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EFFECT OF DIFFERENT CATALYST TOWARDS THE EPOXIDATION OF NEEM OIL VIA IN SITU PERACIDS MECHANISM

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Abstract— Currently, concern arises regarding the depletion of fossil fuels forcing us to find an alternative. Epoxidized product from vegetable oil via epoxidation process are one of the alternatives nowadays. Type of catalyst are one of the important parameters to be identify. Epoxidation of neem oil are set up where 100g of neem oil, 1:1 ratio of formic acid and 4:1 ratio of hydrogen peroxide towards neem oil are used, while the temperature to be fix at 700C and stir at 300 RPM for the whole process. Only catalyst is change for both experiment, which are amberlite 120 IR and zeolite ZSM-5 1g each. Results for both show promising relative conversion oxirane (RCO) where amberlite IR 120 at 49.5% meanwhile zeolite ZSM-5 at 47.34%. Epoxidation is successful because the FTIR spectra show formation of C-O which indicates epoxide bond at 1210cm^{-1} and OH group which are the by product also observed at 3450cm^{-1}. Therefore, both catalysts can produce high RCO since the difference are only 2%. However, DHSA form from the degradation of oxirane ring can be focus on for the optimization of vegetable oils usage in the industry.

I. Introduction

Epoxidation processes are completed when both carbon atom and alkyl group are attached next to each other on the same oxygen atom and form three cyclic member structure [1] known as epoxides or oxiranes. Peracid plays an important role in epoxidation process. Peracid is formed from mixture of hydrogen peroxide with formic acid which is known as performic acid or by mixing hydrogen peroxide with acetic acid and be known as peracetic acid. Another method can be carried out with different procedures such as epoxidation with organic and inorganic peroxides, by molecular oxygen and epoxidation with using hypohalous acids and their salts respectively [3]. The application of epoxidized has been widely used in industries such as stabilizers or plasticizers in plastic industry glossy effect for polyacrylate and as reactant for polyols production[4]. Other than that, epoxidized ester can be used to replace the volatile organic solvent in paints [5].

There is abundant research on epoxidation that uses different types of renewable materials. Most common method are epoxidationis generatedable oils by either performic or peracetic acid which generated by in situ process [4]. Epoxidation of camelina oil is also involved with formic acid and hydrogen peroxide where the results show optimum epoxy content obtained are 7.52wt% with a conversion rate of 76.34% by using excess hydrogen peroxide and a molar ratio of formic acid of less than 1 for 5 hr at 50°C [6].

Recently, epoxy originated from non-renewable fossil fuel. However, these sources are not renewable and would surely be depleted later and humans need to have other alternatives in figuring out the solution to this kind of crisis. Thus, instead of wasting more energy and cost to find more sources of fossil fuel in the future, natural based feedstock such as edible or non-edible vegetables oils can be studied. Natural and renewable feedstock has been greatly commercialized and increased in demand as the products from natural resources are more eco-friendly to the environment.

Thus, the objective of this paper is to determine the epoxidation rate by different catalysts, which are amberlite and zeolite toward the epoxidation process of neem oil.

II. Method

A. Materials

All the chemicals used in this study are neem oil, formic acid (85%), hydrogen peroxide, (50%), zeolite ZSM 5 catalyst (95%) are all supplied by Merck Sdn. Bhd while amberlite IR 120 was purchased from Sigma Aldrich.

B. Experimental Set-up

The study on epoxidation process was done by preparing all the chemicals as in Table 1.

Table 1: Materials used

Neem Oil	Formic Acid	Hydrogen Peroxide	Catalyst	Temperature	RPM
100 (gram)	1 to neem oil ratio	4 to neem oil ratio	Amberlite 120 IR	700°C	300
			Zeolite ZSM-5		

For starting, catalyst and performic acid form are added simultaneously into the beaker after temperature of neem oil reach 700°C as shown in Figure 1. Stirring speed is maintained at 300rpm and 700°C conditions were maintained throughout the process. The sample taken for every 10 minutes are mixed with a few drops of crystal violet and 10mL acetic acid before titration process to determine the optimum rate of epoxidation in this study. Titration is done by hydrobromic acid (HBr) that is filled into pipette. Amount of (HBr) needed to obtain the colour changes from blue to yellowish green are recorded.

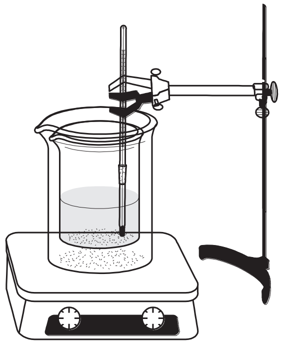

Figure 1: Experimental Set-Up

C. Epoxidation Process

AOCS Tentative Method Cd 9-57 are chosen to determine the oxirane oxygen content experimental (OOCe). Equation 1 shows the equation used to compute the (OOCe) in moles/100g.

$$OOC_e = \frac{T \times N_{HBR} \times 1.6}{W} \qquad (1)$$

where:

T = volume of HBr in ml required to titrate the sample

N_{HBR} = hydrogen bromide's normality

W = sample's weight in grams

The oxirane percentage conversion was calculated using Equations 2 and 3.

$$RCO = \frac{OOC_e}{OOC_t} \times 100\% \qquad (2)$$

$$OOC_t = \left[\frac{\left({IV_0}/{2A_I} \right)}{100 + \left({IV_0}/{2A_I} \right) A_o} \right] A_o \times 100 \qquad (3)$$

where:

OOC_t = optimum oxirane oxygen that could be obtained theoretically and determined at 1.8213

IV_0 = initial iodine value of oleic acid sample

A_o = oxygen molar mass

A_I = iodine molar mass

100g of oleic acid taken as basis for calculation.

III. Result And Discussion

Both epoxidation processes are repeated with the same parameter, and only catalyst are changes. Both catalyst, zeolite and amberlite are in solid form with 1g weight each are used. Epoxidation is optimum when relative conversion oxirane is the highest, where the double bond of vegetable oils is converted into oxirane ring. Figure 2 shows the epoxidation rate both by using amberlite and zeolite.

In Figure 2, relative conversion oxirane for using amberlite IR 120 catalyst at 49.5% meanwhile zeolite ZSM 5 at 47.34%. are at 70 minutes time. This clearly prove that heterogenous catalyst have better water adaptability where it does not effect the selectivity since epoxidation reaction produce water as their side reaction [7]. Other benefit of heterogenous catalyst is minimal cost involve since it was easier for purification and recyclable.

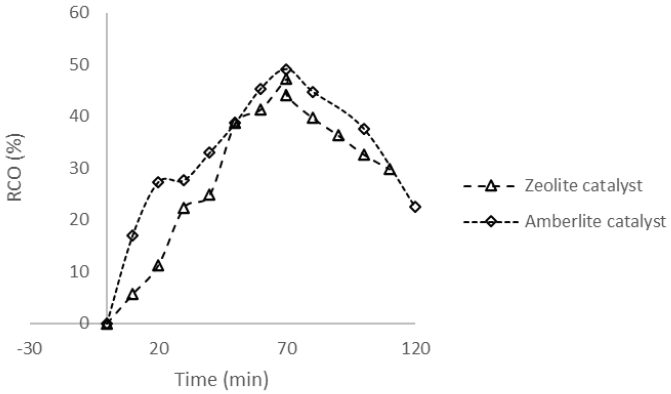

Figure 2: RCO (%) by Using Zeolite and Amberlite Catalyst

In this research, amberlite catalyst produce slightly higher RCO which are 2% compared to when using amberlite. This is due to the slightly increase crosslinking structure indicates a smaller size of pore, thus providing more surface area and promote higher chances for active site attack [8]. Meanwhile, Yunus *et. al* [9] proved that at higher temperature of reaction, higher RCO are obtained, mainly because of the aluminium contain in zeolite helping in lower the activation energy of reaction.

At final stage of the reaction, the epoxide produces and raw neem oil was analysed by (FTIR) to determine the availability of oxirane ring and hydroxyl group which are by product of epoxidation process. FTIR spectrum of non-epoxidized neem oil and epoxidized neem oil in Figure 3.

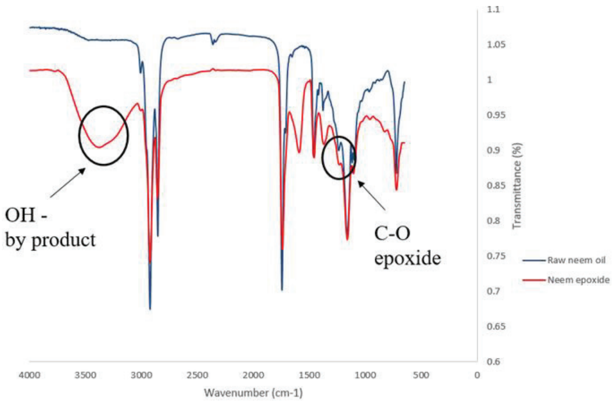

Figure 3: FTIR Spectra of Non Epoxidized Neem Oil and Epoxidized Neem Oil

Based on the spectra above, epoxide bond C-O at 1210cm^{-1} indicates that epoxidation process of neem oil was a success. Formation of OH group also observed at 3450 cm^{-1}. This further confirm the formation of epoxide since water are the intermediate product for epoxidation. Furthermore, according to Yunus *et. al* [9], the ability of oxirane ring to retain its shape decrease at higher reaction temperature which lead to ring opening. The sudden decrease of RCO show the epoxidation reaction rate had achieve its optimum level.

However, the phenomenon of oxirane ring opening would lead to production of DHSA, which are derivatives for cosmetic industries. DHSA can be produce by continuous water additional by the system towards the epoxidized neem oil. This are a potentially beneficial to the industry since DHSA produce from vegetable oils are renewable compared to the conventional method, which petroleum based DHSA are produce which clearly from non-renewable resources and higher in cost [10].

IV. Conclusion

The efficiency of heterogenous catalyst in epoxidation of neem oil could not be denied. However, the temperature must be above or maintain at 700°C to get maximum RCO. Catalyst properties such as its porosity, crosslinking need to be consider while choosing for epoxidation process and DHSA form from the degradation of oxirane ring can be focus on for the optimization of vegetable oils usage in the industry.

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