BIOTRANS
LA ROCHELLE 2023

N°605 / PC
TOPIC(s) : (Chemo)enzymatic strategies / Industrial biocatalysis

APPLICATION OF GREEN METRIC PARAMETERS TO THE EVALUATION OF THE SUSTAINABILITY OF A BIOCATALYTIC SOLVENT-FREE SCALE-UP PROCESS

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PURPOSE OF THE ABSTRACT

Chemistry has contributed to society's evolution and well-being by means of providing different commodities. However, nowadays the environmental burden of chemical transformations is in the spotlight of government agencies and society itself, because of the impact on the biosphere and the depletion of resources that mortgages future generations.
The current compromise of chemists is the development of more sustainable strategies based on the more efficient use of renewable resources and energy and with a lower environmental impact as advocated by the Twelve Principles of Green Chemistry. Nonetheless, merely the application of some of those principles is not enough, being necessary to quantitatively certify the sustainability of the processes. For this, different Green Metrics Parameters have been developed as tools to measure different aspects of the upstream and downstream stages of a process.
This work describes how the application of some Green Metrics Parameters can be very useful in the optimization of a biocatalytic process for synthesizing new non-ionic surfactants based on the direct selective mono-esterification of a poly-alcohol (panthenol), as well as to assess the sustainability of the intensified strategy after a scaling-up process (1).
As can be seen in Table 1, while the Atom Economy (AE), Stoichiometric Factor (S), and Yield are parameters that exclusively refer to the reactivity of the process, the Material Recovery Parameter (MRP), Reaction Mass Efficiency (RME), Process Mass Intensification (PMI), Total Carbon Release (TCR) and E-factor, also consider auxiliary reagents and downstream processes of purification and wastes treatments. In addition, the EcoScale is a tool that integrates ecological and economical aspects to perform a preliminary study of the Life Cycle Assessment (LCA) of a process (2).
An initial study performed with AE, S, Yield, MRP, and RME permitted to identify the optimal molar ratio panthenol : FFA in order to achieve the higher yield in the synthesis of specific panthenyl monoesters. Figure 1.A. shows a radial diagram, as proposed by Andraos, where it is assumed that as the values of the Green Metrics plot a balanced pentagon with a radius close to 1, the greener is the process (3). These results highlight that the

maximum yield is achieved with an equimolar ratio of substrates and that an excess of either substrate only leads to the accumulation of wastes or non-desired products. In addition, these values point to the high economy of the strategy based on the direct esterification in solvent-free system since the negligible mass weight water, as the only by-product, improves the economy of the process, to which must be added the recovery and reuse of the biocatalysts.

To compare the impact of the synthesis with different set-ups, the PMI, TCR, E-factor and EcoScale parameters were used (Figure 1B). Again, the values of these parameters support the sustainability of the process due to its´ high efficiency, the lack of solvent, and that no purification step is needed, as non-reacted substrates are also cosmetic ingredients. However, best productivity and selectivity because of the intensification at higher reaction scales, points to the reactor system at 500 g size as the most sustainable and economical set-up. This intensification seems to be related to a more efficient agitation (that improves mass transfer) and water removal (because of the coupled vacuum system) along the reaction.

This study evidence that the use of Green Metric Parameters is highly recommended whenever a (bio)chemical process is being developed for industry implementation.

Acknowledgments

This work was partially supported by 21640/PDC/21 and 21884/PI/22 (Fundación SENECA-CARM), and by MICINN-FEDER-AEI 10.13039/501100011033 (PID2021- 124695OB-C21/C22 and PDC2022-133313-C21/C22), MICINN –European Union Next Generation EU-PRTR.

FIGURES

Parameter	Calculation	Definition
Atom Economy (AE)	$AE = \frac{Products\ Mw}{\Sigma \text{ Reactants Mw}}$	Quantifies the atoms incorporated into the final product and the amount of waste produced in a reaction
Stoichiometric Factor (SF)	$SF = 1 + \frac{Mass\ of\ Excess\ of\ Reactives\ (g)}{Mass\ of\ Stoichiometric\ Reactives\ (g)}$	Refers to the molar ratio of substrates and permits to perform calculations when using one or more reactants in excess with respect to a limiting one
Yield of Panthenol Monoesters (ε)	$\varepsilon = \frac{MSP}{MMP}$	Provides an insight into the reactivity of substrates and quantifies the selective (bio)catalytic productivity of the reaction
Material Recovery Parameter[b] (MRP)	$MRP = \frac{1}{1 + \frac{\varepsilon \cdot AE \cdot (C+S+W)}{SF \cdot MSP}}$	Shows the loss of auxiliary materials not recovered along the reaction and downstream steps
Reaction Mass Efficiency (RME)	$RME = \frac{\varepsilon \cdot AE \cdot MRP}{SF}$	Mass-based metric, similar to AE, but also considers yield and use of excess reagents
Process Mass Intensification (PMI)	$PMI = \frac{1}{AE\ \varepsilon \frac{1}{SF} \left(\frac{1}{1+AE\ \varepsilon \frac{1}{SF} \frac{(C+S+W)}{MSP}}\right)} = \frac{1}{RME}$	Determines the overall material efficiency in a process, facilitating the analysis of the input-output mass balance
E-factor	$E = \frac{1 - RME}{RME}$ $E = PMI - 1$	Quantifies the amounts of waste formed per kg product
Total Carbon Dioxide Release (TCR)	$TCR = (PMI\ organic\ x\ 2.3 + PMI\ water\ x\ 0.63)$	Represents the kilograms of CO_2 generated per kilogram of product

[a] MSP: Mass of synthesized monoester products; MMP: Maximum mass of synthesized products

[b] C: Catalyst (g); S: Substrates (g); W: Wastes (g)

FIGURE 1

Table 1.

Green Metric Parameters, equations, and definitions. (1,4,5)

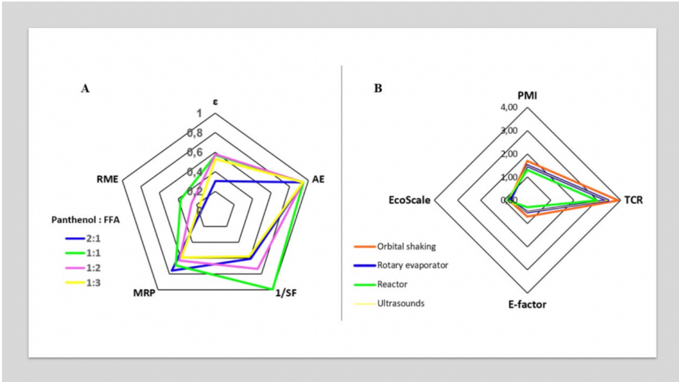

FIGURE 2

Figure 1. Diagram representations of the Green Metrics analyses.

A. Radial pentagon in the optimization analysis of substrates molar ratios. B. Assessment of the environmental impact of different set-ups.

KEYWORDS

biocatalysis | green metrics | optimization | scaling-up

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