Tandem Process Intensification utilizing microwave irradiation and heterogeneous catalysis in the epoxidation of vegetable oils

Adriana Freites Aguilera[1*], Pasi Tolvanen[1], Sebastien Leveneur[1,2], Jyri-Pekka Mikkola[1,3], Timothy Marchant[4], Tapio Salmi[1]

1 Åbo Akademi, Johan Gadolin Process Chemistry Centre, Industrial Chemistry & Reaction Engineering, FI-20500 Turku/Åbo, Finland;

2 Normandie Université LSPC-Laboratoire de Sécurité des Procédés Chimiques, EA4704, INSA/Université Rouen, BP08, Avenue de l'Université, 76801 Saint-Etienne-du-Rouvray, France.

3 Technical Chemistry, Chemical-Biological Centre, Umeå University, SE-90187 Umeå, Sweden.

4 Department of Mathematics, University of Wollongong, Wollongong, New South Wales 2522, Australia

**Corresponding author: afreites@abo.fi*

Highlights

- The reaction was enhanced by employing a solid resin catalyst.
- The special mixing technology (Spinchem^{TM}) minimized external mass transfer limitations
- Microwave irradiated experiments were compared with conventionally heated experiments
- A kinetic model for the epoxidation reaction was developed

1. Introduction

Oil extracted from plants, seeds and wood is a vast biomass resource that can be used to elaborate a wide range of products, for instance, by epoxidation. Epoxidized vegetable oils are used upon development of bio-lubricants, PVC-derived plastic-ware, as well as intermediates for the synthesis of polyols, glycols, olefinic compounds and stabilizers for polymers. Moreover, microwave irradiation (MW) is considered as one of the most innovative process intensification technologies [1]. The Prileshajev oxidation is the most common method to epoxidize vegetable oils, by using peroxycarboxylic acid formed in situ from hydrogen peroxide and acetic acid. To enhance the reaction rate, a solid catalyst can be used.

The aim of this work was to develop an improved method for producing epoxidized vegetable oils with high yields, using less energy and shorter reaction times, applying MW technology combined with special mixing technology and a solid catalyst. Finally, a kinetic model was developed for the epoxidation reactions describing the intrinsic kinetics under various reaction conditions.

2. Methods

Epoxidation of oleic acid was performed in a semi-batch reactor, by the so called Prileschajew oxidation [2]. The perhydrolysis reaction (peroxyacetic acid formed in situ from acetic acid and H_2O_2) was enhanced by using a solid catalyst resin. The reactor system comprised a loop where the mixture was pumped through a cavity in which (single-mode) microwave irradiation took place and immediately recirculated back to the collector vessel/reactor. Experiments conducted under MW were compared with identical experiments carried out under conventional convective/conductive heating. A special mixing technology (Spinchem^{TM}) was incorporated, which allowed to minimize the external mass transfer limitations of the bifacial system and to immobilize the solid resin catalyst. The reaction kinetics was modeled mathematically by applying numerical methods for the solution of stiff differential equations and optimization algorithms for parameter estimation. With the help of this model, the numerical values of the kinetic parameters were obtained and the model could be used to predict the progress of the reaction. Maxwell's equations were included to describe the microwave heating in the energy balance, which defines the interaction of each substance present in the reaction under microwave irradiation.

3. Results and discussion

A clear enhancement of the epoxidation kinetics was accomplished with microwave heating in comparison to conventional heating when performing comparable experiments at 40 ºC without the solid catalysts [3]. When using the Spinchem RBR (Rotating Bed Reactor), external mass transfer limitations were minimized. The yields were further improved when immobilizing the solid Amberlite catalyst into the mixer.

The kinetic model for epoxidation of vegetable oil showed to have a good correspondence between experimental and calculated values. Rate constants and activation energies for the reactions involved were obtained by nonlinear regression analysis.

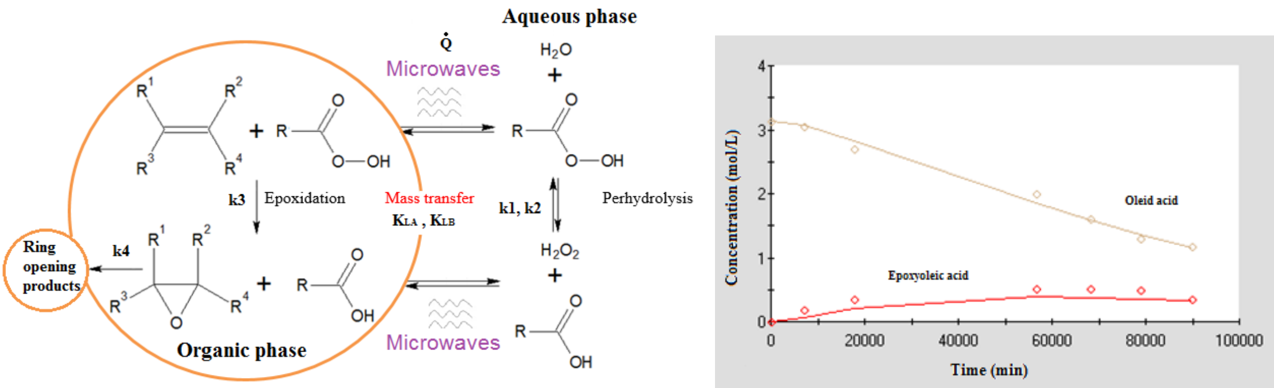

Figure 1. LEFT: Epoxidation reaction scheme. RIGHT: Data fitting for experiment under conventional heating at 40°C.

4. Conclusions

The performance upon epoxidation of vegetable oil was significantly improved by using a combination of microwave technology, special mixing technology (Spinchem^{TM}), and solid resin catalyst. A good fit of the kinetic model to the experimental data was achieved. Estimated rate constants and activation energies for the reactions involved with conventional heating showed to be in the same order of magnitude as the ones reported in the literature.

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Keywords
Epoxidation; mathematical modelling; vegetable oils; microwaves.