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Synthesis Epoxy Fatty Acid Methyl Ester Using Combined Acid Catalyst

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Abstrak

Senyawa epoksi untuk plasticizer dapat disintesis dari metil ester asam lemak. Proses sintesis telah dilakukan dalam reaktor batch pada suhu operasi 60ºC. Sumber oksigen yang digunakan dalam proses epoksidasi adalah hidrogen peroksida. Katalis yang digunakan adalah senyawa berbasis asam, yaitu asam format, asam asetat dan kombinasi keduanya. Parameter yang digunakan untuk menilai kinerja proses reaksi adalah nilai bilangan iod dan konversi ikatan rangkap atom C, dan didukung oleh sifat fisik seperti viskositas, densitas dan titik nyala. Kinerja asam format menunjukkan bahwa konversi maksimum yang dapat dicapai adalah 87,47% dengan bilangan iod 5,84 g-I2/100g pada konsentrasi katalis 10%-wt. Penggunaan katalis asam asetat memberikan konversi maksimum 68,96% dengan bilangan iod 14,57g-I_2/100g pada konsentrasi katalis 20%-wt. Untuk katalis kombinasi, konversi maksimum yang diperoleh adalah 79,30% dengan bilangan iod 9,64 g-I2/100g pada konsentrasi katalis 15%-wt dengan rasio FA:AA=30:70. Katalis terbaik adalah asam format, karena memiliki kinerja konversi tertinggi dan penggunaan konsentrasi minimal. Hasil analisis produk diperoleh senyawa metil 9,10 epoksioktadekanoat epoksida dengan konsentrasi 12,30%-berat.

Kata kunci: FAME, Asam Format, Asam Asetat, Epoksidasi, EFAME

Abstract

Epoxy plasticizer compounds can be produced from fatty acid methyl esters through an epoxidation reaction. In this study, synthesis was conducted in a batch reactor at 60 °C using hydrogen peroxide as the oxygen donor. Acidic catalysts, including formic acid, acetic acid, and their combination, were applied to evaluate reaction performance. Performance was assessed based on iodine value and carbon–carbon double bond conversion, supported by physical properties such as viscosity, density, and flash point. The use of formic acid resulted in the highest conversion of 87.47% with an iodine value of 5.84 g I_2/100 g at a catalyst concentration of 10 wt%. Acetic acid achieved a maximum conversion of 68.96% with an iodine value of 14.57 g I_2/100 g at 20 wt%. For the mixed catalyst system, the highest conversion reached 79.30% with an iodine value of 9.64 g I_2/100 g at a total catalyst concentration of 15 wt% and a formic acid to acetic acid ratio of 30:70. Overall, formic acid was identified as the most effective catalyst due to its superior conversion efficiency at lower concentrations. Product analysis confirmed the formation of methyl 9,10-epoxyoctadecanoate with a yield of 12.30 wt%.

Keywords: FAME, Formic Acid, Acetic Acid, Epoxidation, EFAME

1. Introduction

Fatty Acid Methyl Ester (FAME) is an methyl-ester compound derived from vegetable oils such as crude palm oil through an esterification process using an acid-based catalyst such as H_2SO_4 and/or a trans-esterification process using a base-based catalyst such as NaOH (Hendriyana and Andini, 2024). Most FAME is currently used as fuel for diesel engines with a mixture content of 5%-v, 20%-v and 30%-v with terms known in the market or in the community as B5, B20 and B30. For example, B30 is a diesel fuel whose content consists of 30%-v FAME and 70%-v petroleum-based diesel oil (Soni et al, 2024; Fardilah et al, 2023).

In addition to being a fuel, FAME has also been developed into several chemical products. These products include lubricating oil, solvents and plasticizers. The synthesis of lubricants from FAME has been developed by Shohibulloh et al (2022) and reviewed by Godfred et al (2021). The use of FAME as a solvent is considered environmentally friendly because it is able to degrade easily, has a low level of toxicity and is not flammable (Medina et al, 2007). A plasticizer are materials used to increase the flowability and moulding of polymer materials, such as PVC. Di(2-ethylhexyl) phthalate (DOP) is the most commonly used plasticizer in the industry, however that the products of DOP are able to act as potential carcinogenic agents (Galli et al, 2014; Rodrigo et al, 2010). Phthalate-based plasticizers as mentioned can be replaced by epoxidized fatty acid methyl ester (EFAME) which is renewable and environmentally friendly (Pravin et al, 2024).

Several researchers have developed FAME into epoxy with various raw material sources and catalysts. Pamela et al (2020) developed microalgae as a source of FAME which was then converted into epoxy using hydrogen peroxide as a reagent and formic acid as a catalyst. Junyang et al (2017) used soybean oil as the raw material for epoxidized FAME with formic acid as a catalyst and hydrogen peroxide as a reagent. Meanwhile, Guodong et al (2019) synthesized epoxidized fame from used cooking oil using formic

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acid and H_2SO_4 as catalysts combined. A combination of heterogeneous and homogeneous catalysts has also been developed by Andri et al (2023) in the conversion of used cooking oil into epoxy, the catalysts are acetic acid and amberlite IR-120. Heterogeneous catalysts have advantages in the separation process between the catalyst and the product mixture, but homogeneous catalysts can still be applied because of their high performance. Dekai Liu et al used a mixture of phosphoric acid and acetic acid as catalysts (Dekai et al, 2020). Hong et al (2024) used acetic acid and sulfuric acid combined catalyst for epoxidation.

The combination of catalysts allows for increased performance of the FAME epoxidation process. Catalysts that can be combined are acetic acid and formic acid. Srikanta et al et al (2008) studied these two catalysts and compared them independently. The acetic acid catalyst has advantages in reaction selectivity towards oxirane formation, but its conversion is low. While formic acid has advantages in increasing C=C conversion, but its selectivity is lower. Therefore, the objective of this work was to study the combination of the two catalysts at various concentrations of the mixture.

2. Materials and Methods

2.1. Materials

The main raw materials used in this study were FAME obtained from the market place. Hydrogen peroxide (30%), acetic acid (AA) at 99% and Formic acid (85%) were obtained from a chemical store. Furtheremore, to analyze the iodine number in the sample using Wijs solution, 99.5% cyclohexane, 98.5% sodium thiosulfate, 99.995% potassium iodide and amylum indicator.

2.2. Experimental

The epoxidation reaction process experiment was carried out in a 500 mL glass reactor. The reactor was equipped with a magnetic stirrer for stirring the material so that it was homogeneous and mass transfer occurred quickly. The heating process and stirring control used a hot plate. An alcohol thermometer was used to measure the operating temperature. Other supporting tools used in this study were analytical scales, separating funnels, vacuum pumps, beakers, erlenmeyers, micro burettes and volume pipettes.

2.3. Epoxidation Process

One hundred grams of FAME was weighed and added into the reactor placed on a hotplate. Then a magnetic stirrer was inserted into the reactor, and the reactor was sealed using aluminium foil. To measure the reaction temperature, a thermometer is placed, which is held by a stative. Hydrogen peroxide, formic acid and acetic acid are mixed in a separating funnel, which is then placed on the top of the reactor. Where the bottom of the separating funnel is inserted into the reactor through an aluminium foil cover.

The reaction is started by heating FAME to an operating temperature of 60^{o}C with stirring at 500 rpm. A mixture of hydrogen peroxide, formic acid, and acetic acid was added drop-wisely into the reactor about 1 hour after reaching the reaction temperature. The reaction time is 6 hours after all the mixture in the separating funnel has been fed. The reaction is exothermic, during the reaction, the reaction temperature is always controlled and controlled to maintain it at the set reaction temperature.

The epoxy product obtained is then washed with warm water at a temperature of 50^{o}C until the washing water has a pH of 7. Product drying was carried out under vacuum conditions and stopped when it no longer formed water vapour bubbles in the epoxy.

2.4. Product Characterization

Epoxidized FAME products were characterized using several methods, including iodine number, density, viscosity, flash point and gas chromatography mass spectrophotometry (GCMS). The Wijs method is used to measure the iodine number, where iodine reacts selectively with carbon-carbon double bonds (Edy et al, 2025). The conversion of double bonds of FAME (XC=C) calculated from the iodine value follows the following equation (Lei et al, 2020):

$$X_{C=C}(\%) = \left(\frac{IV_0 - IV_f}{IV_0}\right) \times 100\% \quad (1)$$

While IVF is the iodine number in the epoxy product (the remaining unreacted C double bond) at the end of the reaction. For density, measurements were made using a 25 mL pycnometer. The mass of a 25 mL sample was recorded at 25 °C and then calculated using equation (2).

$$\rho = \frac{m}{V} \quad (2)$$

The ASTM D-445 standard method is used to measure the kinematic viscosity of raw materials and products using a Cannon-Fenske viscometer. To maintain temperature uniformity during measurement, the Viscometer is immersed in a thermostatically controlled water bath.

The GC-MS QP2010 Ultra Shimadzu was used to analyze the composition of the EFAME. Identification of the products was achieved by comparing the observed mass spectra to those in the mass spectral library.

3. Results and Discussion

3.1. Properties of FAME

Properties of FAME related to epoxy synthesis include iodine number, density, kinematic viscosity and flash point. The properties of the methyl ester were used presented in Table 1. The iodine number is estimated to have a value of 46.6 g-I_2/100g. The density at 25°C is 0.871 g/mL. The kinematic viscosity and flash point are 4.96 cSt and 185°C, respectively.

Table 1. Properties of FAME

Parameter	Value
Iodine value (g-I_2/100g)	46.6
Density at 25°C (g/mL)	0.871
Viscosity Kinematic at 25°C (cSt)	4.96
Flash Point (°C)	185

3.2. Effect of Formic Acid Catalyst Concentration

The concentration of formic acid catalyst varied 10%-wt, 15%-wt and 20%-wt of the FAME oil mass. In Table 2, the iodine number value of the product is smaller than that of the feed. This indicates that the number of double bonds in the feed is released reacting with oxygen to form epoxide bonds. The reaction mechanism follows the equation as shown below (Yuchen et al, 2020):

$$HCOOH + H_2O_2 \rightleftharpoons \mathrm{HCOOOH} + H_2O \quad (3)$$

$$HCOOOH \rightarrow H_2O + CO_2 \uparrow \quad (4)$$

$$R_1 - C = C - R_2 + HCOOOH \rightarrow R_1 - COC - R_2 + HCOOH \quad (5)$$

Table 2. Effect of Formic Acid Catalyst Concentration

Formic acid Conc. (%wt)	Iodine Value	$X_{C=C}$ (%)	Viscosity at 25°C, cSt	Density at 25°C, g/cm^3	Flash Point (°C)
FAME	46.60		4.96	0.871	185
10	5.84	87.47	6.06	0.890	198
15	7.36	84.21	8.68	0.887	195
20	8.38	82.03	9.07	0.891	182

From the Table 2 the iodine number value increased after the concentration of formic acid catalyst was increased from 10%-wt to 15%-wt and 20%-wt. This is certainly not in line with the C=C conversion. Where the conversion decreases with the addition of formic acid concentration. This can be caused by excess formic acid reacting with the epoxy chain as presented in equation (4) to form a 1,2-diol compound (two -OH groups on adjacent carbons), where one of the -OH groups has reacted to form an ester with formic acid (HCOOH). In addition, the performic acid compound formed in reaction equation (3) also reacts with epoxide to form an unstable compound as written in equation (7) (Edy et al, 2020; Yuchen et al, 2020):

$$R_1 - COC - R_2 + HCOOH \rightarrow R_1 - CH(OH) - CH(OCOH) - R_2 \quad (6)$$

$$R_1 - COC - R_2 + HCOOOH \rightarrow R_1 - CH(OH) - CH(OOOCOH) - R_2 \quad (7)$$

The viscosity of the product at 25°C increases with increasing concentration of formic acid. This is due to the formation of saturated compounds as a result of the reduction of C=C bonds. The addition of oxygen atoms to the double C chain causes the density and flash point of the product to be higher than the feed.

3.3 Effect of Acetic Acid Catalyst Concentration

To study the effect of acetic acid catalyst concentration on iodine number, C=C conversion and physical properties of EFAME, the catalyst concentration was varied from 10%-wt, 15%-wt and 20%-wt. The reactions that occur during the epoxidation process follow the equations as presented in equations (8) to (11) (Srikanta et al, 2008).

$$CH_3COOH + H_2O_2 \rightleftharpoons CH_3COOOH + H_2O \quad (8)$$

$$R_1 - C = C - R_2 + CH_3COOOH \rightarrow R_1 - COC - R_2 + CH_3COOH \quad (9)$$

$$R_1 - COC - R_2 + H_2O + H^+ \rightarrow R_1 - CH(OH) - CH(OH) - R_2 \quad (10)$$

$$R_1 - COC - R_2 + CH_3COOH \rightarrow R_1 - CH(OH) - CH(OCOCH_3) - R_2 \quad (11)$$

Table 3. Effect of Acetic Acid Catalyst Concentration

Acetic acid Conc. (%wt)	Iodine Value (g-I_2/100g)	$X_{C=C}$ (%)	Viscosity at 25°C cSt	Density at 25°C g/cm^3	Flash Point (°C)
FAME	46.60		4.96	0.871	185
10	14.97	67.87	5.39	0.868	190
15	15.48	66.78	5.17	0.856	194
20	14.47	68.96	5.78	0.874	196

The results of the experiment are presented in Table 3. The iodine number increased from 14.97 g-I_2/100g to 15.48 14.97 g-I_2/100g or the C=C conversion decreased from 67.87% to 66.78% when the acetic acid concentration was increased from 10%-wt to 15%-wt. This is in line with the research of Srikanta et al (2008), where the higher acetate concentration causes the stability of the oxirane ring to be very low and can react with acetate to form by-products such as α-glycol. Then the changes in viscosity and density of the product to the feed conditions are relatively small.

3.4. Effect of Combined Catalyst Concentration

Acetic acid and formic acid catalysts were combined in the FAME epoxidation process with a total catalyst concentration of 10%-wt, 15%-wt and 20%-wt. While the ratio of acetic acid to formic acid was varied at 30:70, 50:50 and 70:30. Where the experimental results are presented in Table 4.

Table 4. Effect of Combined Catalyst Concentration

Catalyst Conc. (%wt)	Catalyst Ratio FA:AA	Iodine Value	$X_{C=C}$ (%)	Viscosity at 25°C, cSt	Density at 25°C, g/cm^3	Flash Point (°C)
FAME		46.60		4.96	0.871	185
10	70:30	13.20	71.68	6.17	0.885	196
	50:50	14.21	69.50	6.53	0.883	190
	30:70	15.23	67.32	6.60	0.881	198
15	70:30	11.17	76.04	8.56	0.885	182
	50:50	10.91	76.58	7.80	0.890	183
	30:70	9.64	79.30	7.00	0.893	180
20	70:30	12.44	73.31	8.50	0.899	188
	50:50	11.17	76.04	7.06	0.901	183
	30:70	11.67	74.95	8.50	0.900	184

Increasing the catalyst concentration from 10%-wt to 15%-wt at various catalyst ratios, the C=C conversion increased. However, when the catalyst concentration was added to 20%-wt, the conversion decreased. This is in line with the use of a single catalyst above. Most likely the catalyst reacts with epoxide compounds and others to produce by-products.

3.5. Gas Chromatography and Mass Spectroscopic of Epoxidized Products

The samples analyzed to determine the content of EFAME were under formic acid catalyst conditions with a concentration of 10%-wt. The main composition of EFAME products from GC-MS analysis is shown in Figure 1 and Table 5. In the analyzed product there were large amounts of saturated chain-methyl ester components such as hexadecanoic acid-methyl ester (RT 19.109 min), octadecanoic acid-methyl ester (RT 21.180 min) and 17-Octadecynoic acid-methyl ester (RT 22.539 min). In the product there is also an unsaturated compound 9-octadecenoic acid-methyl ester (RT 21.003 min) with a fairly high concentration of 26.59%-mass.

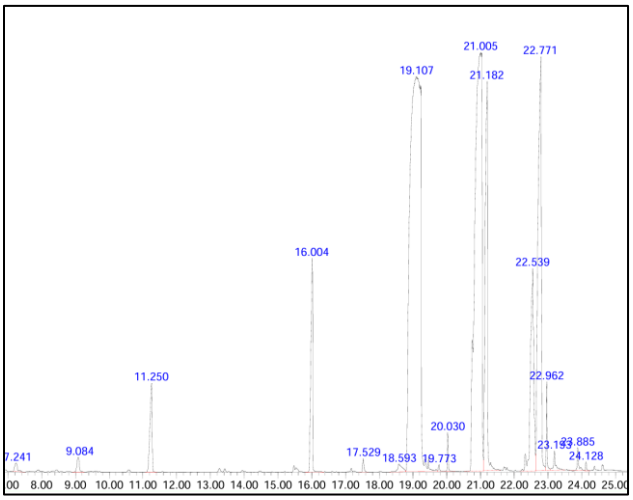

Figure 1. Chromatograms of Epoxidized Fatty Acid Methyl Esters

Table 5. Main Compositions of EFAME by GC-MS Analysis

No.	Retention time (min)	Chemical structural formula	Area (%)
1	9.086		0.32
2	11.251		1.81
3	16.004		3.23
4	18.592		0.32
5	19.109		39.0
6	20.033		0.32
7	21.003		26.59
8	21.180		8.30
9	22.539		5.92
10	22.768		12.30
11	22.962		0.69
12	23.191		0.35
13	23,886		0.27

Epoxy compound was found at a retention time of 22.962 min with a concentration of 12.30%-wt. The epoxy compound formed from this process is methyl 9,10 epoxyoctadecanoate. The chemical compounds formed in this process are in line with the research results of Guodong et al (2019).

Conclusions

Synthesis of epoxide compounds from FAME has been carried out at a temperature of 60oC using formic acid, acetic acid and a combination of both catalysts. Formic acid catalysts provide better performance with a conversion that can be achieved 87.47% at the lowest concentration. The addition of concentration to various types of catalysts can actually reduce the performance of the reaction process, this is due to the side reaction between the catalyst and

the epoxide compound. The results of GCMS analysis of the best sample showed the presence of methyl 9,10 epoxyoctadecanoate epoxide compounds with a concentration of 12.30%-wt.

List of Notations

IV_0 = the amount of iodine at the beginning of the reaction (FAME raw material)
ρ = density of epoxy
m = mass of epoxy [g]
V = volume of epoxy [mL].

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