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Chemical Modification of Oleic Acid Derived Palm Oil as Chemical Processor for Polyols Production

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In recent years, research on the epoxidation of fatty acids has attracted considerable attention due to the growing demand for eco-friendly epoxides generated from vegetable oils. Commercially available epoxides are primarily derived from petroleum and animal fats, which are non-environmentally friendly sources. Epoxide is a crucial chemical precursor for the manufacture of alcohols, glycols, and polymers such as polyesters and epoxy resin. The optimal process parameters were determined using the one factor at a time (OFAT) technique. This study's purpose is to identify the optimal process parameter for agitation speed in relation to the oxirane ring opening of epoxidized oleic acid. The result at 100 rpm and sulfuric acid as catalyst are the optimal process setting for achieving maximal relative oxirane conversion (93 %). Then, the ring opening formation's identity was validated using Fourier Transform Infrared (FTIR).

1. Introduction

Concerns regarding fossil fuels, which have uncertainties in global production and supply, as well as environmental concerns due to carbon emissions and the increasing price of petroleum products, are the best indicators to find alternatives to fossil fuels. Vegetable oils are one of the most favorable resources due to their renewable sources and lower pollutant emissions. Oil palm tree, *Elaeis guineensis*, is one of the ancient tropical plants that originated from West Africa (Resul, 2021). Palm oil and palm kernel oil are triacylglycerols produced from the oil palm tree. Palm oil does not only provide nutrients and medicine for human beings, but it is also important in the oleochemical industry. Basic oleochemicals that are produced from palm oil consists of methyl esters, fatty acids, fatty alcohol and glycerin. Palm oil has become the world's most important oil due to a tremendous growth in production over the past 20 y. Oil varies from many other vegetable oils in that it has a high percentage of palmitic acid which is about 44 %. Palm oil comprises around 50 % saturated fatty acids (SFA), 40 % monounsaturated fatty acids (MUFAs), and 10% polyunsaturated fatty acids (PUFAs) in general (Tuan Ismail et al., 2018). The adaptability of the epoxy group toward a wide range of chemical reactions and in producing useful qualities in the finished products is the root of the widespread interest in epoxy resins. The oxirane ring, often known as the epoxy group, is highly reactive and goes through ring opening processes. It easily breaks down into polyols through hydrolysis in the presence of acid catalysts and alcoholysis in the presence of alcohols or thiols. By hydrogenation, polyols are also produced. For polyvinyl chloride and other plastics, epoxidized vegetable oils are utilised as plasticizers and stabilizers.

Epoxidation process method is used to transform vegetable oils and their unsaturated fatty acids into intermediate compounds. During the production of polyvinyl chloride epoxidized vegetable oils are employed as lubricants, intermediates for polymers used in more common syntheses, plasticizers, and scavengers (Jalil et al., 2022). Moreover, the use of vegetable oils to manufacture epoxy is appealing because it provides a

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sustainable alternative to petroleum as a basic material for a variety of applications. Due to the vegetable oil's high oxirane ring reactivity, many reactions are needed using epoxidation process. In the epoxidation process, commonly sulfuric acid is used as a catalyst for alcoholises. Moreover, in the presence of pyridine, the resultant hydroxy group is further reacted with acid anhydride through alcoholises (Carvalho et al., 2021). In other situations, the initial stage of ring opening was accomplished by adding acetic acid, perchloric acid, or formic acid, followed by esterification process of the resultant hydroxyl group with acid anhydride using pyridine (Lee et al., 2021). Due to the low cost, peracids are extensively used as oxidising agents and powerful mineral acids are used as catalysts in the epoxidation of vegetable oils that are most regularly used in industry. These procedures, however, are hampered by epoxy ring-opening reactions that are acid-catalysed, and the concentrated peroxyacid is unstable and explosive. These epoxidation operations are often carried out utilising peracids generated in-situ at low concentrations to minimise the undesirable epoxide ring opening happened, which is important from a safety perspective. The oxirane ring's highly reactive characteristics have made it a useful intermediate for synthesis with other compounds (Agu et al., 2022). Protonation of the epoxide oxygen atoms in an acidic environment opens the oxirane, which then interacts with various types of nucleophiles via back side assault to produce an anti-orientation type product. One of the most typical procedures for creating seed oil-based polyols involves the epoxidation of seed oils followed by an oxirane ring opening utilising nucleophilic reagents like amines, alcohols, carboxylic acids, and halogenated acids. To produce corn oil-based polyurethane, these polyols are further reacted with diisocyanatos. Most of the secondary hydroxyl groups in polyols generated through epoxidation/oxirane ring-opening processes are substantially less reactive toward isocyanates than primary hydroxyl groups (de Haro et al., 2016).
Moreover, another study depicts the epoxidation of palm olein by using peroxide acids. Performic acid ($HCOOOH$) and peracetic acid (CH_3COOOH) as epoxidation agents were synthesised in situ in the presence of sulphuric acid as a catalyst to produce epoxidized palm olein (Nagendran et al., 2000). The reaction system uses formic acid ($HCOOH$) or acetic acid (CH_3COOH) as an oxygen carrier and hydrogen peroxide (H_2O_2) as an oxygen donor. The use of performic acid as an epoxidation agent resulted in a 95.5 % conversion of the oxirane ring after 150 min of reaction time. In the past, epoxides were mainly produced from petroleum-based sources. This approach is not sustainable in the long term because petroleum is a non-renewable source. The objective of this study to determine the best process parameters of agitation speed on the oxirane ring opening of epoxidized oleic acid. This study can enhance the use of renewable sources to produced epoxy while using in situ performic acid mechanism.

2. Chemicals and method

2.1 Chemicals and materials

The formic acid of concentration (FA) of 85 %, 100 % acetic acid and hydrogen peroxide (HP) of 30 % will be used for this experiment and, while the crystal violet will be used as an indicator for determining the experimental oxirane oxygen content. The overall chemists used for epoxidation oleic acid was tabulated in Table 1

Table 1: List of chemicals used for production of epoxidized oleic acid

Materials	Range/Amount	Purity/ Molarity	Supplier
Oleic acid	100g	75%	QReC Sdn. Bhd
Formic acid molar ratio	1.0	23.6M	QReC Sdn. Bhd
Hydrogen peroxide molar ratio	1.0	30, 35 and 50%	QReC Sdn. Bhd
Sulfuric acid	0.5g	18.0M	QReC Sdn. Bhd
Hydrochloric acid	0.5g	18.0M	QReC Sdn. Bhd

2.2 Epoxidation process by peracid mechanism

The epoxidation method is performed in a 1 L beaker fitted with a stirrer and a thermometer. 100 g dated palm oil was combined with a particular molar ratio formic acid to oleic acid (1.5). A thermostatic water bath was used to keep the beaker warm. The mixture was then heated to the necessary temperature (75 °C) while being agitated at a certain speed (100 – 200 rpm). A 30 % of hydrogen peroxide is added dropwise into the mixture (Arif et al., 2022). The reaction temperature should be monitored throughout the experiment, to avoid the vaporisation of acetic acid which have a boiling point of 118 ◦C and runaway reaction. The reaction will be carried out for 1 hour by stirring using magnetic stirrer.

2.3 Determination of experimental relative conversion to oxirane (RCO)

The experiment was carried out to estimate the RCO value by theoretically calculating oxirane oxygen content (OOC) and empirically calculating OOC using direct titration of hydrobromic (HBr) acid solution to identify the degree of unsaturation in PKO. As the RCO Eq(1) includes both the theoretical Eq(2) and empirically Eq(3) OOC values.

$$RCO = \frac{OOC_{experiment}}{OOC_{theoretical}} \; x \; 100 \qquad (1)$$

$$OOC_{the} = \left\{ \left(\frac{X_0}{A_i}\right) / \left[100 + \left(\frac{X_0}{2A_i}\right)(A_o) \right] \right\} x \; A_o \; x100 \qquad (2)$$

$$OOC_{exp} = 1.6 \; x \; N \; x \frac{(V - B)}{W} \qquad (3)$$

Where X_o represents the initial iodine value, A_i represents the molar mass of iodine, A_o represents the molar mass of oxygen, N represents the normality of HBr, V represents the volume of HBr solution used for the titration, and W represents the weight of the sample.

2.4 Identification of best process parameters on the rate of reaction

To investigate the effect of the process parameters on the epoxidized oleic acid production, the details of several parameters were studied as tabulated in Table 2.

Table 2: Experimental design for DHSA production

Process Parameter	Range/Type	Unit
Agitation speed	100, 300	rpm
Type of catalyst	Sulfuric acid, hydrochloric acid	-

2.5 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectroscopy is an efficient technique for identifying the chemical and inorganic substances present in a test sample. A change in the characteristic pattern of absorption bands clearly indicates a change in the composition of the material or the presence of contamination. In this work, an FTIR spectrometer was utilized to determine the functional groups of the materials (Spectrum One, PerkinElmer, USA). The crude oleic acid and epoxidized oleic acid were examined by FTIR spectroscopy to detect the presence of epoxide groups and the elimination of absorption peaks (attributed to =CH stretching). Within a wavenumber range of 400 – 4000 cm^{-1}, which corresponds to the fundamental vibration modes of the molecules, FTIR spectra were obtained.

2.6 Kinetic modeling

Kinetic study of the epoxidation process can be defined by modelling development through an assumption of the epoxidation process takes in two phases to avoid distribution constant for qualification of different species in aqueous and oil phase. The formation of epoxidized oleic acid is shown in Eq(4-5). Literally, MATLAB simulation was used for this research that include all the statistics, data analysis, optimization and also partial different equations.

$$\mathrm{FA + HP} \; \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} \; \mathrm{PA + Water} \qquad (4)$$

$$\mathrm{PA + OA} \xrightarrow{k_2} \mathrm{EOA + FA} \qquad (5)$$

PA is performic acid and EOA is epoxidize oleic acid. The kinetic model of the epoxidation process and epoxide ring degradation can be developed based on the following constants: k_{11}, k_{12} and k_2, The following rate equations were modelled, and the set of simultaneous differential equations is given as follows:

$$\frac{d[\mathrm{FA}]}{dt} = -k_{11}[\mathrm{FA}][HP] + k_{12}[\mathrm{PA}][\mathrm{Water}] + k_2[\mathrm{PA}][\mathrm{OA}] \qquad (6)$$

$$\frac{d[\mathrm{HP}]}{dt} = -k_{11}[\mathrm{FA}][\mathrm{HP}] + k_{12}[\mathrm{PA}][\mathrm{Water}] \qquad (7)$$

$$\frac{d[\mathrm{PA}]}{dt} = +k_{11}[\mathrm{FA}][\mathrm{HP}] - k_{12}[\mathrm{PA}][\mathrm{Water}] - k_2[\mathrm{PA}][\mathrm{EOA}] \qquad (8)$$

$$\frac{d[\text{Water}]}{dt} = +k_{11}[\text{FA}][\text{HP}] - k_{12}[\text{PA}][\text{Water}] - k_3[\text{OA}][\text{Water}] \quad (9)$$

$$\frac{d[\text{POOA}]}{dt} = -k_{21}[\text{PA}][\text{OA}] \quad (10)$$

$$\frac{d[\text{EOA}]}{dt} = +k_2[\text{PA}][\text{OA}] - k_3[\text{EOA}][\text{Water}] \quad (11)$$

3. Results and discussions

3.1 Epoxidation via performic acid

The influence of stirring speed on the percentage relative conversion to oxirane (RCO) must be examined to determine that the overall reaction was conducted under a kinetically regulated regime (Salzano et al., 2012). Epoxidation is a reaction where an oxygen atom replaces the double bond between two carbon atoms to form an oxidized unsaturated fatty acid known as epoxide. Epoxidation is commonly carried out using performic acid (HCOOOH), which is generated in situ by mixing formic acid (HCOOH), which acts as an oxygen carrier, with hydrogen peroxide (H_2O_2), which acts as an oxygen donor. In other words, the effect of stirring speed is essential for ensuring that the reaction is free of external mass transfer constraints in the form of diffusion (Jalil, 2022). Figure 1 depicts the effect of slower agitation speed on the percentage relative conversion to oxirane (RCO) at 65 °C reaction temperature and 1:1 mole ratio of formic acid to hydrogen peroxide. Due to the constraints of the existing experimental setup, the maximum limit of 300 rpm was chosen. In addition, the highest RCO of 65 % was achieved at the highest agitation speed of 100 rpm to produced epoxidized oleic acid. The RCO was determined to be 32 % at a stirring speed of 300 rpm. Therefore, a stirring speed of 100 rpm was deemed optimal and adopted for all subsequent experimental runs in this investigation.

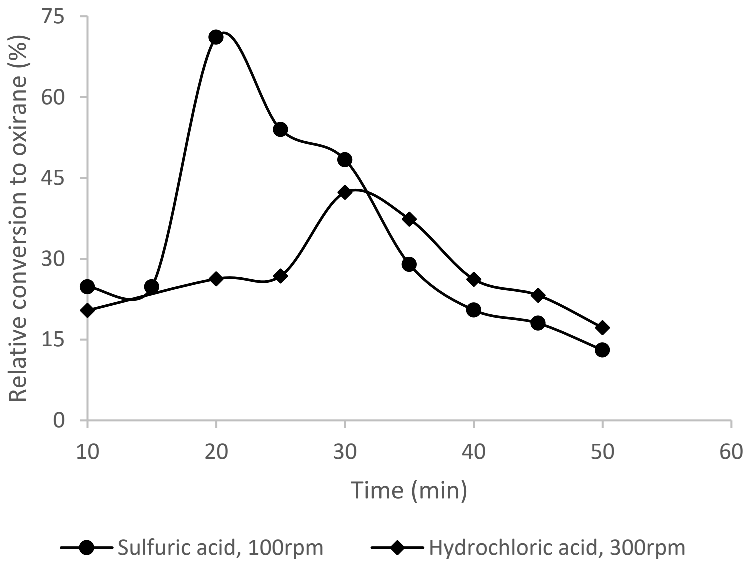

Figure 1: Different catalyst and different agitation speed

Utilizing Fourier Transform Infrared (FTIR) spectroscopy, the chemical characteristics of epoxidized oleic acid were analyzed. In general, the presence of an oxirane ring can be recognized within the wavenumber range of 750 to 880 cm^{-1}. In The unsaturated =CH stretching vibration peak seen in the crude oleic acid sample is no longer visible in the FTIR spectrum of the epoxidized oleic acid as shown in Figure 2. The adaptability of the epoxy group toward a wide range of chemical reactions and in producing useful qualities in the finished products is the root of the widespread interest in epoxy resins. The oxirane ring, often known as the epoxy group, is highly reactive and goes through ring opening processes. It easily breaks down into polyols through hydrolysis in the presence of acid catalysts and alcoholics in the presence of alcohols or thiols.

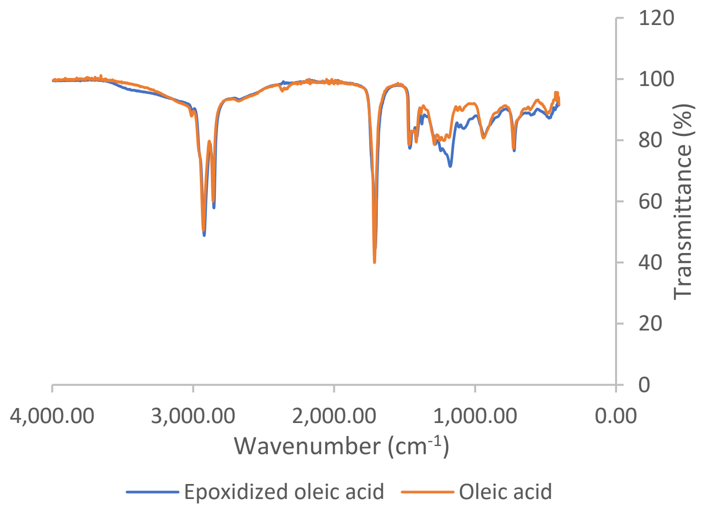

Figure 2: FTIR spectrum for epoxidized oleic acid

3.2 Kinetic modeling

Kinetic is the study of rates of chemical reactions which allow chemist to predict how the speed of a reaction will change under a certain condition. Kinetic study is important because it can provide a prediction and information about the mechanism of reaction and allow chemist to be more efficient in the laboratories. Another importance of kinetics is that it provides evidence for the mechanism of chemical process. Chemical reaction is one in which chemical substances are transformed into another substances which means that chemical bonds are broken and formed so that there are changes in the relative positions of atoms in molecules. To establish the best reaction conditions for the epoxidation process.

A helpful technique for better understanding response mechanisms is kinetic modelling. Designing, assessing, and upgrading gasifiers require knowledge of the kinetic mechanisms that define the conversion during biomass gasification, which is provided by kinetic models. Kinetic modelling was carried out using MATLAB, and the data of response rate, k, obtained from simulation is k_{11}= 0.37, k_{12}= 13, and k_2= 1.45. The kinetic data for the epoxidation and degradation of palm oil was accorded to the initial concentration. Besides, the used of optimization tool in MATLAB simulation where genetic algorithm method was used to fit the experimental data and optimize the reaction, while Range Kutta Fourth Order Method was applied by using ODE 45 tool to solve the complex system of the differential equations. The reaction rate, k, reflects a specific reaction; the greater the number, the faster the reaction takes place. While the lower the mean simulation error, the better the simulation outcome. The key factor influencing the reaction rate of all samples is the molar ratio of formic acid and hydrogen peroxide to oleic acid and the result show the differences between simulation and experiment is lower and acceptable as shown in Figure 3.

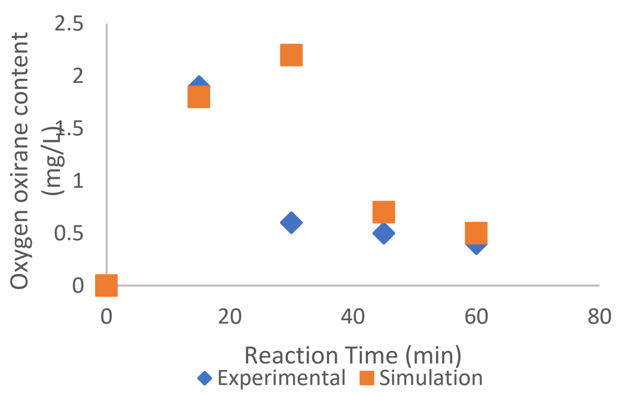

Figure 3: Experiment vs simulation of molar ratio formic acid

4. Conclusions

Vegetable oil triglycerides undergo a chemical or biological reaction known as epoxidation, in which they are converted into more reactive molecules. These will then be further developed into a wide range of goods with excellent potential for industrial uses. Although the era of technology thrives each second during the day, most industries use petroleum to produce epoxidized resin for the paints, coatings, adhesives, and structural applications. On the well-known Prilezhaev reaction, in which peracid is reacted with olefins, is the most popular epoxidation technique. Conventionally, peracid is created in place using hydrogen peroxide and a short-chain carboxylic acid and extremely acidic catalysts. Initially, this research concentrated on statistical analysis to optimize palm oleic acid by varying the agitation speed, formic acid molar ratio, and hydrogen peroxide molar ratio to oleic acid unsaturation molar ratio. At a constant temperature of 65 ˚C and a retention duration of 60 min, three sets of experiments were done for each of the three parameters to determine the percentage of RCO and the best selection of molar ratio of formic acid and hydrogen peroxide. Furthermore, bio-lubricant production by alcoholics was carried out utilizing the optimized epoxidized oleic acid. FTIR is used to identify the functional group of epoxies by examining the infrared spectra of liquid emission. Even though the objectives of this study have been achieved, there are still avenues for further research and improvement, which is because epoxides are very active compounds, it is recommended to explore other value-added capability after ring opening of the epoxidized oleic acid. This research is expected to offer the significant contribution towards the epoxidation process development and applications of epoxidized oleic acid. The advancement of technology opened a new greener route in synthesis of epoxidized resin by using vegetable oil. The unsaturated structure of the vegetable oil can be altered to target specific desired features by complicated reaction known as epoxidation.

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