BIODIESEL PRODUCTION FROM ETHANOLYSIS OF BABASSU OIL: A COMPARATIVE STUDY EMPLOYING HETEROGENEOUS CATALYSTS

Adilson M. Oliveira[1], Matheus R. A. Andrade[1], Giovanna M. Sant´Ana[1], João V. C. Martins[1], Heitor B. S. Bento[2], Luiz F. Gorup[3,4], Bruno C. Gambarato[5], Tales A. Costa-Silva[6], Ana K. F. Carvalho[1]

[1]*Engineering School of Lorena- University of São Paulo – EEL-USP, Lorena, Brazil.*
[2]*School of Pharmaceutical Sciences - UNESP, Araraquara, Brazil.*
[3]*Federal University of Juiz de Fora – UFJF*, Juiz de Fora, Brazil.
[4]*Federal University of Rio Grande – FURG*, Rio Grande, Brazil.
[5]*University Center of Volta Redonda – UniFOA, Volta Redonda, Brazil.*
[6]*Federal University of ABC – UFABC, Santo André, São Paulo, Brazil*

** Corresponding author's email anacarvalho@usp.br*

ABSTRACT

This study aims to compare the production of biodiesel from ethanollysis of babassu oil using a biological catalyst (*Candida rugosa* lipase immobilized in magnetic-chitosan-lipase beads) and a chemical catalyst (niobium with heteropolyacid). In order to achieve this objective, the biological catalyst reaction was carried out batch reaction, while the heterogeneous catalyst was carried out in a Parr reactor. The biodiesel yield using H_3PMo/Nb_2O_5 as catalyst was 98% after 6h of reaction and for immobilized lipase the value was 95% after 72h of reaction time. The biodiesel viscosity from chemical and biologic catalyst was 4.5 and 5.3 ($mm^2.s^{-1}$), respectively. Based on the findings, both transesterification methodologies proved effective in converting babassu oil into biodiesel. The viscosity of the resulting biodiesel from both methods complied with the standards set by the national gas and oil regulatory agency.

Keywords: Biodiesel. Babassu oil. Lipase. Enzyme immobilization. Chemical catalysts.

1 INTRODUCTION

Biodiesel emerges as a promising alternative to fossil fuels[1], notable for its renewable origin and reduced environmental impact. Obtained from either plant or animal sources, biodiesel production has garnered increasing interest driven by the pursuit of more sustainable energy sources[2]. In this context, the utilization of babassu, a native palm species of Brazil, gains significance as a promising feedstock for biodiesel production[3]. Babassu stands out for its abundance in various tropical regions, particularly in the Brazilian northeast, offering substantial potential for biodiesel production. Moreover, the use of babassu in biodiesel production can serve as a significant source of income for local communities, fostering sustainable practices and promoting regional economic development.

Regarding the production process, enzymatic catalysis emerges as an innovative and efficient approach. Unlike traditional methods employing chemical catalysts, enzymatic catalysis utilizes specific enzymes to facilitate the necessary reactions in transesterification, a fundamental step in biodiesel production. This technique offers advantages such as increased selectivity, reduced environmental impact, and milder operational conditions, thereby contributing to a more sustainable and economically viable production process.

On the other hand, the utilization of heterogeneous catalysts in the production of biodiesel through the ethanolysis of babassu oil is a promising and efficient approach. These catalysts, typically solid, offer various advantages, including their capacity for reusability and ease of biodiesel separation. Throughout the ethanolysis process, the heterogeneous catalyst facilitates the reaction between babassu oil and ethanol, resulting in the production of ethyl esters, which constitute biodiesel. Additionally, the use of heterogeneous catalysts may diminish operational costs and environmental impacts associated with biodiesel production. This approach proves promising for large-scale biodiesel production from babassu oil, contributing to the pursuit of more sustainable and renewable energy sources.

2 MATERIAL & METHODS

Feedstock and catalyst: The source of raw materials consists of babassu oil, Chitosan-immobilized lipase (biocatalyst)[6] and H_3PMo support in Nb_2O_5 [7]. The procedure of *Candida rugosa* lipase immobilization was carried-out according to Costa-Silva et al.[6] In brief, Fe_3O_4-chitosan beads (Fe_3O_4/chitosan ratio: 1/4 w/w) were generated by acid chitosan solution containing 0.5 g of *Candida rugosa* lipase. The acetylated chitosan solution + lipase was extruded dropwise by a syringe coupled to a peristaltic pump into solution of cross-linking agent ($Na_5P_3O_{10}$ - 10% w/v). The magnetic-chitosan-lipase beads produced were recovered by filtration and oven dried at 35 °C for 24 h.

Synthesis: The biochemical catalysis was carried out over a period of 72 hours, using a reactor with a capacity of 50 ml, under magnetic stirring, which contained 30 grams of reaction medium - following the proportion of 12 mol of ethanol to 1 mol of oil - and 15% of biocatalyst in relation to the reaction medium. The chemical catalysis was performed in a pressurized reactor (Parr

series 5000 multiple reactor system) with stirring (300 rpm) at 200ºC for 6h using an ethanol to oil molar ratio of 120:1 with (H_3PMo / Nb_2O_5) added at 10%.

Purification: After the end of reaction, the product was put in Falcon tubes for purification. The Falcon tube was centrifuged for 7 minutes at a rotation speed of 2600 rpm. Then, the supernatant, composed of ethyl esters, was separated from the catalyst. The glycerol formed as a by-product was removed with chamotte and the excess ethanol was evaporated in a rotary evaporator at 80°C for 30min.

Analysis: The determination of density values was carried out using a digital densimeter, Model DMA 35n EX (Anton Paar), at a temperature of 20°C. As for viscosity, the Brookfield Viscometer Model LVDVII (Broofield Viscometers Ltd, England) was used at 40°C.

Morphology of the support material was analyzed using scanning electron microscopy (SEM). A Zeiss Supra 35VP microscope with a field emission gun (FEG-SEM), operating at 5 to 10 keV, was employed for this analysis. Sample preparation involved depositing a drop of the sample suspension (5 $mg.mL^{-1}$) onto a silicon substrate using a micropipette. The samples were then dried in an oven at 40°C for 12 hours.

The conversion of transesterification of the heterogeneous catalyst was analysed by Ethyl fatty esters (FAEE) was determined according to the methodology previously established by Urioste et al. (2008)[8].

3 RESULTS & DISCUSSION

The bioencapsulated *Candida rugosa* lipase obtained by the cross-linking technique show a residual lipase activity of 75.6%. This biocatalyst was compared to with a heterogeneous catalyst for biodiesel production using Babassu oil as substrate. The properties of biodiesel are listed on table 1**.**

Table 1 Biodiesel properties obtained from Babassu oil: comparison of catalysts

Catalysts	Properties			
	Reaction time (h)	Viscosity ($mm^2.s^{-1}$)	Density ($kg.cm^{-3}$)	Yield (%)
Chitosan-immobilized lipase	72	5.3	0.8803	95 ± 0.5
H_3PMo/Nb_2O_5	6	4.5	0.8750	98 ± 0.5

The results presented in the table serve as indicators of the produced biodiesel's quality. According to the guidelines established by the National Petroleum Agency (ANP), biodiesel should exhibit a viscosity within the range of 3 to 6 $mm^2.s^{-1}$. The initial viscosity of babassu oil is notably high at 29.59 $mm^2.s^{-1}$. The significant decrease in viscosity observed after the reaction highlights the process's effectiveness, resulting in biodiesel samples that meet the ANP's specified parameters.

Scanning Electron Microscopy (SEM) images shown in Figure 1 demonstrate the efficiency of the immobilization preparation procedure. The presence of well-formed spheres is evident, which correlates with the high yield results obtained.

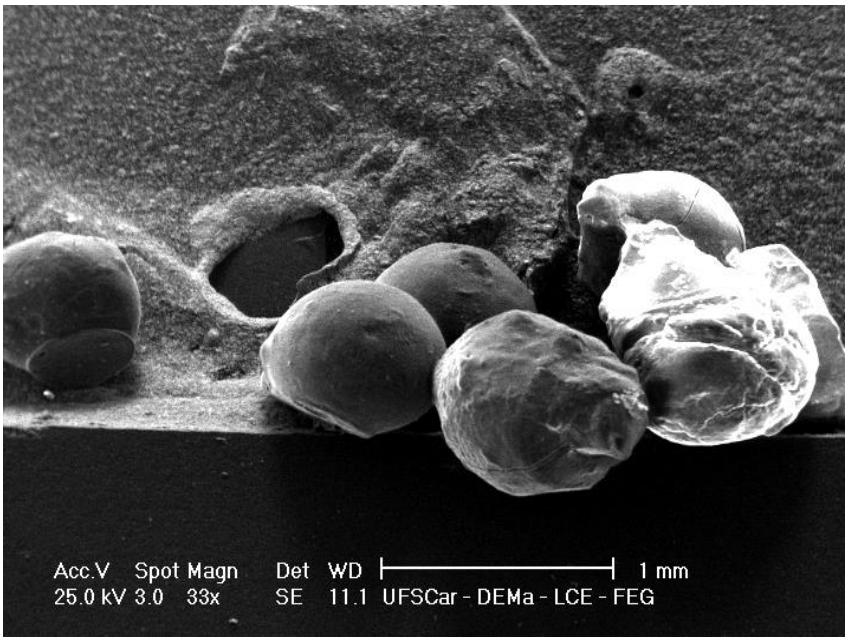

Figure 1 Scanning Electron Microscopy images of supports

It is important to note that the enzymatic reaction required a longer reaction time compared to the chemical method. This disparity in reaction duration could be addressed by employing non-conventional heating techniques, such as microwaves or ultrasound,

which have shown potential to accelerate the enzymatic process, thereby enhancing its competitiveness with the chemical pathway.

4 CONCLUSION

Based on the findings, both transesterification methodologies proved highly efficacious in converting babassu oil into biodiesel. The viscosity of the resulting biodiesel from both methods adhered to the stringent standards set by the national gas and oil regulatory agency, ensuring its suitability for use as a fuel. These results underscore the reliability and efficiency of both chemical and enzymatic transesterification processes. To further enhance the competitiveness of the enzymatic route, several improvements in the bioencapsulation process could be pursued. Increasing the enzyme load would enhance the overall catalytic activity, potentially leading to faster reaction times and higher yields. Additionally, addressing diffusion limitations within the encapsulated matrix could improve substrate accessibility and reaction efficiency. Ensuring greater retention of enzyme activity over multiple cycles would also contribute to the economic feasibility and sustainability of the enzymatic method. However, it is crucial to consider the issue of environmental safety in the production of biodiesel, regardless of the route employed. Both chemical and enzymatic pathways must be evaluated for their environmental impact, particularly concerning the use of solvents, catalysts, and other reagents. Sustainable practices and green chemistry principles should be integrated into the process design to minimize any potential adverse effects on the environment. This holistic approach not only enhances the environmental profile of biodiesel production but also aligns with broader goals of sustainable development and regulatory compliance.

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