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TOWARD BIO-BASED EXTENDED SURFACTANTS OBTAINED BY CHEMO-ENZYMATIC PATHWAY

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PURPOSE OF THE ABSTRACT

Surfactants, classically described as amphiphilic molecules, have many applications in various industries, like biomaterials, pharmacology, biocontrol. Fatty acid sugar esters are non-ionic biobased surfactants, obtained from naturally occurring resources, and able to reduce surface tension. Surfactants, such as rhamnolipids, are nowadays mainly obtained by chemical or microbial means. The use of microorganisms does not allow significant yields and generates almost high production costs, particularly because of purification step [1]. The alternative, particularly for synthetic cost, should be classical chemistry synthetic pathway. Nevertheless, conventional chemistry is difficult to implement with carbohydrates, the basis of many "green" surfactants. Glucose esters have been produced by classical chemistry to measure the "complexity" of the syntheses, especially for the polydispersity of the obtained products (Figure 1). It is in this perspective that biocatalysis appears as a possible solution to synthesize biosourced molecules.

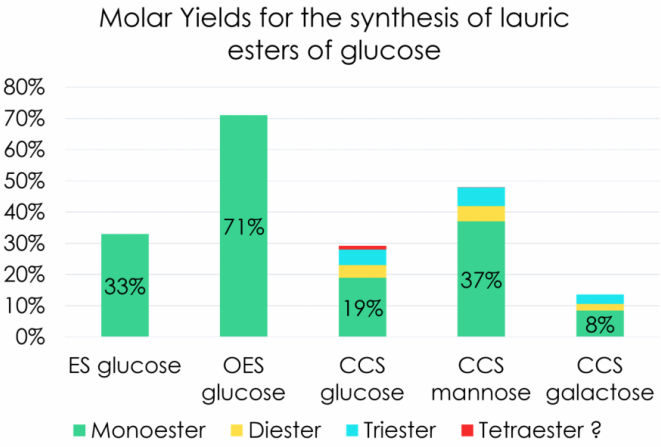
Ecological problem, desire for naturalness, climate change has led to a growing awareness of the need for a more sustainable and renewable consumption. Biocatalysis can be a global answer, with more sustainable industrial processes that comply with the principles of green chemistry [2]: energy saving, product selectivity, monodisperity, reduction of the deviations of the synthesis scheme, in correlation with the life cycle assessment, allowing a decrease of the global energy consumption in reagents and a decrease of residue productions. Enzymes have a great versatility, can be used in mild conditions and in alternative solvents. Thus, biosourced products such as carbohydrates (mono-, di-, polysaccharides), extracted from biomasses such as beet or starch crops, are used as platform entities to obtain high added value products.

For instance, modulating different parameters, such as the solvent used for solubility aspect and water distribution, has done an optimization of monosaccharide ester synthesis. The synthesis of linolenic ester of glucose allowed to determine the interest of using tertiary alcohols as reaction solvent. Reaction parameters of temperature (56°C), medium stirring (240 rpm), reaction time (72h), enzyme ratio (1% lipase Aspergillus Niger), desiccant in the reaction medium (1g 3Å sieve), and Ose:Fatty Acid (FA) ratio (1:3) were determined after several trials. Moreover, by adding a solubilizing agent, as diméthylsulfoxide at different concentrations, the yields could be improved. These optimal parameters were applied to other FA and allowed to determine a relative affinity for long hydrocarbon chains (C18 saturated or unsatured) compared to shorter chains. These operating conditions were transposed to transesterification using ethyl laurate instead of the corresponding FA, and better molar yields were obtained (44% versus 32% with lauric acid). An optimization of this reaction was carried out by modifying the ratio, the reaction time, and the stirring. The results indicates the importance of the ratio, 48h of reaction time and a high agitation, as well as an activation temperature of catalytic activity between 50°C and 60°C (Figure 2). A variation of the osidic moiety shows an identical affinity for all glucose epimers and this lipase.

The current syntheses aim at the formation of a platform molecule having an esterifiable group with different

enzymes. Adding a spacer arm between polar head and hydrophobic part should improve the properties by an increase of the amphiphilic properties and a lower CMC values (critical micelle concentration) [3]. Our main objective is to use enzymatic engineering to produce this type of molecule by decreasing the steps, the residues, and to reuse enzymes. Diethyl glutarate, succinic acid and different propanediol isomers are tested as spacer arms on different sugars and are to be functionalized soon by addition of a hydrocarbon chain.

FIGURES



ES: enzymatic synthesis
OES: optimized enzymatic synthesis
CCS: classical chemical synthesis

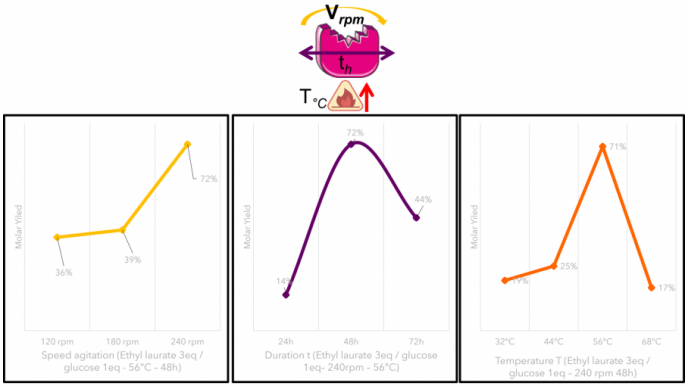


FIGURE 1

Figure 1: Interests of enzymatic synthesis instead of conventional chemistry for aspect of monodisperity

FIGURE 2

Figure 2: Optimization of 3 parameters for the synthesis of lauric ester glucose with Aspergillus Niger 1% in 2M2B (2methyl-2butanol) with 20% DMSO

KEYWORDS

Biobased | Biocatalysis | Chemo-enzymatic | Optimization

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