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Enzymatic epoxidation of oleic acid ? a green pathway to chemical intermediates

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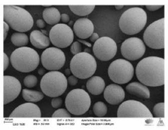
PURPOSE OF THE ABSTRACT

The need for switching from fossil-based raw materials to renewables has led to discovering new technologies for producing the demanded chemical products. Epoxidized vegetable oils have a great potential to replace traditional fossil-based products since they are biodegradable, renewable, and non-toxic. Non-edible plant oils are an option for the production of epoxidized oils, which are used as chemical intermediates for the production of biolubricants, plasticizers, biobased rigid foams and non-isocyanate polyurethanes. The market for oleochemical fatty acids and their derivatives has been growing in the recent years, and the growth is projected to continue during the next few years. The source of vegetable fatty acids can be soybean, palm, rapeseed, sunflower, linseed, and cottonseed. In Northern Europe, Tall Oil Fatty Acids (TOFA) are a large and sustainable source of fatty acids. Tall oil is mainly obtained as a valuable side product in Kraft pulping of wood.

For the time being, the most common technology used in industrial scale for producing epoxidized vegetable oil is the Prileschajew epoxidation. This method comprises a reaction between the unsaturated fatty acid and a peroxy acid in the oil phase, the latter being generated in situ in the aqueous phase with an added short-chain carboxylic acid (e.g. formic acid or acetic acid) and hydrogen peroxide. Despite being both an economic and environmentally friendly method, the epoxides produced by Prileschajew epoxidation are sensitive to ring-opening and the product selectivity is limited. Therefore the recent research has switched its focus towards enzymatic epoxidation which occurs in a mild reaction environment by forming peroxy acids in situ directly from the carboxylic group of the fatty acid and hydrogen peroxide as the oxidant.
We have studied enzymatic epoxidation of unsaturated fatty acids originated from renewable, plant-based resources. Oleic acid as a model molecule for fatty acids is used as feedstock for the epoxidation. The epoxidation reaction is catalyzed by Candida Antarctica lipase B, meaning that the reaction can be carried out under mild reaction conditions with no need of an additional carboxylic acid in the reaction mixture. In this kind of enzymatic epoxidation, only the fatty acid, an oxidant and immobilized lipase are needed for transforming the double bond of the fatty acid into an epoxy group; no reaction carrier (like formic acid or acetic acid) is needed, which is a green leap compared to the Prileschajew epoxidation process.

This work was focused on the epoxidation of oleic acid using immobilized lipase Novozym® 435 as the catalyst and hydrogen peroxide as the epoxidation agent. An extensive series of kinetic experiments were carried out in a laboratory-scale batch/semibatch reactor. Different reactant molar ratios, temperatures, stirring rates and hydrogen peoxide addition policies were evaluated. Acoustic irradiation was implemented in some experiments for process intensification and different ultrasound amplitudes were tested. Novozym® 435 revealed to be an efficient and durable catalyst for fatty acid epoxidation. The experimental results showed that almost complete conversions of the double bonds in oleic acid are achievable in isothermal batch operation, with low concentrations of ring-opening by-products formed. Ultrasound irradiation was successfully applied for enhancing the reaction rate, and higher conversions were reached compared to silent experiments. The catalyst preserved its activity and selectivity well, which was confirmed by catalyst recovery experiments conducted in the absence and presence acoustic irradiation. The product distribution was studied with nuclear magnetic resonance (NMR) spectroscopy, confirming that the main ring-opening agent is the fatty acid itself, which resulted in the formation of esters.

FIGURES



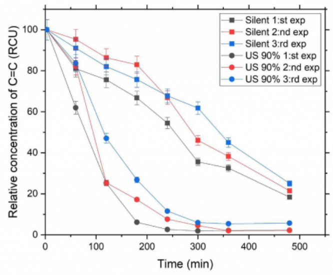


FIGURE 1

Lipase catalyst

SEM image of lipase catalyst particles

FIGURE 2

Kinetic experiments

Effect of ultrasound on kinetics: considerable enhancement

KEYWORDS

Epoxidation | Vegetable oil | Enzyme | ultrasound

BIBLIOGRAPHY