

Modeling using box behnken design for optimization of biodiesel production from low grade cooking oil

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Abstract. The demand to an alternative for the depletion of diesel oil, has steered to the production of biodiesel as an alternative fuel. Nowadays, there is a growing need for biodiesel, which is typically produced using a base-catalyzed transesterification reaction. Therefore, this research utilizing a low-grade cooking oil as the biodiesel feedstock and Ca/Mg/Al₂O₃ as a heterogenous base catalyst using wetness impregnation method. The potential catalyst was optimized using response surface methodology (RSM) by varying parameters of calcination temperature, catalyst dosage and reaction time. The optimum parameter obtained from the RSM are 800°C calcination temperature, 6 wt.% catalyst dosage and 1hour reaction time. The validation is carried out using optimum parameter and it gave 48.30 % of biodiesel production.

Keywords: low-grade cooking oil, heterogeneous-base catalyst, transesterification, biodiesel, RSM.

Classification numbers: 2.4.2, 3.4.1, 4.10.4

1. INTRODUCTION

The primary sources of the world's energy supply are fossil fuels, also referred to as non-renewable energy sources, such as coal, gas, and crude oil. Furthermore, when fossil fuels are burned, hazardous chemicals including carbon dioxide, greenhouse gases, and other organic compounds are emitted [1]. As the result, the quest for clean and renewable energy sources is now very valuable because of the shortage of fossil fuels and current environmental problems [2].

Biodiesel is the best alternative to substitute fossil fuel due to its advantages such as low carbon emission, eco-friendly and environmentally safe to be used. Most of the biodiesel is produced from vegetable oil which consists of mixture of long chain alkyl esters. Transesterification is a process where triglyceride from vegetable oil reacts with alcohol to give methyl ester and glycerol. Heterogeneous catalysts are increasingly studied in the

transesterification process for biodiesel production due to their regenerability and reusability, making them a sustainable and cost-effective option. According to Baskar *et al.* [3], solid base catalysts such as alkaline earth metal are generally preferred due to their strong basic sites and activity. The doped metal oxides catalyst has piqued the interest of researchers in order to improve the stability and activity of the synthesise material since the doping metal tends to improve the surface area, strength, and pore size of the synthesise material. Alkaline earth metal has a potential as solid based catalyst in transesterification process. Nor *et al.* [4] used CaO catalyst using jatropha seed oil as a feedstock in producing biodiesel. The biodiesel yield achieved 94 % with optimum parameter of 1.5 wt.% catalyst dosage and 700 °C calcination temperature. Another research was conducted and showed that CaO catalyst doped with Lanthanum gave a higher biodiesel yield (96.3 %) using canola oil with optimum parameter of methanol to oil ratio (15:1), reaction temperature 65 °C, 5 wt.% catalyst dosage and 2.5 hours of reaction time [5]. Similar to this research, CaO has been doped with iron (Fe) and it gave 98.3 % of biodiesel yield with methanol to oil ratio (18:1), reaction temperature 65 °C, 3 wt.% catalyst dosage and 3 hours reaction time [6].

Alkaline earth metal oxides also used for the synthesis of biodiesel utilizing palm oil with the ideal reaction conditions, of BaO catalyst to make 95% biodiesel, 180 minutes of reaction time, a methanol to oil ratio of 9:1, and reaction temperature of 60 °C [7]. Waste cooking oil (WCO) is frequently utilized in the manufacturing of biodiesel. About 98.2 % of biodiesel were produced from waste cooking oil under ideal conditions of 16:1 methanol to oil molar ratio, 3 wt.% catalyst dosage, and 150 min reaction time [8]. Other than that, the maximum biodiesel conversion of 96.74 % was also observed using WCO with optimum reaction conditions were 20:1 methanol to oil molar ratio, 5 wt.% catalyst loading, 65 °C reaction temperature, and 4 hours of reaction time [9]. The majority of alkaline earth metal oxide has been studied for transesterification of various oils, however the usage of low-grade cooking oil remains limited. As a result, the goal of this study was to create heterogeneous base catalysts of alkaline earth metal oxides by a wetness impregnation approach for catalytic transesterification by using low-grade cooking oil.

RSM is one of the most effective statistical optimization designs for capturing optimal conditions in multivariable systems. Degfie *et al.* [10] investigated the effects of four process variables on WCO biodiesel. When the reaction temperature was 50 °C, the catalyst concentration was 1 wt.% , the molar ratio, 1:8, and the reaction time was 90 minutes, the biodiesel yield decreased. Kolakoti *et al.* [11] also has employed RSM analysis to optimize the utilization of leftover chicken eggshells as a heterogenous catalyst for the synthesis of biodiesel from WCO. According to RSM optimization study, the best conditions for producing biodiesel were catalyst concentration of 1.5 wt.%, a molar ratio of 10:1, a reaction period of 120 minutes, and a temperature of 50 °C. Moreover, in the study of Soria *et al.* [12], they have used the Box-Behnken design (BBD). The reactions with 98.5 % biodiesel yields were accomplished under ideal circumstances at catalyst dosages of 8.75 % particle sizes of 2 mm, and methanol to oil ratios of 8.72:1.

Therefore, in this research, a low-grade cooking oil was chosen as not many reported about potential low grade cooking oil to produce biodiesel and also due to inexpensive and readily market. Low grade cooking oil is the refined cooking oil that being produced from the used cooking oil. The CaO catalyst doped with Mg was selected mainly due to their basic properties and Response Surface Methodology (RSM) with Box Behnken design was chosen to optimize the parameter that yield higher biodiesel.

2. MATERIALS AND METHODS

2.1. Materials

The chemical reagents that have been used in this research were commercial calcium nitrate tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, methanol, CH_3OH , magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and alumina oxide. All chemical reagents were ordered from the same brand, (Sigma Aldrich Chemical).

2.2. Catalyst preparation

The $\text{Ca/Mg/Al}_2\text{O}_3$ was prepared using wetness impregnation method. A 0.586 g calcium nitrate tetrahydrate and 0.3818 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was weighed and dissolved with 40 mL distilled water. Then, 3.8 g of alumina was soaked in the catalyst solution and stirred for 6 hours to ensure that the catalyst had completely covered the alumina support. After that, the coated alumina was dried in an oven 90 °C for 24 hours to remove any extra water. Then, the catalyst was further calcined in furnace for 5 hours at 400, 700, and 1000 °C to remove any remains.

2.3. Biodiesel production

The transesterification reaction was conducted in a batch type reactor with a heterogeneous-base catalyst, $\text{Ca/Mg/Al}_2\text{O}_3$, and methanol in a 250 mL round-two bottom neck flask furnished with a magnetic stirrer connected with a cooler condenser thermometer. The process was carried out at 60 to 65 °C with 6 wt.% of catalyst dosage for 1 hour. Next, the mixture was transferred into a separating funnel and left it to separate for 24 hours. Then, the separated solution with biodiesel on top and the glycerol at the bottom of the funnel was filtered. The biodiesel yield was calculated using Equation 1.

$$\% \text{ Biodiesel yield} = \frac{\text{Weight of biodiesel}}{\text{Weight of oil sample used}} \times 100 \%. \quad (1)$$

2.4. Statistical analysis

RSM was used for statistical analysis. Box-Behnken Design (BBD) of RSM is chosen using Design Expert software 7.1.6. The three independent variables were selected which were calcination temperature, catalyst dosage and reaction time. Total 17 runs of the experiment were examined with the response biodiesel yield.

3. RESULTS AND DISCUSSION

3.1. The chemical composition of Low-Grade Cooking Oil (LGCO) using GC-MS

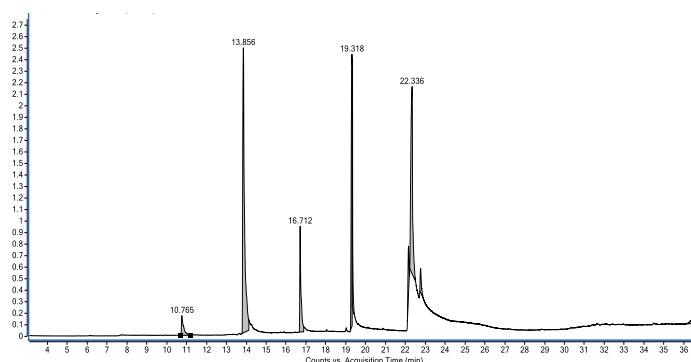


Figure 1. GC-MS Chromatogram of Low-Grade cooking oil (LGCO).

Figure 1 shows the GC-MS chromatogram of the low-grade cooking oil. The identified peaks were capric acid, methyl ester, lauric acid, palmitic acid, and stearic acid. Meanwhile, the acid value obtained for low-grade cooking oil for this study is 1.56 mg KOH/g which is within the range of ASTM method [13]. Therefore, the base catalyst does not require pretreatment.

3.2. Catalytic activity of biodiesel

3.2.1. Effect of calcination temperature

The calcination temperature parameter was investigated by varying temperatures of 600, 700, 800, and 900 °C. The catalyst loading and reaction time were constant at 6 wt.% and 1 hour, respectively. Figure 2 showed the trend of Ca/Mg/Al₂O₃ catalyst at various calcination temperature.

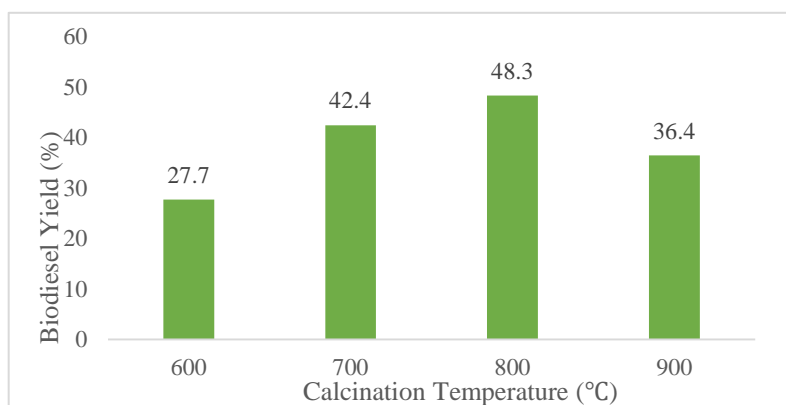


Figure 2. The trend of biodiesel yield at various calcination temperatures.

From the graph it can be observed that when calcination temperature was increased to 800 °C, the biodiesel yield was increased up to 48.3 %. However, at 900 °C, the biodiesel yield started to decreased to 36.43 %. This might due to larger particle formed on the catalyst surface as the temperature is increased as similar obtained by Mat Rosid *et al.* [14]. Therefore, the larger particle would decrease the active sites which decreased the catalytic activity.

3.2.2. Effect of catalyst dosage

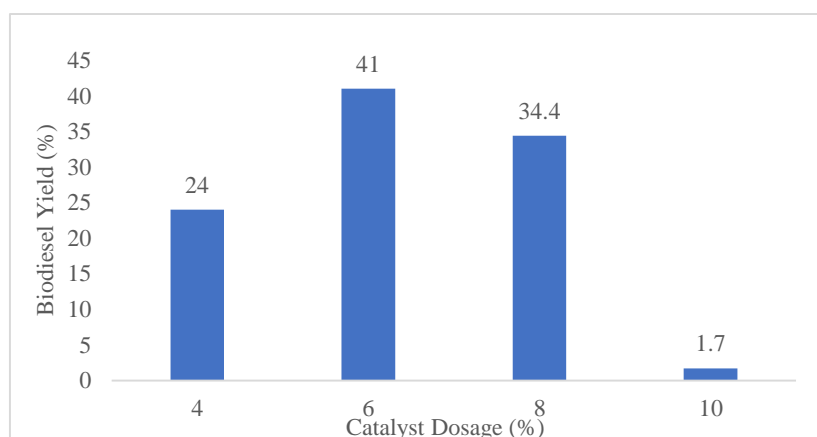


Figure 3. The effect of catalyst dosage.

Catalyst dosage is also one of the important parameters in biodiesel yield. In this work, the range of catalyst dosage with 4 wt.% to 10 wt.% Ca/Mg/Al₂O₃ catalyst was selected. Figure 3 shows the trend of biodiesel yield with various catalyst dosage.

As can be seen, when catalyst dosage was increased from 4 wt.% to 6 wt.%, the biodiesel yield was increased. This might be because more active sites for the transesterification reaction were provided by the catalyst during the process. However, when the catalyst dosage was further increased to 10 %, the biodiesel yield started to decrease accordingly. This might be due to when the optimum active site is achieved, further addition of catalyst would block the process [15].

3.2.3. Effect of reaction time

The effect of reaction time was evaluated by varying it from 1 hour to 3 hours. The methanol to oil ratio was set at 18:1 and 6 wt.% catalyst dosage. Figure 4 shows the decreasing trend of biodiesel production when the time is increased to 3 hours. The tendency for biodiesel yields to decrease over time might due to reversed reaction that occurred when the reaction is longer than optimum time. Thus, the reaction will yield more glycerol than methyl ester [16]. Other than that, according to Lee *et al.* [17] the ratio of methanol to oil also affects the reaction time. This is because at higher molar ratios there is sufficient methanol present to drive the reaction into high yields, thus shortening the turnaround time.

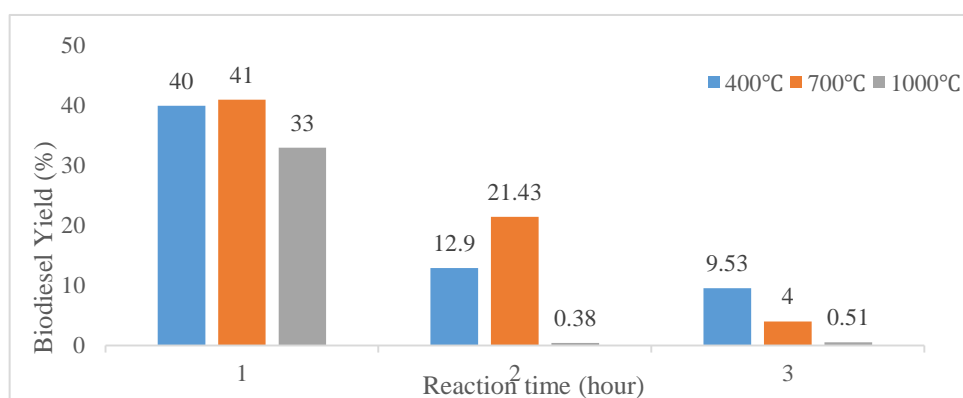


Figure 4. Effect of reaction time.

3.3. RSM based predictive model

The coded and uncoded values for Behnken Design (BBD) approach were displayed in Table 1. The results of the preliminary study served as the foundation for the level selection. Meanwhile, Table 2 provides an overview of the findings from the 17 experimental runs that were conducted using the BBD with three variables.

Table 1. Coded and uncoded value for BBD.

Coded variables values			Variables
-1	0	1	
5	6	7	Catalyst dosage (wt.%)
1	2	3	Reaction time (hour)
700	800	900	Calcination temperature (°C)

Table 2. BBD matrix of three variables along with experimental and predicted response.

Run	Factor variables			Experiment	RSM
	A: Catalyst dosage % (wt/wt)	B: Reaction time (hour)	C: Calcination temperature (°C)		
1	5	1	800	45.60	46.40
2	7	1	800	46.30	45.88
3	5	3	800	26.20	27.03
4	7	3	800	40.60	40.20
5	5	2	700	27.00	26.61
6	7	2	700	38.00	38.84
7	5	2	900	37.30	36.06
8	7	2	900	36.50	36.49
9	6	1	700	42.50	42.69
10	6	3	700	31.00	30.36
11	6	1	900	45.40	46.44
12	6	3	900	33.50	33.71
13	6	2	800	36.00	37.20
14	6	2	800	37.00	37.20
15	6	2	800	37.00	37.20
16	6	2	800	38.00	37.20
17	6	1	800	48.30	46.70

Table 3. Analysis of variance for biodiesel yield.

Source	Sum of squares	Degree of freedom (df)	Mean square	F-value	p-value	
Model	642.41	9	71.38	48.38	< 0.0001	significant
A-catalyst dosage	80.01	1	80.01	54.23	0.0002	
B- time	345.13	1	345.13	233.93	< 0.0001	
C- calcination	25.21	1	25.21	17.08	0.0044	
AB	46.92	1	46.92	31.80	0.0008	
AC	34.81	1	34.81	23.59	0.0018	
BC	0.040	1	0.040	0.027	0.8739	
A ²	1.33	1	1.33	0.90	0.3747	
B ²	43.92	1	43.92	29.77	0.0009	
C ²	19.15	1	19.15	12.98	0.0087	
Residual	10.33	7	1.48			
Lack of fit	8.33	4	2.08	3.12	0.1883	not significant
Pure error	2.00	3	0.67			
Cor total	652.74	16				

A statistically significant association between variables was indicated by a p-value of the model (less than 0.05). The proposed linear model was found to fit well, as indicated by the p-value for the lack of fit being higher than 0.05 ($p = 0.1883$) and not significant. Furthermore,

Table 3 shows that the parameters A, B, C, AB, AC, B², and C² are significant as their p-values are less than 0.05 quadratic.

Furthermore, Table 4 shows a low coefficient of variation (CV, 3.20). This shows that its value is less than 10 %, demonstrating the lower reliability of the experimental value of the response model. A coefficient of determination (R²) of 0.9842 indicates a strong accuracy model and can be used to measure the fit of the resulting regression equation.

Table 4. The statistical data for the ANOVA response value.

Std dev	1.21	R ²	0.9842
Mean	38.01	Adj R ²	0.9638
CV %	3.20	Pred R ²	0.8678
PRESS	86.26	Adeq Precision	21.563

A second order of polynomial regression equation was developed using coded units. While for the final developed model based on coded units for biodiesel yield represented by Eq. 2.

$$\text{Biodiesel Yield (\%)} = 37.20 + 3.16A - 6.26B + 1.77C + 3.42AB - 2.95AC - 0.100BC - 0.56A^2 + 3.24B^2 \quad (2)$$

where, A is catalyst dosage (wt.%), B is reaction time (hours) and, C is calcination temperature (°C).

As can be seen in Figure 5, the normal probability plots showed good agreement between the experimental and RSM data. All points lie close to the straight line, indicating that the RSM accurately predicts the experimental data in the plausible region.

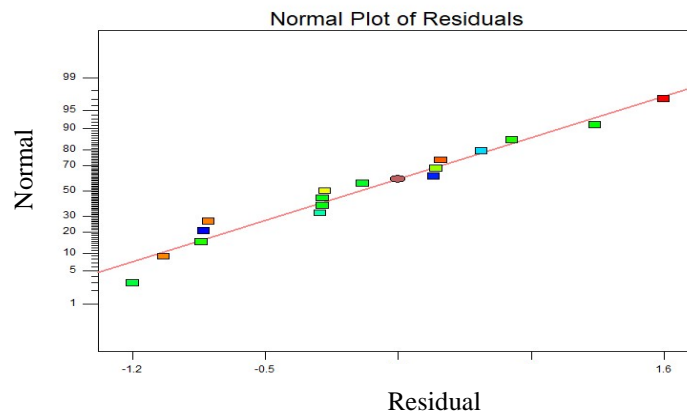


Figure 5. Normal probability plot of response.

Figure 6 (a) illustrates the effects of catalyst dosage and reaction time on the biodiesel yield when the methanol to oil ratio was fixed at 18:1. The maximum amount of biodiesel was produced as a result of the prolonged reaction period and optimum catalyst loading. Figure 6 (b) depicts the effect of calcination temperature and catalyst dosage on biodiesel yield. According to Toemen *et al.* [18], the calcination temperature is one of the most crucial parameters for optimization utilizing the Box-Behnken design. It was noticed that biodiesel production increased to 48.30 % at 800 °C calcination temperature. However, the biodiesel yield decreased when calcination temperature was increased beyond than 800 °C.

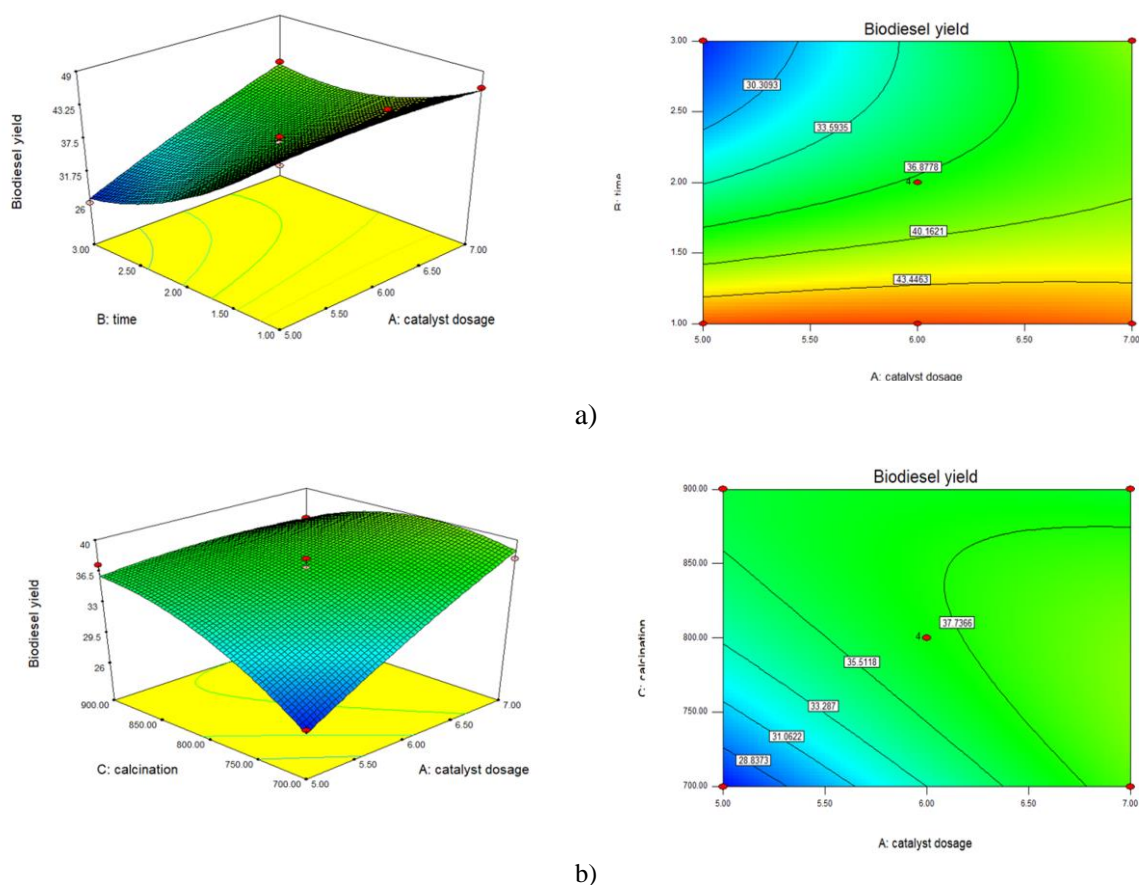


Figure 6. a) The effect of reaction time and catalyst dosage and b) The effect of calcination temperature and catalyst dosage.

3.4. Optimization

The optimization of individual response was performed to achieve maximum biodiesel yield based on respective developed mathematical equations. It was found that the predicted response is in good agreement with experimental results and biodiesel yield of 48.30 % was achieved with 6 wt.% catalyst dosages, 1hour reaction time and 800 °C of calcination temperature.

4. CONCLUSIONS

The transesterification of low-grade cooking oil into biodiesel was optimized using a Ca/Mg/Al₂O₃ catalyst. The effect of operational parameters on the biodiesel yield was evaluated using the Box-Behnken design. According to RSM, the optimal catalyst dosage reaction time, and calcination temperature were 6 wt.% , 1 hour, and 800 °C, respectively; which yield 48.30 % of biodiesel yield. The value from the analysis of variance, $R^2 = 0.9842$, allowed the second-order regression model to be appropriately adjusted using the experimental data. Additionally,

the RSM optimization model demonstrated good efficiency and accuracy in predicting the ideal biodiesel output with error under 0.5.

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CRedit authorship contribution statement. Nursyamimi Zulkurnain: Methodology, Investigation, Funding acquisition. Aisyah Fathiah Ahmad: Analyze data. Salmiah Jamal Mat Rosid: Supervision. Azman Azid: Editing; Susilawati Toemen: Editing

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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