

PRODUCTION OF BIOLUBRICANT BASES BY ENZYMATIC HYDROESTERIFICATION OF BABASSU AND CASTOR OILS: INFLUENCE OF THE CARBON TAIL LENGTH AND UNSATURATION DEGREE ON THE BIOESTERS' PHYSICOCHEMICAL AND TRIBOLOGICAL PROPERTIES

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ABSTRACT

Biolubricants have emerged as an attractive alternative for petroleum-based lubricants. Castor and babassu oils can be used as unsaturated and saturated fatty acid sources, respectively, to produce biolubricant bases (bioesters) with different physicochemical and tribological properties. Enzymatic route has been widely studied as an environmentally friendly substitute to the traditional chemical route. The enzyme Eversa Transform 2.0 (a liquid formulation of *Thermomyces lanuginosus* lipase) has attracted the attention of researchers due to its excellent performance, particularly in the biodiesel (alkyl fatty acid esters) field, besides its low cost compared to others lipase formulations. In a biorefinery context, the use of by-products is a practice that will tend to be increasingly common worldwide due to the current needs of sustainability and reduction of environmental pollutants. In the production of renewable biolubricant bases, fusel oil (a by-product of ethanol distilleries) can serve well as source of alcohols (mainly isoamyl alcohol) to produce bioesters. In this context, this work aimed to produce biolubricant bases from castor and babassu oils by enzymatic hydroesterification with fusel oil as alcohol source. Castor and babassu oils were majorly composed of ricinoleic and lauric acids, and fusel oil mainly composed of isoamyl alcohol. In the first step (hydrolysis), yields up to 80% could be achieved with only 4 hours of reaction using Eversa as biocatalyst. In the same way, this enzyme allowed achieving ester yields up to or more than 80% with 12 hours of reaction. The biolubricant bases exhibited physicochemical and tribological properties comparable to industrial lubricant bases.

Keywords: Biolubricant base. Babassu oil. Castor oil. Fusel oil. Enzymatic hydroesterification.

INTRODUCTION

Lubricant oils are used to reduce friction and wear between moving mechanical components. They can increase the equipment operating time and allow common and industrial applications¹. Approximately 95% of lubricants are produced by petroleum sources². Biolubricants have emerged as an attractive alternative from an environmental perspective^{2,3}. Biolubricants consist of an organic base (>90 wt.%) and additives (<10 wt.%)⁴. The organic base of biolubricants consists of bioesters (alkyl fatty acid esters), which can be obtained through the hydroesterification of triglycerides and alcohols^{5,6}. The chemical characteristics of the reagents influence the properties of the product⁷. Castor and babassu oils can be used for evaluating the influence of the chemical composition of the oils (acyl donors) on the physicochemical and tribological properties of biolubricant bases. As a source of alcohol (acyl acceptor), fusel oil emerges as an attractive option⁶. Fusel oil is a byproduct of ethanol production, it has low-cost product, it has few applications, and its use is aligned with green economy concepts⁸. As a catalyst, the enzyme Eversa Transform 2.0 (a commercial liquid formulation of *Thermomyces lanuginosus* lipase genetically modified)⁹ exhibits good performance in hydroesterification reactions⁵. Thus, this study aimed to obtain biolubricant bases from castor and babassu oils by enzymatic hydroesterification with fusel oil as source of acyl acceptors. The study also aimed to evaluate the influence of the chemical characteristics of the oils on the biolubricant base properties.

MATERIAL & METHODS

Babassu oil was purchased from COPPALJ (Lago do Junco, MA, Brazil). Castor oil was purchased from 21 QUIMICA (Barueri, SP, Brazil). Fusel oil was kindly donated by Usina Sao Martinho (Araraquara, SP, Brazil). Liquid Eversa Transform 2.0 (Novozymes) and molecular sieves (3 Å, 1.6 mm, pellets) were purchased from Sigma-Aldrich (St. Louis, MO, EUA). All other reagents were analytical grade and were used as received.

The acid (AV), saponification (SV), and iodine (IV) values of castor and babassu oils were characterized according to AOCs Cd 3d-63¹⁰, Cd 3-25¹¹, and Cd 1-25¹² methods, respectively. The fatty acid (FA) composition was determined according to AOCs Ce 2-66 method¹³. Alcohol composition of the fusel oil was determined according to Dias et al.⁸. Briefly, a mass of 0.15 g of fusel oil was diluted in 1.0 g of hexane and it was injected in a GC-FID chromatograph (7890 model, Agilent, Santa Clara, CA, EUA) equipped with a Supelco column (SP 2569, 100 m x 250 μm x 0,2 μm, Bellefonte, PA, EUA). Hydrolyses of castor and babassu oils were performed at 40 °C, using an oil:water molar ratio of 1:13, under 250 rpm¹⁴. The enzyme concentration used was 0.5 or 5 wt.%, regarding to the oil mass. The free fatty acids yield (hydrolysis yield, in %) was monitored by the increase in the acid value by acid-base titration using phenolphthalein as indicator¹⁴. At the end of the hydrolysis reaction, the mixture was centrifuged (EPPENDORF, 5810 R, São Paulo, SP, Brazil) for 5 min at 10,000 rpm. The upper phase, rich in free fatty acids (FFA-rich phase), was washed with water twice, followed by drying (FANEM Orion 515, São Paulo, SP, Brazil) at 60 °C for 24 hours. For the esterification step, FFA-rich phase and fusel oil were previously dehydrated with molecular sieves. Then, the reaction was carried

out with 0.5 wt.% enzyme (based on the total mass of the reaction medium), at 40 °C and 250 rpm^{15,16}. Molecular sieves were also added to the reaction medium to avoid water accumulation in the reaction medium, thus preventing the reverse reaction (hydrolysis). Different molar ratios of alcohol and FFAs were evaluated (1:1, 3.5:1, 5:1 and 7:1), as well as the total mass of the mixture (20 and 100 g of whole reaction medium). The conversion of FFAs (esterification yield, in %) was monitored by decrease of the acid value. At the reaction end, the mixture was filtered, and the liquid phase was distilled at 260 mmHg to remove unreacted fusel oil. After, castor-fusel oil esters (CFOE) and babassu-fusel oil esters (BFOE) were analyzed by gas chromatography, injecting 0.15 g of the bioesters diluted in 1.0 g of ethyl acetate in a GC-FID chromatograph¹⁷. The bioesters properties were analyzed by LABELT-SENAI (Lençóis Paulista, SP, Brazil). The properties and tests analyzed were kinematic viscosity (ν) at 40°C and 100°C, viscosity index (VI), pour point, four ball wear test, and rotating pressurized vessel oxidation test (RPVOT). The analyses followed the ABNT AND ASTM standards: NBR 10441:2014, NBR 14358:2012, NBR 11349:2009, ASTM D2266:2015, and ASTM D2272:2014, respectively.

RESULTS & DISCUSSION

Fusel oil was mainly composed of isoamyl alcohol (73.6 wt.%), isobutanol (14.1 wt.%), ethanol (7.1 wt.%), propanol (3.5 wt.%), and butanol (0.6 wt.%). Isoamyl alcohol has been used to synthesize lubricant bases^{6,15,18}, thus fusel oil can be an attractive source of this alcohol for lubricant base market.

Regarding to oil composition (Table 1), castor and babassu oils are mainly composed of ricinoleic acid (C₁₈, 68.5 wt.%), an hydroxylate and unsaturated fatty acid, and lauric acid (C₁₂, 43.2 wt.%), a saturated fatty acid, respectively. The differences in their tail-length and saturation degree could confer lubricant bases with different physicochemical and tribological properties. For example, bioesters produced from babassu oil had poor viscosity index and pour point (Table 2), probably because of reduction in the intermolecular interactions between the tails of the bioesters.

The parameters listed in Table 1 are close to the expected values, except iodine value and amount of linoleic acid in castor oil. These two values exceeded the average values reported in the literature^{19,20}. Linoleic acid has two double bonds, which explains the higher iodine value obtained in this work. The higher double bonds amount in the castor oil had a positive impact on the viscosity and pour point, and a negative impact on the oxidative stability of the bioesters (Table 2). Babassu oil has saponification matter 43.5% higher than the castor oil that can be converted to fatty acid esters. But the iodine value of castor oil is 6.3 times higher than the babassu oil (an expected response due to double bonds in the castor oil). Noteworthy, is the presence of a hydroxyl group in the C₁₂ of castor oil' ricinoleic acid that increased the viscosity of the lubricant base (Table 2) and it can enhance the solubility of additives. However, the oxidative stability of the bioesters produced from castor oil was lower than those produced from babassu oil (Table 2).

Table 1 Chemical composition and characteristics of castor and babassu oils.

Oil	Fatty acid (%wt)	Acid value (mg _{KOH} .g ⁻¹)	Saponification value (mg _{KOH} .g ⁻¹)	Iodine value (mg _{I₂} .g ⁻¹)
Castor	Ricinoleic (68.5%), Linoleic (15.4%)	1.25±0.77	169.3±1.5	130.6±11.4
Babassu	Lauric (43.2%), Myristic (15.8%), Oleic (12.1%)	0.56±0.07	243±15	20.8±3.7

Figure 1(a) shows the hydrolysis profiles of castor and babassu oils using different enzyme loads in the reactor. The hydrolysis of castor oil was kinetically better than the babassu oil, reaching hydrolysis yields of 50% after 4.5 and 10.5 hours (for 0.5 wt.% enzyme load), respectively. When the enzyme load was increased 10 times, maximum hydrolysis yields could be achieved with only 4 hours of reaction (80% and 70% for castor and babassu oils, respectively). The mass of oil in the reactor (Figure 1(b)) slightly influenced the esterification velocity, but a maximum esterification yield very close to 80% could be reached after 25 hours of reaction, even using an oil mass 5 times lower. Regarding to alcohol:FFA molar ratio (Figure 3(c)), the esterification kinetic of FFA from both oils was favored with an excess of alcohol, being 3.5:1 molar ratio sufficient to achieve maximum yield of ca. 80% after 26 hours of reaction. Similar behavior of Eversa Transform 2.0 was previously reported using other oils, alcohols and molar ratios close to 3.5:1^{15,16}.

Figure 2 shows the GC-FID chromatograms of the castor-fusel oil esters (CFOE, Figure 2(a)) and babassu-fusel oil esters (BFOE, Figure 2(b)). The CFOE chromatogram showed fewer expressive peaks compared to BFOE chromatogram. The CFOE is majorly composed of ricinoleic acid esters (ca. 55 wt.%, regarding to peaks with 40-68 min retention time). On the other hand, BFOE is composed of several fatty acid esters, but mainly by lauric acid esters (the greater peak between 30-35 min retention time). No peaks were observed between 7-11 min in the BFOE chromatogram, indicating absence of isoamyl alcohol in the product, because it was previously distilled. For CFOE, the amount of isoamyl esters was around 1.8 wt.%, showing that a distillation step is necessary to purify the product, because the presence of isoamyl alcohol could probably affect the physicochemical and tribological properties desirable of lubricant bases.

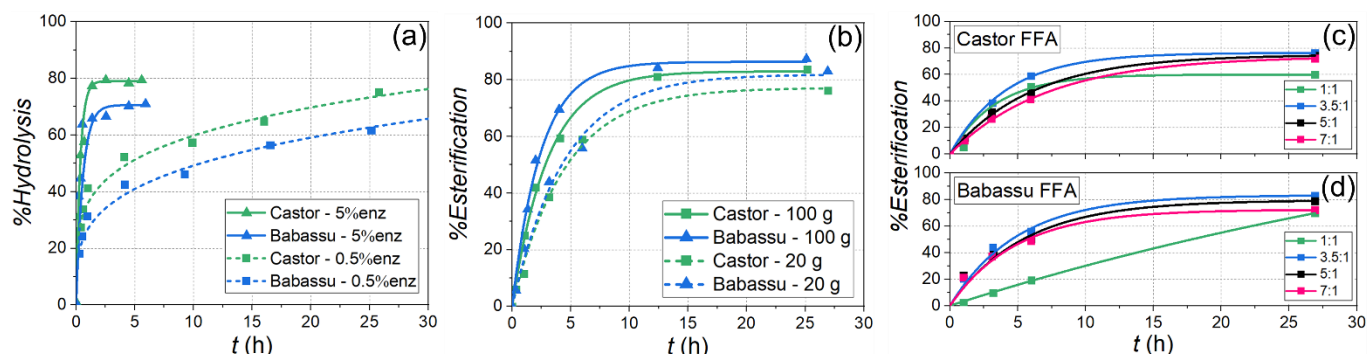


Figure 1 (a) Hydrolysis profiles varying the enzyme load in the reactor, %enz. (constant variables: 13 mol_{H₂O}:1 mol_{oil}, 250 rpm, 40 °C), (b) esterification profiles varying the mixture total mass (constant variables: 3.5 mol_{OH}:1 mol_{FFA}, 0.5%enz, 250 rpm, 40 °C), and alcohol:FFA molar ratio for (c) castor oil FFA (d) babassu oil FFA (constant variable: 100 g, 0.5%enz, 250 rpm, 40 °C).

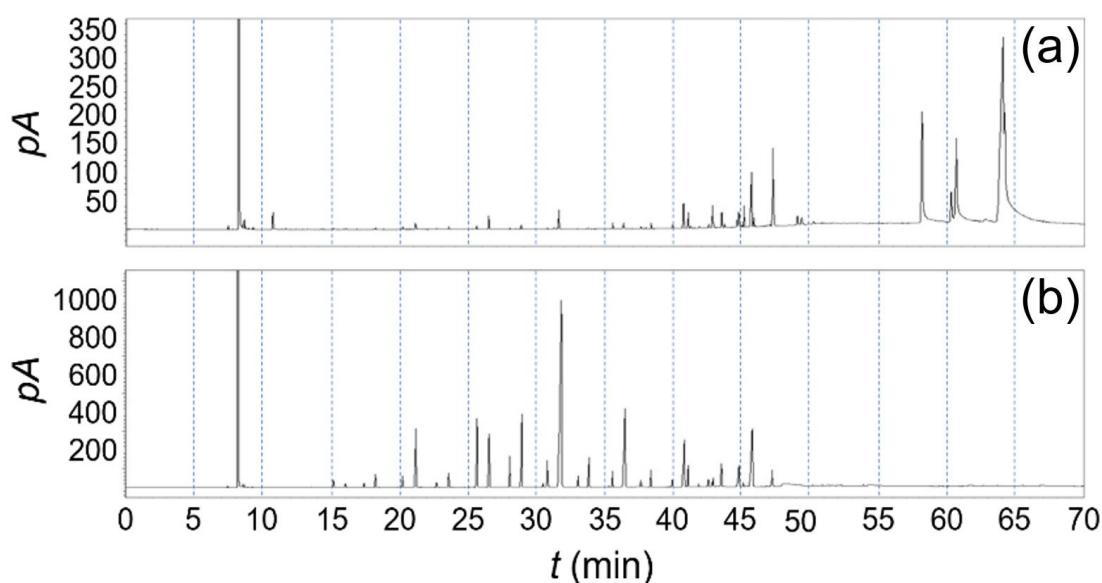


Figure 2 GC-FID chromatogram of the (a) castor-fusel oil esters and (b) babassu-fusel oil esters.

Table 2 presents the physicochemical and tribological properties of the biolubricant bases. The acid values were high (5.4 and 15.6 mg_{KOH}/g for CFOE and BFOE, respectively), being necessary a polishing step (e.g., neutralization)²¹ aiming to prevent metal corrosion for any application. The pour point of CFOE was approximately two times lower than that of BFOE, due to higher unsaturation amount of fatty acid esters in the CFOE⁷. The bioester bases exhibited a pour point comparable to industrial lubricants^{7,22}. At 25 °C, CFOE showed a grease-lubricating behavior, whereas BFOE showed an oil-lubricating behavior, showing that the number of double bonds, hydroxyl groups, and carbon tail length influenced the viscosity of the bioesters. The CFOE had a viscosity index (VI) of 171, whereas the BFOE exhibited VI less than 50. Additives to enhance the VI of CFOE are unnecessary, whereas they would be necessary for BFOE^{7,22,23}. Furthermore, BFOE can be employed as additive to enhance the VI of other lubricants. The wear scar diameter (WSD) of BFOE was 0.678 mm, a value comparable to commercial lubricants^{7,23}. The WSD for CFOE was significantly higher than for BFOE. Common additives, such as ZDDP (zinc dialkyldithiophosphate), can reduce the WSD to acceptable values²³. Both biolubricant bases showed an oxidative induction time (OIT) of approximately 30 minutes, indicating low oxidation resistance, a common characteristic of biolubricant bases²⁴. In addition to reducing the WSD, ZDDP can also increase the OIT by 2 to 4 times, allowing the application of these biolubricant bases^{23,25}.

Table 2 Physicochemical and tribological properties of castor- and babassu-fusel oil esters. VI is the viscosity index; WSD is the wear scar diameter; OIT is the oxidative induction time

Bioesters	Acid value (mg _{KOH} .g ⁻¹)	Pour point (°C)	VI	$\nu - 40\text{ }^{\circ}\text{C}$ (mm ² .s ⁻¹)	$\nu - 100\text{ }^{\circ}\text{C}$ (mm ² .s ⁻¹)	WSD (mm)	OIT (min)
CFOE	5.4	-27	171	25.5	5.64	1.031	31
BFOE	15.6	-15	< 50.0	10.6	1.84	0.678	30

CONCLUSION

This work showed that castor, babassu and fusel oils are suitable raw material to produce biolubricant bases, being more attractive than petroleum-based lubricant from an environmental and sustainable point of view. The hydroesterification process could be more advantageous than traditional transesterification because each step (hydrolysis and esterification) can be optimized

regarding operational parameters, in addition to recovery marketable glycerol in the first step, as well as allow more flexibility to the plant, producing free fatty acids or biolubricant bases, according to market demand. For this purpose, the commercial liquid formulation of lipase Eversa Transform 2.0 proved to be an excellent choice, both for its good performance in both process stages (hydrolysis and esterification) and the cost of the biocatalyst. The lubricant bases produced presented physicochemical and tribological properties suitable to lubricant market, at least for those evaluated in this work.

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