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Supercritical carbon dioxide biocatalysis as a novel and green methodology for the enzymatic acylation of fibrous cellulose in one step

Stavros Gremos, Dimitris kekos, Fragiskos kolisis *

Biotechnology Laboratory, School of Chemical Engineering, National Technical University of Athens, Zografou Campus, 15780 Athens, Greece

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ABSTRACT

Aliphatic esters of cellulose have recently raised the interest on the field of biopolymers. The objective of this work is to develop a methodology for the enzymatic acylation of cellulose with long chain fatty groups in one step. Therefore we designed a system at which fibrous cellulose was enzymatically acylated with vinyl laurate in supercritical carbon dioxide ($scCO_2$) and as a result cellulose laurate was formed. The biocatalysts used for this reaction were immobilized lipase *Candida antarctica*, immobilized esterase from hog liver and the immobilized cutinase *Fusarium solani*. The ester content of the product varied on the specificity of the biocatalyst used, reaching a maximum of 4.1% after 9 h of reaction. In our knowledge, it is the first time where fibrous cellulose is enzymatically acylated by a long chain aliphatic group in one step, without the necessity of any pretreatment.

1. Introduction

Nowadays, the global elimination of crude oil reserves and the environmental effects caused by the broad use of petrochemical products, lead to the valorization of alternative raw materials. Thus, in the field of fuels there is a significant evolution and as a result biofuels will meet more than a quarter of world fuel demand by 2050. Another significant sector of chemical industry, plastics, derives mostly by petrochemicals and there also prevails a trend to produce them by alternative ways. Ideally the related raw material should be cheap, abundant, non toxic, degradable and recyclable. These criteria are well fulfilled by the class of native polymers called cellulosics (Lee and Wang, 2006; Perez and Samain, 2010; Wibowo et al., 2006). Indeed thermosoftening plastics, also known as thermoplastics, can be produced by cellulose derivatives (Edgar et al., 2001; Wibowo et al., 2006).

Actually native cellulose does not exhibit any thermoplastic behaviour, due to strong intermolecular hydrogen bonding. But cellulose derivatization with several chemical groups gives a number of products with predesigned and wide-ranging properties. In particular cellulose fatty esters have a potential as feedstock in the industry of thermoplastics. Several publications until now have shown that acyl esters of cellulose are used effectively in the production of fibers, plastics, films, membranes, modern coatings, cosmetics and drugs (Edgar, 2007; Edgar et al., 2001). The resulting cellulose esters are not synthetic polymers; they are made from a naturally occurring polymer, cellulose, which is obtained from wood pulp and cotton linters.

Several literature references studying the physical, mechanical and thermoplastic properties of cellulose esters indicate that they depend strongly on the degree of substitution and the chain length of the acyl group. More specifically, longer substituent and higher degree of substitution are expecting to lead to better thermoplastic properties and higher thermal stability. This can be attributed to the fact that relatively long fatty chains act as internal plasticizers without any addition of external ones (Crepy et al., 2011; Edgar et al., 2001; Jandura et al., 2000) .

The main bottleneck on the production of cellulose acyl esters is that cellulose is highly crystalline, therefore its structure does not permit easily a chemical manipulation. Commercially, such products are prepared by the use of heterogeneous reaction systems containing tough and hazardous substances like pyridine, N,N-dimethylacetamide and acid chloride. In addition these techniques are usually limited to the esterification of cellulose with acyl groups up to six carbon atoms. Nevertheless there are a few successful attempts on esterifying cellulose derivatives and even cellulose with long chain fatty acids by enzymes, using non conventional biocatalysis (Gremos et al., 2011; Sereti et al., 1998, 2001). Bioconversion can be obtained as a simple, efficient and 'green' approach on cellulose esterification because these systems do not require the use of tough solvents; in addition the enzymes themselves exhibit some remarkable advantages as catalysts. They

Abbreviations: $scCO_2$, supercritical carbon dioxide; XRD, X-ray diffraction; CrI, crystallinity index; SEM, scanning electron microscopy.

* Corresponding author. Address: Iroon Polytechniou 9, Zografou Campus, 15780 Athens, Greece. Tel.: +30 210 7723156.

E-mail address: kolisis@chemeng.ntua.gr (F. kolisis).

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