BABASSU OIL AS RAW MATERIAL FOR THE ENZYMATIC SYNTHESIS OF BIOFUEL AND BIOLUBRICANT: A REVIEW

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ABSTRACT

This study used systematic mapping (MS) to review the literature on the use of babassu oil in the synthesis of biodiesel and biolubricants. The results showed the use of a variety of lipases, with PS lipase (*Burkholderia cepacia*) being the most used by researchers. These different lipases produced similar product yields, with higher enzyme loads being strongly correlated with increased productivity. Transesterification reactions were favored using immobilized lipases, showing higher yields and operational stability than using soluble lipases. Reaction parameters were generally standardized with variations in oil-to-alcohol molar ratios, type of alcohol, and reaction time. Notably, the alcohol carbon chain length and the oil/alcohol molar ratio significantly influenced the yield and productivity of the reaction. Finally, the structure, network distribution, and frequency of co-occurrence between lipases and supports are elucidated to determine possible hotspots and hitherto unexplored advances in knowledge.

Keywords: Biodiesel. Babassu Oil. Biolubricants. Lipase. Systematic mapping.

1 INTRODUCTION

Since their discovery, fossil fuels such as coal, oil, and natural gas have been widely used as primary sources of energy, particularly in recent decades. However, their prevalence is intrinsically linked to adverse consequences for the environment, especially in terms of atmospheric pollution and global warming. After the 28th United Nations (UN) Climate Change Conference - COP28, it was agreed to start the transition away from fossil fuels and prepare for a rapid and fair shift towards creating to clean sources. This decision was supported by significant reductions in emissions and increased financing related to this transition, replacing the use of fossil fuels with renewable ones, will be a basis for developing and implementing national climate plans by 2025, with a budget of at least $100 million per year. COP28 recognizes the need to control and reduce global greenhouse gas emissions by 43% by 2030, limiting global warming to 1.5°C. The expansion of renewable energy sources is crucial in achieving the global goals of reducing fossil fuel consumption. [1]

With this new scenario, biodiesel and biolubricants derived from renewable sources such as vegetable oils and animal fats are gaining prominence as a promising option. It is possible to synthesize esters with biolubricating properties through the transesterification of vegetable oils or through the esterification reaction of long-chain fatty acids with long-chain alcohols and the choice between synthesis methods depends on process preferences, cost and environmental considerations. Babassu oil is a prominent oil in the agroenergy sector. It is extracted from the seeds of the babassu palm (*Orbignya phalerata* Martius), a species native to the Amazon region. The main producers of this oil are the states of Maranhão and Piauí, with Tocantins, Ceará and Pará also significant contributors.[2] The use of babassu oil as a base for biodiesel and biolubricant presents environmental and economic benefits, while promoting development sustainable. in regions where the babassu palm tree is abundant. Furthermore, the low saturation of fatty acids in babassu oil contributes to greater stability of the biodiesel produced. [3]

Enzymatic transesterification is a promising method to synthesize biodiesel and biolubricants. This method offers easier recovery of esters and glycerol at the end of the reaction. It requires mild operating conditions in terms of temperature and pressure and has simultaneous catalytic activity for triglycerides and free fatty acids.[3] Lipases are a group of enzymes highly used by laboratories and industries due to their efficiency, specificity due to their ability to function in aqueous and non-aqueous without the need for cofactors. [4] Systematic mapping analysis is a crucial tool for understanding trends and gaps in a given field of research. This approach involves the application of mathematical and statistical techniques, together with qualitative analyses, to determine the characteristics of scientific production in this area. [5] Therefore, this study aimed to gather data and systematically review findings on the production of biodiesel and biolubricants from babassu oil using lipases as biocatalysts.

2 MATERIAL & METHODS

The SM analysis utilized the scientific databases Scopus and Web of Science. The search string included the terms "Biodiesel" OR "Biolubricant" AND "Babassu Oil" AND "Lipase" OR "Eversa Enzyme". A total of 21 documents were found in the Web of Science database and 17 in the Scopus database as of January 15, 2024. The scope for the evaluation of articles was limited to English language publications without any specific publication date range and was not limited to categories of work in order to broaden the research field. Coverage and overlap analysis of duplicates were conducted using RStudio software. No subjective evaluations were included in the analysis. After removal of duplicates, the database was reduced to 26 papers, and then to 20 studies that met all the inclusion criteria after title, abstract, and keywords screening: i) studies that used babassu oil as raw material for biofuels and/or biolubricants; ii) production via lipase catalysis. A descriptive bibliometric analysis of the data was performed using the Bibliometrix package to assess research trends, co-authorship networks, and other aspects of scientific

production. Finally, the full text of the remaining 20 studies was evaluated. All evaluated articles used babassu oil as the raw material for biodiesel production and the transesterification reactions were catalyzed by lipases, specifically Lipase Eversa® Transform 2.0 (liquid formulation of lipase from *Thermomyces lanuginosus* from Novozymes).

3 RESULTS & DISCUSSION

Research on the subject discussed in this review started in 2007 and remains ongoing. Only 20 documents have been found addressing the proposed theme. The data collection involved 75 authors, 62 author keywords, and 299 additional keywords. It is worth noting that after analyzing the 20 selected articles, none of them addressed the production of biolubricants using babassu oil as raw material. This approach can be seen in the analysis of co-occurrences and their respective degree of occurrence, which can be observed in the scale values (Figure 1), where among the keywords that most appeared in the articles, none of them contemplated the production of biolubricants. The study focuses on co-occurrence assessment, which involves counting paired data within a "sampling unit".[6] Examining the term “Lipase” in the context of biodiesel and biolubricant production, we can identify “Biocatalysis” and “Enzymatic Catalysis” as co-occurrences when mentioned in the same text. Data from three different “sample units” were analyzed, which will be discussed later: Lipases, lipase immobilization and reaction conditions for the production of biodiesel or biolubricant from babassu oil. The study uses the VOSviewer software to generate a graph of main keywords with icon size indicating frequency of occurrence and color representing clusters. Objects are grouped based on similarity, with thicker connecting lines indicating stronger relationships.[7]

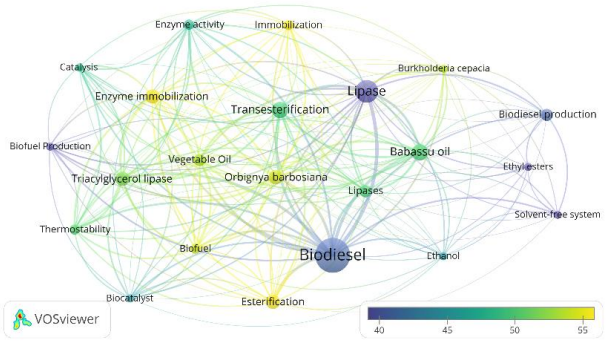

Figure 1 - Keywords co-occurrence analysis

This study revealed that several lipases are used in the production of biodiesel with babassu oil. These enzymes are versatile, functioning well in both aqueous and non-aqueous systems due to their hydrophobic structure.[4] Lipase PS from *Burkholderia cepacia* is widely used due to its efficiency and high yield in transesterification reactions for biodiesel production from babassu oil. On the other hand, Eversa® lipase aroused interest in new projects for biodiesel production due to its effectiveness in solvent-free media, which aligns with the principles of green chemistry. The use of different lipases on the production of biodiesel affected the yield and the productivity of the process. Freitas et al. (2009) conducted screenings to find a lipase for integrated biodiesel and monoglycerides production. They tested various lipases immobilized in a silica-PVA composite using babassu oil and alcohols in solvent-free systems. The PS lipase from *Burkholderia cepacia* showed the best performance, with a transesterification yield of 90.9% and a productivity of 7 mg biodiesel/g/h at a 1:7 oil-to-ethanol molar ratio and 39°C for 48 hours. Lipase AK from *Pseudomonas fluorescens* and liquid lipase B from *Candida antarctica* (CALB L) had lower transesterification yields (70.28% and 61.67%, respectively) than the PS lipase, while Lipase G from *Penicillium camembertii* yielded less than 10%, possibly due to its preference for mono- and diglycerides. This difference in ester yield for biodiesel production by various lipases can be primarily attributed to their structural characteristics, biochemical properties, and specific interactions with the substrate and reaction conditions.

The reviewed studies indicated that the immobilization of enzymes for biodiesel production is predominantly done by covalent bonding and physical adsorption, facilitating the reuse of enzymes and maintaining their stability. [9] There is no universal immobilization method, but the hydrophobicity of the support is crucial for lipases, which can be intensely activated on hydrophobic surfaces. Of the methods analyzed, 55% used covalent bonding, 40% physical adsorption and only 5% encapsulation. Lima et al. (2015) demonstrated the use of different immobilization supports for the Lipase AK from *Pseudomonas fluorescens* enzyme in the production of biodiesel from babassu oil and soybean oil, without solvents. Immobilization on octyl-silica proved to be more effective, with a hydrolytic activity of 650 U/g and an almost complete conversion of babassu oil into biodiesel (>97.5%) in 24 hours. Meanwhile, immobilization on XAD 7HP and polystyrene resulted in maximum transesterification yields of 83% and 80%, respectively, after 48 hours. Lipase AK immobilized on octyl-silica showed great promise for adsorption capacity during the reactions, unlike polystyrene which showed the lowest capacity. In the study by Shimada et al. (1999), crucial parameters for the production of biodiesel by enzymatic catalysis were investigated. They highlighted the importance of the minimum presence of water to maintain the structure of the lipases, and the non-addition of water to the reaction medium, as evidenced after the addition of 0.2% of water to the reaction medium, when the conversion of esters dropped by 10.5%, 3 times less than in the first reaction in which neither addition nor complete removal was performed (ester conversion of 30.9%). Furthermore, they tested different reaction temperatures, observing that the ideal range was between 50°C and 60°C, as the conversion of esters in 6 hours

increased with an increase in the temperature. The molar ratio of oil-to-alcohol was also analyzed, concluding that at least 3 molar equivalents of methanol are needed to completely convert the oil into esters. By adding 1 molar equivalent of methanol every 24 hours, they achieved a conversion of 98.4% in 72 hours, showing the effectiveness of the gradual addition of methanol to complete the oil conversion.

In the study by Souza (2008), it is highlighted that methanol and ethanol are the main alcohols used in the production of biodiesel, with methanol being more common due to its low cost and chemical advantages. However, the ethanol route is being promoted due to the availability of renewable raw materials, such as sugar cane, and Brazil's self-sufficiency in the production of alcohol from this source. Anhydrous ethanol is preferred due to its short carbon chain and effectiveness in removing water from the reaction medium, although excess alcohol can unbalance the reaction in favor of the products, which has been considered harmful.[9] The specification of biodiesel for blending with diesel oil is established by ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis do Brasil) Resolution Nº 920, dated April 4, 2023. Some properties related to the quality of biodiesel obtained from babassu oil were estimated in the study developed by Rodrigues (2017). The estimated cetane index value (63.7) exceeded the standards for biodiesel, which prescribe a minimum of 47 or 51. Regarding the iodine index, the EN 14214 standard, one of the most stringent in this regard, it requires a maximum value of 120 g(I_2)/100 g (biodiesel), and the estimated value for biodiesel from babassu oil is at a very safe level (16.9). For the Cold Filter Plugging Point (CFPP), the value of minus 8.5 °C is excellent, since Brazilian standards require a minimum of 5 °C. These results indicate a strong potential for biodiesel production from babassu oil and the results of this work came from the synthesis of the database, which was only possible to obtain after refining the results of the search string used, reinforcing that the systematic review is an effective method for obtaining data on a given subject, optimizing processes, and facilitating searches assertions.

4 CONCLUSION

This work offered a comprehensive and accurate review of biodiesel production from babassu oil, highlighting the careful searches carried out by the systematic review. A considerable variety of lipases were observed for these reactions, as well as different supports with different levels of hydrophobicity, influencing conversion rates and reaction yields. Some gaps deserve attention, such as the lack of studies on the use of babassu oil in the production of biolubricant esters and the promising, but little explored, enzyme Eversa Transform 2.0 in the biodiesel sector. Therefore, this systematic review is extremely important, as it outlines research related to the production of biodiesel from babassu oil catalyzed by lipases, identifies challenges, and proposes solutions, highlighting the effectiveness of this method in several areas of research.

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