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Green biocatalytic approaches for solid substrates transformation in solvent-free systems

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PURPOSE OF THE ABSTRACT

The best solvent for chemical reactions is no solvent. However, the solid character and/or physical-chemical properties of many substrates (e.g. high melting point and/or mutual immiscibility) hamper the necessary dynamics of molecules for chemical transformations in solvent-free systems, being necessary to develop green and clean solutions.[1] Nevertheless, two different green tools that may help to overcome these hindrances, as they are presented in this communication.

The eutectic behavior of some mixtures of solid substrates, which produces a depression in their melting temperature, may be considered as a useful approach for developing solvent-free liquid reaction media. As an illustrative example, the enzymatic synthesis of panthenol monoacyl esters by direct esterification between panthenol (solid) and free fatty acids (solid) was demonstrated in solvent-free media. Panthenol is a bioactive molecule of great relevance for the pharmaceutical and cosmetic industries, and panthenol ester derivatives are of high interest for pharmacological and cosmetic preparations, because of their improved physical properties. Mixtures of panthenol with free fatty acids form deep eutectic solvents (DESs), and were shown to be excellent reaction media for the biocatalytic synthesis of panthenyl monoacyl esters (i.e. up to 83% conversion and 98% selectivity in the case of the panthenyl monolaurate), remaining the enzymatic activity unchanged for seven consecutive cycles of reuse. This DES approach, based in enzyme-catalyzed direct esterification between renewable raw materials under solvent-free conditions, can be considered as a green and useful process for the sustainable industrial scaling up of panthenyl acyl ester production. [2]

Alternatively, ultrasound-assistance was shown to be a key tool to overcome the handicap imposed by both the mutual immiscibility of fatty acids and xylitol substrates, and the semisolid character of the initial reaction mixtures (see Figure 1). In such semisolid systems, ultrasonic irradiation may enable the transport of substrate molecules to the biocatalytic-site, leading to the efficient synthesis of xylityl fatty esters by direct esterification (e.g. up to 95% yield after 90 min at 40 ºC), with xylityl monoacyl ester and xylitol diacyl ester appearing as the main products (greater than 96%) Astonishingly, this combination resulted even more efficient at higher scale (200 folds the reaction mass) affording the reaction time shortening (30 min), and a better selectivity with almost the same energy input. (Fig. 2) The separation of products was carried out by heating and simple centrifugation of the reaction medium, which was possible due to different densities of the resulting fractions.[3]

In both examples, the nature of substrates, the high yields and selectivity and the absence of reaction media permits the direct use of the products without the need of additional steps of extraction and purification, which is a clear plus for the economic and environmental sustainability.

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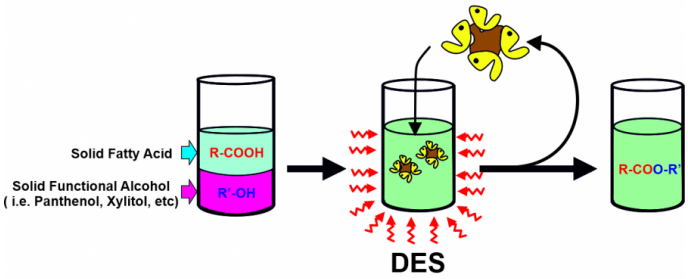
FIGURES



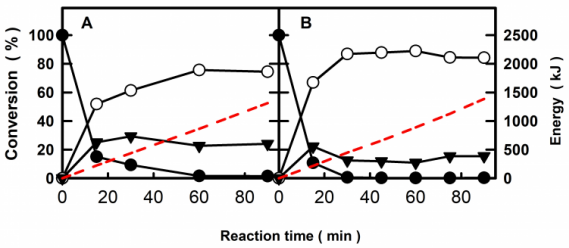


FIGURE 1

Figure 1

Ultrasonic-assistance of biocatalytic synthesis of functional esters by esterification of a solid alcohol with a solid fatty acid under solvent-free media

FIGURE 2

Figure 2

KEYWORDS

DES | ultrasonic-assistance | clean biocatalysis | solvent-free

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