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Avant-garde process intensification in the production of epoxidized fatty acids and fatty acid esters

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PURPOSE OF THE ABSTRACT

Introduction

Oil extracted from plants, seeds and wood is one of the vast biomass resources which can be used to elaborate a wide range of products. Particularly in Nordic countries, tall oil fatty acids represent an abundant feedstock, because large areas of these countries have an enormous annual growing stock volume (103 million m3 /year, Finland, 2012). Fatty acids originating from tall oil do not compete with the food chain. Epoxidized fatty acids and fatty acid esters are used for developing PVC-derived plastic-ware, as well as intermediates for the synthesis of biolubricants, polyols, glycols, olefinic compounds and stabilizers for polymers; their demand is increasing constantly.

The goal of the work was to develop intensified process technology for the production of epoxidized vegetable oils from fatty acids and hydrogen peroxide. Three aspects of process intensification were in focus: application of microwave irradiation (MW) [1], heterogeneous catalysts (cation exchange resins) and new mixing technology (Rotating Fixed Bed). The complex multiphase reaction system is displayed in Figure 1. Acetic acid (RCOOH, AA) was chosen as the oxidant carrier according to the Prileschajew principle [2], and tall oil fatty acids and distilled tall oil were used as reactants.

Materials and Methods

The reaction was executed by peroxyacetic acid (PAA) formed in situ from acetic acid (AA) and H2O2 (HP). Epoxidation of model molecules (pure fatty acids, such as oleic acid) and tall oil was performed in a recycled semi-batch loop reactor. The core of the reactor system was a vigorously stirred tank. A tailored microwave source was implemented in the system; the reacting mixture of oil and the aqueous phase were circulated in a loop through the microwave cavity. The microwave effect was compared with experimental results obtained in with parallel heating. The reactor system was equipped with a special mixing technology (SpinchemTM), which allowed to minimize mass transfer limitations of the bifacial oil-aqueous system and to immobilize solid resin catalysts. An extensive series of kinetic experiments were carried out in the presence and absence of microwave irradiation and heterogeneous catalysts. Typical reaction temperatures were 40-60oC. From the separated aqueous and organic phases, the concentrations of AA, HP, PAA, oil and epoxidized oil were determined by titrations. The ring-opening products were identified by NMR. The liquid flow in the loop reactor was characterized

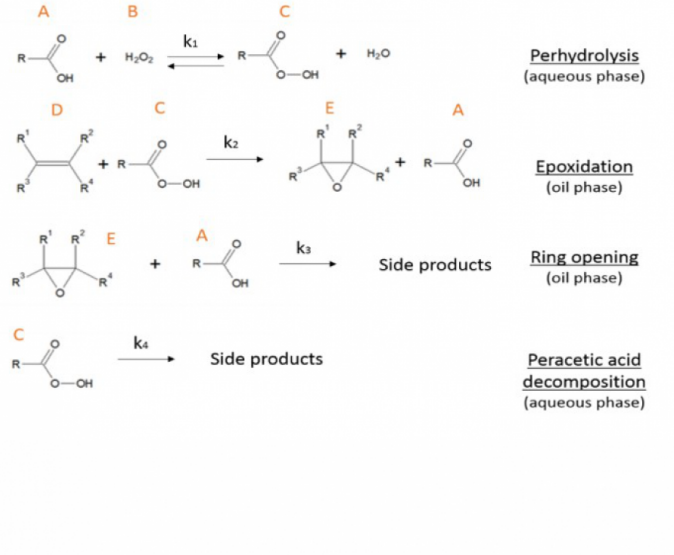
by tracer experiments.

Results and Discussion

The results obtained for epoxidation showed that temperature, acetic acid amount and hydrogen peroxide amount accelerated both rate of epoxidation and ring opening. A clear enhancement of the epoxidation kinetics was accomplished with microwave heating in comparison to conventional heating in the absence of the solid catalyst [3]. By introducing a heterogeneous catalyst (cation exchange resin, e.g. Amberlite or Dowex) the reaction rate was even more enhanced. Several heterogeneous catalysts were screened to find the highest performance (Figure 2).

Advanced kinetic modelling of the multiphase system was carried out, starting from first principles. Detailed kinetic models based on reaction mechanisms were derived and the model parameters were estimated by non-linear regression analysis. The models for epoxidation with conventional heating and microwave irradiation had a good correspondence between experimental and calculated concentrations of fatty acid and epoxide. The rate constants and activation energies for the perhydrolysis, epoxidation and ring-opening reactions were obtained.

FIGURES



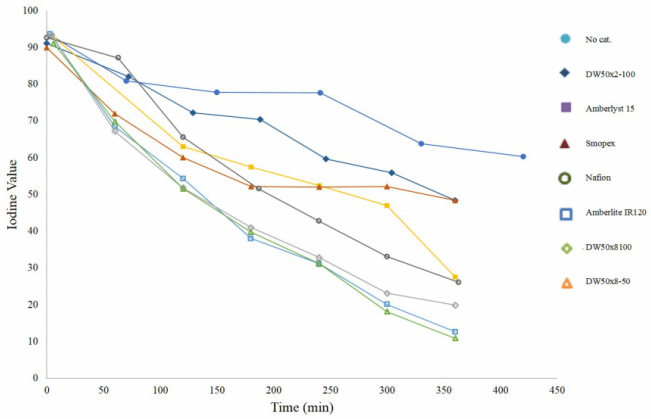


FIGURE 1

Figure 1

Reaction scheme for epoxidation of fatty acids

FIGURE 2

Figure 2

Epoxidation kinetics of a fatty acid (oleic acid) in the absence and presence of heterogeneous catalyst

KEYWORDS

Process intensification | fatty acid | epoxidation | catalysts and kinetics

BIBLIOGRAPHY

[1] A. Freites Aguilera, P. Tolvanen, V. Sifontes Herrera, J-N. Tourvielle, S. Leveneur, T. Salmi, Aspects on reaction intensification by microwave and ultrasound techniques in some chemical multiphase systems. In: Process Synthesis and Process Intensification: Methodological Approaches, Berlin, Boston: De Gruyter (2017) 111-142.

[2] N. Prileschajew Ber. Dtsch. Chem. Ges. 42 (1909) 4811.A. Bianchi, N.C. Jones, Chem. Eng. J. 157 (2019) 326–337.

[3] A. Freites Aguilera, P. Tolvanen, K. Eränen, S. Leveneur, T. Salmi, Epoxidation of oleic acid under conventional heating and microwave radiation, Chemical Engineering and Processing: Process Intensification, 102 (2016) 70-87.