Life Cycle Assessment of the Enzymatic Reaction for Xylose Ester Synthesis

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Resumo/Abstract

RESUMO - Este estudo propõe um processo enzimático sustentável para a produção de ésteres de xilose utilizando solventes eutéticos profundos (DES) à base de xilose, que atuam simultaneamente como solvente e substrato. A reação foi realizada em reatores encamisador a 60°C, 550 rpm, carga enzimática de 500 TBU/g xylose e razão molar de 5:1 (ácido oleico:xilose). O processo foi modelado utilizando balanços de massa e energia no software EMSO, alcançando ~85% de conversão de xilose em ésteres. A Avaliação do Ciclo de Vida (ACV), conduzida com SimaPro e o banco de dados Ecoinvent 3.0, demonstrou menores impactos ambientais em comparação com rotas convencionais de biossurfactantes, especialmente em categorias como esgotamento de recursos fósseis e potencial de aquecimento global. O uso de DES permitiu um meio de reação anidro e biocompatível, favorecendo a esterificação catalisada por lipase em condições moderadas. Esses resultados destacam o potencial da integração de biocatálise e solventes verdes para a produção de surfactantes de base biológica de alto valor a partir de biomassa lignocelulósica. No entanto, mais pesquisas são necessárias sobre as etapas de purificação para melhorar a qualidade do produto e a competitividade do processo. Este trabalho apoia o desenvolvimento de tecnologias eficientes e ecológicas alinhadas aos princípios da bioeconomia e da economia circular.
Palavras-chave: Ciclo de vida, éster de açúcar, xilose.

ABSTRACT - This study proposes a sustainable enzymatic process for the production of xylose esters using deep eutectic solvents (DES) based on xylose, which act simultaneously as solvent and substrate. Reactions were carried out in a jacketed reactor, at 60 °C, 550 rpm, 500 U of tributyrin hydrolysis activity (TBU)/g of xylose and molar ratio of 1:5 (xylose: oleic acid). The process was modeled using mass and energy balances in EMSO software, achieving ~85% conversion of xylose into esters. Life Cycle Assessment (LCA), conducted with SimaPro and the Ecoinvent 3.0 database, demonstrated lower environmental impacts compared to conventional biosurfactant routes, especially in categories such as fossil resource depletion and global warming potential. The use of DES enabled an anhydrous and biocompatible reaction medium, favoring lipase-catalyzed esterification under mild conditions. These results highlight the potential of integrating biocatalysis and green solvents for producing high-value bio-based surfactants from lignocellulosic biomass. However, further research is needed on purification steps to enhance product quality and process competitiveness. This work supports the development of efficient and eco-friendly technologies aligned with the bioeconomy and circular economy principles.
Keywords: Life cycle, sugar ester, xylose.

Introduction

Sustainable product and process solutions have been increasingly demanded by the market as a response to societal challenges such as climate change, environmental pollution, and food insecurity (1,2). To this end, a transition from products derived from finite raw materials, such as petroleum, to those derived from renewable resources, such as biomass, is essential (2). The concepts of bioeconomy and biorefineries offer strategies to address these demands, such as the development of integrated production chains based on renewable raw materials. In this approach, waste and energy generated in each production line can be reused as inputs for the generation of other products, thereby enhancing the overall efficiency in resource utilization (1–3).

Surfactants are amphiphilic molecules widely used in numerous industrial processes, ranging from cleaning to product formulation, due to their critical properties such as emulsification, wetting, foaming, and cleaning action (4). Sugar esters (SEs) have emerged as an alternative to

petrochemical surfactants (5,6); they are produced through an esterification reaction between a sugar and a free fatty acid (7). Furthermore, sugar ester surfactants exhibit superior stability under extreme conditions compared to petrochemical surfactants (8).

Five-carbon sugars (C5-SEs) have been gaining prominence in the scientific and industrial fields due to their excellent lubricating and antimicrobial properties, positioning them as promising molecules for skin moisturizing formulations (9). Furthermore, five-carbon sugar esters, particularly xylose esters, have potential as environmentally friendly and sustainable, as xylose can be obtained from renewable biomasses such as wood, sugarcane bagasse, straw, and other lignocellulosic residues. Therefore, they have potential for use in xylose residues from biorefineries or second-generation ethanol plants (10,11).

Despite the use of reactants from renewable sources highlighting the properties of sugar esters (SEs), their traditional production via chemical processes requires acidic and metal catalysts at high pressures and temperatures (12). Additionally, this method presents low selectivity and specificity, leading to colored derivatives as side products, which may affect their applications in food, cosmetic, and pharmaceutical products (5,12).

Enzymatic catalysis may provide a suitable method to overcome this drawback by using lipases in a single esterification step. Moreover, the enzymatic route offers mild reaction conditions and environmentally friendly processes, in addition to providing high specificity and regioselectivity, which prevent issues such as substrate degradation and the formation of unwanted products (5,13).

Among the biocatalysts used, the commercial preparation of Candida antarctica lipase B immobilized on Lewatit VP OC 1600 (N435) has been widely employed in the production of sugar esters. This biocatalyst consists of Candida antarctica lipase B physically immobilized on an acrylic resin support (Lewatit VP OC 1600) via interfacial activation (10,11). Oleic acid has been used as an acyl donor group in the production of sugar esters, enabling greater conversion due to the selectivity of the biocatalyst (10,11).

Selecting an appropriate reaction medium is critical for applying enzymes in SEs production, due to the low water activity required to favor the esterification reaction and the significant difference in polarity between the substrate and the solvent (8). Deep eutectic solvents (DES) have been proposed as a suitable solvent for lipase-catalyzed reactions (8,14,15).

This new class of solvents consists of two or three chemical compounds that act as hydrogen bond donors and acceptors, and have a lower melting point than their pure components (14,15). DES present a promising alternative to conventional organic solvents due to their non-toxicity, biodegradability, non-flammability, and low volatility (16,17). Furthermore, DES formed by sugars as hydrogen bond donors can be used simultaneously as solvents and substrates, creating an anhydrous reaction medium containing both sugars and fatty acids, which favors lipase-catalyzed esterification (14,18,19).

Life Cycle Assessment (LCA) serves as a powerful tool for evaluating the environmental impacts associated with various processes. Through the analysis of energy and material flows across all stages of a process, LCA makes it possible to measure environmental burdens and pinpoint the most impactful steps. This comprehensive approach facilitates the identification of environmental hotspots and informs the creation of strategies to reduce harmful effects while promoting the sustainability of the entire system (20,21).

In this context, the present study aims to evaluate the sustainable production of xylose esters, focusing on enzymatic catalysis and the use of xylose-based deep eutectic solvents that act simultaneously as both substrate and solvent.

Material and Methods

Materials

Novozym® 435 (N435), tributyrin were purchased from Sigma-Aldrich (St. Louis, MO, USA). Xylose and oleic acid was obtained from Synth (São Paulo, Brazil). Choline chloride were acquired from Neon (São Carlos, Brazil). All other reagents and solvents were of analytical grade and were used without any prior treatment.

Preparation of the xylose-based DES

The xylose-based deep eutectic solvent (DES) was prepared by mixing xylose and choline chloride in equimolar proportions under continuous stirring at 70 °C in a closed bottle. The mixture was stirred for approximately two hours until a homogeneous and transparent liquid was formed (22). This mixture was used as both substrate and solvent in further studies.

Enzymatic synthesis of xylose oleate

The synthesis of xylose oleate was performed through the enzymatic esterification of commercial xylose and commercial oleic acid (C18:1) at a molar ratio of 1:5 (xylose: oleic acid), using different solvents for xylose solubilization, as described previously. Reactions were carried out in a jacketed reactor with a flat-blade impeller, at 60 °C, 550 rpm, and 500 U of tributyrin hydrolysis activity (TBU)/g of xylose. Samples were collected at 0 and 24 hours, and the concentration of oleic acid was measured by gas chromatography. All reactions were performed in duplicate.

Modeling and Simulation

The modeling framework was based on mass and energy balances, along with pressure-related constraints. The process was simulated under steady-state conditions, meaning that system variables remained constant over time. The simulation was carried out using the open-source EMSO software.

Life Cycle Assessment (LCA)

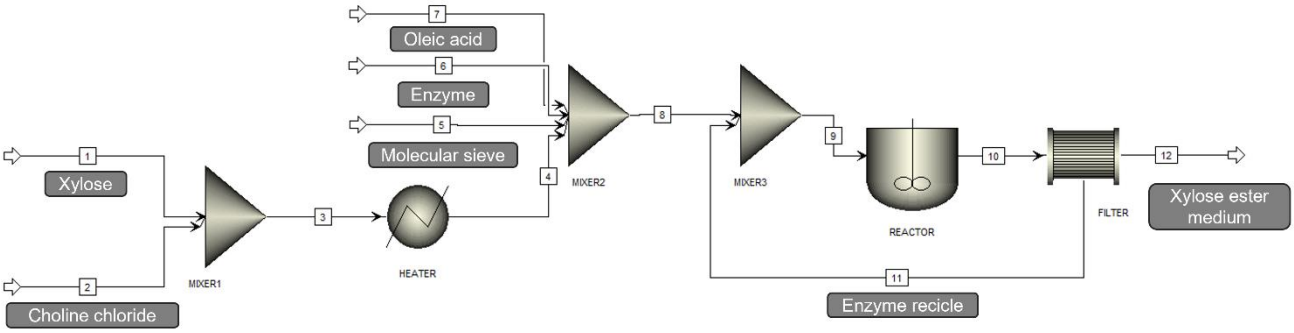


Figure 1. Process diagram for simulation of xylose ester production.

The environmental performance of the process was evaluated through Life Cycle Assessment (LCA), a systematic approach for quantifying environmental impacts. This evaluation utilized the Ecoinvent 3.0 inventory and was carried out in the SimaPro 9.0.0.35 platform. To characterize the impacts, the CML-IA baseline V3.04 (World 2000) method was adopted, covering ten categories: fossil resource depletion (AD), climate change potential over a 100-year horizon (GWP100), ozone depletion (ODP), human toxicity (HT), ecotoxicity in freshwater (FWAET), marine (MAET), and terrestrial (TET) environments, photochemical smog formation (PO), acidification (AC), and nutrient enrichment or eutrophication (EU). The inventory parameters were subsequently linked to the EMSO simulation environment to enable the quantification of these impact metrics. Table 1 shows the indicator values for reagents and electricity.

Tabela 1. Parameter values of each indicator for reagents and utilities used in the process, from SimaPro database. GWP 100a: Global Warming Potentials 100 years; AD: Abiotic depletion - fossil fuels; ODP: Ozone layer depletion; HT: Human toxicity; FWAET: Freshwater aquatic ecotoxicity; MAET: Marine aquatic ecotoxicity; TET: Terrestrial ecotoxicity; PO: Photochemical oxidation; AC: Acidification; EU: Eutrophication.

	Choline Chloride	Fatty Acid	Xylose	Enzyme	Eletricity
GWP 100a (kg eq CO_2)	1.88	2.59	0.973	1.19	0.156
AD (MJ)	50.6	23.8	0.901	39.6	1.6
ODP (kg CFC-11 eq)	1.55 x 10^{-7}	1.12 x 10^{-7}	3.20 x 10^{-8}	3.23 x 10^{-10}	0
HT (kg 1,4-DB eq)	6.54 x 10^{-1}	1.54	1.52	4.91 x 10^{-2}	4.19 x 10^{-4}
FWAET (kg 1,4-DB eq)	0.331	21.1	0.209	0.0145	0
MAET (kg 1,4-DB eq)	1180	1140	-204	53.4	0
TET (kg 1,4-DB eq)	1.54 x 10^{-3}	9.27	1.28 x 10^{-2}	2.89 x 10^{-3}	0
PO (kg C_2H_4 eq)	7.85 x 10^{-4}	1.34 x 10^{-3}	6.19 x 10^{-3}	2.71 x 10^{-4}	1.71 x 10^{-5}
AC (kg SO_2 eq)	1.07 x 10^{-2}	8.78 x 10^{-3}	4.21 x 10^{-3}	2.51 x 10^{-3}	2.67 x 10^{-4}
EU (kg PO_4 eq)	2.35 x 10^{-3}	8.38 x 10^{-3}	2.1 x 10^{-3}	2.3 x 10^{-4}	4.57 x 10^{-5}

Results and Discussion

The experiments resulted in a conversion of 17% of oleic acid to ester. Note that this is the excess component; if we evaluate the conversion in terms of xylose, the conversion is 85% for this reaction. Based on this conversion data and all the experimental conditions evaluated, the simulation was generated for a larger-scale process, as illustrated in Figure 1. Xylose and choline chloride were introduced into the process and solubilized by adding heat to the stream. Soon after, the oleic acid, enzyme, and molecular sieve were added to the process and went to the reactor where the esterification occurs. Finally, a filter was used to separate the enzyme, in solid phase, from the rest of the process, and it was reused for a total of 10 cycles. Although the simulation is continuous, it only represents the experimental batches in the laboratory.

The outcomes of the LCA were determined using the mass and energy balance data generated by the simulation.

Figure 2 illustrates the indicators computed for the production of 1 kilogram of the final product. The plant operated with a baseline of 10 kmol/h of xylose consumption and 10 kmol/h of solvent input, resulting in approximately 3000 kg/h of total mass entering the process. Over 24 hours, the mass conversion of oleic acid reached 85%, reaching 1400 kg/h of xylose ester medium.

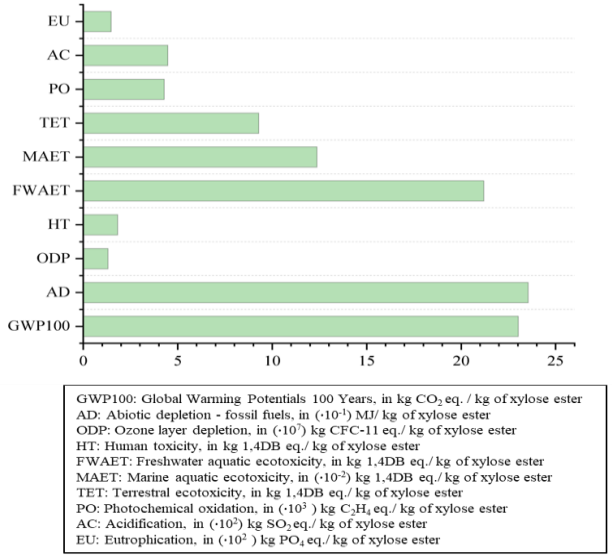
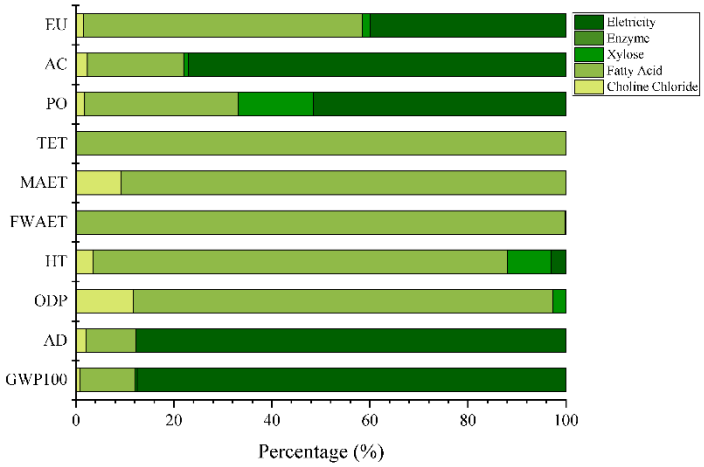


Figure 2. Environmental impact assessed through absolute LCA scores for the biosurfactant production process

When compared to GWP100, the present work resulted in ~23 kg eq CO2/ kg xylose ester, being lower than that presented by Casian *et al.,*(2024) (23) (34.43 kg eq CO2/ kg xylose ester) and 24 (735 kg eq CO2/ kg sophorolipids), and higher than Guilbot *et al.,*(2024) (25) (9.58 kg eq CO2/ kg Alkyl polyglucoside), Lokesh *et al.,* (2017) (26) (1.87 kg eq CO2/ kg Alkyl polyglucoside) and Elias *et al.,* (2021) (27) (17.1 kg eq CO2/ kg sophorolipids). Apart from MAET (1.24 x 103 kg 1,4-DB eq/ kg xylose ester), all other environmental indicators (AD: 2.35 x 102 MJ/ kg xylose ester; ODP: 1.31 x 10-7 kg CFC-11 eq/kg xylose ester; HT: 1.82 kg 1,4-DB eq/kg xylose ester; FWAET: 21.2 kg 1,4-DB eq/kg xylose ester; TET: 9.29 kg 1,4-DB eq/kg xylose ester; PO: 4.49 x 10-3 kg C2H4 eq/kg xylose ester; AC: 4.48 x 10-2 kg SO2 eq/kg xylose ester; EU: 1.48 x 10-2 kg PO4 eq/kg xylose ester) reached values lower than those calculated at (23–27).

Finally, Figure 3 shows the relative values of the environmental indicators, broken down by the percentage contributions from energy and reagents. Electrical energy significantly impacts the GWP100, AD, PO, AC, and EU indicators. On the other hand, oleic acid has the most



significant impact on the ODP, HT, FWAET, MAET, and TET indicators.

Figure 3. Environmental impact with percentage scores of the LCA for the process, separated by utilities and raw materials.

Thus, environmental impacts can be reduced by optimizing the thermal use of the process and reducing the proportion of oleic acid as an excess reagent. Another critical point to highlight is the enzyme, which has practically no impact on calculations. Finally, the choline chloride solvent is also not representative of the LCA, which indicates its potential use in this reaction.

Conclusions

The enzymatic processes for biosurfactant production were precisely modeled: xylose ester from oleic acid and xylose. The simulation accurately described the esterification reaction, converting ~85% of xylose into esters. The Life Cycle Assessment (LCA) indicates lower impacts than other biosurfactants, highlighting the value of an alternative process. However, a study of the purification of the process needs to be carried out to make it competitive in its use.

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