9	34.56979	-3.69979
5	43.6	46.79806	-3.19806
6	37.5	44.08924	-6.56924
7	32.5	30.59902	1.900977
8	45.6	45.38896	0.261039
9	50.2	45.2418	4.958199
10	41.4	37.87618	3.493817
11	40.8	49.45362	-8.65362
12	46.6	46.09396	0.466039
13	38.0	42.56251	-4.56251
14	59.1	56.70161	2.398387
15	61.2	55.90362	5.29638
16	44.3	42.81507	1.494928
17	60.1	59.51584	0.584158
18	52.9	61.27952	-8.31952
19	36.2	31.84847	4.351532
20	41.4	45.33674	-3.91674
21	41.8	43.88791	-2.08791
22	34.7	40.75813	-6.05813
23	62.1	56.80806	5.311935
24	61.2	57.92091	3.279095
25	45.5	45.23402	0.285977
26	63.8	63.84563	-0.04563

27	66.4	67.52013	-1.12013
28	55.3	56.70161	-1.43161
29	56.6	56.70161	-0.10161
30	64.1	56.70161	7.438387
31	56.1	56.70161	-0.60161
32	59.2	56.70161	2.498387

Table C-5 Actual experimental data and predicted experimental data for oxirane oxygen content

Standard Order	Actual Value	Predicted Value	Residual
1	1.9	1.975556	-0.07556
2	2.5	2.359722	0.120278
3	2.2	2.303889	-0.10389
4	2.4	2.386389	0.013611
5	2.5	2.632222	-0.13222
6	2.4	2.438056	-0.00806
7	2.4	2.370556	0.049444
8	2.5	2.478056	0.061944
9	2.2	2.145556	0.074444
10	2.4	2.306667	0.123333
11	2.7	2.736667	-0.05667
12	2.8	2.726667	0.053333
13	2.6	2.723333	-0.16333
14	3.0	3.015	-0.015
15	2.9	2.866667	0.053333
16	2.7	2.713333	-0.02333
17	2.6	2.866667	-0.22667
18	2.5	2.58	-0.12
19	2.1	2.121111	-0.02111
20	2.6	2.596944	-0.04694
21	2.6	2.632778	0.007222
22	2.5	2.543611	-0.00361

23	2.8	2.881111	-0.06111
24	2.7	2.778611	-0.05861
25	2.6	2.539444	0.100556
26	2.7	2.738611	-0.01861
27	2.6	2.497778	0.102222
28	3.2	3.015	0.185
29	3.0	3.015	0.065
30	3.0	3.015	-0.015
31	3.0	3.015	0.035
32	3.1	3.015	0.105

Table C-6 Empirical model selection for conversion

Sequential Model Sum of Squares

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	75266.18	1	75266.18			
Linear vs Mean	1707.45	3	569.15	9.07	0.0002	
2FI vs Linear	336.60	3	112.20	1.97	0.1436	
Quadratic vs 2FI	906.94	3	302.31	12.95	< 0.0001	Suggested
Cubic vs Quadratic	189.04	7	27.01	1.25	0.3380	Aliased
Residual	324.54	15	21.64			
Total	78730.74	32	2460.34			

Lack of Fit Tests

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Linear	1704.71	23	74.12	7.07	0.0193	
2FI	1368.11	20	68.41	6.53	0.0234	
Quadratic	461.17	17	27.13	2.59	0.1487	Suggested
Cubic	272.14	10	27.21	2.60	0.1519	Aliased

Pure Error	52.40	5	10.48

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	7.92	0.4928	0.4385	0.3507	2249.46	
2FI	7.54	0.5900	0.4916	0.3538	2238.71	
Quadratic	4.83	0.8518	0.7911	0.6756	1123.88	Suggested
Cubic	4.65	0.9063	0.8064	0.2628	2553.93	Aliased

Table C-7 Empirical model selection for oxirane oxygen content

Sequential Model Sum of Squares

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	220.66	1	220.66			
Linear vs Mean	0.45	3	0.15	1.76	0.1782	
2FI vs Linear	0.26	3	0.085	1.00	0.4078	
Quadratic vs 2FI	1.86	3	0.62	52.57	< 0.0001	Suggested
Cubic vs Quadratic	0.084	7	0.012	1.03	0.4518	Aliased
Residual	0.18	15	0.012			
Total	223.48	32	6.98			

Lack of Fit Tests

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Linear	2.35	23	0.10	17.26	0.0025	
2FI	2.09	20	0.10	17.69	0.0024	
Quadratic	0.23	17	0.014	2.29	0.1833	Suggested
Cubic	0.15	10	0.015	2.47	0.1653	Aliased
Pure Error	0.030	5	5.910E-003			

Model Summary Statistics

Source	Std.	R-Squared	Adjusted	Predicted	PRESS

	Dev.		R-Squared	R-Squared		
Linear	0.29	0.1584	0.0683	-0.0705	3.02	
2FI	0.29	0.2489	0.0686	-0.3750	3.88	
Quadratic	0.11	0.9080	0.8704	0.8064	0.55	Suggested
Cubic	0.11	0.9379	0.8716	0.7413	0.73	Aliased

Empirical Model Development for Conversion and Oxirane Oxygen Content

Based on the above criteria experimental values were fitted by a quadratic polynomial model and the model equation that correlates the responses to the reaction process variables in terms of actual value after excluding the insignificant terms were given below.

Empirical Model Development for Conversion

The quadratic model equetion for conversion of double bond based on predicted data and actual data was given in Eq. C-1. for the selection of quadratic model see Appendix C Table C-4. Final Equation in Terms of Coded Factors:

$$\mathrm{conversion} = +56.54 + 6.95 * \mathrm{A} + 5.31 * \mathrm{B} + 4.73 * \mathrm{C} + 2.98 * \mathrm{A} * \mathrm{B} + 1.49 * \mathrm{A} * \mathrm{C} + 3.81 * \mathrm{B} * \mathrm{C} - 7.28 * \mathrm{A}^2 - 2.03 * \mathrm{B}^2 - 4.71 * \mathrm{C}^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq. 4-1}$$

Where: A= temperature B= Time C= hydrogen peroxide/oil ratio

Empirical Model Development for Oxirane Oxygen content

The quadratic model equetion for oxirane oxygen content on predicted data and actual data was given in E.q. C.2. for the selection of quadratic model see Appendix C Table C-5.

Final Equation in Terms of Coded Factors:

$$OOC = +2.98 + 0.072 * A + 0.065 * B + 0.11 * C - 0.10 * A * B + 0.029 * A * C - 0.011 * B * C - 0.19 * A^2 - 0.18 * B^2 - 0.26 * C^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq. 4-2}$$

Where: A= Temperature B= Time C= hydrogen peroxide/oil ratio

Table C-8 Statistical determination of optimal value for oxirane oxygen content

Constraints Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Temperatur	is in range	45	75	1	1	3

time	is in range	2	6	1	1	3
Hydrogen peroxide/Oil	is in range	1	2.5	1	1	3
Conversion	is in range	30.87	66.4	1	1	3
OOC	maximize	1.9	3.2	1	1	3

Solutions

Number	temperatur	time	Hydrogen peroxide/Oil	conversion	OOC	Desirability	
1	62.36	4.21	1.94	59.26	3.03	0.877	Selected

Table C-9 Valedation experiment data

Experimental run	Volume	Sample weight	OOC
1	7.2	0.41	2.82
2	7.5	0.4	3.0
3	7.8	0.43	2.92
Average	7.5	0.413	2.91

Appendix D Epoxidation Reaction Kinetics

If it is assumed that the reaction is pseudo-first order with respect to double bonds, the rate equation for the pseudo-first order can be expressed as:

$$-\frac{d[DB]}{dt} = K[DB]$$

Where: $K = K3[PAA]^{n2}$

According to reaction engineering concept: the double bond of oil can be expressed by using conversion (Levenspiel, 1999). That is:

$$[DB] = DB_0(1 - X_{DB})$$

Where: $DB_0 = \text{initial concentration of double bond}$

$X_{DB} = \text{conversion of double bond}$

The above equation can be simplified as:

$$-\frac{d[DB]_0(1 - X_{DB})}{dt} = K[DB_0](1 - X_{DB})$$

$$\frac{dX_{DB}}{dt} = K[DB_0](1 - X_{DB})$$

Integration at $t = 0 \rightarrow X_{DB} = 0$ and $t = t \rightarrow X_{DB} = X_{DB}$

$$\int_0^{X_{DB}} \frac{dX_{DB}}{1 - X_{DB}} = \int_0^t K[DB_0]dt$$

$$\ln(1 - X_{DB}) = -K[DB_0] * t$$

Table: D-1 Time vs Ln (1- X_{BD}) data

Temperature 45°C			Temperature 60 °C			Temperature 75 °C		
time	(X_{BD})	Ln (1- X_{BD})	Time	X_{BD}	Ln (1- X_{BD})	time	X_{BD}	Ln (1- X_{BD})
0	0	0	0	0	0	0	0	0
2	0.3752	-0.318599	2	0.408	-0.52425	2	0.4142	-0.53478
4	0.436	-0.5727	4	0.591	-0.89404	4	0.6212	-0.97075
6	0.4565	-0.60973	6	0.61	-0.94161	6	0.638	-1.01611

Initial concentration of the reacting components is calculated using the following equation

$$C_o = \frac{n_o}{v}$$

Where: $C_o = \text{concentration of component};\ n_o = \text{number of mole};\ v = \text{volume of mixture}$

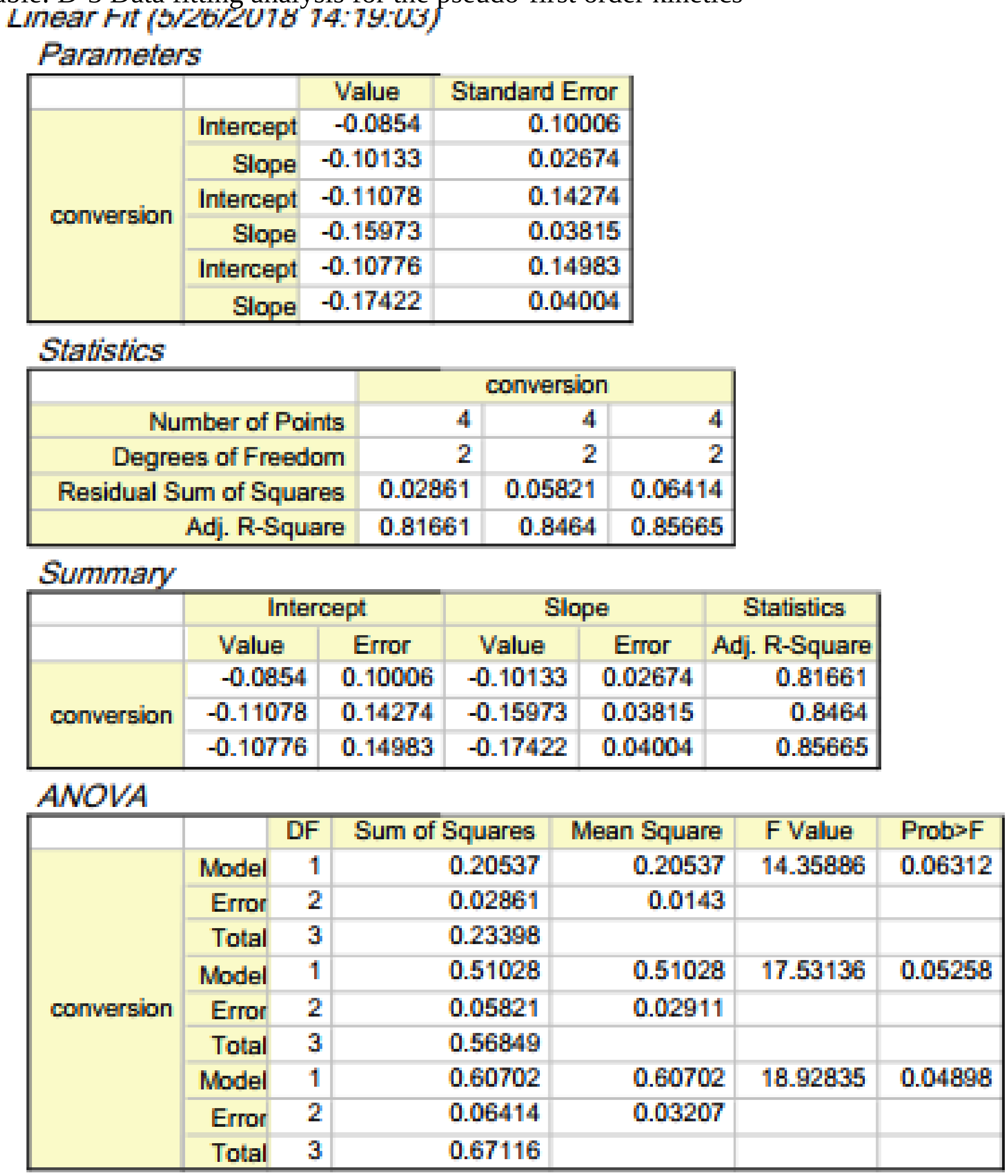
$$n_o = \text{mass/molecular mass}$$

$$\text{Mass} = \text{density} * \text{volume liquid used in reaction}$$

Table: D-2 Initial data and property of the component (feed material Calculation)

Reacting component	Density	Molecular mass	Volume	n_o (mole)	C_o (mol/l)
Oil	918.9 kg/m3	274.68 g/mol	15	0.05	1.95
H2O2	1.11 g/cm3	34.01 g/mol	9.13 ml	0.09	3.5
Acetic acid	1.05 g/cm3	60.1 g/mol	1.5ml	0.0262	1.02

Table: D-3 Data fitting analysis for the pseudo-first order kinetics



Linear Fit (5/26/2018 14:19:03)

Parameters

		Value	Standard Error
conversion	Intercept	-0.0854	0.10006
	Slope	-0.10133	0.02674
	Intercept	-0.11078	0.14274
	Slope	-0.15973	0.03815
	Intercept	-0.10776	0.14983
	Slope	-0.17422	0.04004

Statistics

	conversion		
Number of Points	4	4	4
Degrees of Freedom	2	2	2
Residual Sum of Squares	0.02861	0.05821	0.06414
Adj. R-Square	0.81661	0.8464	0.85665

Summary

	Intercept		Slope		Statistics
	Value	Error	Value	Error	Adj. R-Square
conversion	-0.0854	0.10006	-0.10133	0.02674	0.81661
	-0.11078	0.14274	-0.15973	0.03815	0.8464
	-0.10776	0.14983	-0.17422	0.04004	0.85665

ANOVA

		DF	Sum of Squares	Mean Square	F Value	Prob>F
conversion	Model	1	0.20537	0.20537	14.35886	0.06312
	Error	2	0.02861	0.0143		
	Total	3	0.23398			
	Model	1	0.51028	0.51028	17.53136	0.05258
	Error	2	0.05821	0.02911		
	Total	3	0.56849			
	Model	1	0.60702	0.60702	18.92835	0.04898
	Error	2	0.06414	0.03207		
	Total	3	0.67116			

Kinetics constant determination detail work

$$\ln(1 - X_{DB}) = -K[DB_0] * t$$

The above equation has slope $-K[DB_0]$ and the slope of each graph is given in statistical -0.10133, -0.15973, and -0.17422 at 45 ^{o}C, 60 ^{o}C and 75 ^{o}C respectively. So,

$-K[DB_0] = -0.10133$ and the initial concentration of cottonseed oil was determined in Table F-2 ($[DB_0] = C_o = 1.95$ mol/l

$$-K = -0.10133/1.95$$

$$K = 0.051964 = 5.19 * 10^{-2} l/(mol.s)$$

And then $K = 0.051964 = K3[PAA]o$ according to mole-mole relationship, mole of PAA=mole of acetic acid that is 0.0262 mole. Then the concentration of peracetic acid is calculated by using the following equation.

$$[PAA]o = C_{PAA} = \frac{n_{PAA}}{\text{volumeof the solution}}$$

$$= 0.0262/25.7$$

$$= 0.001021 \frac{mol}{ml} = 1.02 mol/l$$

Now we can calculate K3:

$$K3 = \frac{K}{[PAA]o}$$

$$K3 = \frac{5.19 * 10^{-2} \frac{l}{mol.s}}{1.02 mol/l}$$

$$K3@45 = 0.050908 = 5.09 * 10^{-2} l^2 mol^{-2}. s^{-1}$$

Based on this procedure the pseudo second order kinetics and other value was calculated.

Appendix E Experimental set up and instruments

Figure E-1 Epoxidation experimental Set-up

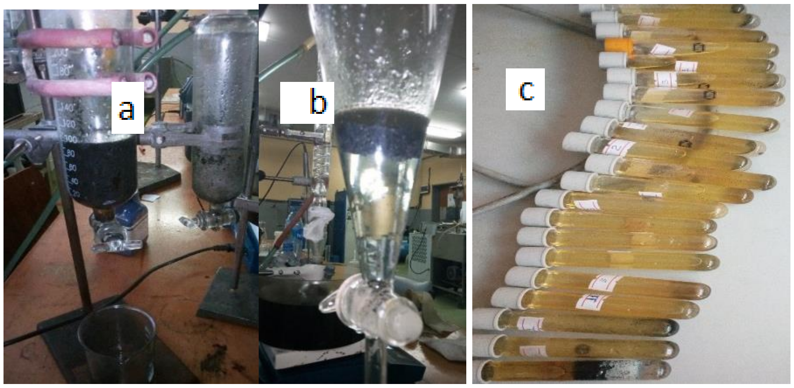
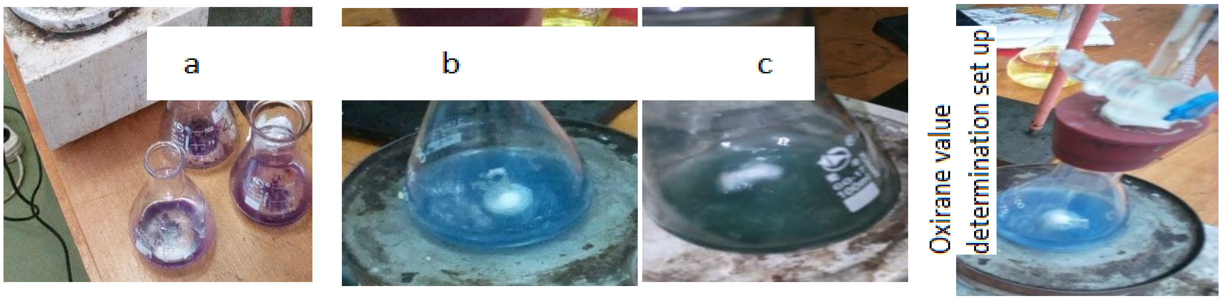


figure E-2 epoxidized oil a) before washed, b) after washed with water and c) final product

Figure E-3 iodine value determination



a) before titration b) Intermediate c) After titration

figure E-4 oxirane oxygen content determination

Instrument used in synthesize and characterize

Figure E-5 FT-IR instrument

Method: *Brix
Sample: *Brix_epoxy

11:22:13 AM
Administrator

Density: 0.9207 g/cm³
Density: 920.7 kg/m³
Density Temperature: 20.02 °C
Density Condition: valid

Figure E-6 Density meter

Figure E-7 pyrolizer

Figure E-8 Elemental Analyzer

Figure E-9 TAG instrument