



Research article

Optimisation of CaO-Al₂O₃-SiO₂-CaSO₄-based catalysts performance for methanolysis of waste lard for biodiesel production using response surface methodology and meta-heuristic algorithms

E.O. Ajala^{a,*}, A.B. Ehinmowo^b, M.A. Ajala^a, O.A. Ohiro^{b,c}, F.A. Aderibigbe^a, A.O. Ajao^a

^a Department of Chemical Engineering, University of Ilorin, Kwara State, Nigeria

^b Department of Chemical and Petroleum Engineering, University of Lagos, Lagos, Nigeria

^c Department of Chemical Engineering, University of Michigan, USA

ARTICLE INFO

Keywords:

Transesterification

Vegetable oil

Animal fat

Genetic algorithm

Particle swarm optimisation

Firefly algorithm

Fatty acid methyl esters

ABSTRACT

The CaO-Al₂O₃-SiO₂-CaSO₄-based solid catalysts developed from calcium carbide residue (CCR) was investigated for biodiesel production using waste lard in optimisation and regeneration studies. The catalysts were synthesized by calcination of the CCR at the temperature of 500, 700 and 900 °C and sulphonation, to give Cat₅₀₀, Cat₇₀₀ and Cat₉₀₀ respectively. The catalysts were studied to optimise the biodiesel yield from waste lard using combinations of response surface methodology (RSM) and meta-heuristic algorithms such as particle swarm optimisation (PSO), genetic algorithm (GA) and firefly algorithm (FA). The process parameters investigated were methanol: oil molar ratio (6–12 w/w), reaction temperature (50–60 °C), reaction time (1–4 h), catalyst quantity (5–15 % (w/w)) and catalyst type (Cat₅₀₀, Cat₇₀₀ and Cat₉₀₀). The study revealed that the 12:1 MeOH: oil molar ratio, 59.97 °C reaction temperature, 1 h reaction time, 5% (w/w) catalyst quantity and Cat₅₀₀ catalyst type gave biodiesel yield of 96.35%. The performance of the meta-heuristic algorithms based on the optimisation output compared well with that of the RSM. This study concludes that the catalyst developed from the CCR can be regenerated after the ninth cycle of usage and re-utilised for efficient biodiesel production.

1. Introduction

Humongous diminution of fossil fuel reservoirs due to increased energy demand as a result of increasing global social economy is escalating energy crisis [7]. Also, the use of fossil fuel is generating toxic and hazardous materials into the environment [3] and escalating global greenhouse gas emissions [37]. These have necessitated emphasis on the development and utilisation of alternative, renewable and sustainable green energy sources [7]. Biodiesel, an example of a green energy source has several benefits which include non-toxicity, biodegradability, renewability and being environmentally benign [35].

Biodiesel is a mono-alkyl ester of long-chain fatty acids which contains mainly fatty acid methyl esters (FAME) that are synthesised through transesterification reaction of vegetable oils or animal fats and primary alcohols in the presence of a catalyst [19,35]. Samuel et al. [39] gave an account of several researchers that produced biodiesel from edible oils (soyabean oil, palm oil, corn oil, sunflower oil and groundnut oil) and non-edible oils (animal fat and waste cooking oil). However, the

use of edible oil for biodiesel production is not sustainable as it is responsible for the increase in food price and affects its availability [25,39]. Whereas, the use of non-edible oils as feedstocks for biodiesel production can deal with food security and significantly reduce production costs [25,26]. Therefore, the sustainability of biodiesel production depends on low-cost feedstock such as waste cooking oil and animal fats (waste lard, mutton fat, duck tallow and chicken fat).

Waste lard is a low-cost animal fat that is cheaply available and suitable as a feedstock for biodiesel production [3]. Buchori et al. [9] utilised lard for biodiesel production and obtained an optimum yield of 92.69% in a two-stage trans-esterification process by CaO-HCl catalytic process. Ezekannagha et al. [15] also achieved an optimum yield of 96% biodiesel from waste lard in the presence of KOH catalyst using Response Surface Methodology (RSM). The authors concluded that lard is a good feedstock suitable and sustainable for biodiesel production. In another study, the RSM demonstrated high efficiency to optimise lard for biodiesel production at a high yield of 97.8 ± 0.6% with a high-quality product that satisfied the standards for biodiesel [23]. Given that the

* Corresponding author.

E-mail address: ajala.oe@unilorin.edu.ng (E.O. Ajala).

<https://doi.org/10.1016/j.fuproc.2021.107066>

Received 19 July 2021; Received in revised form 1 October 2021; Accepted 12 October 2021
0378-3820/© 2021 Elsevier B.V. All rights reserved.

waste lard as a feedstock offers a promising future in the biodiesel industry, it contains high amounts of free fatty acids (FFA) (> 1 wt%), moisture content (> 0.5 wt%) and other impurities [18]. As such, it is difficult to use basic homogenous catalysts, because they are highly sensitive to high FFA and moisture content, as it forms undesirable by-products such as soap [4]. The acidic homogeneous catalysts by nature are very corrosive, difficult to recover and results in an increase in the cost of biodiesel production due to purification processes [18]. Therefore, heterogeneous catalysts are preferred due to their ease of separation and lower corrosion. These and many more benefits of the heterogeneous catalysts over homogenous catalysts have necessitated more research efforts on the former for biodiesel production [32].

Researchers have reported the use of different oxides of metals as support for the development of a heterogeneous catalyst for biodiesel production. Among these catalysts are $\text{Nb}_2\text{O}_5/\text{SO}_4$, $\text{SO}_4^{2-}/\text{ZrO}_2$, $\text{SO}_4^{2-}/\text{TiO}_2\text{-SiO}_2$, $\text{Fe}_2\text{O}_3\text{-MnO-SO}_4^{2-}/\text{ZrO}_2$, $\text{CaO}/\text{Fe}_2(\text{SO}_4)_3$, $\text{Li-CaO}/\text{Fe}_2(\text{SO}_4)_3$, $\text{CaFe}_2\text{O}_4\text{-Ca}_2\text{Fe}_2\text{O}_5$, $\text{MgFe}_2\text{O}_4/\text{CaO}$ and $\text{CaO-}\gamma\text{-Fe}_2\text{O}_3$ [3–5]. However, Fattah et al. [17] stated that the alkaline earth metal oxides demonstrated high activity as heterogeneous catalysts for biodiesel production than other oxides of metal, due to their stronger basic sites. This effectively promotes the reaction, as the number of basic sites in a unit mass is approximately equals to the surface area of the catalyst. According to their findings, the amount of basic sites in alkaline earth metals follows the order: $\text{CaO} > \text{MgO} > \text{SrO} > \text{BaO}$ which indicates that the CaO-based catalysts are more active than the others. This corroborates the claims of Latchubugata et al. [29] that the CaO-based catalysts are the most studied for biodiesel production due to their many advantages. These include long catalyst life, low solubility in methanol, relatively high basic strength, low cost, moderate reaction conditions, high activity and not actively leach into the reaction medium [3,29,38]. Moreso, CaO is relatively available in high amounts in numerous waste materials (such as snail shells, chicken eggshells, animal bones and calcium carbide) which have been explored for catalysts development [3,5]. Laskar et al. [28] synthesised CaO-based solid catalyst from waste snail shells for biodiesel production and obtained a biodiesel yield of 98%. Ajala et al. [5] and Odetoye et al. [32] reported the use of chicken eggshell for the development of CaO-based catalysts for biodiesel production and achieved a maximum biodiesel yield of 97.10% and 90.2% respectively. In other studies by Ajala et al. [2] and Ajala et al. [6], calcite and dolomite rocks were developed into CaO-based catalysts for biodiesel production and attained maximum biodiesel yield of 97% and 98.69% respectively. In the previous study by Ajala et al. [3], CCR was used as a precursor to synthesise $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaSO}_4$ heterogeneous acid catalysts for biodiesel production. The synthesis was carried out by thermal modification of the CCR at 500, 700, and 900°C, followed by sulphonation, to develop $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2/\text{SO}_4^{2-}$ solid-acid catalysts known as Cat₅₀₀, Cat₇₀₀ and Cat₉₀₀ respectively. However, the study did not investigate the optimisation of catalysts performance for biodiesel production. As the catalysts performance can depends on various parameters such as reaction temperature, catalyst quantity, methanol: oil molar ratio and thermal treatment for catalyst development [11]. Successful optimisation of these parameters are bound to overcome challenges of the costs of raw material (fats/oils, methanol and catalyst) and cost of processing (time and temperature) associated with biodiesel production [37]. However, heterogeneous catalysts generally have deactivation drawbacks due to leaching of the active site during

transesterification which can be solved by reactivation after repeated uses [35]. This study therefore, investigates the reusability and reactivation of the spent catalyst.

Meanwhile, optimisation of the transesterification parameters for the maximum biodiesel yield requires enormous experimental runs which is a serious challenge [35]. The RSM which is an effective mathematical and statistical technique can overcome this drawback by designing a minimum number of experimental runs, developing models and optimising the parameters [1,35]. However, the RSM may not be applicable to optimise all processes despite its many advantages. As it can only develop first-degree and second-degree models which are considered a disadvantage, especially for data that could be fitted better on other models [26]. To solve this problem of RSM, some optimisation algorithms known as meta-heuristics can be deployed. Meta-heuristics are developed to solve all optimisation problems with no or minimum adjustment on the algorithm [30]. Also, a meta-heuristic algorithm can be modified to the characteristics of a specific problem to give superior performance and convergence than the generic or black-box design [34].

Meta-heuristic algorithms are higher-level procedures that produce approximate solutions to problems in parameter spaces that are too large to be fully sampled, such as material spaces [12]. They have become an integral part of modern optimisation with a wide variety of them becoming increasingly popular, such as particle swarm optimisation (PSO), genetic algorithm (GA), firefly algorithm (FA). The PSO is one of the most well-known populations intelligence-based evolutionary computation techniques. It is based on swarm behaviour such as bird flocking and nature schooling as seen in fishes. This approach searches for the optimum solution utilising individuals or entities referred to as particles whose trajectories are modified by deterministic and stochastic components [45]. The GA on the other hand is a randomised search algorithm designed to mimic the mechanics of natural selection and natural genetics. It is a meta-heuristic search algorithm based on the concepts of the natural competition between individuals for the appropriation of finite natural resources [21]. The FA was proposed by Yang [48] and was categorised as intelligent, meta-heuristic and nature-inspired swarm. It is based on the animation of the actions of tropical fireflies displaying characteristic light flickering behaviours to attract mates, communicate and serve as a danger warning for predators. These algorithms have been successfully utilised to maximise biodiesel yield as reported in the literature; PSO [24,31,43], FA and GA [8]. Noteworthy is that the meta-heuristic algorithms can be employed in the hybridisation of more than one algorithm instead of one, to optimise engineering design and other application areas [30]. Even though the RSM has been reported for biodiesel production using waste lard, the aforementioned algorithms have not been explored, at least to the best of the authors' knowledge.

Therefore, this study aimed at optimisation of biodiesel production using waste lard and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaSO}_4$ -based solid catalysts by RSM and meta-heuristic algorithms such as GA, PSO and FA. The parameters that may significantly affect the process such as methanol: oil molar ratio (MeOH: oil ratio), reaction temperature, reaction time, catalyst quantity and catalyst types, CATs (Cat₅₀₀, Cat₇₀₀ and Cat₉₀₀) were considered for the optimisation. The catalyst with optimum biodiesel yield was investigated for its reusability, de-activation and reactivation studies, using the optimal parameters.

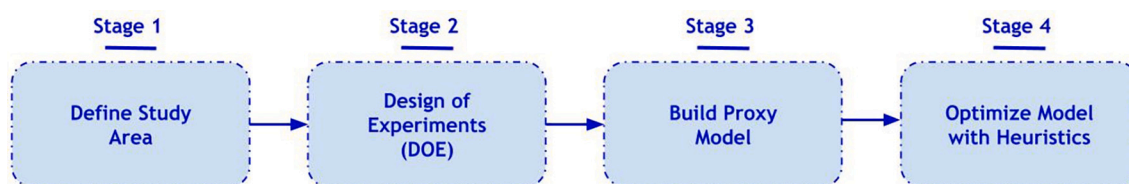


Fig. 1. Workflow of the study.

Table 1

Experiment parameters.

Parameter	Code	Unit	Uncertain range
Methanol: oil molar ratio	A	w/w	6–12
Temperature	B	°C	50–60
Time	C	h	1–3
Catalyst quantity	D	m ³	5–15
Catalyst type	E	Categorical factor	Cat ₅₀₀ , Cat ₇₀₀ , Cat ₉₀₀

Table 2

Central composite experimental design matrix for maximum biodiesel yield.

Run	A: MeOH: oil molar ratio	B: temperature	C: time	D: Catalyst quantity	E: Cat type
1	6	55	2	5	Cat ₅₀₀
2	12	60	3	15	Cat ₇₀₀
3	6	60	1	15	Cat ₇₀₀
4	12	60	1	5	Cat ₇₀₀
5	12	60	1	15	Cat ₅₀₀
6	6	60	3	15	Cat ₅₀₀
7	12	50	1	5	Cat ₅₀₀
8	9	55	3	10	Cat ₇₀₀
9	9	55	2	15	Cat ₅₀₀
10	9	50	3	10	Cat ₅₀₀
11	6	55	3	10	Cat ₉₀₀
12	6	50	3	5	Cat ₉₀₀
13	9	55	1	10	Cat ₇₀₀
14	6	50	3	15	Cat ₇₀₀
15	9	60	2	15	Cat ₉₀₀
16	6	50	1	5	Cat ₇₀₀
17	6	60	1	5	Cat ₉₀₀
18	9	55	1	10	Cat ₇₀₀
19	12	60	3	5	Cat ₉₀₀
20	6	60	3	5	Cat ₇₀₀
21	12	50	3	5	Cat ₇₀₀
22	9	50	1	10	Cat ₅₀₀
23	12	50	3	15	Cat ₉₀₀
24	12	50	1	15	Cat ₇₀₀
25	6	50	2	15	Cat ₅₀₀
26	12	50	2	10	Cat ₉₀₀
27	6	60	1	5	Cat ₅₀₀
28	9	60	2	15	Cat ₉₀₀
29	9	55	1	5	Cat ₉₀₀
30	12	50	2	10	Cat ₉₀₀
31	12	60	1	15	Cat ₉₀₀
32	6	55	3	10	Cat ₉₀₀
33	9	55	1	5	Cat ₉₀₀
34	6	50	1	15	Cat ₉₀₀
35	12	55	3	5	Cat ₅₀₀

2. Methodology

2.1. Materials

The CATs obtained from calcium carbide residue (CCR) that was synthesised in Chemical Engineering Laboratory, University of Ilorin, Ilorin, Nigeria was used in this study. Waste lard that was collected from a local butchery industry in Ilorin Metropolis was processed by heating at 100 °C until it melted. The oil was collected by filtering under reduced pressure after sieving the solid residue from the mixture. The free fatty acid (FFA) of the purified lard was evaluated as 6.68% using the AOAC standard method. Analytical grades of methanol (98%), n-hexane (99%) and sulphuric acid (98.99%) used as reagents for the study were purchased from Sigma–Aldrich, India.

2.2. Workflow for the optimisation process

Fig. 1 shows the activities of workflow that was followed for the study, from stages 1 to 4. Stage 1 is the parameterisation of the experimental process of catalytic conversion of waste lard to biodiesel. Stage 2

is the formulation of the design of the experiment to accurately capture the interactions of the parameters. Stage 3 focuses on building the model while Stage 4 incorporates various optimisation algorithms in scanning through the model search space for their optimal performances.

2.3. Design of experiment

Proxy models were developed, and their performance were tested to assess the efficacy of the RSM in correctly predicting the output of the catalytic conversion process. The first challenge in implementing this aim was to plan the studies, to analyse the factors of the model underpinning the catalytic conversion process and to minimise the number of experimental runs needed to build such models. A central composite design (CCD) was adopted to design the experiment for the development of a second-order (quadratic) model for the response variable without the need to use a maximum 3 factorial experiment. Using the Design-Expert 6.0 software, actual levels of factors were determined, and an experimental program was developed. Process parameters investigated are MeOH: oil ratio (6–12 w/w), reaction temperature (50–60 °C), reaction time (1–3 h), catalyst quantity (5–15% w/w of the oil) and catalyst types, CATs (Cat₅₀₀, Cat₇₀₀, Cat₉₀₀) as shown in Table 1. The CCD generated a total of 35 experimental matrices as shown in Table 2, using the process parameters in Table 1.

2.4. One-pot trans-esterification of high FFA waste lard using CATs

The procedure described by Ajala et al. [3] was adopted for the trans-esterification of the high FFA (6.68%) waste lard in a one-pot synthesis using methanol in the presence of CATs. A flat-bottom flask connected to a Liebig condenser to aid the reflux of methanol vapour was used for the study. One hundred grams (100 g) of the purified waste lard and corresponding MeOH: oil molar ratio of 6, 9 or 12 (w/w) were weighed into the flask with a catalyst quantity of 5, 10 or 15% (w/w of the lard). The mixture was heated to a temperature of 50, 55 or 60 °C with continuous agitation speed at 600 rpm using a magnetic stirrer for a reaction time of 1, 2 or 3 h. At the end of the reaction time, the mixture was poured into a separatory funnel for the separation of excess MeOH, glycerol and biodiesel. The crude biodiesel was recovered and purified using the method of Komintarachat & Chuepeng [27]. The percentage yield of biodiesel was evaluated using Eq. (1):

$$\text{Yield (\%)} = \frac{\text{Weight of biodiesel}}{\text{Weight of waste lard}} \times 100 \quad 1$$

2.5. Optimisation studies

2.5.1. Response surface methodology (RSM)

The RSM attempts to link a response to the variety of input parameters or factors that affect it using adequate design layout and analysis of experiments. The RSM was used to model the curvature in the relationship between the factors and the response. At the end of 35 experimental runs, regression models were built based on experimental results. Variance Analysis (ANOVA) was used for the graphical analysis of the results. Interactions between variables and reactions have been analysed. The fitness of the polynomial model was represented by the coefficient of determination and the statistical significance of the polynomial model was verified using the Fisher-test. Three-dimensional (3D) plots were obtained based on the results of the two-factor stage.

In general, an optimisation challenge requires choosing the right solution from all available solutions. In the simplest case, the optimisation problem consists of maximising or minimising the function by systematically selecting input values from within the permitted range and calculating the value of the function. For instance, given Ackley's function in Eq. (2):

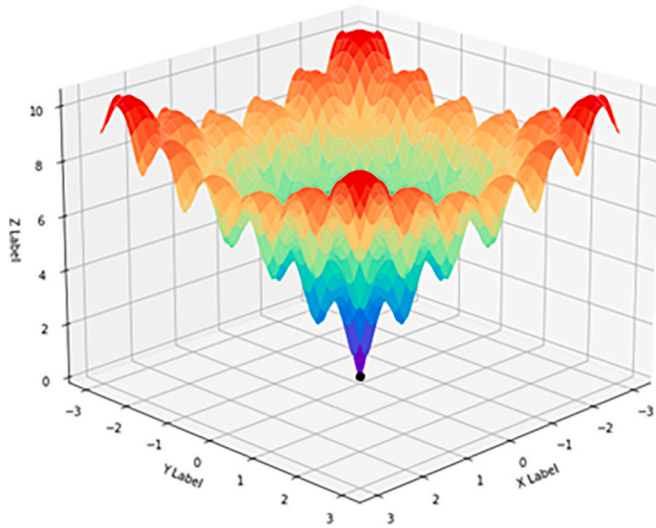


Fig. 2. Graph of Ackley's function.

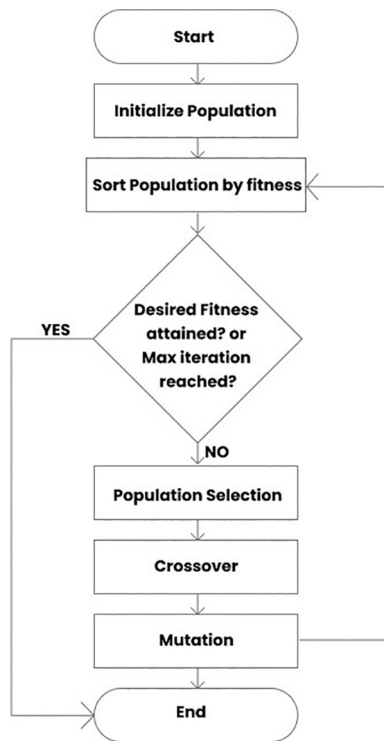


Fig. 3. Genetic Algorithm (GA) flowchart.

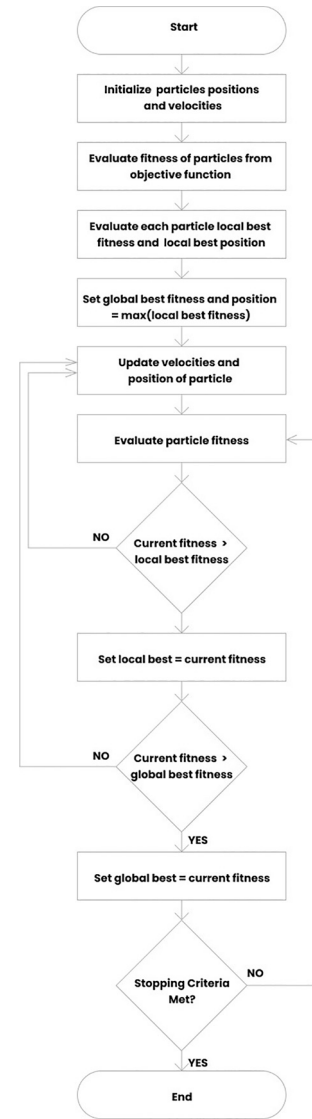


Fig. 4. Particle Swarm Optimisation (PSO) flowchart.

2.5.2. Meta-heuristic optimisation algorithms

Meta-heuristics is a class of algorithms developed to expand on heuristics. A meta-heuristic is a problem-independent, high-level algorithm that offers a series of instructions or techniques to create algorithms for heuristic optimisation [34]. Meta-heuristic algorithms can be categorised into local and global search algorithms. Local search algorithms strive to converge towards a local optimum, not always a global optimum, and such an algorithm is often deterministic and cannot avoid

$$z = f(x, y) = -20 \exp \left[-0.2 \sqrt{0.5(x^2 + y^2)} \right] - \exp[0.5(\cos 2\pi x + \cos 2\pi y)] + e + 20$$

2

The surface model is presented in Fig. 2 with each point on the response surface corresponding to a solution from any combination of the input parameters. As previously stated, the main goal of optimisation is maximising or minimising a function, for Eq. (2), this is represented by the 'black dot' with a maximum value of $Z = 0$, and input variables set to $X = 0$ and $Y = 0$.

local search optimisation. On the other hand, for global optimisation, local search algorithms are not sufficient and global search algorithms must be used. In most cases, modern meta-heuristic algorithms appear to be ideal for global optimisation, although not always effective or efficient. This paper studies the effectiveness of Genetic Algorithm (GA), Particle Swarm Optimisation (PSO), and Firefly Algorithm (FA) for biodiesel production using waste lard in the presence of CATs.

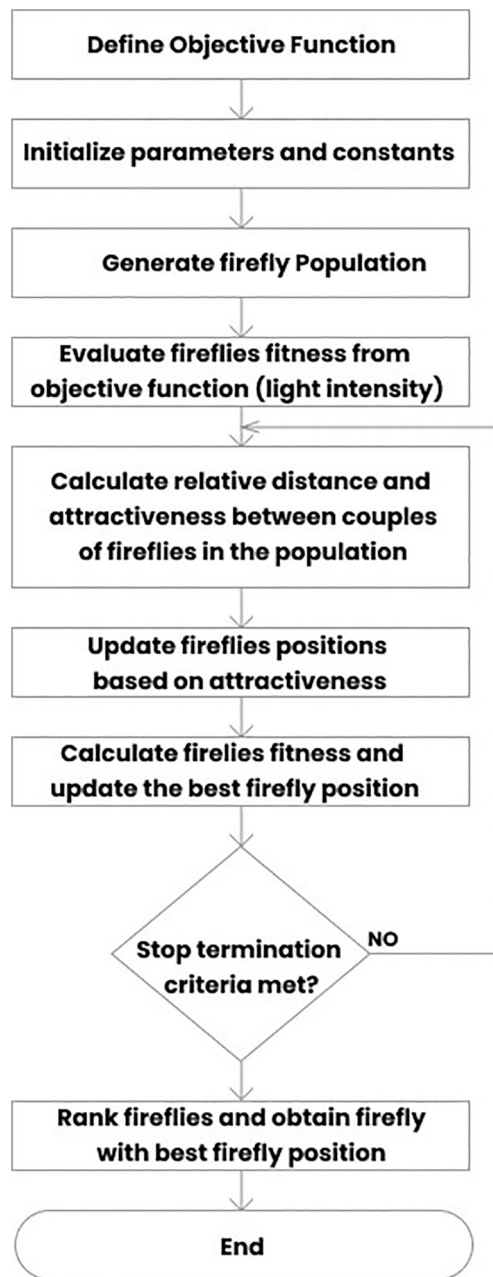


Fig. 5. Firefly Algorithm (FA) flowchart.

2.5.2.1. Genetic algorithm (GA). Fig. 3 shows the flowchart of the genetic algorithm that was followed to simulate the RSM model in this study. The GA is a randomised search algorithm designed to mimic the mechanics of natural selection and natural genetics. It is a metaheuristic search algorithm based on the concepts of the natural competition between individuals for the appropriation of finite natural resources. The survival of the individual typically depends on their genes, and the reproduction by those individuals ensures the gene is propagated through generations. The algorithm randomly chooses individuals from the existing population to be parents and uses them to make children into the next generation through a process of selection, crossover and mutation. By successively choosing superior individuals to become parents and to induce reproduction from one generation to another, the population approaches an optimum solution. Since superior parents produce good offspring while the bad individuals are excluded from the generation.

Table 3

Experimental design matrix with the actual and predicted biodiesel yield results.

Run	A	B	C	D	E	Biodiesel yield		Residual
						Actual	Predicted	
1	6	55	2	5	Cat ₅₀₀	65.58	65.95	-0.37
2	12	60	3	15	Cat ₇₀₀	73.65	71.14	2.51
3	6	60	1	15	Cat ₇₀₀	78.58	77.67	0.91
4	12	60	1	5	Cat ₇₀₀	86.75	89.48	-2.73
5	12	60	1	15	Cat ₅₀₀	90.09	92.36	-2.27
6	6	60	3	15	Cat ₅₀₀	84.96	83.49	1.47
7	12	50	1	5	Cat ₅₀₀	83.29	84.81	-1.52
8	9	55	3	10	Cat ₇₀₀	73.34	78.56	-5.22
9	9	55	2	15	Cat ₅₀₀	87.41	86.59	0.82
10	9	50	3	10	Cat ₅₀₀	70.41	70.04	0.37
11	6	55	3	10	Cat ₉₀₀	73.57	73.83	-0.26
12	6	50	3	5	Cat ₉₀₀	68.00	68.85	-0.85
13	9	55	1	10	Cat ₇₀₀	83.10	80.46	2.64
14	6	50	3	15	Cat ₇₀₀	70.92	79.14	-8.22
15	9	60	2	15	Cat ₉₀₀	85.25	83.14	2.11
16	6	50	1	5	Cat ₇₀₀	92.20	84.20	8.00
17	6	60	1	5	Cat ₉₀₀	68.00	69.27	-1.27
18	9	55	1	10	Cat ₇₀₀	83.91	80.46	3.45
19	12	60	3	5	Cat ₉₀₀	80.90	73.65	7.25
20	6	60	3	5	Cat ₇₀₀	73.20	74.33	-1.13
21	12	50	3	5	Cat ₇₀₀	70.20	74.78	-4.58
22	9	50	1	10	Cat ₅₀₀	70.06	71.94	-1.88
23	12	50	3	15	Cat ₉₀₀	75.33	74.61	0.72
24	12	50	1	15	Cat ₇₀₀	60.00	55.64	4.36
25	6	50	2	15	Cat ₅₀₀	65.90	65.16	0.74
26	12	50	2	10	Cat ₉₀₀	75.76	75.06	0.70
27	6	60	1	5	Cat ₅₀₀	70.00	71.49	-1.49
28	9	60	2	15	Cat ₉₀₀	86.30	83.14	3.16
29	9	55	1	5	Cat ₉₀₀	80.10	82.19	-2.09
30	12	50	2	10	Cat ₉₀₀	75.00	75.06	-0.057
31	12	60	1	15	Cat ₉₀₀	65.00	73.52	-8.52
32	6	55	3	10	Cat ₉₀₀	74.07	73.83	0.24
33	9	55	1	5	Cat ₉₀₀	78.83	82.19	-3.36
34	6	50	1	15	Cat ₉₀₀	84.22	82.01	2.21
35	12	55	3	5	Cat ₅₀₀	95.57	91.43	4.14

2.5.2.2. Particle swarm optimisation (PSO). The PSO is one of the most well-known population intelligence-based evolutionary computation techniques. It is based on swarm behaviour such as bird flocking and nature schooling as seen in fishes. This approach searches for the optimum solution using individuals or entities referred to as particles whose trajectories are modified by deterministic and stochastic components. Each particle is guided by its best position (particle best cost function solution) and the best position of the swarm or population but continues to move randomly. Each particle is defined by its position vector and velocity vector. At each iteration of the algorithm, each particle changes its position according to its velocity vector interaction between its current position, its best position and the population best position. Fig. 4 describes the flowchart that was followed to run the PSO algorithm of the RSM model.

2.5.2.3. Firefly algorithm (FA). The FA was created by Yang [46] and is categorised as intelligent, meta-heuristic and nature-inspired swarm. It is based on the animation of the actions of tropical fireflies, displaying light flickering behaviours to attract mates, communicate and serve as a danger warning for predators. The algorithm is predicated on the fireflies as unisexual in such a manner that they all can attract each other and the attractiveness is directly proportional to the degree of the individual's light. Thus, the dimmer fireflies attract the brighter ones to move towards each other. In cases where no firefly is brighter than a certain firefly, it moves randomly. To maximise the objective function, individuals in the population are required to move systematically or randomly true search space. In this way, it is assured that all fireflies migrate towards more appealing ones, which have a brighter flash before the population converges towards the brightest. Fig. 5 shows the flowchart of the FA algorithm that was employed to simulate the RSM

Table 4

ANOVA results for the biodiesel of the quadratic model.

Source	Sum of Squares	df ^a	Mean Square	F Value	p-value Prob > F	Remark
Model	2084.15	20	104.21	3.38	0.0118	sig. ^b
A-MeOH: oil molar ratio	71.73	1	71.73	2.33	0.1493	
B-Temperature	158.84	1	158.84	5.16	0.0395	sig.
C-Time	22.08	1	22.08	0.72	0.4114	
D-catalyst quantity	0.21	1	0.21	0.007	0.9346	
E-catalyst type	4.74	2	2.37	0.077	0.9264	
AB	48.00	1	48.60	1.58	0.2297	
AD	319.18	1	319.18	10.36	0.0062	sig.
AE	451.82	2	225.91	7.33	0.0066	sig.
BD	21.50	1	21.50	0.70	0.4175	
BE	306.41	2	153.20	4.97	0.0234	sig.
DE	228.00	2	114.00	3.70	0.0513	
A ²	79.59	1	79.59	2.58	0.1303	
B ²	27.16	1	27.16	0.88	0.3637	
D ²	59.88	1	59.88	1.94	0.1850	
ABE	184.16	2	92.08	2.99	0.0830	
Residual	431.34	14	30.81			
Cor total	2515.49	34				
R ² 0.8285	Adj. R ² 0.5836	BIC 261.89		AICc 300.31		C.V. (%) 7.20

^a Degree of freedom.^b Significant.

model.

2.6. Reusability, de-activation and regeneration studies of Cat₅₀₀

The catalyst with the optimum biodiesel yield was investigated for its reusability, de-activation and regeneration studies. The de-activation, being one of the characteristics of an heterogeneous catalyst, its recovery and re-utilisation are crucial factors to evaluate the economic application on an industrial scale [40]. Therefore, optimal parameters obtained from the optimisation studies for Cat₅₀₀ (Table 5) was used for the reusability study. After every cycle, the Cat₅₀₀ was separated through filter paper, rinsed with n-hexane to remove glycerol and excess oil attached to the catalyst, and dried in a hot air oven at 100°C for 1 h [3–5]. At the end of the ninth cycle, portion of the spent catalyst was

collected for re-activation by washing with n-hexane, oven-dried at 100 °C for 1 h and calcined at 500 °C. The analysis of the physical and chemical properties of the fresh, spent and re-activated samples of the catalyst were carried out using X-ray diffraction (XRD, model Bruker AxSD8), high-resolution scanning electron microscope (HRSEM, Zeiss Auriga), surface area (Brunauer–Emmett–Teller, BET Nova Quantachrome version 11.03) and basic strength using the method described by Ajala et al. [3–5].

3. Results and discussion

3.1. Response surface methodology (RSM) analysis

The effects of independent parameters of MeOH: oil molar ratio (A),

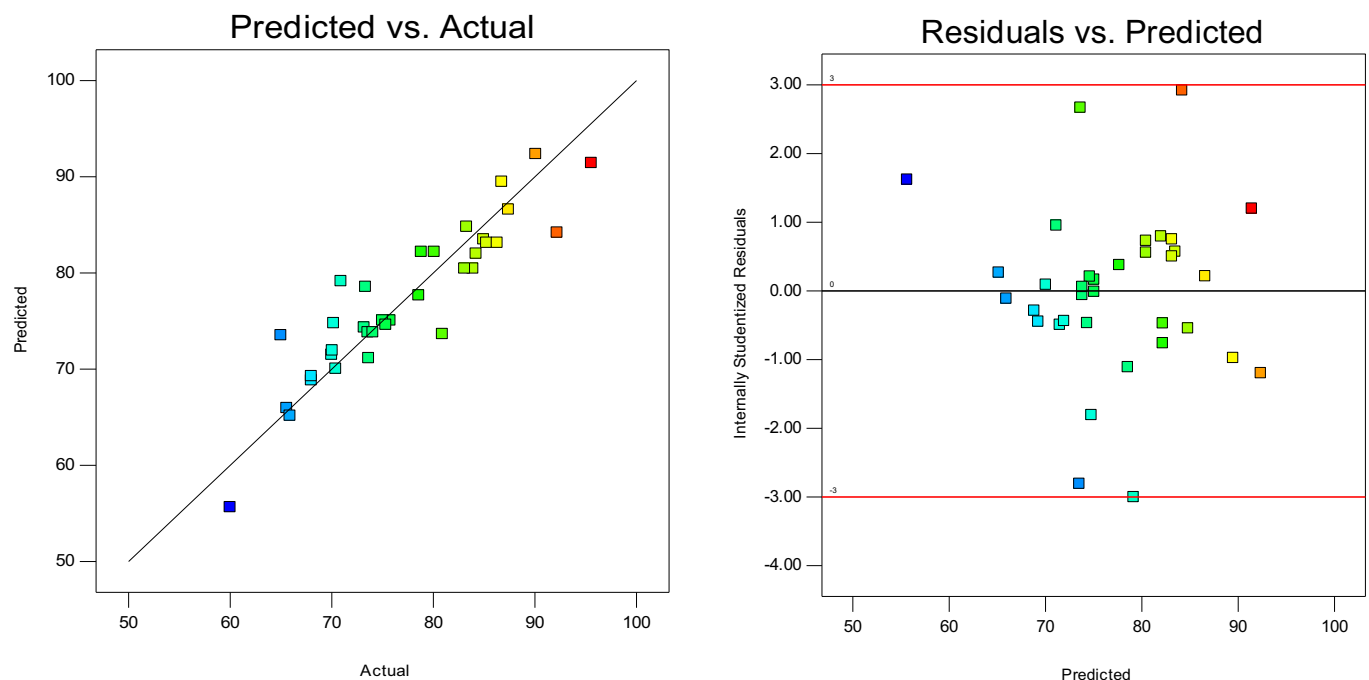


Fig. 6. (a) Actual versus predicted the plot of biodiesel yield and (b) residual plot.

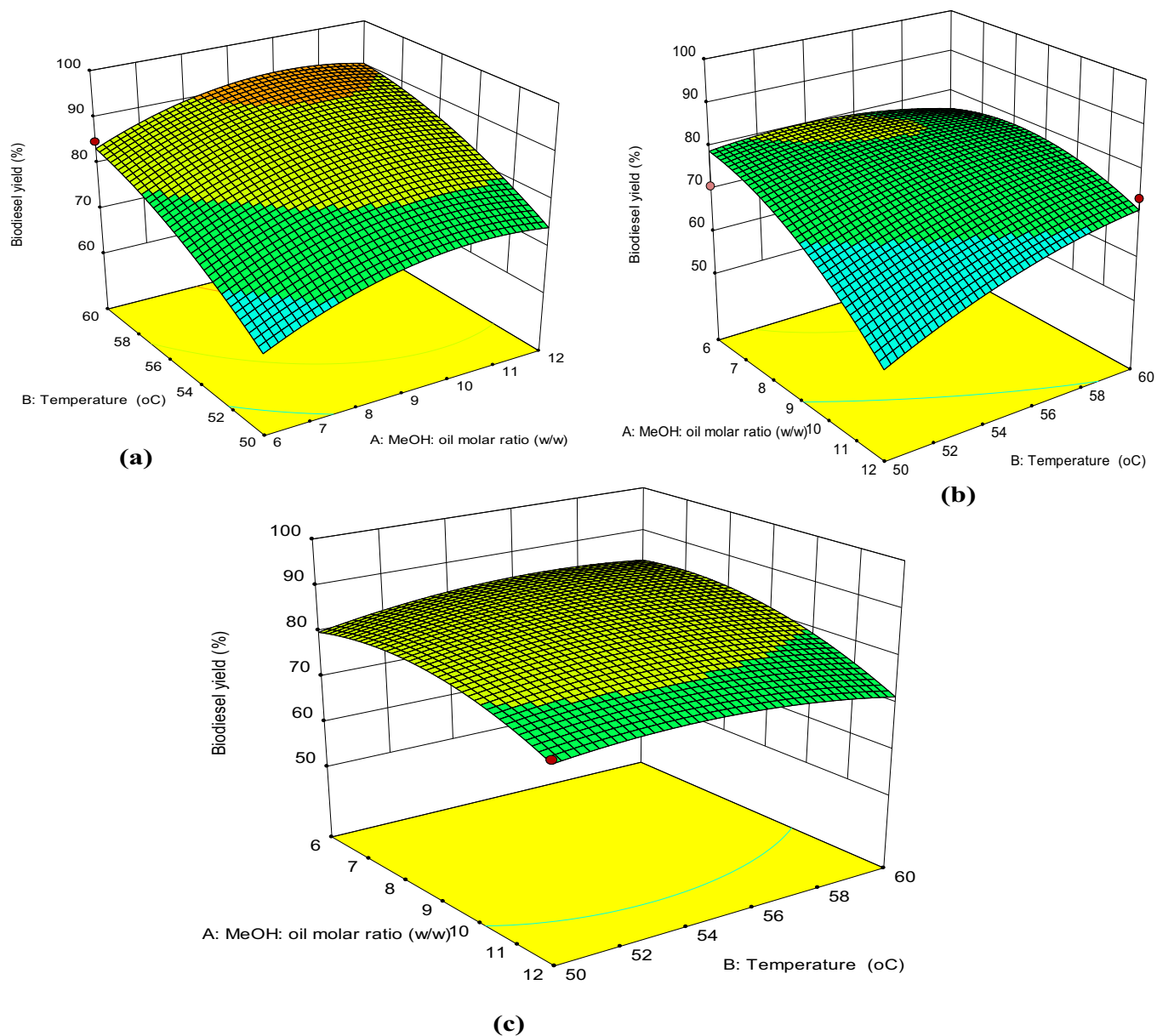


Fig. 7. 3D surface plots of interaction between MeOH: oil molar ratio and temperature against biodiesel yield using (a) Cat₅₀₀, (b) Cat₇₀₀ and (c) Cat₉₀₀.

reaction temperature (B), reaction time (C), catalyst quantity (D) and CATs on the biodiesel yield (%) were studied in an optimisation process using the CCD of an experimental matrix of 35 runs. The experimental runs were carried out to analyse the impacts of the individual parameters and their interactions on the biodiesel yield as shown in Table 3.

The table shows that the response item of the actual biodiesel yield varies between 60.00% (run 24) and 95.57% (35), which are not so different from the predicted biodiesel yield of 55.64% and 91.43% respectively. Thus, indicates the close relationship between actual and predicted values of the biodiesel yield with the residual values showing minimal differences.

The linear, interaction and quadratic effects of the process parameters were performed to obtain the optimal conditions. The linear relationship was evaluated using the analysis of variance (ANOVA) as presented in Table 4. The quadratic model was suggested as the most appropriate for the analysis by the design expert with the corresponding parameters indicating the significance of the model. The best regression model obtained from the experimental data for biodiesel yields for respective CATs are given in Eqs. 2(1–3):

$$Y_{Cat500} = -418.495 + 0.530 \times (A^2) + 0.110 \times (B^2) + 0.152 \times (D^2) + 0.949 \times (A \times B) - 0.298 \times (A \times D) + 0.045 \times (B \times D) \quad 2.1$$

$$Y_{Cat700} = -116.558 - 7.536 \times A + 9.008 \times B - 0.949 \times C - 3.873 \times D + 0.346 \times (A \times B) - 0.298 \times (A \times D) + 0.045 \times (B \times D) - 0.530 \times (A^2) - 0.110 \times (B^2) + 0.152 \times (D^2) \quad 2.2$$

$$Y_{Cat900} = -323.924 + 18.175 \times A + 12.344 \times B - 0.949 \times C - 2.432 \times D - 0.102 \times (A \times B) - 0.298 \times (A \times D) + 0.045 \times (B \times D) - 0.530 \times (A^2) - 0.110 \times (B^2) + 0.152 \times (D^2) \quad 2.3$$

Where Y_{Cat500} , Y_{Cat700} and Y_{Cat900} are the biodiesel yield (%) for the Cat₅₀₀, Cat₇₀₀ and Cat₉₀₀, respectively; A, B, C and D are the independent parameters, while AB, AC, AD, BC, BD and CD are interaction terms between parameters, and A^2 , B^2 , C^2 and D^2 are the quadratic terms.

From the ANOVA results, a *p*-value of 0.0118 was gotten for the model as shown in Table 4. This indicates that the process parameters based on the quadratic model have significant effects on the biodiesel yields and that the model is statistically significant.

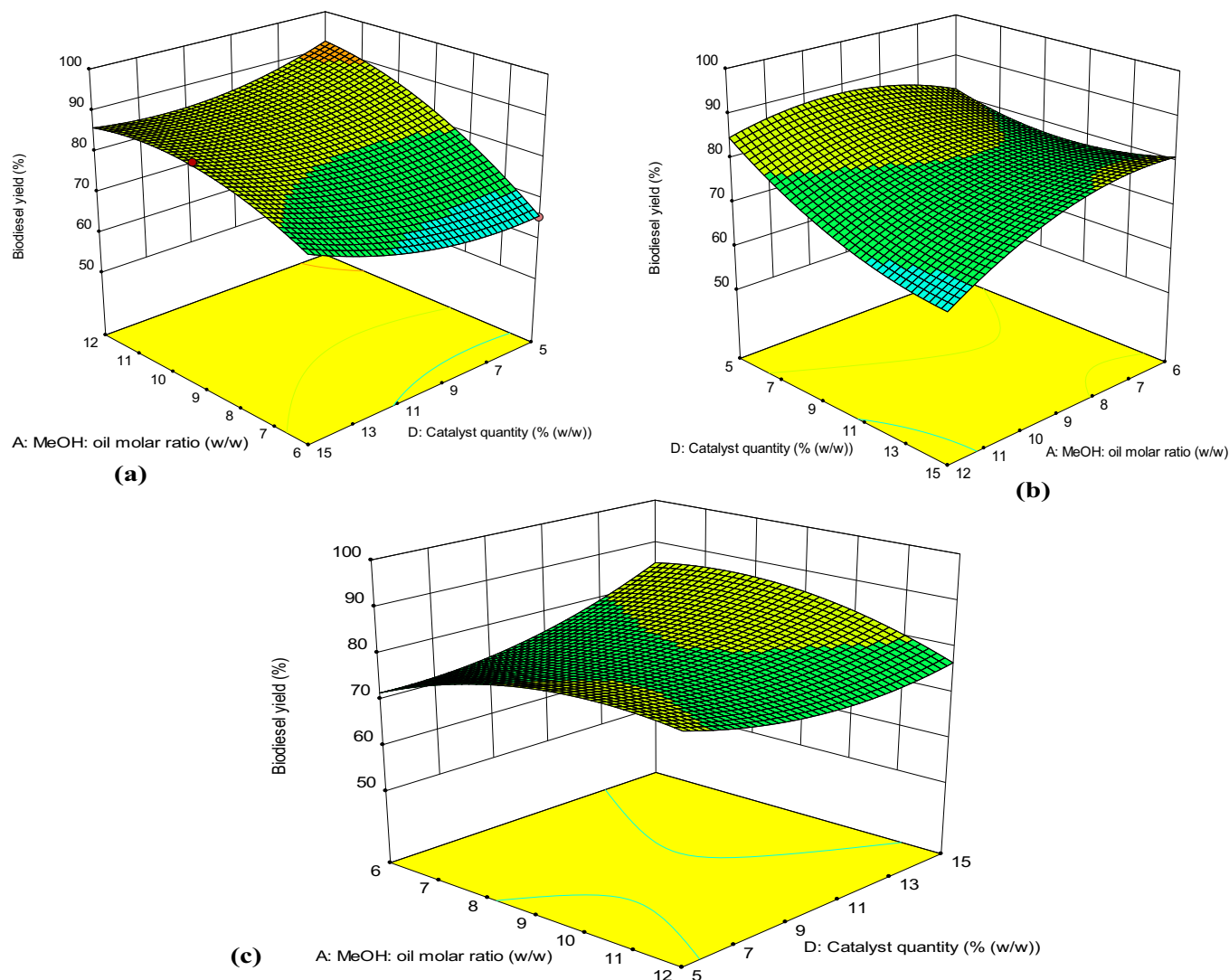


Fig. 8. 3D surface plots of interaction between MeOH: oil molar ratio and catalyst quantity against biodiesel yield using (a) Cat₅₀₀, (b) Cat₇₀₀ and (c) Cat₉₀₀.

According to Table 4, the model terms of A, B, C, AB, AD, AE, BD, BE, DE, A², B², D² and ABE are significant with p -values <0.5, hence, influenced the biodiesel yields by the CATs.

The coefficient of determination (R^2) and adjusted R^2 obtained was 0.8285 and 0.5836 (Table 4) respectively. The R^2 value obtained advocates that the model could estimate the 82.85% conversion in the biodiesel yield confirmed by the equation(s). This shows that there is a relationship between the experimental and predicted biodiesel yields for the quadratic model. A low value of the variation coefficient (C.V., %) of 7.20% shows low deviations between the experimental and predicted values, which makes the model reliable. This justifies that the quadratic polynomial regression model shows an acceptable fit of the experimental data and credibly evaluates the response within the studied space of the independent parameters. The actual and predicted plot of the biodiesel yield is presented in Fig. 6a, which reveals the perfect fit and indicates minimal operational error between the actual and predicted data. Fig. 6b shows the plot of studentized residuals versus predicted biodiesel yield with a random scattering of data, an indication that the proposed model is a good description of the process [20]. Therefore, all the aforementioned results reaffirm the capacity of the quadratic model to predict the biodiesel yield of waste lard in the presence of the CATs.

3.2. Effects of interactions between process parameters on the biodiesel yield

Figs. 7a, b and c show 3D surface plots of the biodiesel yield against the interaction of MeOH: oil molar ratio and temperature for Cat₅₀₀, Cat₇₀₀ and Cat₉₀₀ respectively. The figures show an increase in the biodiesel yield by increasing both the MeOH: oil molar ratio and reaction temperature. The maximum biodiesel of 89.65% at MeOH: oil molar ratio of 12:1 and temperature of 60 °C was achieved when Cat₅₀₀ was used as shown in Fig. 7a. This shows that an increase in the amount of MeOH for Cat₅₀₀ transesterification of waste lard moves the reaction equilibrium towards higher biodiesel yield. The maximum yield of biodiesel at the molar ratio of 12:1 can be attributed to sufficient alcohol that created more cavities in the reaction, leading to enhanced yield for Cat₅₀₀ [39]. However, increasing the amount of MeOH: oil molar ratio from 9:1 to 12:1 did not favour waste lard transesterifications by Cat₇₀₀ and Cat₉₀₀, as shown in Fig. 7b and c respectively. The maximum biodiesel yield of 79.90% and 79.83% was achieved at the MeOH: oil molar ratio of 7.5:1 and 9:1 as well as the reaction temperature of 55 °C for Cat₇₀₀ and Cat₉₀₀ respectively. The increase in the MeOH: oil molar ratio beyond 9:1 declines the biodiesel yield gradually. This is because the excess MeOH dilutes the catalyst concentration of Cat₇₀₀ and Cat₉₀₀, resulting in a decrease in the concentration of active sites per unit volume [20,35]. Also, excess MeOH increases the solubility of glycerol,

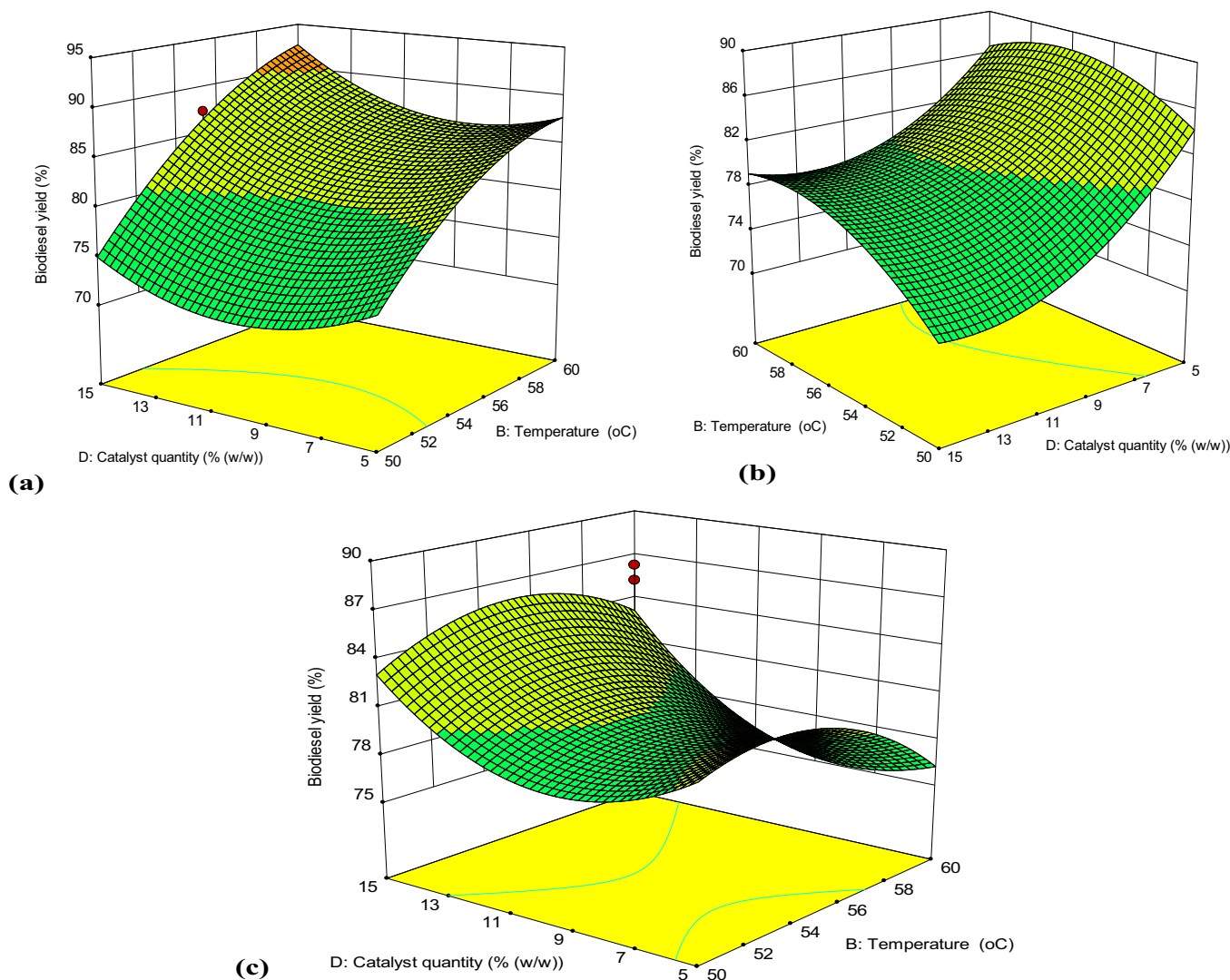


Fig. 9. 3D surface plots of interaction between temperature and catalyst quantity against biodiesel yield using (a) Cat₅₀₀, (b) Cat₇₀₀ and (c) Cat₉₀₀.

which complicates the separation process and reduces biodiesel yield [35]. According to Fig. 7b and c, an increase in the temperature beyond 55 °C for Cat₇₀₀ and Cat₉₀₀ for the transesterification of waste lard lead to a decrease in production efficiency which justifies that the temperature has a significant effect on the biodiesel yield [37]. As the appropriate temperature has a direct influence on the advancement of the reaction through the Arrhenius law rate constants [24]. Therefore, the decrease in the biodiesel yield at a higher temperature in the catalysed transesterification by Cat₇₀₀ and Cat₉₀₀ might be due to the evaporation of the alcohol [10].

Figs. 8a, b and c illustrate 3D surface plots of the biodiesel yield against the interaction of MeOH: oil molar ratio and catalyst quantity for Cat₅₀₀, Cat₇₀₀ and Cat₉₀₀ respectively. Figs. 8a and b show that the MeOH: oil molar ratio of 12:1 and 9:1, as well as the catalyst quantity of 5% (w/w) gave the highest biodiesel yield of 92.30% and 88.11% for Cat₅₀₀ and Cat₇₀₀ respectively. As the catalyst quantity increases to 15% (w/w), the biodiesel yield decreases to 86.27% and 80.52% for Cat₅₀₀ and Cat₇₀₀ respectively. The decline in the yield could be attributed to the soap formation instead of biodiesel production, which resulted from the use of higher catalyst quantity [39]. The excessive quantity of catalyst in the reaction can also lead to the formation of an emulsion, which increases the viscosity and causes gels formation that hinders glycerol separation, hence, reducing the biodiesel yield [10]. Also, the increased viscosity of reactants due to excess catalyst quantity can delay

mass transfer to active sites of the catalyst and reduce the rate of reaction [3–5,20]. Thus, 5% (w/w) of the catalyst quantity for Cat₅₀₀ and Cat₇₀₀ was sufficient to prevent a diffusion resistance during the reaction. However, Fig. 8c reveals that the MeOH: oil molar ratio of 8:1 and catalyst quantity of 15% (w/w) gave the highest biodiesel yield of 86.72% for Cat₉₀₀. This shows that a higher quantity of Cat₉₀₀ catalyst is required for maximum biodiesel yield compared to Cat₅₀₀ and Cat₇₀₀ catalysts. This is probably due to the difference in the activity of the various CATs as a result of the differences in thermal treatments during catalyst preparation. Because, the different thermal treatments could give different catalytic capabilities such as surface area, pore structure, favourable homogeneity and high purity [35]. A catalyst would be more active due to its large surface area and porous structure which simplifies the interaction between MeOH and oil to give a high yield of biodiesel [20].

Figs. 9a, b and c are 3D surface plots of the biodiesel yield against the interaction of reaction temperature and catalyst quantity for Cat₅₀₀, Cat₇₀₀ and Cat₉₀₀ respectively. Fig. 9a shows that the temperature and high catalyst quantity of 60 °C and 15% (w/w) respectively, yielded 92.44% of biodiesel for Cat₅₀₀. While 60 °C and catalyst quantity of 5% (w/w) gave a biodiesel yield of 88.34% for Cat₇₀₀, as shown in Fig. 9b. Also, Fig. 9c presents a maximum biodiesel yield of 85.73% for Cat₉₀₀ at a reaction temperature of 55 °C and a catalyst quantity of 15% (w/w). The results reveal that a reaction temperature of 60 °C promotes mass

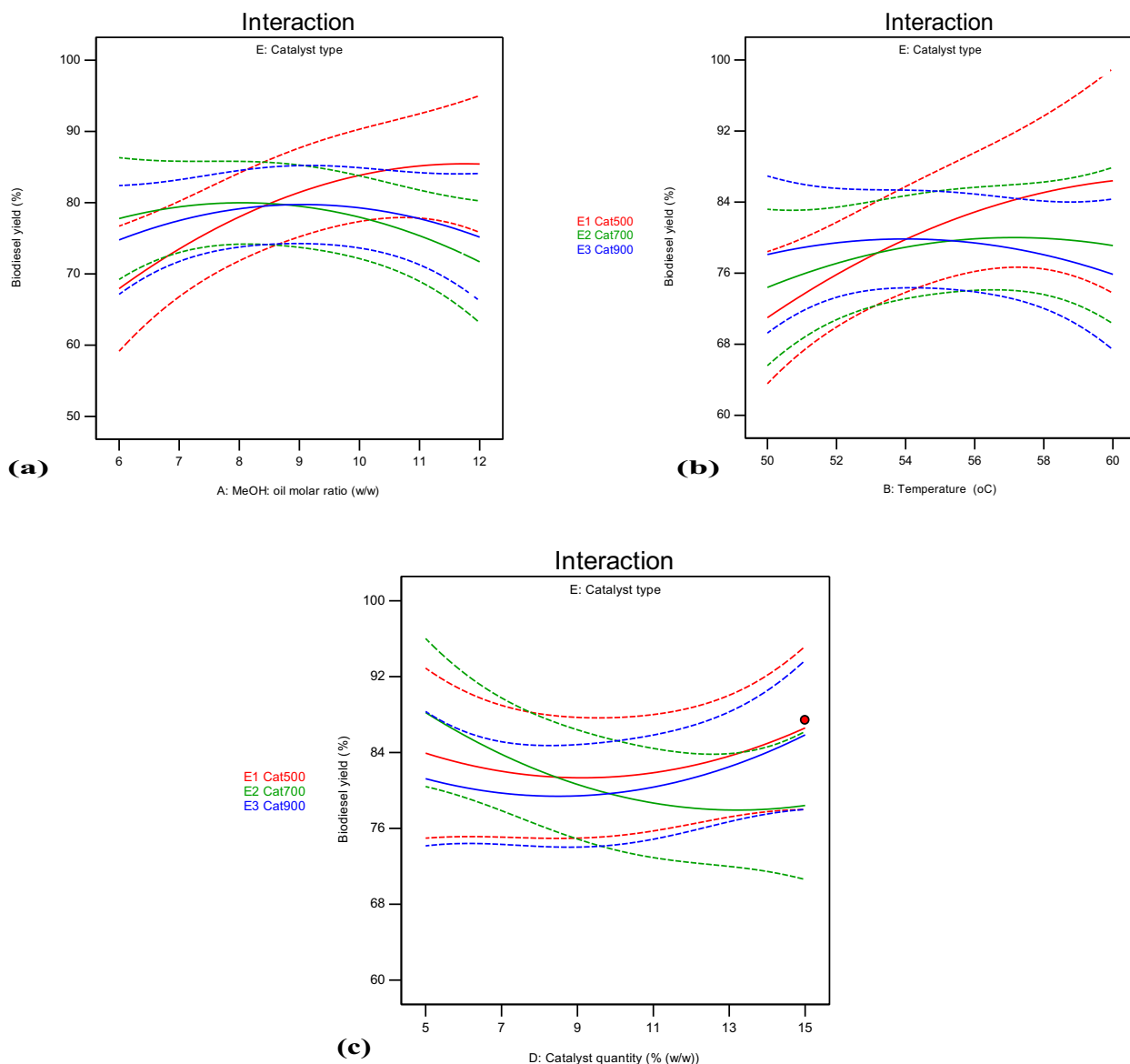


Fig. 10. Plots of interaction between catalyst type and (a) MeOH: oil molar ratio, (b) temperature and (c) catalyst quantity, against biodiesel yield.

transfer of reactant to the surfaces of the Cat₅₀₀ and Cat₇₀₀, which permit the dispersion of the catalyst particles [47]. This further justified the significant effects of temperature and catalyst quantity, as adequate temperature is required to effectively mobilise reactants into the catalyst pores. Although, excess catalyst quantity of 15% (w/w) may increase the viscosity of the reactants for Cat₅₀₀ and Cat₉₀₀, however, the increased reaction temperature could have improved the fluidity of the MeOH. Hence, improve the mass transfer of reactants to active sites of the catalyst and prevent diffusion resistance during the reaction [3,20].

Figs. 10a, b and c show plots of the biodiesel yield against the interactions of CATs with other variables such as MeOH: oil molar ratio, reaction temperature and catalyst quantity respectively. Fig. 10a shows that a maximum biodiesel yield of 94.90% was obtained for Cat₅₀₀ at a MeOH: oil molar ratio of 12:1. Whereas, Figs. 10b and c revealed that the Cat₇₀₀ and Cat₉₀₀ gave their highest biodiesel yield of 86.30% and 85.12% at MeOH: oil molar ratios of 6:1 and 9:1 respectively. The inconsistency in the performance of the CATs with the MeOH: oil molar ratio indicates that each catalyst possess different characteristics which are responsible for their behaviour to alcohol quantity. As aforementioned, the increased MeOH: oil molar ratio increases the biodiesel yield based on Le Chatelier's principle for Cat₅₀₀. However, excess MeOH

Table 5
Optimisation algorithms parameters.

GA	PSO	FA
Crossover probability = 0.5	Learning constant = 2	Attraction coefficient = 2
Mutation probability = 0.2	Initial weight	Light absorption coefficient = 1
Tournament selection of size = 3	Max velocity = 3 Min velocity = -3	Mutation coefficient = 0.2 Mutation coefficient damping ratio = 0.98
Generations = 100 Population = 50	Generation = 100 Population = 50	Generation = 100 Population = 50

reduces the viscosity of the reaction medium, thereby, encourages mass transfer of the reactants, and eventually improve the performance of the CATs to increase the biodiesel yield [3]. Though, MeOH: oil molar ratio of 6:1 and 9:1 were sufficient to attain maximum biodiesel for Cat₇₀₀ and Cat₉₀₀ respectively, MeOH: oil molar ratio beyond 6:1 and 9:1 for respective CATs decreases the yield. This may be attributed to the high solubility of glycerol in alcohol at a higher MeOH: oil molar ratio for the

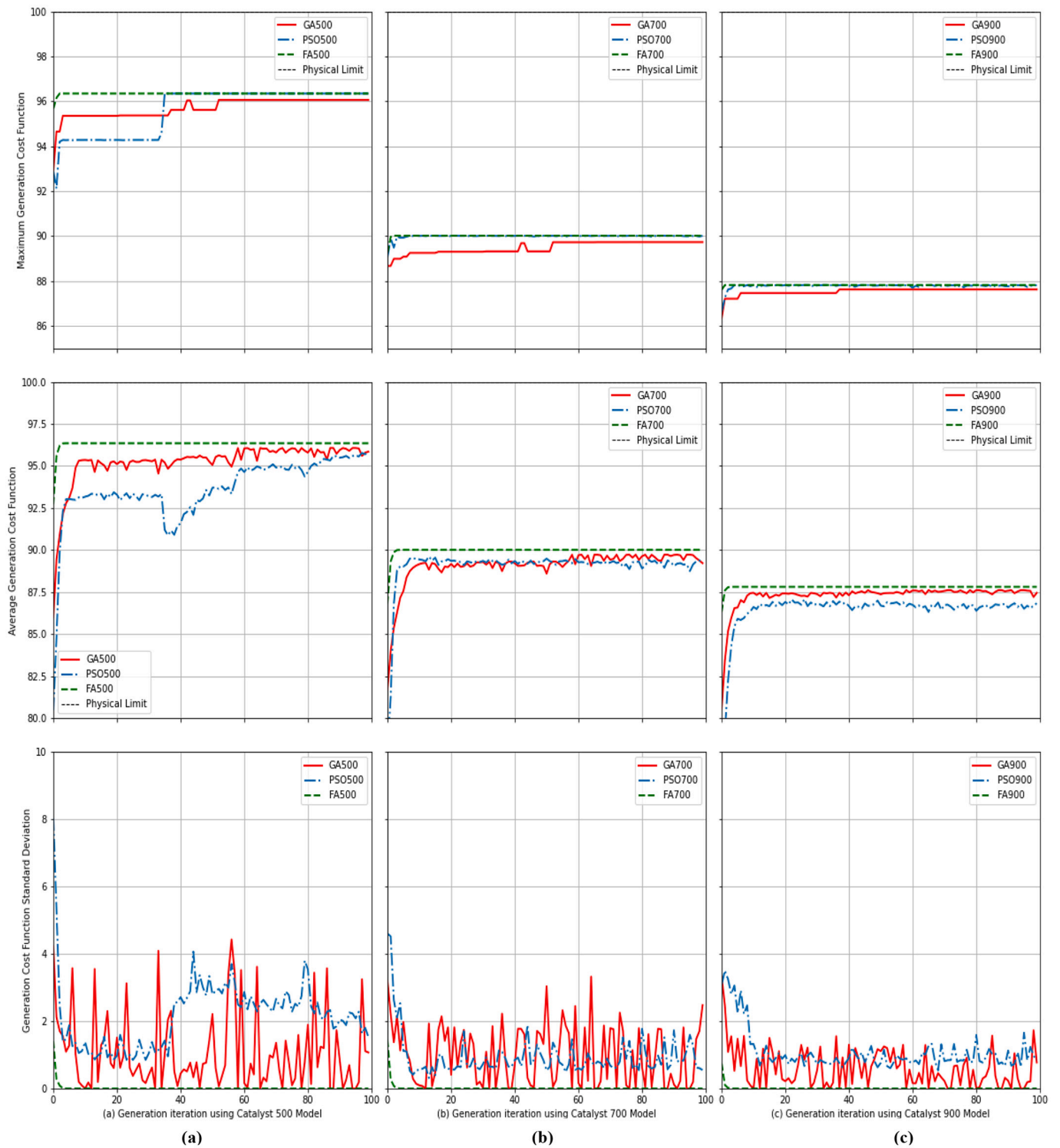


Fig. 11. Biodiesel yield conversion metrics of GA, PSO and FA for (a) Y_{Cat500} , (b) Y_{Cat700} and (c) Y_{Cat900} models.

Table 6a

Performance metrics of optimisation algorithms on catalyst models at 100th generation.

Biodiesel yield metrics	Y_{Cat500}			Y_{Cat700}			Y_{Cat900}		
	GA	PSO	FA	GA	PSO	FA	GA	PSO	FA
Maximum generation cost function	96.07%	96.35%	96.35%	89.73%	90.01%	90.01%	87.62%	87.81%	87.82%
Average cost function	95.85%	95.80%	96.35%	89.22%	89.36%	90.01%	87.46%	86.84%	87.82%
Standard deviation	1.07	1.53	0.00	2.48	0.55	0.00	0.78	0.84	0.00

Table 6b
Statistical evaluation.

Statistical measure	RSM	GA	PSO	FA
Chi-Square	1.02	0.09	0.08	0.08
SEP (%)	8.68	2.50	2.40	2.40
RMSE	5.62	1.62	1.55	1.55
MSE	31.53	2.62	2.42	2.42
MRPD	5.69	1.44	1.51	1.51
MAE	5.20	1.29	1.36	1.36

Cat₇₀₀ and Cat₉₀₀ catalysed reactions. The high solubility of glycerol in MeOH poses a serious separation problem that usually results in a reduction in biodiesel yield [16].

Fig. 10b reveals that the Cat₅₀₀ has the highest biodiesel yield at a reaction temperature of 60 °C. This corroborates the earlier results and justifies the significant effect of temperature in the reaction. This shows that the reaction temperature of 60 °C promotes the mass transfer of reactant to the surface of Cat₅₀₀ and permit dispersion of the catalyst particles [47]. Also, because activation of the triglyceride is very difficult and to favour MeOH nucleophilic attack on the triglyceride, a relatively high reaction temperature of 60 °C is required to activate this carbonyl group [36]. Fig. 10c shows that either 5% (w/w) or 15% (w/w) of the catalyst quantity can produce the highest yield of biodiesel. This is because almost the same value of biodiesel yield was obtained at 5% (w/w) and 15% (w/w) catalyst quantity. Therefore, 5% (w/w) catalyst quantity has provided sufficient basic sites and the reaction has already reached an equilibrium condition, thus, increasing the catalyst quantity to 15% (w/w) has no significant effect on the biodiesel yield [41].

Hence, at every parameter investigated, Cat₅₀₀ was the most effective catalyst with the highest biodiesel yield from the waste lard. Although all the CATs performed well, the optimisation study suggested Cat₅₀₀ as the best catalyst for biodiesel production from the waste lard. This indicates that the preparation method and calcination temperature of the CATs are crucial to the catalytic performances in transesterification [35,42].

Table 7
Optimal parameters for the catalysts models.

Optimal variables	$Y_{Cat_{500}}$			$Y_{Cat_{700}}$			$Y_{Cat_{900}}$		
	GA	PSO	FA	GA	PSO	FA	GA	PSO	FA
Methanol: oil molar ratio	11.99	12.00	12.00	10.69	10.68	10.66	7.74	7.58	7.59
Temperature	59.74	60.00	60.00	58.82	58.74	58.71	55.62	55.74	55.68
Time	1.06	1.00	1.00	1.01	1.00	1.00	1.06	1.00	1.00
Catalyst quantity	5.10	5.00	5.00	5.10	5.00	5.00	14.95	15.00	15.00

3.3. Combinatorial study of the RSM and meta-heuristic optimisation algorithms

The model of the respective CATs was obtained by fitting a quadratic model from the Design Expert™ to generate the response surface. The final equations for the 3 catalytic models are given by Eqs. (2.1), (2.2) and (2.3) for $Y_{Cat_{500}}$, $Y_{Cat_{700}}$ and $Y_{Cat_{900}}$ respectively. To evaluate the performance metric for the optimisation algorithms of PSO, GA and FA such as convergence criteria, average generation performance, and best solution, the initialisation parameters (population size and number of generations) across all three algorithms were kept constant. The specific parameters of each algorithm used are given in Table 5. Statistical results, such as best, average and standard deviations, have been used in both tests to determine the consistency of the solutions. When comparing the algorithms, they were contrasted with the mean value for the three biodiesel yields. Figs. 11a, b and c show the performance of GA, PSO and FA on the maximum objective function, average objective cost function and the standard deviation of all generation solutions for $Y_{Cat_{500}}$, $Y_{Cat_{700}}$ and $Y_{Cat_{900}}$ for the biodiesel yield efficiency as modelled in Eqs. (2.1), (2.2), and (2.3) respectively. Table 6a shows the performance metrics of the algorithms on the CATs under consideration at the end of the 100th generation. Figs. 11(a, b and c) show that the FA optimisation reaches maximum objective function (biodiesel yield efficiency) at the shortest number of generations, followed by PSO and then GA.

It can also be observed that the FA solutions of individuals (Standard deviation) in a generation converges to a singular solution quicker than PSO. The convergence of the GA does not undergo smooth convergence to a single solution as this is an inherent property of the crossover and mutation effect. For the biodiesel yield, metrics of maximum generation cost function and average generation cost function of the $Y_{Cat_{500}}$ model are shown in Fig. 11a and Table 6a. It was observed that the Cat₅₀₀ gave the highest functions compared to Cat₇₀₀ and Cat₉₀₀. The GA, PSO and FA optimisation algorithms obtained maximum biodiesel yield solutions before their 10th generation and achieve a conversion efficiency of 96.07%, 96.35% and 96.35% by the 100th generation respectively. Of all the meta-heuristic algorithms considered, PSO and FA have the same biodiesel yield efficiency and performed the best above the GA for all the

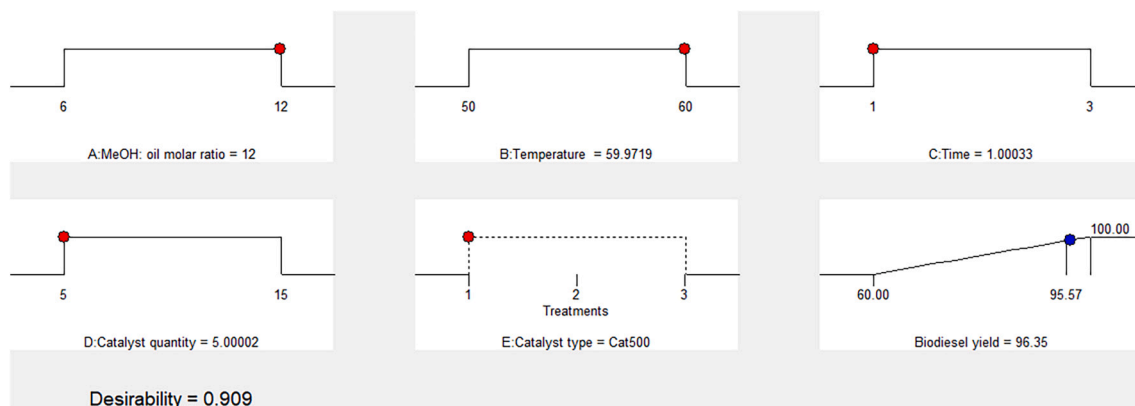


Fig. 12. Optimal parameters by the RSM for maximum biodiesel yield of waste lard in the presence of CATs.

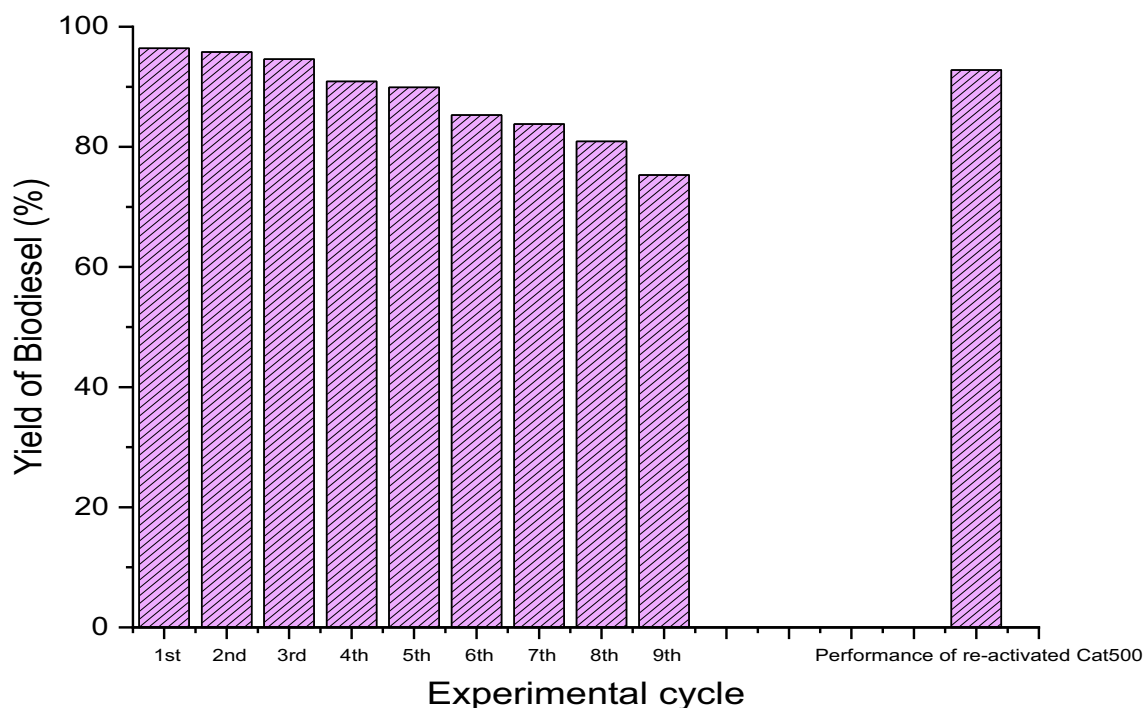


Fig. 13. Reusability and testing of re-activated Cat₅₀₀ for biodiesel production.

Y_{Cat500} , Y_{Cat700} and Y_{Cat900} models. However, in maximising the cost function, FA performed the best among the three algorithms, with GA performing slightly lower than PSO in Y_{Cat500} and Y_{Cat900} . Whilst PSO performing slightly better than GA in Y_{Cat700} as shown in Table 6a. The optimal model parameterisation obtained by each algorithm within the set boundaries (Table 4) is given in Table 7 for each CATs model (Y_{Cat500} , Y_{Cat700} and Y_{Cat900}).

The developed model was further tested using some statistical quantities, including Mean square error (MSE), chi-square, root mean square error (RMSE), mean absolute error (MAE), mean relative per cent deviation (MRPD) and standard error of prediction (SEP). The values for each of the statistical quantities obtained are shown in Table 6b. Details of these statistical measures can be found in Ishola et al. [22] and Ong et al. [33]. The SEP and MAE were used to measure the deviation of the predicted values from the experimental value. The lowest SEP value of 2.4% was recorded for PSO and FA models, while 2.50% and 8.68 % were obtained for GA and RSM models respectively. This shows that the RSM model has the highest divergence from the actual values.

The lowest chi-square value of 0.08 also reveals that the PSO and FA models are far superior in performance compared with the RSM model. The GA model also performed higher than the RSM model but slightly lower than PSO and FA models. The MAE and MRPD values obtained for all the models are low which suggests that the models are reliable. From the results, PSO and FA models with the lowest error values are the most accurate, followed by the GA model and the RSM model being the least. Therefore, the PSO and FA models are better than the RSM model which corroborate findings in the literature [13,14].

3.4. Optimal conditions of the biodiesel yield and models' validation

From the results in Table 7, it is evident that the Cat₅₀₀ produces better catalytic biodiesel conversion efficiency than Cat₇₀₀ and Cat₉₀₀ with all optimisation algorithms converging towards the same optimal solution of parameters. This study showed the usefulness of heuristic algorithms in providing a satisfactory solution and demonstrated the ability of nature-inspired algorithms in solving complex systems of models. The optimal parameters obtained from the modelling and

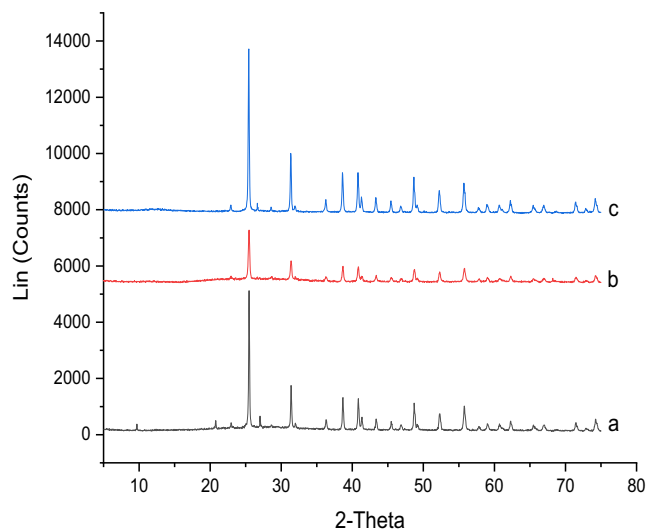


Fig. 14. XRD patterns of Cat₅₀₀ when (a) fresh, (b) degenerated and (c) re-generated after nine cycles of biodiesel production.

optimisation was used to validate the operating parameters to fully maximise biodiesel yield.

Fig. 12 presents the optimal parameters obtained from the RSM for the transesterification of waste lard to biodiesel in the presence of CATs. As shown in the figure, optimum biodiesel yield of 96.35% was obtained at the optimal parameters of MeOH: oil molar ratio of 12: 1, reaction temperature of 59.97 °C, reaction time of 1 h, catalyst quantity of 5% (w/w) and catalyst type of Cat₅₀₀. These findings are the same as obtained for the PSO and FA while the GA have slightly deviated values compared with the RSM. The optimal parameters obtained by the RSM, PSO and FA were tested for validation and yielded biodiesel of 96.40%. The percentage error between the predicted (96.35%) and actual (96.40%) values of the biodiesel yield was 0.05%, which is a low value

Table 8Comparative analysis of fresh, degenerated and regenerated Cat₅₀₀.

Cat ₅₀₀	Crystallite size (nm)	BET surface area (m ² /g)	Basic strength (mmol/g)	Reference
Fresh	32.79	94.48	4.92 ± 0.03	Ajala et al. [3]
De-activated	38.22	53.75	10.14 ± 0.02	This study
Regenerated	31.85	78.42	6.37 ± 0.03	This study

and an indication that the model developed by the RSM was accurate and confirmed by the PSO and FA. The percentage error obtained for the GA was 0.34% which is also a low value. Since the percentage error is <0.5%, it is evident that there is an agreement between the actual and predicted values of the biodiesel yield using RSM, PSO, FA and GA. These results revealed that the parameters investigated in this study were effective for biodiesel production using waste lard in the presence of Cat₅₀₀. This justifies that the choice of optimal parameters for maximum biodiesel yield is important to optimise the process to reduce the cost of production.

3.5. Reusability, deactivation and regeneration studies of the best-performing CATs (Cat₅₀₀)

Fig. 13 shows the reusability of the Cat₅₀₀ for biodiesel production over nine cycles and its re-usability after the regeneration of the spent catalyst. The performance of the catalyst is similar to the report of Ajala et al. [3], however, the yield of the first cycle was 96.40%, a value higher than 94.8% in the literature. The higher value is due to the implementation of the optimal parameters in the reusability study.

It can be seen from Fig. 13 that the activity of the Cat₅₀₀ decreased from 96.40% to 75.30% after nine cycles, which represents a loss of 21.10% biodiesel yield. Although the catalyst performed excellently at the initial cycles of the investigation, the loss of the activity at the 9th cycle is very huge which is due to the deactivation of the catalyst. Another factor that could cause the loss of the activity may be the blockage of active sites by the reactants and products, thereby, reduces the mass transfer of triglycerides into the catalyst's pores [40]. It could also be due to partial deactivation and structural changes of the catalyst as a result of water in the reaction mixture [3].

The spent Cat₅₀₀ was investigated for its re-activation after nine cycles of its usage for biodiesel production. Fig. 14a shows XRD pattern of fresh Cat₅₀₀ which revealed sharp reflections at different diffraction peaks of $2\alpha = 22.9, 25.4, 28.7, 31.2, 32.0, 36.4, 38.7, 40.8, 41.4, 47.4, 52.9, 71.5$ and 74.0 as reported by Ajala et al. [3]. The XRD pattern of

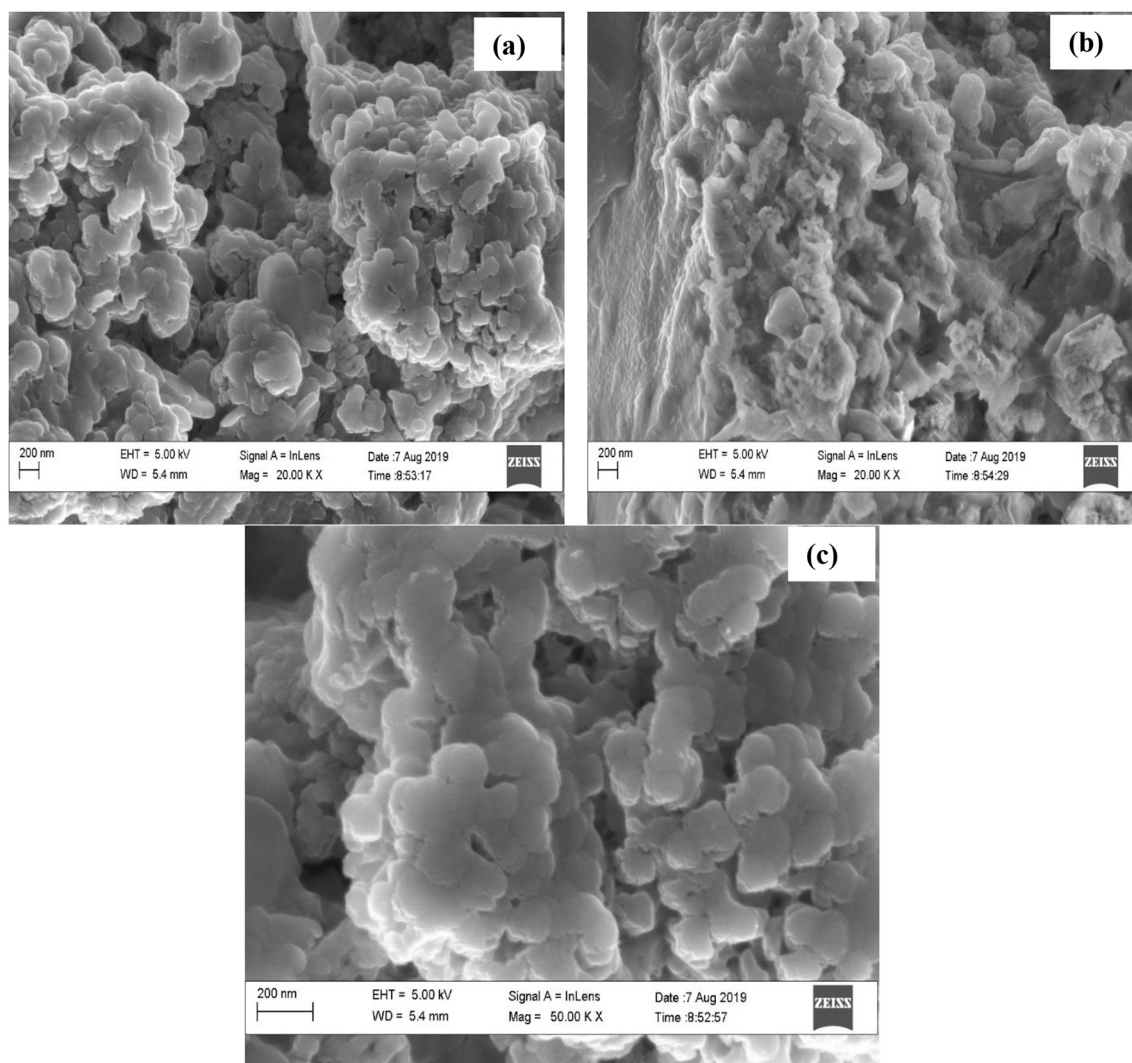


Fig. 15. HRSEM of Cat₅₀₀ when (a) fresh, (b) degenerated and (c) regenerated after nine cycles of biodiesel production.

the fresh Cat₅₀₀ shows some active compounds suitable for transesterification which includes CaSO₄ (JCPDS No.: 00-037-1496) and Ca_{2.62}Al_{9.8}Si_{26.2}O₇₂H_{4.56} (JCPDS No.: 01-075-1518). Fig. 14b shows XRD pattern of degenerated Cat₅₀₀ with diffraction peaks of $2\alpha = 22.9, 25.4, 31.4, 38.6, 40.8, 45.5, 48.7, 52.3, 59.0, 66.9$ and 71.5 . The XRD pattern of the degenerated Cat₅₀₀ shows a significant decrease in the active compounds compared to the fresh Cat₅₀₀. The relative shorter intensity of the peaks of the degenerated Cat₅₀₀ shows a little lesser crystallinity compared to the fresh Cat₅₀₀. Some of the peaks that disappeared from the degenerated Cat₅₀₀ was due to obstruction of the catalyst surface by contaminants which leads to the low accessibility of the active sites to the reactants [44]. Fig. 14c presents XRD spectra of regenerated Cat₅₀₀, showing diffraction peaks at $2\alpha = 22.9, 25.5, 31.4, 36.3, 38.7, 40.9, 43.4, 45.5, 48.7, 52.3, 55.8, 57.8, 59.0, 62.3$ and 74.3 . The peaks observed from the figure is similar to that of the fresh Cat₅₀₀, even in term of the intensity.

Table 8 shows the crystallite size, surface area and basic strength of the fresh, degenerated and re-activated Cat₅₀₀. The crystallite size obtained was 32.79 nm (fresh), 38.22 nm (degenerated) and 31.85 nm (re-activated). Also, the BET recorded were 94.48 m²/g (fresh), 53.73 m²/g (degenerated) and 78.42 m²/g (re-activated) as well as the basic strength of 4.92 ± 0.03 mmol/g (fresh), 10.14 ± 0.02 mmol/g (degenerated) and 6.37 ± 0.03 mmol/g (re-activated). The results showed that the re-activation by washing with n-hexane, oven-dried at 100 °C for 1 h and calcined at 500 °C were effective to regenerate the catalyst for subsequent use.

According to Wahyudi et al. [44], the organic compounds on the catalyst surface tend to convert into carbon and still attach to the surface, which would reduce the activity of the catalyst. The washing of the catalyst by n-hexane would clean up the surface from the contaminants. While the calcination would activate the active sites of the catalyst and improved the crystallinity, surface area and basic strength of the catalyst. The re-activated Cat₅₀₀ showed higher basicity compared to the degenerated which means an improved activity for biodiesel production. Since the basic strength in catalyst deprotonates methanol into methoxide ion ($-\text{OCH}_3$) to reacts with triglyceride to form biodiesel [44].

The HRSEM image of Cat₅₀₀ when fresh, degenerated and regenerated is illustrated in Fig. 15(a–c) respectively. As it can be seen from Fig. 15a, the morphology of fresh Cat₅₀₀ shows spongy and porous structures with a regular geometric shape that can be characterised as spheres with $50 \geq \text{diameters} \leq 200$ nm [3]. Also, the micrograph of the fresh catalyst exhibited better porosity which signifies the effects of calcination and sulphonation processes. However, after the deactivation, the HRSEM image of Cat₅₀₀ changed to a more condensed agglomerate with irregular shapes as shown in Fig. 15b. The change in the structure could be due to the blockage of active sites by contaminants. This indicates low adsorption capability as the space between the agglomerates reduces and can significantly encourage the loss of catalytic activity. The HRSEM image of Cat₅₀₀ after re-activation is shown in Fig. 15c.

The figure revealed that the morphology of the re-activated Cat₅₀₀ improved and compared well with that of the fresh Cat₅₀₀. This shows that the treatments exposed the active sites which can easily be accessed by the reactants during the reaction [44]. The result of the reusability of the re-activated Cat₅₀₀ as shown in Fig. 13 indicated the increase in biodiesel yield from 75.3% (degenerated) to 92.8% (regenerated). This confirms that the catalyst compound of CaO–Al₂O₃–SiO₂–CaSO₄ produced from waste carbide at a calcination temperature of 500 °C and sulphonation can be regenerated after nine cycles and still perform efficiently for biodiesel production.

4. Conclusion

In this study, optimisation of biodiesel production using waste lard in the presence of CaO–Al₂O₃–SiO₂–CaSO₄-based solid catalysts by hybridisation of RSM and meta-heuristic algorithms such as GA, PSO and FA

was investigated. The parameters that significantly affected the biodiesel yield to obtain the maximum output of 96.35% are MeOH: oil molar ratio of 12:1, reaction temperature of 59.97 °C, reaction time of 1 h, catalyst quantity of 5% (w/w) and catalyst type of Cat₅₀₀. The performance of the meta-heuristic algorithms based on the optimisation outputs (GA = 96.07%, PSO = 96.35% and FA = 96.35%) compared well with that of the RSM (96.35%) which justified the application of the algorithms in biodiesel production. The validation study using the optimal parameters gave a percentage error of 0.05% between the predicted and actual values of the biodiesel yield. This confirmed that the model developed by the RSM and simulated by the meta-heuristic algorithms was accurate to predict the optimum biodiesel yield from the waste lard in the presence of Cat₅₀₀. However, a different curve-fitting model equation or more advanced modelling techniques such as Artificial Neural Network (ANN) or Adaptive Neuro-Fuzzy Inference System (ANFIS) can be employed in subsequent studies to better capture the intrinsic relationship of variables in the model and can offer better predictability performance.

It could be noted that the performance of the optimisation algorithms on the optimal variables of time and catalyst quantity is at the variable lower bound threshold, this effect is due to rigid constraints of the optimisation setup. The proxy quadratic developed model should be robust enough to infer accurate solutions of a data point within and outside the boundaries of the experimental variables. This study showed the usefulness of heuristic algorithms in providing a good enough solution and demonstrated the ability of nature-inspired algorithms in solving complex systems of models. This study concludes that the catalyst developed from the CCR at calcination temperature of 500 °C and sulphonation processes can be used over nine cycles and can also be regenerated thereafter for efficient biodiesel production.

Declaration of Competing Interest

All the authors have no conflict of interest whatsoever.

References

- [1] E.O. Ajala, F. Aberuagba, A.M. Olaniyan, M.A. Ajala, M.O. Sunmonu, Optimization of a two-stage process for biodiesel production from shea butter using response surface methodology, Egypt. J. Pet. 26 (4) (2017), <https://doi.org/10.1016/j.ejpe.2016.11.005>.
- [2] E.O. Ajala, M.A. Ajala, O.B. Okedere, F. Aberuagba, V. Awoyemi, Synthesis of solid catalyst from natural calcite for biodiesel production: a case study of palm kernel oil in an optimization study using definitive screening design, Biofuels (2018), <https://doi.org/10.1080/17597269.2018.1532752>.
- [3] E.O. Ajala, M.A. Ajala, A.O. Ajao, H.B. Saka, A.C. Oladipo, Calcium-carbide residue: a precursor for the synthesis of CaO–Al₂O₃–SiO₂–CaSO₄ solid acid catalyst for biodiesel production using waste lard, Chem. Eng. J. Adv. 4 (August) (2020) 100033, <https://doi.org/10.1016/j.cej.2020.100033>.
- [4] E.O. Ajala, M.A. Ajala, I.K. Ayinla, A.D. Sonusi, S.E. Fanodun, Nano-synthesis of solid acid catalysts from waste-iron-filling for biodiesel production using high free fatty acid waste cooking oil, Sci. Rep. 10 (13256) (2020) 1–21, <https://doi.org/10.1038/s41598-020-70025-x>.
- [5] E.O. Ajala, M.A. Ajala, T.E. Odetoeye, F.A. Aderibigbe, O.H. Osanyinpeju, M. A. Ayanshola, Thermal modification of chicken eggshell as heterogeneous catalyst for palm kernel biodiesel production in an optimization process, Biomass Convers. Biorefinery (2020) 1–19, <https://doi.org/10.1007/s13399-020-00636-x>.
- [6] E.O. Ajala, M.A. Ajala, T.E. Odetoeye, A.T. Okunlola, Synthesis of solid catalyst from dolomite for biodiesel production using palm kernel oil in an optimization process by definitive screening design, Braz. J. Chem. Eng. 36 (02) (2019) 979–994.
- [7] S. Basumatary, B. Nath, B. Das, P. Kalita, B. Basumatary, Utilization of renewable and sustainable basic heterogeneous catalyst from *Heteropanax fragrans* (Kesseru) for effective synthesis of biodiesel from *Jatropha curcas* oil, Fuel 286 (P1) (2021) 119357, <https://doi.org/10.1016/j.fuel.2020.119357>.
- [8] M.C. Bobadilla, R.F. Martínez, R.L. Lorza, F.S. Gómez, E.P.V. González, Optimizing biodiesel production from waste cooking oil using genetic algorithm-based support vector machines, Energies 11 (2995) (2018) 1–19, <https://doi.org/10.3390/en1112995>.
- [9] L. Buchori, D.D. Anggoro, F. Tsaniya, M.B. Elyasa, E. Novriyonyo, The effect of catalyst loading on biodiesel production from lard, in: The 3rd International Conference of Chemical and Materials Engineering Vol. 1295, 2019, pp. 1–4, <https://doi.org/10.1088/1742-6596/1295/1/012005>.
- [10] H. Dagne, R. Karthikeyan, S. Feleke, Waste to energy: response surface methodology for optimization of biodiesel production from leather fleshing waste, J. Energy (2019) 1–19, <https://doi.org/10.1155/2019/7329269>.

- [11] S.K. Dinkar, K. Deep, Process optimization of biodiesel production using antlion optimizer, *J. Inf. Optim. Sci.* 2667 (2019) 1–15, <https://doi.org/10.1080/02522667.2018.1491821>.
- [12] T. Dokeroglu, E. Sevinc, T. Kucukilymaz, A. Cosar, A survey on new generation metaheuristic algorithms, *Comput. Ind. Eng.* 137 (September) (2019), <https://doi.org/10.1016/j.cie.2019.106040>.
- [13] A.B. Ehinmowo, O.A. Ohiro, O. Olamigoke, O. Adeyanju, Inferential reservoir modelling and history matching optimization using different data-driven techniques, *J. Eng. Res.* 24 (2) (2020) 91–110.
- [14] Adegboyega B. Ehinmowo, O.O. Ariyo, O.A. Ohiro, O.T. Fajemidude, K.K. Salam, An improved data-driven model for the prediction of minimum transport condition for sand transport in multiphase flow systems, *FUOYE J. Eng. Technol.* 6 (1) (2021) 103–107, <https://doi.org/10.46792/fuoyejt.v6i1.618>.
- [15] C.B. Ezekannagha, C.N. Ude, O.D. Onukwuli, Optimization of the methanolysis of lard oil in the production of biodiesel with response surface methodology, *Egypt. J. Pet.* (2017), <https://doi.org/10.1016/j.ejpe.2016.12.004>.
- [16] O.A. Fadara, O. Falowo, T. Ojumu, E. Betiku, Process optimization of microwave irradiation-aided transesterification of Kariya seed oil by Taguchi orthogonal array: pawpaw trunk as a novel biocatalyst, *Biofuels Bioprod. Bioref.* (2021) 1–15, <https://doi.org/10.1002/bbb.2193>.
- [17] I.M.R. Fattah, H.C. Ong, T.M.I. Mahlia, M. Mofijur, A.S. Silitonga, State of the art of catalysts for biodiesel production, *Front. Energy Res.* 8 (June) (2020) 1–17, <https://doi.org/10.3389/fenrg.2020.00101>.
- [18] J. Gardy, M. Rehan, A. Hassanpour, X. Lai, A. Nizami, Advances in nano-catalysts based biodiesel production from non-food feedstocks, *J. Environ. Manag.* 249 (December 2018) (2019) 109316, <https://doi.org/10.1016/j.jenvman.2019.109316>.
- [19] S.N. Gebremariam, J.M. Marchetti, F. Science, The effect of economic variables on a bio-refinery for biodiesel production using calcium oxide catalyst Shemelis, *Biofuels Bioprod. Bioref.* 13 (2019) 1333–1346, <https://doi.org/10.1002/bbb.2039>.
- [20] M. Helmi, K. Tahvildari, A. Hemmati, P. Aberoomand, Phosphomolybdic acid/graphene oxide as a novel green catalyst using for biodiesel production from waste cooking oil via electrolysis method: optimization using with response surface methodology (RSM), *Fuel* (October) (2020) 119528, <https://doi.org/10.1016/j.fuel.2020.119528>.
- [21] J.H. Holland, Genetic algorithms, *Sci. Am.* 267 (1) (1992) 66–73. <http://www.jstor.org/stable/24939139>.
- [22] N.B. Ishola, A.A. Okeleye, A.S. Osunleke, E. Betiku, Process modelling and optimization of sorrel biodiesel synthesis using barium hydroxide as a base heterogeneous catalyst: an appraisal of response surface methodology, neural network and neuro-fuzzy system, *Neural Comput. & Applic.* 7 (2019), <https://doi.org/10.1007/s00521-018-03989-7>.
- [23] G. Jeong, H. Yang, D. Park, Optimization of transesterification of an animal fat ester using response surface methodology, *Bioresour. Technol.* 100 (2009) 25–30, <https://doi.org/10.1016/j.biortech.2008.05.011>.
- [24] M.A. Kadi, N. Akkouche, S. Awad, K. Loubar, M. Tazerout, Kinetic study of transesterification using particle swarm optimization method, *Heliyon* 5 (February) (2019), e02146, <https://doi.org/10.1016/j.heliyon.2019.e02146>.
- [25] S. Kant Bhatia, R. Kant Bhatia, J.M. Jeon, A. Pugazhendhi, M. Kumar Awasthi, D. Kumar, Y.H. Yang, An overview on advancements in biobased transesterification methods for biodiesel production: oil resources, extraction, biocatalysts, and process intensification technologies, *Fuel* 285 (2021) 119117, <https://doi.org/10.1016/j.fuel.2020.119117>.
- [26] M. Karimi, B. Jenkins, P. Stroeve, Multi-objective optimization of transesterification in biodiesel production catalyzed by immobilized lipase, *Biofuels Bioprod. Bioref.* 10 (6) (2016) 804–818, <https://doi.org/10.1002/bbb.1706>.
- [27] C. Komintarachat, S. Chuepeng, Solid acid catalyst for biodiesel production from waste used cooking oils, *Ind. Eng. Chem. Res.* 48 (2009) 9350–9353.
- [28] I.B. Laskar, K. Rajkumari, R. Gupta, S. Chatterjee, B. Paul, L. Rokhum, Waste snail shell derived heterogeneous catalyst for biodiesel production by the transesterification of soybean oil, *R. Soc. Chem. Adv.* 8 (2018) 20131–20142, <https://doi.org/10.1039/c8ra02397b>.
- [29] C.S. Latchubugata, R.V. Kondapaneni, K.K. Patluri, U. Virendra, S. Vedantam, Kinetics and optimization studies using response surface methodology in biodiesel production using heterogeneous catalyst, *Chem. Eng. Res. Des.* 135 (2018) 129–139, <https://doi.org/10.1016/j.cherd.2018.05.022>.
- [30] T.W. Liao, G. Li, Metaheuristic-based inverse design of materials – a survey, *J. Mater.* 6 (2) (2020) 414–430, <https://doi.org/10.1016/j.jmat.2020.02.011>.
- [31] A.M. Nassef, E.T. Sayed, H. Rezk, M. Ali, C. Rodriguez, A.G. Olabi, Environmental effects fuzzy-modeling with particle swarm optimization for enhancing the production of biodiesel from microalga fuzzy-modeling with particle swarm optimization for enhancing the production of biodiesel from microalga, *Energy Sour. A Recov. Utiliz. Environ. Eff.* 00 (00) (2018) 1–10, <https://doi.org/10.1080/15567036.2018.1549171>.
- [32] T.E. Odetoeye, J.O. Agu, E.O. Ajala, Biodiesel production from poultry wastes: waste chicken fat and eggshell, *J. Environ. Chem. Eng.* (May) (2021) 105654, <https://doi.org/10.1016/j.jece.2021.105654>.
- [33] M.Y. Ong, N. Saifuddin, K. Fitranto, M.H.R. Raja, H.S. Abd, Modelling and optimization of microwave-based bio-jet fuel from coconut oil: investigation of Response Surface Methodology (RSM) and Artificial Neural Network Methodology (ANN), *Energies* 14 (295) (2021) 1–17, <https://doi.org/10.3390/en14020295>.
- [34] A. Prakasham, N. Savarimuthu, Metaheuristic algorithms and probabilistic behaviour: a comprehensive analysis of Ant Colony Optimization and its variants, *Artif. Intell. Rev.* 45 (1) (2016) 97–130, <https://doi.org/10.1007/s10462-015-9441-y>.
- [35] T. Qu, S. Niu, X. Zhang, K. Han, C. Lu, Preparation of calcium modified Zn-Ce/Al₂O₃ heterogeneous catalyst for biodiesel production through transesterification of palm oil with methanol optimized by response surface methodology, *Fuel* 284 (August 2020) (2021) 118986, <https://doi.org/10.1016/j.fuel.2020.118986>.
- [36] K. Ramachandran, P. Sivakumar, T. Suganya, S. Renganathan, Production of biodiesel from mixed waste vegetable oil using an aluminium hydrogen sulphate as a heterogeneous acid catalyst, *Bioresour. Technol.* 102 (15) (2011) 7289–7293, <https://doi.org/10.1016/j.biortech.2011.04.100>.
- [37] M. Reza, S. Mokhtari, M. Saadat, Modelling and optimization of biodiesel production from microalgae in a batch reactor, *Fuel* 280 (May) (2020) 118578, <https://doi.org/10.1016/j.fuel.2020.118578>.
- [38] W. Roschat, T. Siritanon, B. Yoosuk, V. Promarak, Biodiesel production from palm oil using hydrated lime-derived CaO as a low cost basic heterogeneous catalyst, *Energy Convers. Manag.* 108 (2016) 459–467, <https://doi.org/10.1016/j.enconman.2015.11.036>.
- [39] O.D. Samuel, M.O. Okwu, S.T. Amosun, T. Nath, S.A. Afolalu, Production of fatty acid ethyl esters from rubber seed oil in hydrodynamic cavitation reactor: study of reaction parameters and some fuel properties, *Ind. Crop. Prod.* 141 (January) (2019) 111658, <https://doi.org/10.1016/j.indcrop.2019.111658>.
- [40] R. Singh, A. Kumar, Y.C. Sharma, Biodiesel Production from Microalgal Oil Using Barium – Calcium – Zinc Mixed Oxide Base Catalyst: Optimization and Kinetic Studies, 2019, <https://doi.org/10.1021/acs.energyfuels.8b03461>.
- [41] F.E. Soetaredjo, A. Ayucitra, S. Ismadji, A.L. Maukar, KOH/bentonite catalysts for transesterification of palm oil to biodiesel, *Appl. Clay Sci.* 53 (2011) 341–346, <https://doi.org/10.1016/j.clay.2010.12.018>.
- [42] T. Umegaki, Y. Watanabe, N. Nukui, K. Omata, M. Yamada, Optimization of catalyst for methanol synthesis by a combinatorial approach using a parallel activity test and genetic algorithm assisted by a neural network, *Energy Fuel* 17 (4) (2003) 850–856, <https://doi.org/10.1021/ef020241n>.
- [43] M. Valizadeh, S. Syafie, I.S. Ahamad, Multi-objective particle swarm optimization for optimal planning of biodiesel supply chain in Malaysia, *Recent Adv. Soft Comput. Data Min.* (2014) 293–302, https://doi.org/10.1007/978-3-319-07692-8_28.
- [44] A. Wahyudi, W. Kurniawan, H. Hinode, Study on Deactivation and Regeneration of Modified Red Mud Catalyst Used in Biodiesel Production, 2017, pp. 247–258, <https://doi.org/10.4236/gsc.2017.74019>.
- [45] D. Wang, D. Tan, L. Liu, Particle swarm optimization algorithm: an overview, *Soft. Comput.* 22 (2) (2018) 387–408, <https://doi.org/10.1007/s00500-016-2474-6>.
- [46] X. Yang, Nature-Inspired Metaheuristic Algorithms: Success and New Challenges, 2012, <https://doi.org/10.4172/2324-9307.1000e101>.
- [47] A.S. Yusuff, J.O. Owolabi, Synthesis and characterization of alumina supported coconut chaff catalyst for biodiesel production from waste frying oil, *S. Afr. J. Chem. Eng.* 30 (July) (2019) 42–49, <https://doi.org/10.1016/j.sajce.2019.09.001>.
- [48] X.S. Yang, Firefly algorithm, stochastic test functions, and design optimization, *Int. J. of Bio-Inspired Comput.* 2 (2010) 78–84, <https://doi.org/10.1504/IJBIC.2010.032124>.