Epoxidation Reaction Parameter of Palm Olein for Synthesis of Dihydrostearic Acid (DHSA) Via Hydrolysis Reaction

Mohd Jumain Jalil1, Noor Hidayu Abdul Rani2, Aliff Farhan Mohd Yamin3, Nur Radzi Adhary Anuar4, Intan Suhada Azmi1 and Abdul Hadi1

1Chemical Engineering, Universiti Teknologi Mara, Cawangan Pulau Pinang, Malaysia.
2Chemical Engineering, Universiti Teknologi Mara, Cawangan Johor, Kampus Pasir Gudang, Malaysia
3Mechanical Engineering, Universiti Teknologi Mara, Cawangan Pulau Pinang, Malaysia.
E-mail: mjumain0686@ppinang.uitm.edu.my

Abstract. Nowadays, most of the industries in the world such as plastic industries manufacture products based on petrochemicals resources. Epoxidation is a method where fatty acids are converted to a three membered epoxide ring that is called oxirane ring when the double bond of carbons reacts with active oxygen. Thereafter epoxidized vegetable oil was hydrolyzed to form DHSA. Based on the experimental findings, the optimum conditions for epoxidations palm olein temperature at 55oC with the presence of sulphuric acid as catalyst with producing the highest yield of 80.33%. FTIR results shows that the disappearance of double bond carbon C=C group peak at 3,000 cm-1 and formation of oxirane ring in the spectrum of fingerprint region is indicated by the peaks between 815 to 890cm -1. For DHSA synthesis, the conversion of oxirane is decreasing to 16.10% after 5 hours of heating at 60ºC. The FTIR analysis shows the the epoxy group at 837 cm-1 had disappeared and the hydroxyl group which confirmed the formation of DHSA was observed at the region of 3200-3600 cm-1.

1. Introduction
For past decades, chemical production was mainly focused on petroleum but it tends to depletes sooner or later [1]. Therefore, exploitation of renewable must be done by researcher around the world in order to maintain the synthesis of products based on chemicals [2]. Vegetable oil is one of the renewable resources that can be chemically or enzymatically modified as a replacement of petrochemical based product in industries [3]. Vegetable oil is only referred to plant oils that are liquid at room temperature and the oil is extracted by pressing or by solvent extraction [4]. There are many types of vegetable oil produced around the world and palm oil is one of them. Palm oil consists of unsaturated fatty acids such as oleic acid, linoleic acid and linolenic acid with one, two or three carbon-carbon bond present [5]. Oleic acid has the highest percentage in the palm oil, hence oleic acid is applicable for any further research for reaction and chemical modification [6]. Among the chemical modifications of oleic acid, epoxidation is an easy and effective method to produce intermediate product that can be used in a variety of applications [7]. Epoxidation process is one of the newest method where fatty acids are converted to a three member epoxide ring that is oxirane ring when the double bond of carbons reacts with active oxygen [8].
Epoxidized oil can be used as a raw material for a various types of chemicals such as alcohols, alkanolamines, glycols, carbonyl compounds, olefinic compounds, and polymers [9]. Epoxidized oil has been widely used as polymer stabilizer and plasticizer in polyvinylchloride (PVC) [10]. These epoxidized oils are used as intermediate products to manufacture varies of end products that can be useful for industrial purposes. Hence, the economic value of the palm oil is increasing because of the conversion of palm oil into epoxidized palm oil [11]. Epoxidized oils are very important as intermediates in organic synthesis because of the high reactivity of oxirane rings can make them involve in some reactions [12]. By hydrolysis reaction of epoxidized palm olein, a high-value hydroxyl fatty acid called dihydroxystearic acid (DHSA) is produced. DHSA (C18H36O4) is also known as glycolic stearic acid that contains two alcohol groups a carboxylic group in a long hydrocarbon chain [13]. DHSA is derived from in-situ epoxidation of the unsaturated fat in the palm oil with peracetic acid in the presence of catalyst followed with hydrolysis of the epoxide with hydrogen donor such as water. DHSA has been used widely in industry nowadays, as primary and secondary emulsifiers, pigments coating agents and oil gelling agent in cosmetic formulation [14]. The first paragraph after a heading is not indented (Bodytext style).

2. Experimental

2.1. Material
The material used for the epoxidation are fatty acid palm oils as main solvent, acetic acid and hydrogen peroxide (30%) for peracetic formation, sulphuric acid as catalyst, and hydrogen bromide and crystal violet droplet as indicator for titration. For hydrolysis reaction to produce DHPA, distilled water and alumina as catalyst is used.

2.2. In-Situ Epoxidation
In-situ epoxidation is the most common process in epoxidation process. The epoxidation is using peroxy-acids as oxygen donor and carboxylic acid as the oxygen carrier has received concern on its commercial reputation [5]. The epoxidation reaction needs to be accelerated by using strong mineral acid as catalyst to avoid low yield of the epoxidation [15].

Basically, the peroxy-acid is generated in-situ by the reaction of concentrated hydrogen peroxide with carboxylic acid such as acetic or formic acid with the presence of a mineral acid as a catalyst to accelerate the process, according to the following reaction [11].

Peracetic Formation

\[
\text{H}_2\text{O}_2 + \text{HCOOH} \leftrightarrow \text{HCO}_2\text{OH} + \text{H}_2\text{O}
\]  

(1)

Epoxidation Process

\[
\text{R-CH=CH-R'} + \text{HCO}_2\text{OH} \leftrightarrow \text{R-CH-CH-R} + \text{HCOOH}
\]  

(2)

Based on the equation (1) and (2), epoxidation process occurs when palm olein reacted with the peroxy-acid generated in-situ to produce epoxidized palm olein. Both formic and acetic acids are carboxylic acids and therefore it is possible to use either one of these acids for epoxidation [16].

2.3. In-Situ Epoxidation
DHSA is produces by reacting the epoxidized palm olein with water in the presence of catalyst [13]. This reaction is called hydrolysis reaction where oxirane ring opening of the epoxidized palm olein is done to produce crystal-like solid DHSA. The reaction equation for synthesis of DHSA is as shown.
\[
\text{R-CH-CH-R} + \text{H}_2\text{O} \rightarrow \text{R-CH-CH-R} \\
\text{O} \quad \text{OH} \quad \text{OH}
\] (3)

Alumina is used as catalyst for the synthesis of DHSA. Alumina is proven to be an effective catalyst for oxirane ring opening by oxygen-containing and nitrogen-containing nucleophiles [17].

3. Results and Discussions

3.1. Epoxidation palm olein without catalyst

RCO% is calculated from the oxirane oxygen content (OOC) that can be obtained from the direct titration of hydrogen bromide. The RCO% is calculated for the reaction process with different temperature and presence of catalyst. The percentage RCO calculated for epoxidation without presence of catalyst with different reaction temperature shown in table 1.

| Temperature, (°C) | 35°C | 55°C | 75°C |
|------------------|------|------|------|
| Time, (min)      | RCO % | RCO % | RCO % |
| 30               | 12.8756 | 23.1760 | 19.3133 |
| 60               | 21.8884 | 25.1073 | 21.2447 |
| 90               | 26.3949 | 30.2576 | 29.6138 |
| 120              | 32.8327 | 38.6267 | 36.6953 |
| 150              | 50.2147 | 53.4335 | 51.5022 |
| 180              | 59.2275 | 68.8842 | 63.7340 |
| 210              | 52.1460 | 53.4335 | 54.7211 |
| 240              | 33.4764 | 39.2704 | 43.1331 |
| 270              | 25.1073 | 30.2576 | 28.9700 |
| 300              | 19.9571 | 27.6824 | 27.6824 |
| 330              | 18.0258 | 23.1760 | 20.6009 |
| 360              | 16.7382 | 20.6009 | 18.0258 |

From table 1, the percentage relative conversion to oxirane (RCO) is the highest at 30 minutes of the reaction for all three different temperatures that are 59.23% for 35°C, 68.88% for 55°C and 63.73% at 75°C. Percentage of RCO indicated the yield of epoxide from palm. Hence, at the temperature of 55°C, the reaction produces the highest yield of epoxide. Even though there are no presence of catalyst, it still shows high yield of epoxidation. This is due to the presence of acetic acid that acts as a catalyst during the peracetic formation in the epoxidation reaction [7].

3.2. Epoxidation palm olein with catalyst

The percentage RCO calculated for epoxidation with \( \text{H}_2\text{SO}_4 \) as catalyst with different reaction temperature is shown in table 2.
Table 2. The percentage of RCO with H$_2$SO$_4$ as catalyst.

| Temperature, (°C) | Time, (min) | 35°C | 55°C | 75°C |
|------------------|-------------|------|------|------|
| 30               | 15.4507     | 30.2576 | 23.1760 |
| 60               | 30.2576     | 46.3520 | 48.2833 |
| 90               | 53.4335     | 61.1589 | 55.3649 |
| 120              | 61.1589     | 68.8842 | 65.6653 |
| 150              | 68.8842     | 77.2533 | 71.4593 |
| 180              | 70.8155     | 84.3349 | 76.6095 |
| 210              | 53.4335     | 67.5967 | 54.7211 |
| 240              | 38.6267     | 46.3520 | 36.6953 |
| 270              | 30.2576     | 38.6267 | 30.9013 |
| 300              | 23.1760     | 36.6953 | 27.6824 |
| 330              | 20.6009     | 30.9013 | 23.1760 |
| 360              | 15.4507     | 23.1760 | 19.9571 |

From table 2, the percentage relative conversion to oxirane (RCO) is the highest at 30 minutes of the reaction for all three different temperatures that are 70.82% at 35°C, 84.33% at 55°C and 76.61% at 75°C. Percentage of RCO shows the yield of epoxidation process. Hence, at the temperature of 55°C, the reaction produces the highest yield of epoxidation.

3.3. Effect of Reaction Conditions on the Reaction Rate of Epoxidation Palm Olein

3.3.1. Effect of Reaction Temperature.

From figure 1, it shows that reaction at temperature of 55°C produces the highest RCO of 84.34%. The finding shows that at moderate temperature will produces highest yield of epoxidation.

![Figure 1. Effect of different temperature of reaction to RCO % of epoxidation.](image)
The epoxidation rate is increasing with temperature, but it will gradually decrease if the temperature increased higher. It is because RCO will achieve maximum yield faster at high temperature and then will decrease gradually [18]. Other reason is due to the reversible reaction of peracetic acid causes by the high temperature. When the temperature is high, the rate of reaction is also high but the conversion to oxirane is lower because of the reversible reaction of peracetic acid that satisfy the Equilibrium Law. The Equilibrium Law (Le Chatelier’s Principle) stated that when an equilibrium system is disturbed by stress such as temperature, the system will change necessarily to avoid the disturbance.

3.3.2. Effect of Presence of Catalyst.
The RCO is the highest at 55°C whether there is catalyst or no catalyst presence, therefore temperature 55°C is selected for comparison of catalyst for the RCO % of epoxidation reaction. Figure 2 shows the effect of presence of catalyst to the percentage of RCO.

![Figure 2. Effect of presence of catalyst to RCO % of epoxidation.](image)

Various type of catalysts has been utilised in the epoxidation of vegetable oils such as mineral acid catalysts and solid catalysts. It is known that the presence of catalyst in the reaction will decrease the activation energy, which in turn increases the rate of reaction. By referring at Figure 2, it can be seen that the highest rate of reaction was observed when sulphuric acid was used as the catalyst that are with maximum 80.33% RCO. The epoxidation reaction was accelerated when mineral acids such as sulphuric acids used as catalyst because it can avoid low yield of the epoxidation calculated [19]. The result is same with previous research, which that sulfuric acid is determined as the best inorganic catalyst for this system that can produce a high conversion of double bonds to oxirane groups in epoxidation reaction [5].

3.4. Synthesis of DHSA
From the epoxidation process done earlier, the epoxidized oil with H₂SO₄ as catalyst and reaction temperature of 55°C is suitable to be chosen to produce DHSA. Epoxidized palm olein is reacted with distilled water with presence of alumina as catalyst and heated at 60°C. Figure 3 shows the RCO% of the hydrolysis reaction for 5 hours.
Based on figure 3, the percentage of RCO is decreasing with time. After 5 hours, the RCO is decreasing to 16.10%. The progress of the hydrolysis reaction was followed by measuring the RCO and considered as complete when the RCO approaches zero but after 5 hours the RCO is not approaching zero yet [8]. For chemical characteristic, conversion of palm oil to DHSA resulted in lower iodine value (IV) because of conversion of unsaturated fat to saturated fat and higher hydroxyl value (OHV) because of formation of hydroxyl group. For physical characteristic, DHSA crystal size is affected by the cooling modes where higher cooling rate causing high super-saturation through higher temperature, producing smaller crystal and vice versa [20]. It can be concluded that hydrolysis need to takes longer time to decreasing the RCO to zero. The final DHSA product obtained is visually appeared as a white and waxy materials.

3.5. FTIR Analysis
The chemical properties examination of the crude palm oil and the epoxidized palm olein were accomplished by using Fourier Transform Infrared (FTIR) spectroscopy. Thermo Scientific Nicolet 6700 FTIR spectrometer were used to detect the presence of epoxide group that are available at wavenumber 750 - 880 cm\(^{-1}\) and 815 - 950 cm\(^{-1}\) based on theoretical FTIR analysis of palm oil. The disappearance of double bond group peak will be observed at 3000 cm\(^{-1}\) because of the conversion of double bond in linoleic acid to the epoxide group. To optimize the epoxidation reaction, the hydroxyl and double bond peak must be avoided to appear in FTIR spectrum [21]. The FTIR spectrum of the oleic acid and epoxidized palm olein are shown in figure 4 and 5 respectively.
The disappearance of double bond group peak at 3,000 cm$^{-1}$ demonstrate the conversion of double bond in linoleic acid to the epoxy group. Formation of oxirane ring in the spectrum of fingerprint region is indicated by the peaks between 815 to 890cm$^{-1}$[3]. Previous research has stated that to optimize the epoxidation reaction, the hydroxyl and double bond peak must be avoided to appear in FTIR spectrum.

Figure 6 shows the FTIR spectrum of the DHSA produced from epoxidized palm olein. For hydrolysis, the absorption band region of 1210-1320 cm$^{-1}$ (C-O-C stretching) will disappear and hydroxyl group observed at 3200-3600 cm$^{-1}$ [11]. After hydrolysis, the epoxy group at 837 cm$^{-1}$ had disappeared. This shows that the epoxy ring from epoxidized palm olein has reacted by water to
produce secondary hydroxyl compound to form DHSA [13]. The hydroxyl group which confirmed the formation of DHSA was observed at the region of 3200-3600 cm$^{-1}$ as reported in previous research [11].

Figure 6. FTIR spectrum of the DHSA produced.

4. Conclusions
Epoxidized vegetable oils have been researched by many researchers in this past years because of they are derived from renewable and sustainable resources that can be used to replace petrochemical raw material in the future. In this study, palm olein from palm oil has been epoxidized using in-situ formed peracetic acid in order to produce epoxidized oleic acid. The DHSA can be synthesised from the epoxidized palm olein by reacting with water that can decreasing the RCO% and producing hydroxyl fatty acid that can also be used as ramaterial for industries.

References
[1] Jankovic M R et al 2014 Ind. Eng. Chem. Res. 53 9357.
[2] Vanags E et al 2018 J. Renew. Mater. 6 764.
[3] Derawi D et al 2014 J. Anal. Sci. 18 584.
[4] Jalil M J et al 2014 Adv. Mater. Res. 906 125.
[5] Saurabh T et al 2011 Int. J. Adv. Eng. Technol. 2 491.
[6] Jalil M J et al 2017 Recent Innov. Chem. Eng. 10 1.
[7] Derawi D et al 2010 E-Journal Chem. 7 1440.
[8] Gupta S S et al 2016 Int. Res. J. Chem. 1 17.
[9] Salzano E et al 2012 Chem. Eng. Trans. 26 39.
[10] Sun S et al 2011 Ind. Crops Prod. 33 676.
[11] Jalil M J et al 2014 Adv. Mater. Res. 906 125.
[12] Jalil M J et al 2018 Chem.Chem.Technol. 12 296.
[13] Rafizan A et al 2014 J. Appl. Sci. Agric. 9 86.
[14] Koay G F L et al 2006 International Journal of Engineering and Technology 3 115.
[15] Milchert E et al 2008 Czasopismo Techniczne. Chemia 105 283.
[16] Goud V V et al 2007 Chem. Eng. Sci. 62 4065.
[17] Piazza G J Nuñez et al 2003 Journal of the American Oil Chemists' Society 80 901.
[18] Benaniba M T et al 2007 Eur. J. Lipid Sci. Technol. 109 1186.
[19] Milchert E et al 2015 Molecules 20 21481.
[20] Koay G F et al 2011 J. Oleo Sci. 60 237.
[21] Performik A et al 2015 J. Anal. Sci. 19 144.