PRODUCTION OF SUGAR FATTY ACID ESTERS FROM RENEWABLE AGRICULTURAL RESOURCES: AN INTEGRATED OPTIMIZATION OF ENZYMATIC-PURIFICATION PROCESSES AND OF SURFACTIVE PROPERTIES

Fact Sheet

Project Information

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Coordinated by
Institut National Polytechnique de Lorraine
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Objective

The aim of the project is to acquire an improved knowledge of enzymatic and purification processes for the synthesis of sugar fatty acid esters, with a view to develop economically feasible processes for the preparation of new non-toxic biodegradable surface-active agents derived entirely from renewable resources.

The project proposes an integrated and multidisciplinary approach towards the
optimization of enzymatic processes for the production of new sugar fatty acid esters surfactants.

Starting from the sugars sucrose and lactose and from fatty acids of different chain length, it examines the performances of the different reaction and purification steps leading to sugar esters.

The study mainly focuses on the following aspects:

1. the initial enzymatic or chemical alkylation of the sugars;

2. the enzymatic esterification of the saccharides with varying fatty acids and lipases, under different operational parameters

3. the sugar esters purification by liquid and supercritical carbon dioxide extractions, precipitation and chromatography to achieve different degrees of purity

4. the determination of the composition and surface properties of the synthesized sugar esters.

The knowledge gained on these processes are expected to contribute to the development of economically competitive technologies and of novel surfactants interesting as detergents or as additives for cosmetics, food and pharmaceuticals.

This project is investigating both chemical and enzyme based methods of producing surface active materials (surfactants and emulsifiers) based on esterification of any of a number of different sugars with any of a number of different long chain fatty acids. Some such products, such as sucrose esters, are available commercially, finding use in cosmetics and foods. However, in general they are relatively costly due to difficulties in production and purification. These compounds consist of the combination of a sugar molecule, which is water soluble, with a long chain fatty acid which is soluble in organic solvents. The problem is to identify solvents in which both components will dissolve and then react as required. Such reactions may require the production of complex intermediates and reaction sequences. A number of the solvents which can be used are potentially harmful and have to be removed from the products. An alternative is to use enzymes which catalyse esterifications or transesterifications. However, again there is a need to find conditions under which the reactants will dissolve, the enzymes are stable and the products formed in sufficient quantities to be separated from the reaction mixture. Progress in reaching these objectives over the first two years of the project are described.

SYNTHESIS
Studies on synthesis cover both alkylation and acylation reactions, with the objective of optimising both chemical and enzymatic alkylation of sugar and enzymatic
Acylation in organic solvents. In addition the chemical alkylation of lactose was studied with analytical methods developed to determine the various reaction products. The enzymatic alkylation of butyl glycoside and butyl galactoside were also investigated. It was found that:

- Concentration of butyl glycoside increased with the concentration of beta-glycosidase, whereas concentration of butyl galactoside was not affected by the concentration of beta-galactosidase.
- Concentration of both butyl glycoside and butyl galactoside decreased at high temperature (above 60 °C) as a result of the denaturation of the enzymes.
- Decreasing the molar ratio butanol/glucose increased the concentration of butyl glycoside.

This result was due to an increase in the concentration of glucose in the medium. Synthesis of butyl galactoside was not depended on the molar ratio of butanol/galactose because of the poor solubility of galactose in the medium.

The enzymatic acylation of fructose, developed in the first year, was extrapolated to pilot scale, operated under reduced pressure. Yields of about 90% were obtained and fructose oleates concentrations up to 85 g l l were obtained.

Other work focused on the acylation of sucrose in organic solvents and the purification of the resulting esters. Two processes were considered (the synthesis of sucrose monolaureate and sucrose monopalmitate) in order to obtain sucrose esters with different surface active properties. The study of the optimal conditions for the synthesis of sucrose monolaureate was carried out using the lipase from Humicola lanuginosa immobilised on Eupergit C which was tested under various conditions of humidity (water activity, aw). Following this various solvents were assayed. The reaction only took place in solvents (DMSO, DMF, DMA, pyridine) that solubilise sucrose to a significant extent. DMSO was best in terms of production. The molar ratio acylating agent:sucrose was found to be of particular important on the time course of the reaction, due to the low solubility of vinyl laureate in this solvent. Surprisingly, a molar ratio 1.5:1 gave better results than 4:1. It was found that reaction temperature was crucial for the yield of the process, with the reaction proceeding significantly faster at 60 °C than at 40°C. Under optimal conditions, at 60 °C, a productivity of 90 g monoester per litre (175mM) was achieved in about 45 minutes. The biocatalyst (immobilised enzyme) did not loose any activity during the process and could be re-used. Investigations of the synthesis of sucrose monopalmitate showed that the reaction took place at a much slower rate. Several lipases were found to catalysed transesterification. The best results were obtained with the lipase from Humicola lanuginosa immobilised on Celite and with a preparation of lipase from Penicillium sp. obtained from industrial wastes. With the latter biocatalyst a productivity of 95 g.l-1 was obtained in 144 hours using dimethylacetamide as solvent.
SEPARATION
Equilibrium constants, required for process optimisation purposes, were estimated with preliminary results suggesting that the UNIFAC model could be used for the estimation and possibly for the prediction of equilibrium constants. In addition process were developed for the recovery of fatty acid sugar esters through supercritical extraction and liquid liquid extraction and their performance evaluated. Product recovery using supercritical extraction with carbon dioxide appeared promising on the basis of results achieved for the recovery of fructose laureate. For product recovery through liquid liquid extraction, application of the UNIFAC model for the screening of potential solvents gave encouraging results showing a good fit with experimental results.

A liquid chromatography separation process for the recovery of butyl glycoside was developed which gave a very pure product (>99%) with a yield of 70%. A method for the purification of fructose monooleates was developed, resulting in recovery of small quantities of pure sugar esters. The structure and some surfactant properties of these molecules was determined. In addition two purification processes were developed. These combined a filtration step (removal of the immobilised enzyme) and distillation (removal of the solvent) or liquid liquid extraction (removal of the residual sugar). The two methods differed in the separation of the residual fatty acid. The first (analytical scale) used medium pressure liquid chromatography to separate sugar ester from the acyl donor. This method allowed the recovery of pure sugar ester used for structural analysis. The second one used another liquid liquid extraction for the removal of fatty acid. The purification of sucrose monolaureate and monopalmitate was attempted using liquid liquid extraction steps. However, a problem arose from the surfactant properties of the monopalmitate, since the emulsions were very stable and difficult to break.

CHARACTERISATION
The products recovered as above were used in evaluation of the surface active properties. The structural analysis of products demonstrated that the enzymatic synthesis of fructose monooleate led to a mixture of 4 isomers (a and b anomers of 6 fructofuranose and b anomers of l fructofuranose and l fructopyranose). In addition surface and interfacial tensions as well as the foaming and emulsifying powers were determined. Fructose monooleates caused a significant decrease in both surface and interfacial tensions, even at low concentrations. The critical micelle concentration of fructose monooleates was determined as 2.4x10-4 M. This biosurfactant showed a high capacity to stabilise emulsions. In practice, 20% separation of phases were obtained with 0.1 % fructose monooleates previously solubilised in xylene phase. In addition, on beating, this surfactant formed a foam which was very stable with time.

Fields of science
Programme(s)

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324 - Transformation and conservation-combined processing (combination of different process technologies)

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