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Clean biocatalytic processes using sponge-like ionic liquids and supercritical carbon dioxide

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PURPOSE OF THE ABSTRACT

Sustainable chemistry turns around two main axes: the selectivity of catalytic transformations, and the easy and clean separation of pure products. To transfer of the exquisite catalytic efficiency shown by enzymes in nature to chemical processes is an important challenge. The use of enzymes in ionic liquids (ILs) was reported great advantages (i.e. improved activity and enantioselectivity, enhanced stability, etc.), and its combination with supercritical technologies was resulted in synergetic and outstanding platforms for developing (multi)catalytic green chemical processes under flow conditions able to directly provide pure products. [1] This has been demonstrated by several examples of flow synthetic processes in IL/scCO2 biphasic systems at 100-160 bar and 40-100ºC (e.g. DKR of rac-1-phenylethanol,[2] biodiesel,[3] etc., see Fig. 1).

However, the development of more simple and easy protocols to carry out biotransformation, product recovering and biocatalysts/ILs reusing without any loss in the overall greenness character of the process, are encouraged. Sponge-Like Ionic liquids (SLILs) are hydrophobic ILs based on cations with long alkyl side-chains, e.g. octadecyltrimethylammonium bis(trifluoromethylsulfonyl)imide, etc.), which behaves as sponge-like systems by switching from liquid to solid phase with temperature.[4] Based on this new property, the SLILs have been applied for developing straightforward and clean approaches for biocatalytic synthesis and extraction of nearly pure compounds of added value (e.g. terpene esters,[5] biodiesel, [6,7] ,monoglycerides,[8] etc.). The SLILs are able for dissolving (soaking) hydrophobic compounds at temperatures compatible with enzyme catalysis (e.g. vegetable oil and methanol mixtures are monophasic in [C18mim][NTf2] at 50°C)[6]. By cooling reaction mixtures based on these SLILs under room temperature, they are solid phases that can be fractionated by centrifugation, allowing the release (wringing out) of reaction products from the SLIL net, and resulting in two phases: a solid SLIL phase and a liquid phase containing synthetic products (flavour esters, biodiesel, etc.). This approach for product separation can be improved by using centrifugal filters, demonstrating the excellent suitability of this straightforward and green approach for carrying out synthesis and separation of pure products with full recovery and reuse of the reaction system (SLIL and biocatalyst).[5,7]

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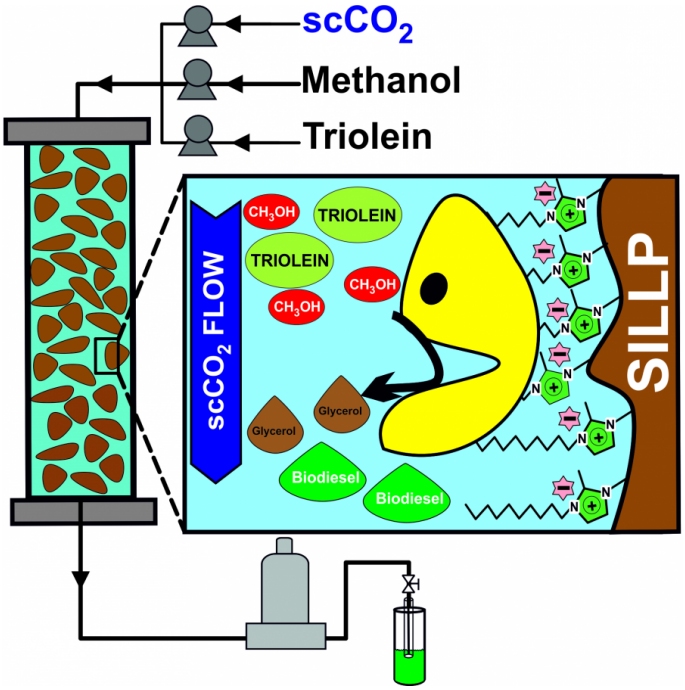
FIGURES



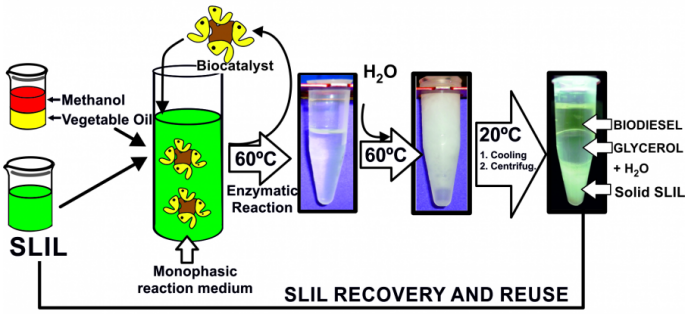


FIGURE 1

Figure 1

Continuous flow reactor based on CALB immobilised on covalently supported ionic liquid-like phases (SILLPs) for the synthesis of biodiesel in scCO2

FIGURE 2

Figure 2

Cyclic protocol for the clean biocatalytic production of pure biodiesel in sponge-like IL (SLIL), including the full recovery and reuse of the enzyme/SLIL system.

KEYWORDS

ionic liquids | supercritical fluids | Applied biocatalysis | Clean processes

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