

SIIC029

Degradation of Catalytic Epoxidation of Oleic Acid Palm Oil by in situ Performic acid

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Abstract:

The world consumption of raw material has been changing from a non-renewable material into a renewable material. The study on the epoxidation has also changed in a much cost-effective and a greener product which is safer than the non-renewable material. The increasing study of vegetable oil has been in demand. Epoxidation of oleic acid was carried out by in situ performic acid to produce epoxidized oleic acid. Since epoxide ring is highly reactive, the degradation of the oxirane was tested by using hydrogen peroxide, formic acid and water. The degradation of the epoxide is mainly focus on the production of DHSA. Therefore, the study on degradation of the epoxide is lacking. Analysis by using FTIR and NMR are conducted to know the characterization of the degradation product. As a result, the degradation is highly effective in an acidic condition such as hydrogen peroxide and formic acid which lead to a formation of side products such as diol and α -glycol (carboxylic acid). Then, the kinetic rate, k parameters obtained by using an ODE45 function on MATLAB software is $k_{11}= 6.6442$, $k_{12}= 11.0185$, $k_{21}= 0.1026$, for epoxidation palm oleic acid, and $k_{31} = 0.0347$, $k_{41}= 0.0154$, $k_{51}= 0.0142$, in degradation process. The minimum error of the simulation is 0.17311.

Keywords:

palm oil, epoxidized oleic acid, oxirane ring, degradation, kinetic rate

Objectives:

- To identify the effect of addition of H₂O, H₂O₂ and FA with the epoxide for the opening of oxirane.
- To determine the physicochemical product of the ring opening of epoxy.
- To determine the reaction kinetic of the ring opening of epoxy.

Methodology:

The epoxidation will be carried out in a 2litre capacity reactor with agitation of 300 rpm. The reaction will take place in a beaker. The molar ratio used will be 1:1:1 of FA-to-OA-to-H₂O₂ [1]. Oleic acid, Formic acid and Sulphuric acid will be added simultaneously in the reactor. The mixture will be continuously stirred at fixed speed. The reaction will be heated gradually to achieve a constant temperature at 55°C. The hydrogen peroxide will be added gradually after the mixture reach 55°C. Time reaction will be taken after the addition of hydrogen peroxide. A 5 mL of sample will be taken every 5 minute during the reaction period to avoid vaporization of FA and a runaway reaction [2]. The sample was retrieved to determine the oxirane oxygen content according to AOCS Tentative Method Cd 957 [3], as in equation (1):

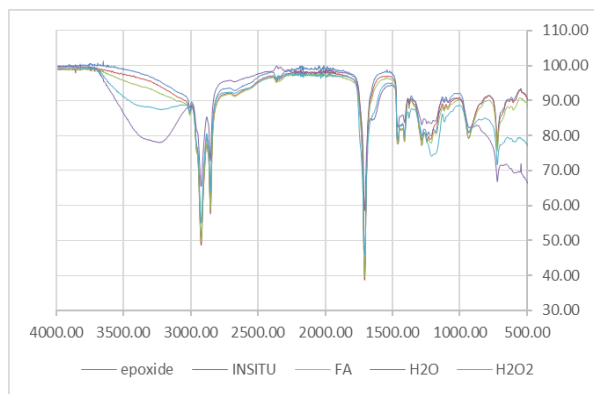
$$OOC_{exp} (\%) = 1.6 \times (V-B) / W \quad (1)$$

where V-B is denoted as the volume of hydrogen bromide in mL that is needed to titrate the sample, NHBR is the molarity of the hydrogen bromide which is 3.56 and W is the weight of the sample which is 2.5 grams. Equations 2 and 3 are used to calculate the relative percentage conversion to oxirane (RCO).

$$RCO = \frac{OOC_{exp}}{OOC_{the}} \times 100\% \quad (2)$$

$$OOC_{the} = \left[\frac{(IV_0 / 2A_I)}{100 + (IV_0 / 2A_I) A_O} \right] A_O \times 100 \quad (3)$$

where OOC_{the} is the theoretical maximum oxirane oxygen and was determined to be 1.8213. Meanwhile, IV₀ is the initial iodine value of WCO sample which is 74.69, A_o (16.0) and A_I (126.9) are the atomic masses of oxygen and iodine, respectively.

Results:

FTIR of the epoxide and degraded epoxide

Estimated rate reactions parameter from MATLAB software

Rate constant of epoxidation process	Value rate constant (mol/L.min)
k ₁₁	6.6442
k ₁₂	11.0185
k ₂	0.1026
k ₃	0.0347
k ₄	0.0154
K ₅	0.142
Summation of Error (%)	0.1731116428
Correlation coefficient, r	0.925544

Conclusion:

The cost-effectiveness and eco-friendly to environment palm oil has makes them as an alternative for the production of epoxide. The present formic acid, hydrogen peroxide and water can cause ring opening of epoxide. From the study, the effect of formic acid toward degradation less active compare to hydrogen peroxide since formic acid is less reactive. Furthermore, deeper study is required to obtain more on oxirane ring degradation reactions, to obtain the correct predictions to fit with the experimental data.