Breakthrough in epoxidation of vegetable oils: from semibatch to continuous technology

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Highlights

- New continuous packed bed reactor technology was developed for the production of epoxidized vegetable oils
- The superiority of the new technology was demonstrated experimentally
- The epoxide production was optimized experimentally and described mathematically with a dynamic axial dispersion model
- The experimental optimization the mathematical model gave a good perspective for future process scale-up actions

1. Introduction

Epoxides are important intermediates for the synthesis of several organic compounds, e.g., di- or polyalcohol, β-hydroxethers, β-hydroxesters and, carbonates. In this scenario, Epoxidized Vegetable Oils (EVOs) represent a noteworthy source to produce chemicals and to obtain intermediates to make polyurethane in an environmentally friendly way. Several technologies have been proposed and tested in the recent years for the direct epoxidation of unsaturated vegetable oils with hydrogen peroxide, such as the use of heterogeneous and enzymatic catalysts. However, the alternative methods are not yet competitive with the classical indirect epoxidation technology according to the principle of N. Prilezhaev. The indirect epoxidation is based on the presence of a short-chain carboxylic acid (e.g. formic or acetic acid) which acts as the reaction carrier forming a percarboxylic acid in a reaction with hydrogen peroxide. This percarboxylic acid transfers from the aqueous phase to the oil phase, where it reacts with the double bonds of the vegetable oil. The short-chain carboxylic acid is regenerated and a new reaction cycle is initiated. The critical issue in the process is the exothermicity of the reaction system and the thermal stabilities of hydrogen peroxide and particularly the percarboxylic acid formed in situ. The current industrial practise still relies on the cumbersome and dangerous semibatch technology: hydrogen peroxide is added gradually to the reaction mixture to avoid a temperature run-away, which could cause fatal consequences: decomposition of hydrogen peroxide and percarboxylic acid. Semibatch technology with long reaction times is the real bottleneck of the current commercial process [1].

In this work, we decided to take the challenge and investigate a technology jump from semibatch to continuous technology, but remaining on the principal concept of N. Prilezhaev, because it works in practise. A new, continuous reactor system was developed, based on very solid fundamental studies of the formation and decomposition kinetics of percarboxylic acids, decomposition kinetics of hydrogen peroxide, determination of component partition coefficients, as well as studies on the epoxidation and ring opening kinetics, determination of residence time distributions in the aqueous and oil phases and evaluation of interfacial mass transfer phenomena. The extensive experimental work culminated in rigorous mathematical modelling of the continuous reactor concept.

2. Methods

A laboratory-scale continuous packed bed reactor was constructed. The reactor was filled with glass beads to spread the aqueous and oil phases and to counteract channeling. The temperature profile inside the reactor was recorded with a thermocouple. The epoxidation experiments were carried out using cardoon seed oil as the model substance. Formic acid was used as the reaction carrier. The dynamic behavior of the system was investigated by taking samples from the oil and aqueous phases at the reactor outlet. ^{1}H-NMR analysis was applied to determine the double bond conversion and the epoxide

selectivity. The Greenspan and MacKeller and the acid-base potentiometric titration methods were used to analyse the concentrations of hydrogen peroxide, formic acid and performic acid. Step-change experiments were carried out with inert tracers (Sudan black for the oil phase and NaCl for the aqueous phase) to determine the residence time distribution and the Péclet number. A dynamic liquid-liquid reactor model was developed, based on intrinsic kinetics as well as on interfacial mass transfer and axial dispersion effects. Levenberg-Marquardt method was used to minimize the objective function in the optimization of the parameters of the model. The computations were performed with gPROMS [1].

3. Results and discussion

The main reactions in the system are displayed below,

$$FA_{Aq} + H_2O_2 \underset{}{\overset{H^+}{\rightleftharpoons}} PFA_{Aq} + H_2O \qquad \text{Perhydrolysis in aqueous phase}$$

$$PFA_{Org} + DB \longrightarrow C(O)C + FA_{Org} \qquad \text{Epoxidation in organic phase}$$

Besides these reactions, some ring-opening of the epoxide took place, probably at the phase interface, thus suppressing the epoxide yield. An example of the model simulation results is provided in Figure 1. Experimental observations revealed that the hydrogen peroxide concentration has a profound influence on the double bond conversion and epoxide selectivity. After gradually increasing the hydrogen peroxide concentration in successive experiments, the double bond conversions exceeding 95% and epoxide selectivities 90% at the organic-to-aqueous volumetric flow ratio 1:9 were reached at a low and safe process temperature, 40°C, clearly exceeding the performance of the current semibatch process.

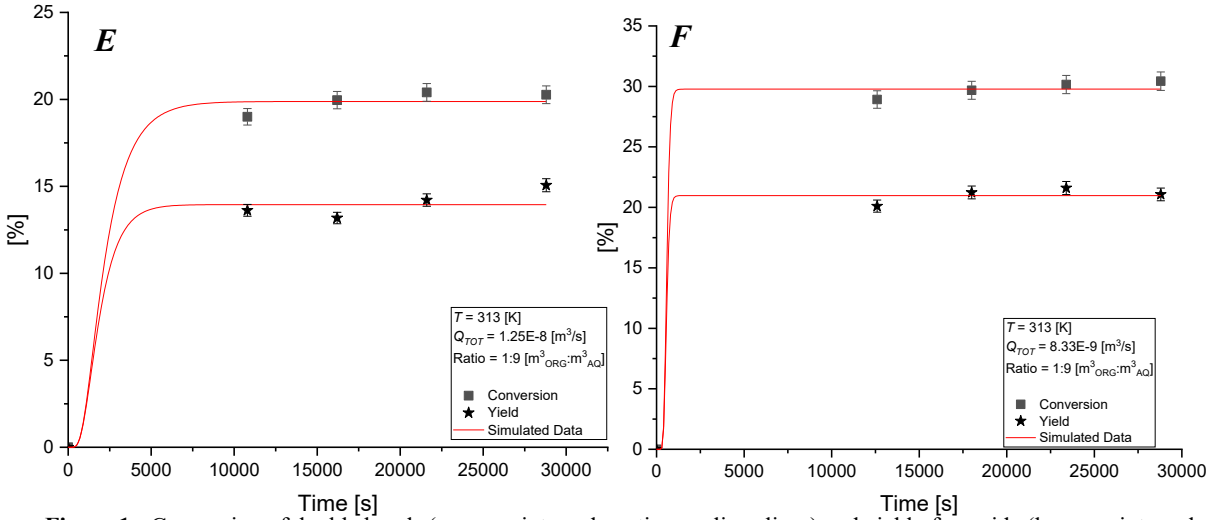

Figure 1. Conversion of double bonds (upper points and continuous lines lines) and yield of epoxide (lower points and continuous lines) in two experiments in the continuous reactor. Reaction temperature: 40°C.

4. Conclusions

Safe and convenient continuous reactor technology was developed for the epoxidation of unsaturated vegetable oils originating from non-edible sources. The process concept was proven experimentally and described mathematically with a multiphase dynamic axial dispersion model, giving the perspective to process scale-up. Further work could be devoted to detailed studies of the ring-opening reactions.

References

Tommaso Cogliano, Epoxidation of vegetable oils: from batch to continuous process, Doctoral thesis, Università di Napoli and Åbo Akademi University, *Acta technologiae chemicae Aboensia 2023 A/4*

Keywords
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