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Enzymatic synthesis of butyl acetate in a packed bed reactor under liquid and supercritical conditions

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ABSTRACT

In this work we studied the synthesis of butyl acetate in an enzymatic packed bed reactor using lipase B, from *Candida antarctica*, immobilized by simple physical adsorption on porous pellets. The enzymatic reaction was carried out in two different solvents: a conventional organic solvent (n-hexane) and a green solvent (supercritical carbon dioxide). The highest ester productivity in hexane (119 μmol min^{-1} $g^{-1}_{pellets}$) was reached at 323 K, whereas in supercritical CO_2, a maximum productivity of 501 μmol min^{-1} $g^{-1}_{pellets}$ was achieved at 333 K and under 12 MPa. The environmental impacts of each process were estimated by means of the *E*-factor (mass ratio of amount of waste produced divided by amount of desired product) and the values obtained under the previous conditions were 28.7 and 12.0 respectively. Results show that replacing hexane by supercritical CO_2 in a continuous process increases ester productivity and reduces environmental impact, thus allowing making a more environmentally friendly process.

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1. Introduction

Short chain esters are natural aroma compounds which are widely used as additives in products of food, cosmetic and pharmaceutical industries [1]. Such molecules are relatively expensive when extracted from vegetals or produced by means of fermentation, so chemical synthesis is traditionally employed for commercial purposes. However, these synthetized esters are directed towards human consumption and the use of toxic organic solvents and acid catalysts has been progressively restricted for this purpose. Indeed, the interest for investigating alternative production paths and more sustainable processes has risen during the last two decades. In this recent field of development of more "natural" products, biocatalyzed reactions have gained high popularity, especially due to the high specificity of enzymes limiting side reactions [2,3]. Furthermore, among various enzymes, lipases have been claimed as the most adequate esterification biocatalyst in various solvents and processes [4–6].

In order to improve production performance, supercritical fluids (SCFs) have been strongly considered for replacing conventional organic solvents. Following the work by Randolph et al. [7], many batch [8–10] and continuous [11–14] processes using SCFs were developed. Indeed, SCFs exhibit gas-like diffusivities and low viscosities, allowing enhanced mass transfer, but also their densities and dielectric constants depend greatly on temperature and pressure, enabling to further improve reaction yields by an accurate control of these operating parameters. Another major advantage of such processes is that downstream processing may be achieved with no additional separation step; SCFs are usually gaseous under standard conditions and a simple depressurization enables a relatively simple separation of the products without any traces of solvent residues [15]. Numerous applications concerning esterification in SCFs have therefore been successfully developed for flavors [16], fatty acids [17–19], chlorogenic acid [20,21] but also chiral compounds such as lactic acid [22] or anti-inflammatory drugs [23,24].

Previous studies have demonstrated that using SCFs instead of organic solvents is a good alternative to operate enzymatic reactions [25,26]. Carbon dioxide (CO_2) is the most common SFC [27] for carrying out such biocatalytic reactions, due to its mild critical conditions (304 K, 7.38 MPa), low toxicity and nonflammable features; moreover it is environmental friendly, naturally abundant and available at high purity. All these characteristics make CO_2 a prime choice over fluoroform, ethane, sulfur hexafluoride,

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ethylene or propane. It has also been proven to be a suitable medium for active enzymes and to allow better yields [19,28–30] than other solvents.

Among the commercially available lipases, *Candida antarctica* lipase B (CalB) has proven to be active for esterification, not only in organic solvents [31] but also in supercritical CO_2 [32,33]. It is noteworthy that enzymes work better when grafted on a support material for use under high pressures [34], since immobilization improves their stability [35]. In addition, it leads to long term reuse of the biocatalyst [36] and reduces process costs. Although, only few works describe in detail the immobilization methods applied [19,32].

Several kinds of reactors have been considered for investigation of processes based on immobilized lipases [37,38]. The most widespread configuration is a packed bed reactor, due to its easy development and operation and despite the well-known drawback of significant pressure drop when working with conventional solvents. However, this issue should be overcome by working with supercritical fluids, because they have lower densities compared to liquids. Furthermore, packed bed reactors are well suited for long term industrial production and continuous processes are adapted for easy supercritical fluid recycling. The combination of all the aforementioned conditions makes packed bed reactors a good choice for the development of a green process.

Many papers detail esterifications carried out in an enzymatic continuous process using a SCF as a solvent [11,19,22]. However, to our knowledge, only the work presented by Marty et al. in 1997 [13] contains a direct comparison of the performances of packed bed reactors using hexane and SC CO_2 as solvents for the esterification of oleic acid with ethanol. Nevertheless, this work mainly focused on the effect of the solvents on water activity and enzyme deactivation through the evolution of conversion with time. Our paper presents a more complete study of enzymatic catalysis carried out in continuous packed bed reactors, aiming to underline the interest of using SC CO_2 as solvent which, on the one hand, enhances the green aspect of the process and on the other hand leads to higher reactor performances.

The aim of this work was to investigate the synthesis of butyl acetate, a short chain ester with tropical fruit flavor chosen as model molecule, catalyzed by CalB immobilized by simple physical adsorption on porous pellets of alumina, in continuous packed bed reactors. Experiments were first carried out in n-hexane, a widely used organic solvent, to determine the influence of different parameters like the reactants ratio, substrate flow rate and temperature. Hexane was chosen as a representative organic solvent as it is known to have a $\log P$ (partition coefficient value between n-octanol and water) close to 4, a value reported as the optimum for lipase catalysis [39]. Furthermore, among many organic solvents hexane exhibits the lowest water content for a given activity [40], which is an important criterion if esterification has to be favored over hydrolysis reactions. Afterwards, syntheses in SC CO_2 were carried out to examine the effect of temperature, pressure and substrate flow rate. Finally, n-hexane and SC CO_2 were investigated as reaction media regarding productivity and yield and were also compared based on their mutual green chemistry metrics quantified by the *E*-factor (mass ratio of amount of waste produced divided by amount of desired product as defined by Sheldon [41]).

2. Materials and methods

2.1. Materials

Commercial solution of *Candida antartica* Lipase B (CalB) was kindly provided by Novo Nordisk (Denmark). Porous γ-alumina pellets were supplied by Alfa Aesar (diameter of 2.5 mm, length of 5 mm, average pore width of 122 Å, total pore volume of 757 $mm^3\,g^{-1}$ and specific area of 249 $m^2\,g^{-1}$). All chemicals: n-hexane (≥97%), vinyl acetate (>99%), 1-butanol (≥99.7%), 1-octanol (>99%) and dichloromethane (≥99.9%) of analytical grade were purchased from Sigma–Aldrich. Pressurized liquid carbon dioxide, under 5.5 MPa and with a purity exceeding 99.998%, was supplied by Air Products.

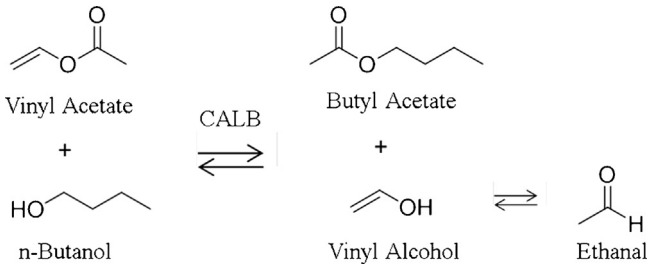

Fig. 1. Schematic pathway of enzymatic synthesis of butyl acetate.

2.2. Reaction and analysis

Transesterification of butyl acetate from vinyl acetate and n-butanol was carried out in hexane and in supercritical carbon dioxide. As presented in Fig. 1, this reaction exhibits the particularity of shifting the equilibrium point of the reaction towards the synthesis of products, owing to vinyl alcohol converting into its tautomer, ethanal.

Reactant and product content was determined by gas chromatography (Agilent 6850) using a flame ionization detector, a Restek Stabilwax-DA capillary column (30 m length × 0.25 mm i.d.) and 1-octanol as internal standard. Hydrogen was used as carrier gas at a flow rate of 1.5 mL min^{-1}; hydrogen was also used for the detector at a flow rate of 25 mL min^{-1}, along with an air flow rate of 300 mL min^{-1} and nitrogen as a makeup gas at 10 mL min^{-1}. The temperature of the column oven was maintained at 323 K for 2.5 min after sample injection, then linearly increased to 358 K (10 K min^{-1}) and finally kept at 423 K for the remaining time of the analysis. Injector and detector temperatures were both set to 523 K. Retention times corresponding to vinyl acetate, butyl acetate, 1-butanol and 1-octanol were 1.9 min, 3.9 min, 4.9 min and 7.9 min respectively.

Collected samples were analyzed multiple times to check repeatability of the measurements. Random deviations between each analysis of the same sample never exceeded 2% of the actual value.

2.3. Enzyme immobilization

Enzymes were immobilized on porous γ-alumina pellets by adsorption. Pellets were initially hydrated for 12 h in a 10 mM phosphate buffer (pH 7.8). Then 200 g of pellets were submerged in 1.5 L of the enzymatic solution (prepared by diluting the commercial solution with the same phosphate buffer to a final concentration of 20% (v/v)) and maintained at 25 °C for 4 h while stirring. Finally, the pellets were rinsed three times with the phosphate buffer and dried in presence of phosphorus pentoxide under vacuum conditions over night; the enzymatic pellets were then stored in a desiccator at room temperature until use.

2.4. Butyl acetate synthesis in n-hexane under atmospheric pressure

Synthesis of butyl acetate from n-butanol and vinyl acetate was carried out in both batch and continuous modes.

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