



Synthesis of Polyol Through Epoxidation and Hydroxylation Reactions of Ricinus Communis L. Oil

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Abstract. Polyols are intermediate compounds used as raw materials to produce highly valuable industrial materials. Generally, the raw materials for synthesizing polyols are petroleum-based, non-biodegradable fossil fuels. In this study, the raw material used is oil from *Ricinus communis* L. (Local name: *jarak kepyar*), a renewable raw material. The fatty acid content of *Jarak Kepyar* oil is dominated by 90% of ricinoleic acid, which could be converted into polyols. The polyols are synthesized through epoxidation and hydroxylation reactions. The products were characterized using FTIR, the ratio of the oil and the polyol's hydroxyl number, the ratio of the oil and the polyol, and the ratio of the iodine value of the oil and the polyol. The percentage of conversion of castor oil to polyol, which was determined based on the ratio of the iodine value of the oil and the product, was 91.43%.

Keywords: Polyol · Epoxidation · Hydroxylation · *Ricinus communis* L.

1 Introduction

Polyols are intermediate compounds used as industrial raw materials, especially in the polymer industry. Conventionally, polyols are synthesized from petroleum derivatives. The use of petroleum, both as fuel and as petroleum-based industrial precursors, raises various problems. Non-renewable natural resources, environmental damage and unstable prices are the main problems of using petroleum. Therefore, the search for bio-renewable resources is very important to reduce the problems arising from petroleum use. Vegetable oils are the main alternative as bio-renewable resources due to their sustainability, biodegradability, low cost, low toxicity, abundance and ease of chemical modification [1, 2].

The main components of vegetable oils are triglycerides, glycerol esters and fatty acids. The types of fatty acids in triglycerides are distinguished by the length of the carbon chain and the number of double bonds. The type of fatty acids is also determined by the type of plant and the conditions where it grows. The double bonds in the structure of the fatty acids can undergo various chemical transformations that allow the formation of new functional groups, such as hydroxyl groups. The synthesis of polyols starts from the

oil's epoxidation reaction, followed by the reaction of opening the oxirane ring through a hydroxylation reaction [2]. Various vegetable oils have been used as raw materials for the production of bio-polyols-based polymers, including soybean oil [3], canola oil [4], palm oil [5] and olive oil [6]. These vegetable oils are edible. Therefore, its use as raw material for non-food industries is not recommended.

One of the plants that can produce vegetable oil is *Ricinus communis* L. (from now on referred to as *jarak kepyar*). On the island of Lombok, West Nusa Tenggara, Indonesia, this plant thrives and is a wild plant. *Jarak kepyar* oil is also known as castor oil or Ricinus oil. Unlike other vegetable oils, the main fatty acid content (90%) of *jarak kepyar* oil is ricinoleic acid, a hydroxyl fatty acid [7]. Due to this hydroxyl content, castor oil is soluble in alcohol and slightly in petroleum ether at room temperature. The content of hydroxyl and double bonds in ricinoleic acid allows the chemical transformation of these two functional groups. The hydroxyl content of the ricinoleic acid chain can be added through epoxidation and hydroxylation of the carbon double bond.

2 Experimental Section

2.1 Materials and Instrument

Oil extracted from *jarak kepyar* seeds and purified using the method developed by [8]. N-hexane, 30% of hydrogen peroxide, methanol, 98% of formic acid, 97% of sulfuric acid, bentonite, sodium bicarbonate, sodium thiosulphate, potassium iodide, chloroform, potassium hydroxide, acetic acid anhydrous and acetone were of analytical grade and purchased from Merck, Germany, and used as received. The instruments used were a rotary evaporator (B-ONE RE-1000VN, China), a water bath stirrer (Biosan W-4MS, England), and an FTIR Spectrophotometer (Perkin Elmer FTIR–Frontier, Waltham, MA, U.S.A.).

2.2 Epoxidation and Hydroxylation of Jarak Kepyar Oil Procedure

Epoxidation and hydroxylation were performed using the procedure developed by [9] and [10] with slight modifications. 60 mL of 98% formic acid, 30 mL of 30% H₂O₂, and 2 mL of 97% H₂SO₄ were slowly put into a three-neck flask while stirring for 1 h. Then, as much as 43.4 g of *jarak kepyar* oil was added to the mixture and the temperature was maintained at 40–50 °C. The reaction lasted for 2 h. Then, the reaction mixture was left for 24 h to separate the oil and water phases. After separation, distilled water is added to the oil phase to remove residual acetic acid and catalyst.

Furthermore, the remaining water in the oil phase was removed using anhydrous magnesium sulfate. The next process is the hydroxylation reaction, which is the reaction of opening the oxirane ring to form a polyol. 150 mL of diethyl ether was added to the purified epoxidized oil and stirred until it dissolved. Then, 25 mL of 2 M NaOH and 25 mL of distilled water were added and stirred until two layers were formed. After being separated, 25 mL of hot distilled water (90–100 °C) was added to the organic phase, the remaining distilled water was evaporated using a rotary evaporator and anhydrous Na₂SO₄ was added and filtered. The polyol formed was characterized using an FTIR spectrophotometer, and the polyol conversion percentage was calculated.

2.3 Characterization

Product characterization was carried out using several tests, including acid number (AOCS-Ca 5a-40 and AOCS-Cd 3d-63), iodine number (AOCS-Cd 1d-92), hydroxyl number (AOCS-Cd 13-60), saponification value (AOCS-Cd 3-25 and AOAC-920.160), peroxide value (AOCS-Cd 8-53 and AOAC 965.33), viscosity determination using an Ostwald viscometer and identification of functional groups using the FTIR spectrum.

3 Results and Discussion

Synthesis of polyols from castor oil is carried out through epoxidation and hydroxylation reactions simultaneously. The epoxidation process is carried out by reacting peracid and *jarak kepyar* oil. Peracid can be produced in situ by reacting formic acid, hydrogen peroxide and sulfuric acid as catalysts. Formic acid dissociates hydrogen ions, so the reaction can run quickly. Meanwhile, hydrogen peroxide serves as an oxygen donor, which donates active oxygen to formic acid to form performic acid. Based on research [11], it was found that 30% of hydrogen peroxide had a positive effect on the rate of epoxidation; therefore, this study used 30% of hydrogen peroxide. Peracid formation reaction can be seen in Fig. 1.

The main function of sulfuric acid in this reaction is accelerating the equilibrium reaction for peracid formation. However, more H⁺ ions will make it easier for the oxirane ring to reopen. Therefore, epoxy compounds are only used as intermediates to form polyols. Meanwhile, hydroxylation is the reaction of opening the oxirane ring in epoxide compounds to form polyols. In this process, the opening of the epoxide/oxirane ring by water begins with the protonation of the oxygen atom in the oxirane ring by H⁺ ions from the sulfuric acid catalyst. After that, the carbon-oxygen bond opens, and a positive charge accumulates on the substituted carbon atom. Next, the nucleophile (from the water) attacks the substituted carbon atom. The final stage of this process is the deprotonation of oxygen to form polyols [14]. The reaction for forming polyols from castor oil is shown in Fig. 2.

3.1 Characteristics of the Product

The iodine number is a value that indicates the degree of unsaturation of fat or oil. The magnitude is directly proportional to the unsaturation of the bonds in the fatty acid chains of the oil or fat; the higher the iodine number, the more C=C bonds there are in the fat or oil. The iodine number of the *jarak kepyar* oil used is 88.83 g I₂/100 g. Meanwhile, the product has an iodine number of 7.61 g I₂/100 g. This significant decrease in iodine

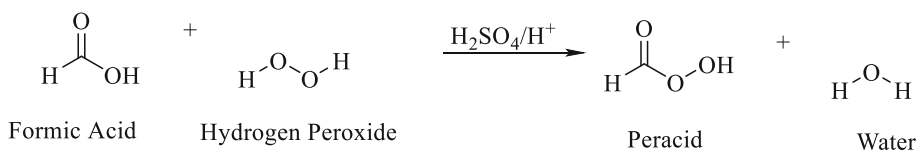


Fig. 1. Peracid formation reaction [12, 13]

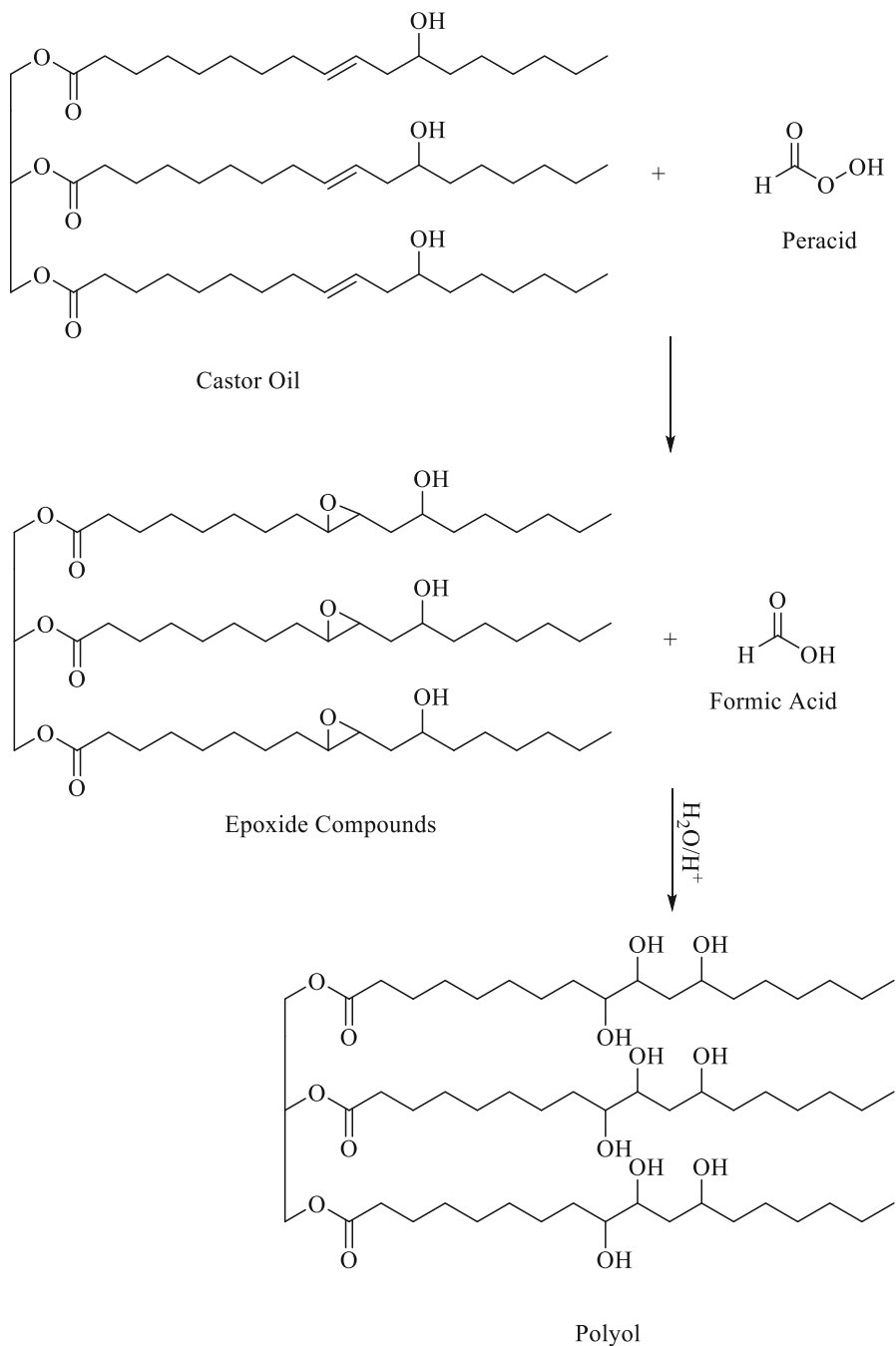


Fig. 2. Epoxidation and hydroxylation reactions of castor oil [12, 13]

number is a strong indicator of breaking the C=C double bond from the fatty acid chain in the oil to form polyol compounds, which previously formed epoxy compounds. Based on the changes in the iodine number of the oil and the product, the polyol conversion percentage was 91.4%. The conversion percentage of this polyol is relatively high when compared to the conversion percentage of canola oil (82.7%), midoleic oil (82.7%), soybean oil (79.4%), linseed oil (82.7%), and sunflower oil (75.5%) [15].

Another parameter to see oil conversion into polyols is the saponification value, which is the number of milligrams of K.O.H. needed to saponify 1 g of oil or fat. The saponification number is also a parameter related to the molecular mass of oil or its derivatives. The saponification value of the *jarak kepyar* oil used was 154.97 mg KOH/g, and this value corresponds to the range of saponification value of *jarak kepyar* oil reported by [16], which is 165.50–187.00 mg KOH/g. Meanwhile, the saponification value of the product was 251.05 mg KOH/g. This increase in the saponification value indicates the increasing number of hydroxy groups in the oil's fatty acid chain, which causes the saponification process to increase.

The peroxide value indicates the degree of damage to the oil or fat. Unsaturated fatty acids in oil or fat can bind oxygen to their double bonds to form peroxides and aldehydes, lactones, and acrolein compounds. The peroxide value of the *jarak kepyar* oil used was 13.40 mEq/Kg. Meanwhile, the peroxide value of the product/polyol was 11.33 mEq/kg. This decrease in peroxide value indicates that there has been oxidation/breaking of the double bonds in the fatty acid chains in the oil. The breaking of this double bond is expected due to the formation of hydroxy groups in the fatty acid chains of the oil.

Another parameter is the hydroxyl number, which measures the content of free hydroxy groups in a compound, especially natural or synthetic fats, oils or esters. In this study, testing of the hydroxyl number aims to ensure that the hydroxylation process of epoxied oil has formed hydroxy groups in the oil. The hydroxyl number of *jarak kepyar* oil is 110.20 mg KOH/g. This large hydroxyl number is due to castor oil containing resinoleic fatty acids with hydroxyl groups in their structure. The hydroxy groups in the ricinoleic fatty acid provide oxidative stability to the oil while making it unique in that it allows various chemical reactions to occur [17]. The hydroxyl number of the product is 132.77 mg KOH/g. This value, of course, is greater when compared to the hydroxyl number of castor oil; this increase in hydroxyl number indicates that hydroxyl groups have been added to the fatty acid chain of *jarak kepyar* oil.

One of the physicochemical characteristics that can indicate the breaking of the double bond in an oil is the oil's viscosity. Viscosity is a measure of the thickness of a fluid. In oils, the viscosity is due to the number of unsaturated bonds in the fatty acid chains. The more double bonds in the fatty acid chain of the oil, the lower the viscosity. Viscosities in oils and products are determined using an Ostwald viscometer. The viscosity value of the *jarak kepyar* oil used was 12.73 cP, while the product was 453.23 cP. This large increase in viscosity indicates that the double bond has been broken in the fatty acid chain in the oil to form a polyol.

3.2 FTIR Analysis

The addition of hydroxy groups to the fatty acid chains of castor oil can be observed by comparing the FTIR spectra of the oil and the product. A comparison of the FTIR

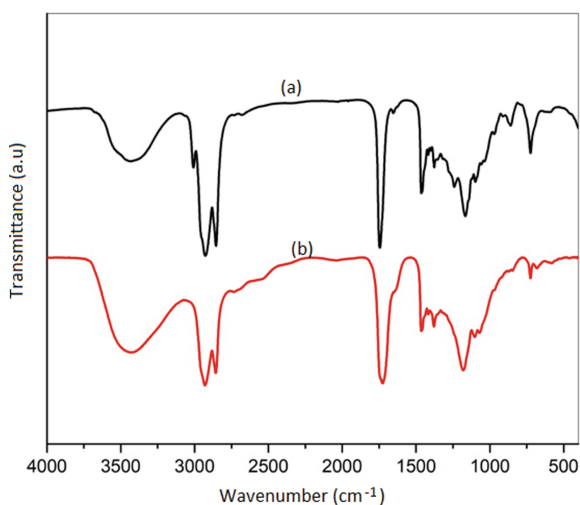
Table 1. Physico-chemical characteristics of *jarak kepyar* oil and products

Parameter	<i>Jarak kepyar</i> Oil	Product
Iodine number (g I ₂ / 100 g)	88.83	7.61
Saponification value (mg KOH/ g)	154.97	251.05
Hydroxyl number (mg K.O.H./ g)	110,20	132.77
Peroxide value (mEq/ Kg)	13.40	11.33
Viscosity (cP)	12.73	453.23

spectra of the oil and the product also shows that the double bond in the fatty acid chain of *kepyar* oil has broken. In the FTIR spectrum of castor oil (Fig. 3a), there is absorption in the region of wave numbers 3434; 3007; 1745; and 1654 cm^{-1} , which indicates the occurrence of vibrations by the $-\text{O.H.}$, $=\text{C.H.}$, $\text{C}=\text{O}$ and $\text{C}=\text{C}$ groups (Table 1).

The absorption was detected in the region of wave number 3434 cm^{-1} , which is the $-\text{O.H.}$ group absorption in the oil (Fig. 3a) caused by ricinoleic acid, which is the main constituent of castor oil. Meanwhile, the absorption in the 3007 cm^{-1} ($=\text{C.H.}$ group) and 1654 cm^{-1} ($\text{C}=\text{C}$ group) indicate the presence of double bonds in the fatty acid chain of *jarak kepyar* oil. These absorptions are typical of *jarak kepyar* oil, following the FTIR spectrum of *jarak kepyar* oil reported by [18, 19].

Meanwhile, in the FTIR spectrum of the product (Fig. 3b), absorption was detected in the region around wave number 3427 cm^{-1} , which is a region of $-\text{O.H.}$ vibration with a higher intensity than oil. This increase in intensity indicates the addition of the number of hydroxy groups in the fatty acid chains of the oil; in other words, the oil hydroxylation process is successful. The result is supported by the absorption loss in the

**Fig. 3.** FTIR spectrum of (a) *jarak kepyar* oil, (b) product/ polyol

region of wave numbers 3007 and 1654 cm^{-1} , which are vibrations of the double bond =C.H. and C=C. The loss of this absorption and the increase in the absorption intensity of the -O.H. group indicates that the hydroxylation process is going well. The data is reinforced by the detection of C=O group vibrations in the product spectrum, indicating that the oxidation reaction (breaking of the double bond) does not occur in the carbonyl group but in the alkene group present in the fatty acids. These data are under the FTIR spectrum of polyols from the study of [20].

4 Conclusion

Polyols have been successfully synthesized from castor oil through epoxidation and hydroxylation reactions. A decrease in the iodine number indicated the success of the synthesis, an increase in the hydroxyl number and viscosity values and a loss of absorption in the region of wave numbers 3007 and 1654 cm^{-1} , which are vibrations of the double bond =C.H. and C=C in the FTIR spectrum of the product. The percentage of conversion above 90% proves castor oil has considerable potential as a raw material for making polyols.

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