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Biocatalytic synthesis of solketyl laurate by using ionic liquids and supercritical carbon dioxide technoloiies

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PURPOSE OF THE ABSTRACT

Because of the increase in the production of biodiesel fuels (e.g. fatty acid methyl esters), an excess of the byproduct glycerol in the market has been ocurred. Glycerol derivatives, like solketal (1,2-isopropylideneglycerol) have been successfully used in the production of new oxygenated fuels, such as the Fatty Acid Solketyl Esters (FASEs), as an interesting approach for enhancing octane number of gasolines. Biodiesel blends up to 20% volume fraction of FASE, exhibiting an excellent suitability as liquid fuel (e.g. viscosity, cetane number, adiabatic flame temperature, etc.),as it was demonstrated by testing in an automotive engine.1

The biocatalytic synthesis of oxygenated biofuels (fatty acid solketal esters, FASEs) can be carried out by immobilized lipase-catalyzed the direct esterification of fatty acids (i.e., lauric, oleic, palmitic, etc) with solketal, or the transesterification of different esters (i.e. vinyl laurate) with the same alcohol. However, the strong deactivation effect of solketal alcohol to the enzyme activity makes necessary to use enzyme stabilization approach for the biocatalytic application.2 It was reported how hydrophobic ionic liquids (ILs) based on cations with long alkyl side-chains (e.g., hexadecyltrimethylammonium bis (trifluoromethylsulfonyl)imide[C16tma][NTf2]), which are excellent monophasic reaction media for producing FASEs reaching almost 100% yield.3 Alternatively, it is noteworthy stand out that biphasic systems based on the combination of ILs (or the use of Supported Ionic Liquid-like Phases, SILLPs) and supercritical carbon dioxide (scCO2) are excellent reaction media for developing continuous green biocatalytic processes.4

A biocatalytic flow reactor, based on C. antarctica lipase immobilized onto SILLPs particles, was used for the synthesis of FASES under supercritical conditions (see Fig.1), resulting in pure product at high yield (up to 99 %). Several SILLPs supports, containing different degree of modification, have been assayed, being resulted in the increase in activity as the alkyl-side chain in cation moieties was increased. 5

For the most appropriate SILLPs, the influence of temperature in the biocatalytic reaction has also been studied under continuous supercritical flow (see Fig.2). As can be seen, a continuous product profile was obtained for all temperatures, without any loss in activity with time. These results clearly show the excellences of the SILLPs to provide a stabilization of the enzyme, which was improved as the temperature was increased. This work clearly shows the suitability of this biocatalytic reactor for continuous production of oxygenated biofuels under supercritical conditions. The unique properties of ILs to enhance the catalytic efficiency of enzymes in scCO2 can be improved by using covalently attached ILs (SILLPs). These results clearly illustrate the potential of SILLP-supported biocatalysts to the production of a green biofuel (e.g. Fatty Acid Solketyl esters), which may be produced by fully green technology under continuous operation.4

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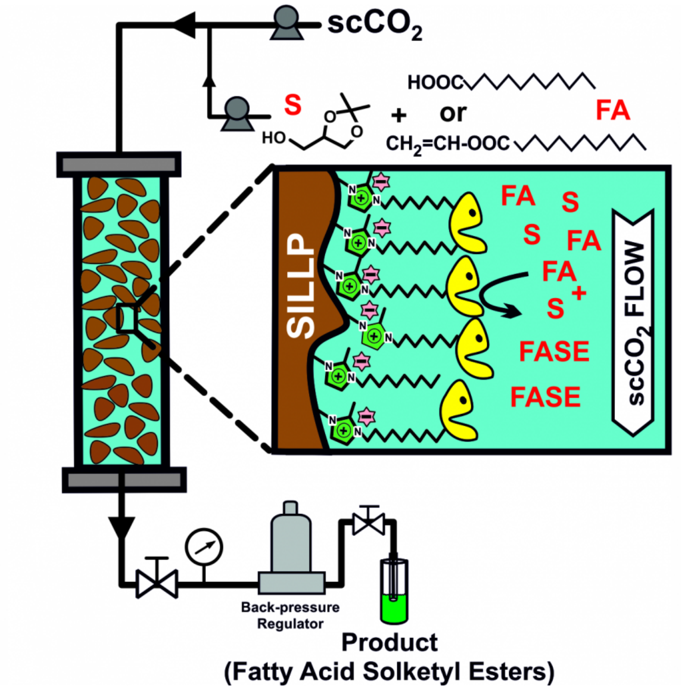
References

1. J. García, H. Garcia-Marin, E. Pires. Glycerol based solvents: synthesis, properties and applicatoins. Green Chem. 2014, 16, 1007-1033.
2. P. Lozano, J.M. Bernal, S. Nieto, C. Gómez, E. Garcia-Verdugo, S.V. Luis. Chem. Commun. 2015, 51, 17361-17374.
3. P. Lozano, E. Garcia-Verdugo, J.M. Bernal, D.F. Izquierdo, M.I. Burguete, G. Sanchez-Gomez, S.V. Luis. ChemSusChem, 2012, 5, 790-798.
4. P. Lozano, C. Gomez, A. Nicolas, R. Polo, S. Nieto, J.M. Bernal, E. Garcia-Verdugo, S.V. Luis. ACS Sust. Chem. Eng. 2016, 4, 6125-6132
5. E. García-Verdugo, B. Altava, M.I. Burguete, P. Lozano, S.V. Luis. Green Chem., 2015, 17, 2693?2713.

FIGURES



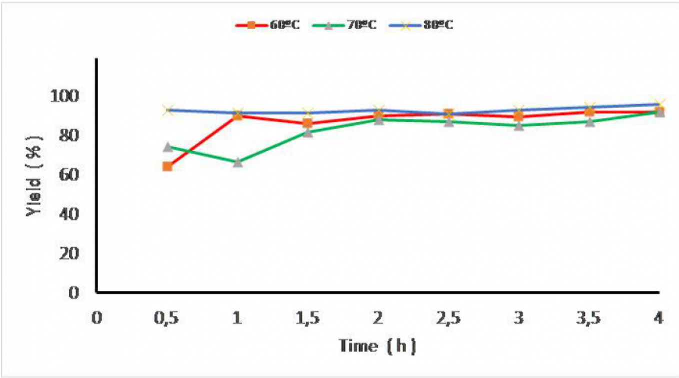


FIGURE 1

Fig. 1

Experimental set-up of the supercritical biocatalytic reactor

FIGURE 2

Fig 2

Product yield profile of the supercritical biocatalytic reactor under continuous flow at 110 bar and different temperatures

KEYWORDS

biocatalysis | ionic liquids | supercritical fluids | biofuels

BIBLIOGRAPHY

1. J. García, H. Garcia-Marin, E. Pires. Glycerol based solvents: synthesis, properties and applicatoins. Green Chem. 2014, 16, 1007-1033.

2. P. Lozano, J.M. Bernal, S. Nieto, C. Gómez, E. Garcia-Verdugo, S.V. Luis. Chem. Commun. 2015, 51, 17361-17374.

3. P. Lozano, E. Garcia-Verdugo, J.M. Bernal, D.F. Izquierdo, M.I. Burguete, G. Sanchez-Gomez, S.V. Luis. ChemSusChem, 2012, 5, 790-798.

4. P. Lozano, C. Gomez, A. Nicolas, R. Polo, S. Nieto, J.M. Bernal, E. Garcia-Verdugo, S.V. Luis. ACS Sust. Chem. Eng. 2016, 4, 6125-6132

5. E. García-Verdugo, B. Altava, M.I. Burguete, P. Lozano, S.V. Luis. Green Chem., 2015, 17, 2693–2713.