DECYL ACETATE SYNTHESIS BY ENZYME CATALYSIS IN SC-CO2

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Abstract

The main purpose of this work was the study of long chain esters production, using decyl acetate as model compound, by enzymatic catalysis in supercritical media, with the aim of developing a sustainable, clean and efficient process as an alternative to the traditional chemical processes. The combination of a sustainable and clean technology, as biocatalysis, with a green/natural solvent, as supercritical CO_2, besides allowing the establishment of processes with less environmental costs, leads to products considered as natural, which results in a significant increase of their market value.

Decyl acetate is a high added value product. It figures in the "Food and Drug Administration" list of authorized flavoring agents and additives, and it also finds applications in the fragrance industry because of its floral essence. Usually, these kind of esters are obtained by extraction from natural expensive oils and waxes or produced through the esterification of carboxylic acids by acid catalysis. In this work, it was synthesized by the transesterification reaction of vinyl acetate with decanol in a high-pressure experimental set-up, equipped with a variable volume batch reactor, operating isothermally at 35 ºC and 100 bar. *Candida antarctica* Lipase B (CALB), immobilized in the macroporous resin Lewatit B (Novozym 435®), was used as catalyst and CO_2 in supercritical conditions was used as solvent.

Results on the enzyme intraparticle distribution, external and internal diffusional limitations, and effect of the feed concentration of substrates in the initial reaction rate are presented. Modeling and simulation results are also addressed in this work. Some important details of the experimental set-up and experimental procedure are described.

The enzymatic content was determined for each particle size of the catalyst. The smallest particles have a larger specific amount of enzyme, with an inversely proportional relation between the enzymatic content and the particle size. The results also show that the enzyme is most probably located in an external shell of the particle, following an "egg-shell" model type, with a thickness of ca. 60 µm (assuming a homogeneous distribution in this outer shell), independent of the particle size.

The mass transfer resistances, both external and internal, were found to be negligible.

The experimental results obtained while varying the concentration of each reactant individually were qualitatively consistent with the Ping-pong bi-bi kinetic model with competitive inhibition by the alcohol: the reaction was enhanced by concentrations of vinyl acetate $\geq$ 100 mM, and inhibited by concentrations of decanol $\geq$ 100 mM.

The reactor behavior was simulated using a simplified Ping-pong bi-bi reaction rate equation with four parameters. These were determined using an adaptative random search optimization algorithm. Simulation results are in very good agreement with experimental data, within the range of concentrations tested (50 – 200 mM).

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