

EXPLORING OIL TRANSESTERIFICATION IN A PACKED BED REACTOR WITH A LOW-COST BIOCATALYST

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ABSTRACT

Heterogeneous enzymatic catalysis can be an interesting alternative to several processes in pharmaceutical, food and biofuels industries. However, low-cost and effective biocatalysts still need to be developed. This study aimed to investigate the application of lipase immobilized in starch–alginate beads by jet cutting for oil transesterification in a packed bed reactor. A bead containing 1% starch, 1% alginate, and 10% Eversa Transform 2.0 was produced by jet cutting technique. X-ray photoelectron spectroscopy showed a concentration of nitrogen ranging from 6.38% to 7.29% at the different levels of the bead, proving that lipase is distributed inner and out the bead. Also, N_2 isotherms demonstrated a Barrett–Joyner–Halenda adsorption pore size of $48.09 \text{ \AA} = 4.8 \text{ nm}$. Moreover, when the biocatalyst was applied in a transesterification oil reaction in a tubular reactor, triacylglycerol conversion of about 45% was found in different runs of the face-centered central composite design. The highest ester productivities were obtained in run 12 ($45 \text{ }^\circ\text{C}$, 12 oil:alcohol molar ratio, $0.075 \text{ cm min}^{-1}$), namely of $2.05 \times 10^{-2} \text{ } \text{g}^{-1} \text{ biocatalyst min}^{-1}$ and $1.5 \times 10^{-4} \text{ } \text{U}^{-1} \text{ min}^{-1}$. After recirculation, the ester yield increased two-fold ($14.57\% \pm 1.23\%$). Then, the results prove that a cheap biocatalyst that can be used in oil transesterification in a packed bed reactor was successfully produced.

Keywords: Enzyme immobilization, entrapment, alginate, corn starch.

1 INTRODUCTION

Enzymatic processes have been reported as ecofriendly and selective. Industrial processes use enzymes in both soluble and insoluble forms. However, a drawback of using soluble enzymes is their incompatibility with continuous processes. As a solution to this limitation, strategies such as enzyme immobilization have been explored to enable the application of enzymes in continuous systems. Heterogeneous enzymatic catalysis can be conducted using different types of reactors, such as stirred tank reactors, fluidized bed reactors, and packed bed reactors (PBR). PBR is easily scalable and has high operational stability, also can be operated in batch, fed batch and continuous modes^{1,2}.

It should be noted that, although immobilization is the strategy of choice for using enzymes in continuous processes, at present, there is no universal support material or immobilization method proven to work for all enzymatic applications³. Jet cutting technique has stood out as an interesting technique that combines both the advantage of gel entrapment and the possibility of producing smaller beads than dripping technique⁴. Moreover, this technique allows the use of cheap wall materials, such as starch and gelatin in bead production⁵.

To the best of our knowledge, no study has been reported in the literature evaluating the use of jet-cutting beads in a packed bed reactor. Then, this study aimed to investigate the application of lipase immobilized in starch–alginate beads by jet cutting for oil transesterification in a tubular reactor.

2 MATERIAL & METHODS

The biocatalyst was produced using a solution containing 1% starch, 1% alginate, and 10% Eversa Transform 2.0 and following the process described by Almeida et al.¹. The biocatalyst was characterized by X-ray photoelectron spectroscopy (XPS) (ThermoScientific K-Alpha spectrometer), and nitrogen (N) physisorption analysis (Micromeritics ASAP 2020 Plus surface area analyzer (Norcross, USA)).

Biodiesel production was performed in a continuous system containing a jacketed glass column ($10 \times 80\text{mm}$) packed with 7 g of biocatalyst, a peristaltic pump, and a water bath. Three independent variables were studied: temperature (30 to $60 \text{ }^\circ\text{C}$), oil: ethanol molar ratio ($1:3$ to $1:12$), and superficial velocity (0.05 to 0.1 cm min^{-1}) using a face-centered central composite design⁶. The products determination was performed by high-performance size exclusion chromatography (HPSEC).

3 RESULTS & DISCUSSION

A biocatalyst containing starch and alginate as wall material to immobilize Eversa Transform 2.0 was produced by jet cutting technique and was physically characterized by XPS and N₂ isotherms. XPS analysis confirmed the presence of lipase since it is possible to see the presence of nitrogen in beads composition. Moreover, it is also possible to note that lipase is distributed in the inner and outer regions of the beads, as nitrogen content ranged from 6.38% to 7.29% at the different levels. The N₂ isotherms obtained by BET area analysis were classified as type IV (Fig. 1), characteristic of mesoporous materials⁷. The presence of hysteresis is suggestive of mesopores⁸. A Barrett–Joyner–Halenda (BJH) adsorption pore size (48.09 Å = 4.8 nm) was found, confirming the N₂ behavior result.

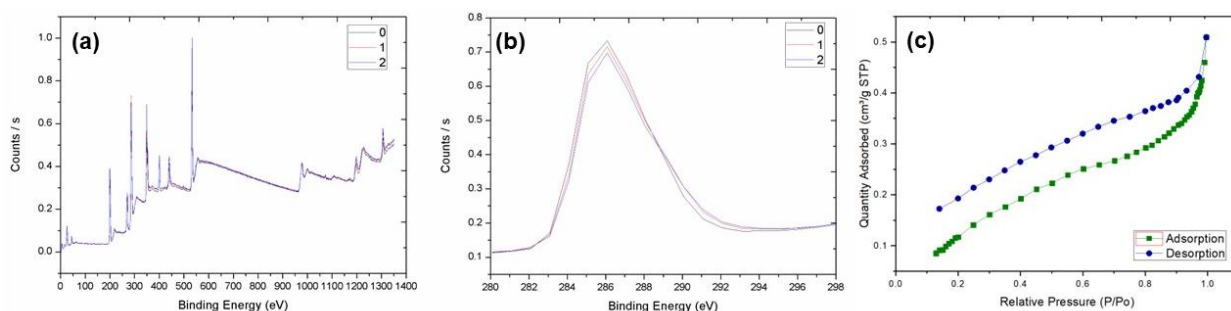


Fig. 1 - X-ray photoelectron spectra (survey (a) and N (b)) and N₂ adsorption/desorption isotherms (c), as determined by Brunauer–Emmett–Teller surface area analysis. 0, etch time = 0 s, etch level = 0; 1, etch time = 5.002 s, etch level = 1; 2, etch time = 10.005 s, etch level = 2

The biocatalyst was applied for oil transesterification in a packed bed reactor. Thus, a face-centered central composite design with 14 runs and 3 repetitions of the center point was applied. Table 1 shows the coded and real values of independent variables and the results for the transesterification process. There were no significant differences in the results of center point runs, demonstrating low error. In all runs, transesterification occurred by the ping-pong bi-bi mechanism, by which a product is released before the addition of the other substrate⁹.

The highest triacylglycerol (TAG) conversion percentages, approximately 45%, were observed in runs 1 (30 °C, 3 oil:alcohol molar ratio, 0.05 cm min⁻¹), 3 (30 °C, 12 oil:alcohol molar ratio, 0.05 cm min⁻¹), 12 (45 °C, 12 oil:alcohol molar ratio, 0.075 cm min⁻¹), and 14 (45 °C, 7.5 oil:alcohol molar ratio, 0.1 cm min⁻¹). The highest productivities were achieved in run 12, namely of 2.05 × 10⁻²% ester g⁻¹ biocatalyst min⁻¹ and 1.5 × 10⁻⁴% ester U⁻¹ min⁻¹. Notably, among these runs, the lowest fatty acid ethyl ester (FAEE) conversion (1.8%) was observed in run 1, conducted with the lowest O:A stoichiometric ratio reported in the literature (1:3).

Table 1. Soybean oil transesterification in a packet bed reactor using a new starch–alginate biocatalyst.

Run	T (°C) (x ₁)	O:A (x ₂)	V (cm min ⁻¹) (x ₃)	TAG %	DAG %	MAG %	FFA %	FAEE %
1	30 (-1)	3 (-1)	0.05 (-1)	55.2	23.6	2.2	17.2	1.8
2	60 (+1)	3 (-1)	0.05 (-1)	65.6	18.6	1.6	11	3.2
3	30 (-1)	12 (+1)	0.05 (-1)	50.5	24.4	2.6	15.1	7.4
4	60 (+1)	12 (+1)	0.05 (-1)	65.2	19.9	0	10.7	4.3
5	30 (-1)	3 (-1)	0.1 (+1)	63	19.8	1.8	11.8	3.6
6	60 (+1)	3 (-1)	0.1 (+1)	85.8	8.3	0	4	1.9
7	30 (-1)	12 (+1)	0.1 (+1)	60.4	20.2	2.3	11.1	6
8	60 (+1)	12 (+1)	0.1 (+1)	66.4	17.9	1.8	8.2	5.8
9	30 (-1)	7.5 (0)	0.075 (0)	64.6	19.2	1.8	10.8	3.6
10	60 (+1)	7.5 (0)	0.075 (0)	57.7	22	2	14.6	3.6
11	45 (0)	3 (-1)	0.075 (0)	66.4	17.7	1.5	10.1	4.2
12	45 (0)	12 (+1)	0.075 (0)	55.7	21.8	2.8	12	7.7
13	45 (0)	7.5 (0)	0.05 (-1)	59.4	20.8	2.1	13.4	4.3
14	45 (0)	7.5 (0)	0.1 (+1)	55.9	22.2	2.4	13.4	6
15 (C)	45 (0)	7.5 (0)	0.075 (0)	62.4	20	1.8	10.8	5
16 (C)	45 (0)	7.5 (0)	0.075 (0)	65.3	18.4	1.9	10	4.4
17 (C)	45 (0)	7.5 (0)	0.075 (0)	63.4	19.6	2	9.3	5.8

C, center point; T, Temperature; O:A, Oil: Alcohol molar ratio; V, superficial velocity; TAG, triacylglycerol; DAG, diacylglycerol; MAG, monoacylglycerol; FFA, free fatty acids; FAEE, fatty acid ethyl esters.

Given that the final product of the reaction is ester, effect analysis was carried out for this compound using regression coefficients and the p-value. A representative model was generated considering a significance level of 10% ($p < 0.1$) ($Y_1 = 5.34 - 1.22x_1^2 + 1.65x_2$). Effect analysis demonstrated that temperature and O:A exerted significant effects on yield. Temperature had a weak negative effect; and O:A, a weak positive effect. ANOVA revealed the model to be valid, with an R^2 of 74.40% and F-value $>$ F-critical. The contour plot constructed using the model is depicted in Fig. 2.

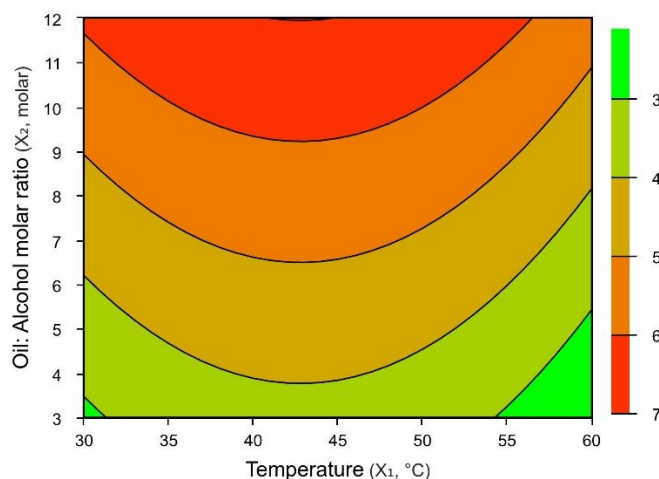


Fig. 2. Contour curve for soybean oil transesterification (FAEE %) in a tubular reactor using lipase immobilized in starch–alginate beads.

The contour plot shows that the highest FAEE yields are obtained in a temperature range of about 35 to 55 °C. Temperature can positively influence enzymatic reaction rates up to a certain point, after which enzymes may be denatured¹⁰. Regarding O:A, it was found that, within the studied range and at a given temperature, the higher the alcohol content, the higher the ester yield. Of note, under the best conditions indicated by the contour plot (38 - 52 °C and 10 - 12 O:A molar ratio), the estimated ester yield was about 7%, which is like that obtained in run 12 whose conditions were selected as the best ones (45 °C and a 12 O:A molar ratio). Given this and aiming to increase the yield of ester and other products, we carried out a recirculating process instead of an optimization process.

After recirculation, the ester yield increased 2-fold ($14.57\% \pm 1.23\%$) and TAG yield decreased from 55.7% to $46.67\% \pm 6.29\%$, demonstrating the potential of the recirculation process. Furthermore, given that the same biocatalyst was used for the main process and recirculation (without any treatment between experiments), it can be said that it shows good reusability. The ester productivity found were $1.96 \times 10^{-2}\%$ ester g^{-1} biocatalyst min^{-1} and $1.42 \times 10^{-4}\%$ ester $U^{-1} min^{-1}$.

4 CONCLUSION

The biocatalyst was successfully applied in oil transesterification in a packed bed reactor. Furthermore, the biocatalyst showed potential to be reused. Thus, in the current study, we produced a low-cost biocatalyst that can be used in continuous reactions.

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