Combination of Temperature and Time in Epoxidation for Producing Epoxidized Palm Oil as Source of Bio Polyol

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Abstract. Epoxidized palm oil is an alternative source of bio polyol. The combination of temperature and time in epoxidation reaction is important to produce qualifying epoxidized palm oil. This study used a combination of the temperatures ranged from 50 - 80 °C and time ranged from 1 - 4 hours. The epoxidized palm oil parameters were Fourier-transform infrared spectroscopy (FTIR), density, oxirane oxygen content (OOC), and iodine value. The result of this study shows that an epoxidation temperature of 70 °C for 3 hours produced the highest OOC, while the epoxidation reaction temperature of 50 °C for 1 hour produced the lowest OOC. Epoxidized palm oil with high OOC is considered to be of better quality. The study also showed that the iodine values were getting lower. It indicates the epoxidation reaction was successful.

Keywords: Combination; Temperature; FTIR; OOC

1. Introduction

Polyols are alcohols that contain two or more hydroxyl groups [1]. The raw material for polyols is usually used petroleum. Petroleum is a natural resource that cannot be renewed and its availability is decreasing over time. Meanwhile, human dependence on petroleum and its derivative products is very high. Therefore, it is necessary to find alternative resources that can replace the function of petroleum to meet human needs. Alternative resources that can be used as raw material for polyols are carbohydrate-based materials, natural phenolic compounds such as tannins, and vegetable oils, but there have been many studies using vegetable oils as raw materials for polyols, for example, soybean oil [2], palm oil [3], castor oil [4], rapeseed oil [5], palm kernel oil [6], and bui oil [7]. Vegetable polyols can replace petrochemical polyols partially or completely in the manufacture of flexible polyurethane foam [8].

The area of palm oil plantations in Indonesia in 2015 was around 11.3 million hectares with a production of around 6.2 million tons, while the area of Indonesian oil palm plantations in 2017 was 12.3 million hectares with production around 7.1 million tonnes [9]. From the data, it can be seen that the area and production of oil palm continue to increase from year to year. This increase was also accompanied by an increase in palm oil production. Palm oil has the potential to replace the role of petroleum as a raw material for polyurethane foam. Palm oil that is produced contains different unsaturated fatty acids which can be determined from the iodine value. The different iodine values will affect the characteristics of the resulting polyol. Palm oil polyols are formed by the hydroxylation reaction. The hydroxylation reaction includes two stages of the reaction, namely the epoxidation reaction of the formation of an oxirane ring (epoxidized vegetable oils) and oxirane ring-opening of epoxidized vegetable oils. The factors that influence the hydroxylation reaction are the reaction temperature, reaction time, catalyst concentration, the type of oxirane ring-opening compound.
Epoxidation of RBD Palm Oil

2. Methods

2.1 Materials

Raw material: Refined Bleached Deodorized (RBD) Palm Oil, Sari Murni brand, produced by PT Incasi Raya. Chemicals: H₂O₂ 50% (PT. Brataco), acetic acid 99.9%, sulfuric acid 98% (Smart Lab), ethylene glycol (Merck), sodium bicarbonate (Merck), NaCl (Merck), HBr (Merck), KOH (Merck), crystal violet for microscopy certistain (Merck).

2.2 Epoxidation of RBD Palm Oil

200 mL of palm oil heated at 50-55 °C together with 47% acetic acid of 0.3 mol in a 250 mL 3-neck flask equipped with a stirrer, then add concentrated sulfuric acid catalyst (98%) as much as 1% of the total oil the total continues to be stirred at a speed of 1200 rpm. Then add 50% hydrogen peroxide (dilute) of 1.7 mol added gradually (keep stirring and maintain temperature 50-55). The reaction time and duration were treated after the addition of H₂O₂. The epoxy as a result of this epoxidation is separated with a separating funnel using a saturated sodium bicarbonate solution to a neutral pH and washed with hot distilled water 2 times. The washing results were dried with sodium chloride. The epoxy obtained is yellowish-white, then tested.

2.3. oxirane oxygen content (OOC) [19]

Oxirane oxygen content (OOC) is a method for determining the number of groups oxiranes contained in epoxy oil, which can be titrated directly with Hydrogen Bromide in Acetic Acid.

The equation for the approximate content:

\[
\text{Oxirane oxygen content (OOC)} = \frac{\text{vol HBr} \times N \text{HBr} \times 1.6}{W}
\]

Remarks:
Vol HBr = volume of the HBr required for titration (ml)
N HBr = Normality of the HBr solution used for titration (N)
W = sample weight
1.6 = Oxirane oxygen content (OOC)

2.4. Iodine Value [20]
The iodine value is expressed as the amount of iodine salt bound by 100 grams of oil or fat. Determination of iodine numbers can be done by the Hanus method or the Kaufmaun method and the Von Hubl method or the Wijs method. In the hanus method, the standard iodine solution is prepared in concentrated (glacial) acetic acid which contains not only iodine but also iodine bromide. The presence of iodine bromide can speed up the reaction. The Wijs method uses a solution of iodine in concentrated acetic acid, but it contains iodine chloride as a trigger for the reaction.

2.5. Fourier Transform Infra-Red (FTIR) [21]
Sample measurement was conducted by directly applied the sample on top of the sample detector and was scanned 40 times under wavelength in the range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). The sample was processed using Perkin Elmer FT-IR Spectrometer Frontier.

3. Results and Discussion

3.1. Raw Material Analysis
The raw materials used in this study was RBD Palm Oil of Sari Murni Brand. It is used because it is the only cooking oil produced in West Sumatra. The results of the analysis of palm oil can be seen in Table 1.

| Parameter                          | Value        |
|-----------------------------------|--------------|
| Acid value (mg KOH / g)           | 0.32 ± 0.03  |
| Iodine value (g I\(_2\) / g oil)  | 42.90 ± 0.36 |
| Density (g / cm\(^3\)) at 25°C    | 0.8896 ± 0.01|

The acid value of cooking oil brand Sari Murni is 0.32 mg KOH / g (Table 1). The acid value of cooking oil has met the requirements of SNI 3741: 2013, namely a maximum of 0.6 mg KOH / g [22].

RBD Palm Oil has an iodine value of 42.90 g I\(_2\) / g oil. The high iodine value of RBD Palm Oil shows contains oleic acid which is predominantly unsaturated fatty acids contained in the liquid fraction of palm oil [23]. The presence of oleic acid makes the oil easily converted to epoxidized palm oil. Refined Bleached Deodorized (RBD) palm oil produces better polyols than using Crude Palm Oil (CPO) [24]. The density of RBD Palm Oil at 25 °C is 0.8896 g / cm\(^3\).

3.2. Epoxidized Palm Oil

3.2.1. Density
Density is a measurement of the mass per unit volume of an object. The higher the density of an object, the greater the mass per volume. The average density of each object is the total mass divided by its total volume. Density of epoxidized palm oil can be seen in Table 2.

| Temperature | 1 hour     | 2 hours   | 3 hours   | 4 hours   |
|-------------|------------|-----------|-----------|-----------|
| 50 °C       | 0.9278 ± 0.0006 | 0.94 ± 0.0024 | 0.9324 ± 0.006 | 0.935 ± 0.0022 |
| 60 °C       | 0.9424 ± 0.0032 | 0.936 ± 0.0048 | 0.9384 ± 0.0076 | 0.9394 ± 0.0026 |
| 70 °C       | 0.9352 ± 0.0004 | 0.9454 ± 0.003 | 0.9476 ± 0.0004 | 0.9374 ± 0.0010 |
| 80 °C       | 0.944 ± 0.00028 | 0.940 ± 0.0016 | 0.9446 ± 0.0022 | 0.9446 ± 0.0066 |
The density values obtained range from $0.9278 \pm 0.0006 - 0.9476 \pm 0.0004$ g / cm$^3$ (Table 2). The density of palm oil produced has almost the same value. This shows that the epoxidation reaction with various levels of temperature treatment and reaction time has been successfully carried out. The difference is in the closure or opening of the oxidation ring due to the temperature and duration of the epoxidation reaction which exceeds the optimum limit.

The density of epoxidized palm oil is higher than the density of palm oil. This shows that the formation of resin through epoxidation reactions occurs. Epoxidized vegetable oils are resin that are widely used in the paint, adhesive, glue, and polymer industries [25]. The density values obtained ranged from $0.9278 \pm 0.0006 - 0.9476 \pm 0.0004$ g / cm$^3$. Density of epoxidized palm oil obtained in this study was not much different from the density of epoxidized oil obtained in the study [17], which was around 0.945 g / mL.

3.2.2. Fourier-transform infrared spectroscopy (FTIR)

FTIR is a technique for obtaining the infrared spectrum from the absorption or emission of solid, liquid, or gas. FTIR is used to identify compounds, detect functional groups, and analyze the mixtures and samples analyzed. The working principle of FTIR is the interaction between matter and energy. When FTIR is used, infrared will pass through the gap to the sample. This gap serves as a control for the amount of energy that will be given to the sample. The sample then absorbs some of the incoming infrared, while the other infrared that is not absorbed is moved through the surface of the sample. The goal is that the infrared rays can pass to the detector. The measured signal is then sent to a computer for later recording. The FTIR used in this study is the Perkin Elmer brand. The FTIR spectrum of epoxidized palm oil can be seen in Figure 1.

![FTIR spectrum of epoxidized palm oil produced from the epoxidation process at temperatures of (a) 50 °C and (b) 80 °C for 2 hours](image)

The epoxidized palm oil produced from the epoxidation process at 50 °C for 2 hours has a sharp absorption in the 2922.09 cm$^{-1}$ and 2861.48 cm$^{-1}$ areas, while the epoxidized palm oil produced from a temperature treatment of 80 °C for 2 hours had a sharp absorption in the area of 2919.95 cm$^{-1}$ and 2859, 78 cm$^{-1}$ (Fig.1). Sharp absorption showed the presence of methylene (-CH$_2$-) and methyl (-CH$_3$) groups which were strengthened by the presence of absorption at 1452.53 cm$^{-1}$ and 1367.50 cm$^{-1}$ (treatment at 50 °C for 2 hours) and 1456.58 cm$^{-1}$ and 1373.25 cm$^{-1}$ (treatment temperature 80 °C for 2 hours). Another strong absorption is found at 1741.78 cm$^{-1}$ (treatment temperature 50 °C for 2 hours) and 1737.23 cm$^{-1}$ (treatment temperature 80 °C for 2 hours) is the wave number for the C = O group which can be esters or ketones. The C-O ether group is present at wave number 1150.05 cm$^{-1}$ (treatment temperature 50 °C for 2 hours) and 1166.85 cm$^{-1}$ (treatment temperature 80 °C for 2 hours). The presence of an absorption area of 833.70 cm$^{-1}$ (treatment temperature 50 °C for 2 hours) and
842.33 cm⁻¹ (treatment temperature 80 °C for 2 hours) is a typical absorption of the vibrational stretching of the oxirane group –COC- on epoxidized oil. Widened absorption at wave number 3422.60 cm⁻¹ (treatment at 50 °C for 2 hours) and wave number 3461.88 cm⁻¹ (treatment at 80 °C for 2 hours) indicated the presence of an OH group from alcohol. The absence of absorption in the 3000-3100 cm⁻¹ region indicates no C-H double bonds.

3.2.3. Oxirane Oxygen Content (OOC)

Oxirane or epoxy ring are cyclic ether compounds with a ring that has three members. The basic structure of an epoxy group contains an oxygen atom bonded to two adjacent carbon atoms derived from a hydrocarbon. The tension from the three-member ring makes the epoxy compound even more reactive. A three-member ring structure can be formed if the oxygen atom adds to the two carbon atoms of the double bond on the same side. The most commonly used peroxy acid is peroxyacetic.

Epoxidized crude palm oil which is solid at room temperature, is obtained from the epoxidation reaction at 50 °C and 60 °C for 4 hours and at 70 °C and 80 °C for 2, 3, and 4 hours. Epoxidized palm oil is yellowish-white which can melt at 50 °C for 5 minutes. Epoxidized palm oil which is liquid at room temperature is obtained from the epoxidation reaction at 50 °C and 60 °C for 1, 2 and 3 hours and the epoxidation reaction at 70 °C and 80 °C for an hour liquid at room temperature whitish-yellow.

**Table 3. Oxirane Oxygen Content (OOC) (%) of Epoxidized Palm Oil**

| Temperature | Time  | 1 hour | 2 hours | 3 hours | 4 hours |
|-------------|-------|--------|---------|---------|---------|
| 50 °C       |       | 3.04 ± 0.08 | 4.48 ± 0.18 | 8.52 ± 0.28 | 2.96 ± 0.08 |
| 60 °C       |       | 3.80 ± 0.02 | 7.40 ± 0.28 | 8.32 ± 0.51 | 5.52 ± 0.18 |
| 70 °C       |       | 6.52 ± 0.80 | 10.60 ± 0.76 | 11.36 ± 0.88 | 11.32 ± 0.34 |
| 80 °C       |       | 5.52 ± 0.36 | 10.76 ± 0.38 | 9.68 ± 0.80 | 9.12 ± 0.34 |

**Figure 2. Graph of Oxirane Oxygen Content with Different Temperature and Time in Epoxidation**

The oxirane oxygen content generated from this study is 3.04 ± 0.08 - 11.36 ± 0.88% (Table 3). The highest oxirane oxygen content is found at a reaction temperature of 70 °C for 3 hours, while the lowest oxirane oxygen content is obtained at a reaction temperature of 50 °C for 1 hour. Different oxirane oxygen content in epoxidized oil will give different physical properties to the resulting polymer [25].

Epoxidation reactions at temperatures of 50 °C, 60 °C, and 70 °C experienced an increase in the oxirane oxygen content from 1 hour to 3 hours of reaction, whereas after 3 hours of reaction the oxirane oxygen content decreased. There is a degradation of the oxirane ring structure after 3 hours of the reaction. The oxirane oxygen content of epoxidized castor oil continues to increase from 1 hour to 3
hours of reaction, after 3 hours of epoxidation reaction the oxidation number of castor oil has decreased [26]. The longer the epoxidation reaction lasts, it can damage the bonds between carbon and oxygen so that the rate of ketone formation is faster and can even lead to ketone decomposition [27].

The epoxidation that took place at a temperature of 80 °C had an increase in the oxirane oxygen content from 1 hour to 2 hours of reaction, after 2 hours of reaction there was a decrease in the oxirane oxygen content. The longer the reaction time, the more likely it is to collide with one another. Collisions between molecules that are too long can cause degradation of the structure of the oxirane ring during the epoxidation reaction [28]. Besides, the degradation of the oxirane group during the epoxidation reaction can also be caused by the presence of an acetic acid derivative in the form of peroxyacetic acid which is reversible. Epoxidation reaction times that exceed the optimum time can also cause side reactions between acetic acid and H₂SO₄ which can produce ketone compounds [29].

It is found that raising epoxidation temperatures will lead to the increasing oxirane oxygen content (Fig. 2). It can be concluded that higher temperature accelerates the epoxidation reaction so that the frequency of collisions between reacting molecules is also greater [30]. The reaction that takes place at 70 °C produces a higher oxirane oxygen content than the epoxidation reaction at 80 °C. This is because at temperatures exceeding 70 °C it causes the structure of the oxirane ring to degrade [18] and possibly side corrections. The higher the reaction temperature used, the more reactive the double bonds in fatty acids from palm oil are to bind with oxygen from peroxy acids. Increasing the temperature of the reaction will increase the kinetic energy of the particles so that the particles will move faster as a result, the collisions that occur will be more frequent. Temperature conditions that exceed the optimum temperature limit of the epoxidation reaction can cause the degradation of epoxy ring. Epoxidation is a reversible reaction and there is a possibility of side reactions, epoxidation is attempted to occur at low temperatures and in a short time [31].

### 3.2.4. Iodine Value

The Iodine number provides an overview of the reactivity and unsaturation of fatty acids. The iodine value indicates the size of the number of double bonds, while the oxirane oxygen content indicates the percentage of epoxy content [32]. An epoxidized oil is said to be of quality if it has a higher oxirane oxygen content with a lower iodine number. A higher iodine value indicates the fatty acid is more reactive and less stable. According to theory, a higher iodine value indicates the number of iodide ions attached to the unsaturated carbon chain [33].

| Temperature (°C) | 1 hour | 2 hours | 3 hours | 4 hours |
|------------------|--------|---------|---------|---------|
| 50               | 40.45 ± 0.76 | 30.44 ± 0.12 | 25.50 ± 0.11 | 22.86 ± 0.35 |
| 60               | 19.34 ± 0.88 | 18.47 ± 0.46 | 17.59 ± 0.35 | 14.07 ± 0.35 |
| 70               | 17.59 ± 0.53 | 16.93 ± 0.77 | 12.31 ± 0.35 | 9.23 ± 0.30 |
| 80               | 12.31 ± 0.35 | 6.16 ± 0.44 | 6.15 ± 0.88 | 5.28 ± 0.18 |

Palm oil has an unsaturated fatty acid composition that is almost equal to the saturated fatty acid content. Palmitic acid (C16: 0 = 44.02%) and oleic acid (C18: 1 = 39.15%) are the main fatty acid components as well as several other fatty acids such as linoleic acid (C18: 2 = 10.12%), stearate (C18: 0 = 4.54%), myristic acid (C14: 0 = 1.09%), and a little linolenic acid (C18: 3 = 0.37%) and lauric acid (C12: 0 = 0.23 %) [34]. Palm oil contains high levels of unsaturated fatty acids, so this oil is the potential to be used as raw material for epoxidized vegetable oil. The double bonds in oleic, linoleate, and linolenic fatty acids react readily with oxygen at high temperatures.

The iodine values obtained ranged from 5.28 ± 0.18 - 40.45 ± 0.76 g I₂ /100g (Table 4). The lowest iodine value was found in epoxidized palm oil obtained at a reaction temperature of 80 °C for 4 hours, while the highest iodine value was found at a reaction temperature of 50 °C for 1 hour.

The higher the reaction temperature and the longer the epoxidation will lead to the decreasing iodine value of epoxidized palm oil (Fig.3). This shows that during the epoxidation reaction the double bond -
C = C- conversion occurs in unsaturated fatty acids into an oxirane ring structure so that the iodine value decreases. The decrease in the iodine value of oil is related to the breakdown of the double bonds in unsaturated fatty acids due to oxidation reactions [35].

The temperatures that exceed the optimal cause the iodine value to be lower. The higher the temperature, the faster the reaction, and the more reactive the double bonds to bind oxygen to form an epoxidized palm oil. It can be concluded that lower the iodine value accelerates the formation rate of epoxidized palm oil.

\[ 50^\circ C \] \[ 60^\circ C \] \[ 70^\circ C \] \[ 80^\circ C \]

\[ 0 \] \[ 5 \] \[ 10 \] \[ 15 \] \[ 20 \] \[ 25 \] \[ 30 \] \[ 35 \] \[ 40 \] \[ 45 \]

1 HOUR 2 HOURS 3 HOURS 4 HOURS

Figure 3. Graph of Iodine Values with Different Temperature and Time in Epoxidation

4. Conclusion

The best combination of temperature and time in epoxidation based on the physicochemical properties of epoxidized palm oil was a temperature of 70 °C for 3 hours. The parameters were oxirane oxygen content at 11.36%, density at 0.9476 g/cm³, and iodine value at 12.31 g I₂/100 g. The FTIR test showed the presence of a distinctive absorption from the stretching vibration of the oxirane group –C-O-C- on the resulting epoxidized palm oil.

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