Structure & Reactivity approach applied to the epoxidation of vegetable

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Abstract

Increasing environmental awareness has underscored the need for sustainable alternatives to fossil-based resources due to global warming, GHG emissions, and the depletion of fossil reserves. The chemical industry, heavily reliant on petroleum-derived feedstocks, significantly contributes to GHG emissions, exacerbating environmental challenges and raising concerns about resource security and market volatility. Biomass, a renewable and carbon-neutral resource, has emerged as a key player in producing biofuels for transportation, electricity, and heat. Among biomass-derived materials, vegetable oils (VOs) are widely recognized for their availability, renewability, and chemical versatility. Their modification, particularly via epoxidation, transforms unsaturated fatty acids into reactive epoxide groups, facilitating the production of bio-based polymers, coatings, adhesives, and other high-value materials. Although various epoxidation methods exist, the Prileschajew method is the most studied, despite drawbacks such as side reactions like ring-opening, which reduce yield and selectivity, and safety concerns when using strong peracids like peracetic and performic acids. This study investigates the epoxidation of vegetable oils (VOs) and their fatty acid methyl esters (VO-FAMEs), addressing key challenges like improving reaction efficiency, minimizing side reactions, and enhancing thermal stability. Using perpropionic acid and Amberlite IR-120 as a solid acid catalyst, the study demonstrates superior performance compared to performic acid. The research compares the structural and kinetic behaviors of different oils and their derivatives, developing a reliable kinetic model and expanding its application to various vegetable oils. The study initially focuses on cottonseed oil (CSO) and its FAME (CSO-FAME). Functional group transformations and structural differences between CSO and CSO-FAME were characterized through FTIR, NMR, SEC, and titration. A comparative analysis of epoxidation kinetics between CSO and CSO-FAME was conducted, revealing that CSO’s three-armed star structure enhances the epoxidation rate compared to the linear structure of CSO-FAME. In the second part, a detailed structural analysis was performed to monitor functional group modifications and structural changes, providing insights into reaction pathways and side reactions. A robust kinetic model describing epoxidation and ring-opening reactions of CSO and CSO-FAME was developed, incorporating mass transfer effects and the biphasic nature of the reaction system. Bayesian methods were employed for parameter estimation, achieving high precision and strong alignment with experimental data. The research further explored soybean oil (SBO), linseed oil (LSO), and their FAMEs in the third part, systematically comparing their epoxidation kinetics and structural transformations. The results showed that CSO exhibited the highest epoxidation rate, followed by SBO and LSO, with similar trends in their FAME derivatives. Despite LSO containing more double bonds, its epoxidation rate was hindered by linolenic acid composition. FAMEs exhibited a stronger linear relationship between initial double bond concentrations and reaction rates, likely due to more accessible reactive sites and reduced steric hindrance. This study establishes perpropionic acid as a superior oxidizing agent for epoxidation, compared to performic acid. The developed kinetic model provides valuable insights into epoxidation dynamics, contributing to the valorization of biomass through the production of epoxidized vegetable oils and their derivatives.