Optimization of enzymatic ethyl ester production from coconut oil in the range of interest of bio-kerosene

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ABSTRACT

In this study, coconut oil with fatty acids within the desired range for bio-kerosene was used to produce ethyl esters, employing lipase as a catalyst and ethanol as an acyl acceptor. The mass of the enzyme and water content were optimized in factorial design (3^2). Coconut oil, characterized by a fatty acid profile primally composed of C12:00 and C14:00, represents a potential raw material for bio-kerosene production. The results of the ethyl ester yield (84.57 %) underscore the statistical significance of enzyme mass and water content in the reaction, with emphasis on water content. The optimized parameters for enzyme mass and water content were determined by 62.5 mg and 2.6667 %, respectively.

Keywords: Lipase. Ethanol. Fatty Acids. Design of Experiments. Surface Response.

1 INTRODUCTION

The transport sector is responsible for significant quantities of pollutants in the atmosphere, with the shipping and aviation sectors contributing 0.71 Gt of CO_2 in 2021[1]. Aviation, in particular, stands out due to its heavy reliance on fossil fuels as a primary energy source [1]. Several initiatives have been promoted to reduce dependence on fossil fuels and consequently pollutants emissions, such as the European Green Deal and ReFuelEU [1].

In this scenario, utilizing esters with a number of carbons within the range of those found in fossil kerosene (, when mixed with the latter, could offer an alternative for the reducing dependence on fossil fuels in aviation [2]. Esters derived from coconut oil, predominantly composed of lauric acid (55.5 %) and myristic acid (14.9 %), were found to be feasible for blending with commercial Jet A1 kerosene up to 10 vol.%, as described in the work of Llamas *et al.* (2012) [2]. Coconut oil was utilized in the production of bio-kerosene through transesterification followed distillation in the study conducted by Saifuddin *et al.* (2016) [3]. According to their findings, the bio-kerosene failed to meet ASTM 1566 standards, particular regarding freezing point and flash point [3]. As suggested by the authors, blending the bio-kerosene with fossil kerosene or aromatic compounds could enhance these parameters [3]. Methyl esters from coconut oil were texted in blends with commercial jet fuel at mass proportions of esters to jet fuels of 5 %, 10 %, 20 % and 100 % in the study conducted by Verastegui *et al.* (2023) [4]. As reported by the authors, blends containing 5%, 10 % and 20 % meet the ASTM standards for jet fuel [4].

The transesterification process for the ester production is primarily conducted via the homogenous alkaline route in the presence of methanol. However, the utilizing lipase as a catalyst offers several advantages over alkaline catalysts, including milder reactions conditions, the potential for simultaneous conversion of triacylglycerol and fatty acids, and the production of high-purity glycerol [5]. Therefore, the objective of this study was to optimize the production of ethyl esters from coconut oil using ethanol with an enzymatic catalyst. The parameters optimized were the water content in the reaction and the enzyme mass percent.

2 MATERIAL & METHODS

Coconut oil was acquired from a local market. The internal standard for chromatography analysis, ethyl tricadecanoate, and lipase from *Burkholderia cepacia*, powder lipase, were purchase from Sigma-Aldrich and other reagents were of analytical grade. Fatty ester composition of coconut oil was determined according to ISO 12966 [6]. For enzymatic ethyl ester production optimization, two parameters were tested in the reaction, mass of powder lipase and water content. For this purpose, a full factorial design 3^2 was used with two independent variables and one dependent variable (Table 1).

Table 1 Full factorial design for ethyl ester prodution optimizatio.

	Codified variables		
Independent variables	-1	0	+1
X_1 = enzyme mass (mg)	10	40	80
X_2 = mass of water relative to oil mass (%)	1.5	2.5	5

It should be noted that in all reactions the oil mass was 3.53 g. Besides that, the oil to ethanol molar ratio was 6:1 and the reaction temperature 40 ºC, with time reaction of 96 h. Equation (1) was used for mathematical modeling of ethyl ester production as a function of enzyme mass and water content.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} {X_i}^2 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} {X_j}^2 + \epsilon \quad (1)$$

Where Y represents the dependent variable (ethyl ester), X_i and X_j represent the enzyme mass and water content, respectively, and β and ε are the estimate parameters.

The ethyl ester was determined by chromatography analysis (SHIMADZU, GC-2010) using an oven temperature of 180 ºC for 15 minutes, followed by 380 ºC for 30 minutes. The FID detector temperature was set to 380 ºC.

3 RESULTS & DISCUSSION

The main components in mass percent of coconut oil were, in ascending order, capric acid (C10:0, 6.5 ± 2.1), caprylic acid (C8:0, 7.3 ± 3.8), oleic acid (C18:1, 7.5 ± 3.5), palmitic acid (C16:0, 8.9 ± 1.9), myristic acid (C14:0, 18.9 ± 3), and lauric acid (C12:0, 49.2 ± 5.7). According to the fatty acid composition, there was a predominance of medium chain fatty acids within the hydrocarbon range present in the fossil kerosene (C6 to C12) [7], demonstrating the potential of the coconut oil for bio-kerosene production.

The results of the ethyl ester production after 96 hours of reaction between coconut oil, ethanol, water, and lipase as catalyst, for the factorial design experiments are present in the Response Surface plot shown in Figure 1.

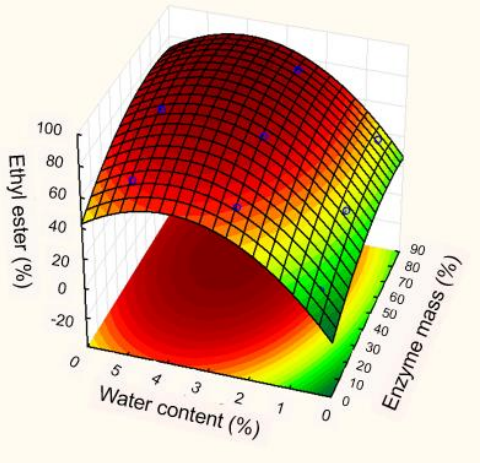

Figure 1 Response Surface for ethyl ester production as a function os enzyme mass and water content.

The optimized paramters, from the Response Surface data, were ethyl ester 84.57 %, enzyme mass of 62.5 mg and water content of 3.8 %. The mathematical model, with a coefficient of determination (R^2) of 99.44%, was $Y = -3.13 + 0.92X_2 - 0.006X_2^2 + 31.96X_1 - 4.05X_1^2$. The Pareto Chart (Figure 2) shows the parameter in order of significance relative to the ethyl ester production.

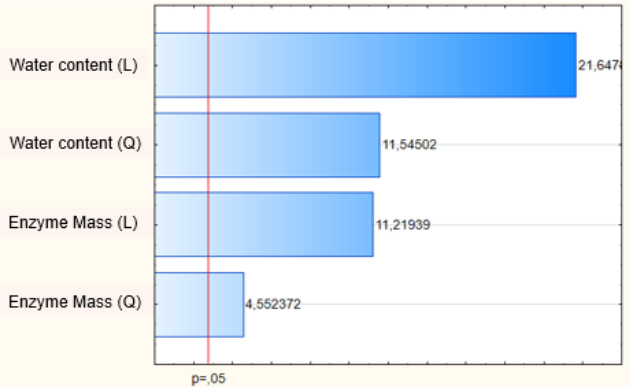

Figure 2 Pareto Chart for the ethyl ester production from coconut oil.

As shown in Figure 2, all parameters are statistically significant for optimizing ethyl ester production, with particular emphasis on water content. Lipases are responsible for catalysis in the reaction through the interaction between substrates (oil and ethanol) and their active sites. Therefore, when more active sites are available for catalysis, more esters are produced. However, increasing enzyme concentration is not favorable to the reaction due to the limitation interfacial area for lipase catalytic performance [8]. Regarding water content, a small amount of water can improve catalytic performance by hydration the enzyme, maintaining its flexibility for catalysis [9]. However, an excess of water can hinder ester production due to the predominance of the hydrolysis reactions [9]. The results of ester concentration (84.57 %), in optimized conditions of reaction, demonstrate the potential of lipase for the bio-kerosene production. These esters can be distilled and used in a blending with fossil kerosene or can be converted into hydrocarbons through different methods such as hydrodeoxygenation, hydrocracking and hydro isomerization [10].

4 CONCLUSION

Coconut oil, containing fatty acids within the desired range of interest for bio-kerosene production, was converted into through enzyme catalysis. The optimized reactions conditions demonstrated the significant influence of enzyme mass and water content, resulting in an ester production yield of 84.57 %. The results underscore the potential of the lipase-catalyzed reactions for ethyl esters production, which can serve as jet fuel as a blend with fossil kerosene or be converted in hydrocarbons, with coconut oil serving as a viable raw material bio-kerosene production.

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