ISBN 978-989-9121-37-9
38th BARCELONA International Conference on "Chemical, Biological and Environmental Sciences" (BCBES-24)
April 24-26, 2024 Barcelona (Spain)

Cleaner Biodiesel Production Technology from Hybrid Feedstock Via Transesterification Process Optimization

Anietie Etim[1], and Paul Musonge[1,2]

[1]Department of Chemical Engineering, Institute of System Science, Durban University of Technology, Steve Biko Campus, Durban, 4001, South Africa
[2]Faculty of Engineering, Mangosuthu University of Technology, Umlazi, South Africa

***Abstract*:** *Increase in energy demand, global warming and environmental threat has incited the global concern on the consequences of fossil fuels over-exploitation and depletion. The thrust into new and hybrid renewable and sustainable energy supply is therefore a promising step to address this situation. The commercialization of biodiesel as an indigenous fuel is impeded by the lack of readily available feedstock, as different feedstock kinds with differing qualities might be found in different places. This study investigates the possibility of green based heterogeneous catalyst obtained from the mixture of banana and avocado waste fruit peels in transesterification of ternary-hybrid oil of used frying oil, marula and linseed oil (UFO/MSO/LO, 3:1:1). The characterization of the calcined catalyst at 600 °C using EDS, and SEM, indicated that it exhibits high amount of potassium. The optimization of the important variables (such as catalyst amount, molar ratio of methanol to oil, and reaction time) of the process was done using the central composite design (CCD). The ideal conditions instituted by the CCD were the process reaction time of 50 min, molar ratio (methanol/hybrid oil) of 14.7:1, and catalyst amount of 2.5 wt% with the experimental yield of 98.7 %. The significance of the generated model was ascertained using an analysis of variance (ANOVA) at 95% confidence level with the probability value (α = 0.05) and the determination coefficient (R^2 = 0.9899). The fuel characteristics of the biodiesel obtained were all within gratifying norms as specified by ASTM D6751, and EN 14214, SANS 1935:2011. The study demonstrates that feedstock hybridization is a viable strategy for addressing the challenges of feedstock supplementation and exploration for biodiesel development.*

Keywords: *Biodiesel, Feedstock Hybridisation, Heterogeneous Catalysts, Transesterification*

1. Introduction

The alarming situation over energy demand, environmental pollution and climate change remain an urgent global stressing challenge, as the consumption of global energy is projected to exceed existing levels in the coming decades. The need to synergise renewable energy with the fossils or even outright displacement as the crisis in Eastern Europe is escalating is no longer to be taken for granted. Fossil fuels persist as the prime source of energy despite significant advances in alternative energy supply. The direct effects of fossil fuel combustion are linked to GHG emissions and climate change [1]. Its non-renewable nature and over-exploitation have wreaked havoc on the environment, triggering air pollution, global warming, ozone layer dwindling, and acid rain. When compared to diesel, biodiesel reduces greenhouse gas emissions by 41%, as well as some other key air pollutants, with negligible effects on the health of both human and environment [2]. Feedstock challenges (both in quality and quantity) is one of the biggest stressing issues encountered by the bio-refinery industries as different feedstock kinds with differing compositions can be found in various locations. Therefore, hybridization of feedstock of biodiesel production is a step in the right direction to ensuring quality feedstock and constant supply.

Biodiesel is widely produced by a simple method of transesterification, involving the reaction of triglyceride over a short chain alcohol (mostly methanol) alongside an effective catalyst [3]. Owing to some disadvantages

that links with the traditional catalysts such as separation and recovering difficulties, equipment corrosion, low yield and increases in the overall cost of production, heterogeneous biomass catalysts can proficiently be utilized to solve these problems in biodiesel production [1]. The reusability potential in several production without any major loss in catalytic activity is another advantage of using heterogeneous catalysts, thus making the production process more economical.

The recent study explores the potential of a green heterogeneous catalyst developed from the combination of two agricultural waste materials: banana and avocado peels, in the transesterification of ternary hybrid oil consisting of used frying oil, marula and linseed oil in the volumetric proportion of 3:1:1. Based on our knowledge, these combinations of oil and catalyst materials have not been investigated or reported. The transesterification of reaction parameters was optimized by varying the catalyst concentration, reaction duration and the ratio of methanol-to-oil using central composite design (CCD). The analytical technique of Electron-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) were used to assess the characteristics of the combined calcined banana-avocado peels ash (CBAP). The fuel characteristics of the resulting ternary hybrid oil biodiesel (THOB) were ascertained and compared with the standard criteria of ASTM D6751 and EN 14214.

2. Experimental

2.1. Materials and Method Submission

Used frying oil (UFO) was acquired from the University of Technology, Durban, South Africa, Steve Biko campus student eateries. The crude marula seed oil (MSO) and linseed oil together with all the analytical grade chemicals and reagents used in this experiment was supplied by Laboquip laboratory suppliers, Durban, South Africa.

2.2. Preparation and Characterization of the Catalyst

Fruit peels from bananas and avocados were utilized to make the catalyst for the ternary oil conversion in this investigation. The two materials were cleaned with water and left overnight in an oven set to 110 ^{o}C. The dried materials were ground and sieved individually through a 0.8 mm mesh sieve to produce a powder. The grams of each material's sieved powder were measured and combined in equal proportions, and then calcined at 600 ^{o}C for 3h in a Muffle furnace. The resulting biochar was then preserved for later use in cork tubes. To ascertain the surface structure and elemental composition of the CBAP catalyst, AURIGA (Zeiss Germany) fitted to the energy dispersive X-ray detector was used to perform SEM and EDS analysis on the produced catalyst.

2.3. Ternary Hybrid Oil Preparation

The UFO obtained was filtered to remove impurities and then mixed with marula and linseed oils in the ratio of 3:1:1 vol %. The hybrid was heated at 60 ^{o}C and then agitate for 10 min to obtain a homogenous solution. The blended oil was left to cool before subjected to physiochemical properties determination, which was performed in accordance with the AOAC standard methods.

2.4. The Transesterification of Reaction of the Ternary-Hybrid Oil

The transesterification was performed by heating the oil to a temperature of 60 ^{o}C and then followed by adding a calculated amount of methanol and catalyst and agitate vigorously at 450 rpm. The experiment was allowed to last within a stipulated time as established by CCD design matric in Table 3. The resultant mixture at the end of the reaction was centrifuged to separate the catalyst and the remaining liquid mixture were transferred to the separating funnel to remove the glycerol, while the produced biodiesel was further processed by rinsing with the distilled warm water and drying at 100 ^{o}C. The biodiesel yield(s) obtained was computed using Eq. 1.

$$FAME\ yield\ (\%) = \frac{weight\ of\ THOB\ produced\ (g)}{weight\ of\ THO\ (g)} \times 100 \quad (1)$$

2.5. Empirical Design and Statistical Analysis

The response surface approach was used to investigate the interaction impacts of transesterification reaction variables, such as the methanol/hybrid oil ratio (6–14), catalyst amount (1.5–5.5), and process reaction duration (40–80), while maintaining constant stirring speed and temperature at 60 ^{o}C and 450 rpm, respectively [4]-[5]. To maximize the biodiesel yield, a five-level central composite design (CCD) with three components was utilized to optimize the process variables. Table 1 displays the range and levels of the independent variables for the ternary hybrid oil transesterification. Using this, 20 transesterification experiments were created, as indicated in Table 2, comprising 23 factorial experiments, 6 axial points, and 6 duplicates at the centre point for the evaluation of pure error. For every independent factor, the software yielded the two extreme alpha values: the lowest (-α) and the highest (+α). The distance between the central and axial point is represented by α = 2n/4, where n is the number of components. Eq. (2) gives the polynomial second order equation defining the link between the response variables (yields) and the input factors.

$$Y = \mathrm{F}_0 + \sum_{i=1}^{n} \mathrm{F}_i X_i + \sum_{i=i}^{n} \mathrm{F}_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} \mathrm{F}_{ij} X_i X_j + \mathrm{z} \quad (2)$$

Where Xi, Xj are the individual terms for the experimental variation, z is the random error, F_0 is the intercept, Fi is the first order coefficient, Fii is the coefficient of interaction, and Y is the biodiesel yield %. The yield in terms of the actual and anticipated values of the independent variables was calculated using Eq. (2) to fit the data.

TABLE I: CCD transesterification factors and levels considered for THOB production.

Factors	**Symbols**	**Coded factor levels**				
		-α	**-1**	**0**	**1**	**+α**
Catalyst loading (wt%)	B	1.5	2.5	3.5	4.5	5.5
Methanol/oil molar ratio	A	6:1	8:1	10:1	12:1	14:1
Reaction time (min)	C	40	50	60	70	80

TABLE II: Experimental transesterification variable conditions and THOB yields

Std order	**Run**	**Met/oil**	**Catalyst Loading (wt%)**	**Time (min)**	**Actual FAME value (%)**	**Predicted value (%)**
16	1	10	3.5	60	90.53	90.80
9	2	6	3.5	60	95.20	95.19
6	3	12	2.5	70	96.33	96.26
17	4	10	3.5	60	90.86	90.80
4	5	12	4.5	50	88.35	88.85
19	6	10	3.5	60	91.10	90.80
13	7	10	3.5	40	92.50	92.18
11	8	10	1.5	60	97.95	98.20
10	9	14	3.5	60	91.50	91.46
12	10	10	5.5	60	92.40	92.10
14	11	10	3.5	80	91.10	91.37
15	12	10	3.5	60	90.95	90.80
7	13	8	4.5	70	90.90	91.08
1	14	8	2.5	50	94.65	94.86
5	15	8	2.5	70	93.80	93.36
2	16	12	2.5	50	92.80	92.67
3	17	8	4.5	50	95.35	95.48
20	18	10	3.5	60	90.83	90.80
18	19	10	3.5	60	90.60	90.80
8	20	12	4.5	70	89.70	89.54

3. Result and Discussion

3.1. Characterization of CBAP Catalyst

The elemental compositions of the prepared banana-avocado-peels catalyst were ascertained by EDS analysis, and the results are presented in Table 3. It is demonstrated that K predominates in the calcined peel ash. According to earlier reports, K performs a vital role in the catalytic activity of the majority of agricultural waste catalysts, including pawpaw peels, cocoa pod husk, and plantain peels [7]-[9]. Cl, P, and Si among other elements are also present in substantial amounts. Fig. 1 displays the SEM image of the developed catalyst, revealing the porous characteristics of the ash particles. Agglomeration and sintering of tiny aggregates of the particles occurred as the outcome of high treatment of the peel during the process of calcination. The fine crystal powder that has formed after calcination suggests good propensity of catalytic activity of the produced catalyst [10]

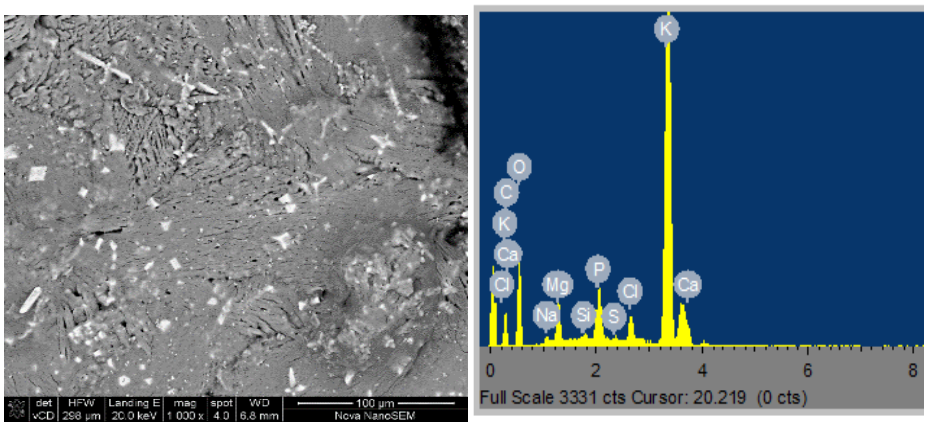

Fig. 1: SEM image and EDX plot of CBAP catalyst.

TABLE III: Elemental composition of CBAP catalyst

Element	O	Mg	Si	P	S	Cl	K	Fe
Mass fractions (%)	35.47	0.4	0.86	1.17	0.28	7.33	54.23	0.27

3.2. Statistical and Regression Analysis

The numerical value of coefficients derived from each process variable at a 95% confidence level were illustrated in terms of the mathematical equation given in Eq. 3, in order to forecast the yield of biodiesel obtained from the ternary hybrid oil (THO). The model accuracy in predicting biodiesel yield is further demonstrated by the plot of projected biodiesel yields against the empirical yield in Figure 2, which shows that the model's predicted responses correspond with the empirical responses.

$$HOB\ Yield\ (\%) = 90.80 - 0.9325A - 1.52B - 0.2012C - 1.11AB + 1.27AC - 0.7225BC + 0.6301A^2 + 1.09B^2 + 0.2426C^2 \quad (3)$$

The obtained results following the empirical matrix established by CCD design are presented in Table 2. The ANOVA for THOB production was indicated by the low P-value (0.05) and high F-value of each process variable input. The model parameters were statistically calculated as the coefficient of determination R^2 (0.9899), adjusted R^2 (0.9809) and predicted R^2 (0.9331). The generated model exhibits good agreement between the projected and actual R^2 values, with an acceptable discrepancy of 0.009, which is smaller than the limit permissible difference of 0.2. The low values of the experimental data deviation standard (0.33) and coefficient of variance (0.36%) were in support of the model's applicability.

3.3. Graphical Interaction of Operational Parameters on the Hybrid Oil Biodiesel Yield

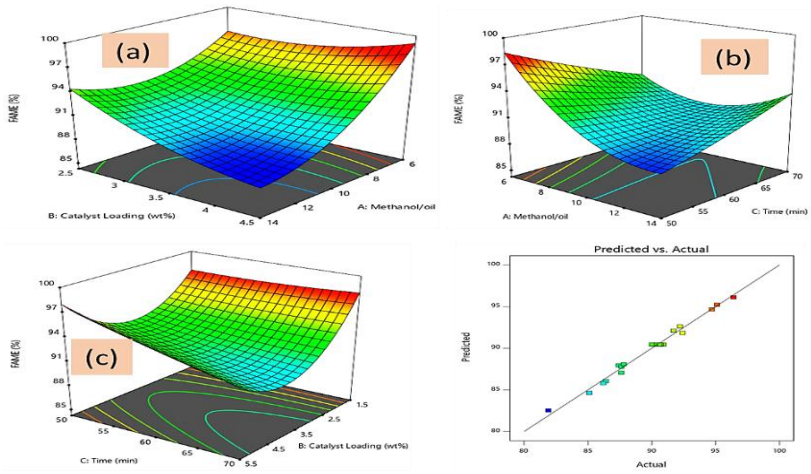

Fig. 2 (a-c): Surface plot explaining the interaction effects of the parameters with THOB yield

Fig. 2a illustrates the strong and significant relationship between catalyst loading and methanol/THO on THOB. The lowest catalyst loading, and methanol/hybrid oil ratio resulted in the highest THOB production. The mixing and mass transfer process will become more challenging if the two parameters are increased above their optimal values. This will cause soap formation and a decrease in yield. Fig. 2b shows the impact of reaction time and the methanol/oil molar ratio on THOB yield. The figure illustrates that both parameters had a substantial interaction effect on the yield. THOB yield was favoured at increase reaction time and lower ratio of methanol/oil. Fig. 2c illustrate the interaction of reaction time and catalyst loading effect on THOB yield. The THOB yield was observed to be dramatically increase at lower catalyst loading and reaction time. Similar observations have been made in literature on the significant impact of the characteristics examined in this study [4], [11]. The CCD established optimal condition for this study was methanol/hybrid oil ratio of 4.7:1, catalyst loading of 2.5 wt% and reaction time of 50 min. This was further validated with triplicate experiments. The average yield achieved was 98.70 wt%. Thus, the difference between the projected and observed yield values was less than 2%, which indicate that the model is accurate and adaptable.

4. Reusability Test of the Catalyst

One key economic aspect of heterogeneous catalyst is its capacity to be reused in successive transesterification experiments. CBAP reusability test was carried out under optimum condition. The spent catalyst after each subsequent experiment was extracted from the mixture by centrifugation, cleaned with hexane, and dried at 120 ^{o}C in an oven. The yield of the THOB after 4th cycle was 92.05%, which demonstrate the good activity of the developed catalyst after several recycling. Thus, the yield(s) of the biodiesel declined following the increasing number of catalysts recycling. This may be attributed to the loss of catalyst during the recovery process and leaching of the active ingredient into the reaction mixture.

5. Characterization of the Produced Biodiesel

The biodiesel produced in this study was evaluated and its quality was juxtaposed with EN 14214 and ASTM D6751 limit standards. Important characteristics of biodiesel have been identified and are shown in Table 4, which include density, acid value, kinematic viscosity, cetane number, flash point, and calorific value. Density is one of key fuel attributes that influences the CIE's functional efficiency of fuel. The EN14214 standard specifies a range of 860 – 900 kg/m^3 for biodiesel at 15 ^{o}C. High density beyond the specified limit can alter the air-fuel-ratio,

performance characteristics and engine burning [11]. The density obtained for the produced fuel in this study was within the limit specified by EN 14214. The biodiesel produced shows lower acidity level, with the calculated acid value of 0.25 mg KOH/g as compared to 0.5 mg KOH/g requirement limit. High viscosity affects fuel atomization and promotes deposits [12]. The kinematic viscosity of 3.07 mm^2/s obtained for THOB was appropriate and within the acceptable limit. The high flash point temperature of THOB indicate that it can be safely handle and stored at room temperature. The cetane number of 60.69 was higher than the minimal limits of both standards, indicating improved performance and a shorter ignition delay. The calorific value obtained indicates that the produced biodiesel has a sufficient capacity, which makes it a potential fuel alternative.

TABLE IV: Physicochemical Properties of THOB in Comparison with standards

Property	Units	THOB	ASTM D6751	EN 14214
Density at 15°C	kg/m^3	875	850	860 – 900
Kinematic Viscosity @ 40°C	mm^2/s	3.07	1.9 – 6.0	3.5 – 5.0
Acid Value	mg KOH/g	0.25	0.5 max	0.5 max
Flash point	°C	178	< 130	< 120
Calorific value	MJ/kg	41.29	N/S	N/S
Cetane number		60.69	47 min	51 min

6. Conclusion

The current study investigates the green technology of bio-feedstock hybridization for biodiesel production via transesterification process. A case study of ternary-hybrid oil comprising of UFO, MSO and LO at the ratio of 3:1:1 g was investigated over banana-avocado peel derived catalyst. The elemental characterization of CBAP catalyst revealed that it contains potassium as the major element behind the good catalyst feat of the catalyst in the transesterification process. The reusability test of CBAP catalyst showed a minimal reduction in the catalyst strength with 92.05% THOB yield after 4 cycles. The statistical analysis was done by CCD with 20 experimental conditions. The input process variables were optimized and at ideal condition of 4.7:1 methanol/hybrid oil ratio, 2.5 wt% catalyst loading, 50 min reaction time and 60 °C constant temperature, an average THOB yield of 98.7 wt% was obtained. The statistical data obtained showed that the model is significant and effective in predicting the yields. The high R^2 value of 0.9899 indicates the high level of reliability between the empirical and projected values. The properties obtained are well conformed with the specification standard limits of biodiesel. With the low quantity of parameters used in this study and the robustness of the hybrid process, the whole protocols appear promising for implementation on an industrial scale, as it will lower the production cost while maintaining maximum output.

7. Acknowledgements

Authors appreciate the South Africa National Research Foundation (NRF) – Durban University of Technology for the financial support.

8. References

[1] A.I. Osman, L. Chen, M. Yang, G. Msigwa, M. Farghali, S. Fawzy, “Cost, environmental impact, and resilience of renewable energy under a changing climate: a review “. Environ. Chem. Lett. 21, 741–764, 2023a https://doi.org/10.1007/s10311-022-01532-8

[2] C. W. Mohd Noor, M. M. Noor, and R. Mamat, “Biodiesel as alternative fuel for marine diesel engine applications: A review,” *Renew. Sustain. Energy Rev.*, vol. 94, no. June, pp. 127–142, 2018. https://doi.org/10.1016/j.rser.2018.05.031

[3] H. H. Mardhiah, H. C. Ong, H. H. Masjuki, S. Lim, and H. V. Lee, “A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils,” *Renew. Sustain. Energy Rev.*, vol. 67, pp. 1225–1236, 2017. https://doi.org/10.1016/j.rser.2016.09.036

[4] A. O. Etim, P. Musonge, and A. C. Eloka-eboka, “Process optimization of bio-alkaline catalysed transesterification of flax seed oil methyl ester,” *Sci. African*, vol. 16, p. e01275, 2022. https://doi.org/10.1016/j.sciaf.2022.e01275

[5] I. Fatimah, D. Rubiyanto, A. Taushiyah, F.B. Najah, U. Azmi, Y.L. Sim, ‘’Use of ZrO 2 supported on bamboo leaf ash as a heterogeneous catalyst in microwave-assisted biodiesel conversion.’’ Sustain. Chem. Pharm. Vol. 12, pp. 100-129, 2019. https://doi.org/10.1016/j.scp.2019.100129

[6] B. Nath, B. Das, P. Kalita, and S. Basumatary, “Waste to value addition: Utilization of waste Brassica nigra plant derived novel green heterogeneous base catalyst for effective synthesis of biodiesel,” *J. Clean. Prod.*, vol. 239, p. 118-112, 2019. https://doi.org/10.1016/j.jclepro.2019.118112

[7] C. Zhao, P. Lv, L. Yang, S. Xing, W. Luo, Z. Wang, “Biodiesel synthesis over biochar-based catalyst from biomass waste pomelo peel “. Energy Convers. Manag. 160, 2018. https://doi.org/10.1016/j.enconman.2018.01.059

[8] E. Betiku, A. O. Etim, O. Pereao, and T. V. Ojumu, “Two-Step Conversion of Neem (Azadirachta indica) Seed Oil into Fatty Methyl Esters Using a Heterogeneous Biomass-Based Catalyst: An Example of Cocoa Pod Husk,” *Energy & Fuels*, vol. 31, no. 6, pp. 6182–6193, Jun. 2017. https://doi.org/10.1021/acs.energyfuels.7b00604

[9] A. O. Etim, A. C. Eloka-Eboka, and P. Musonge, “Potential of Carica papaya peels as effective biocatalyst in the optimized parametric transesterification of used vegetable oil,” *Environ. Eng. Res.*, vol. 26, no. 4, pp. 200–299, 2021. https://doi.org/10.4491/eer.2020.299

[10] A. O. Falowo and E. Betiku, “A novel heterogeneous catalyst synthesis from agrowastes mixture and application in transesterification of yellow oleander-rubber oil : Optimization by Taguchi approach,” *Fuel*, vol. 312, no. December 2021, p. 122-999, 2022. https://doi.org/10.1016/j.fuel.2021.122999

[11] A. M. Ashraful *et al.*, “Production and comparison of fuel properties, engine performance, and emission characteristics of biodiesel from various non-edible vegetable oils: A review,” *Energy Convers. Manag.*, vol. 80, pp. 202–228, 2014. https://doi.org/10.1016/j.enconman.2014.01.037

[12] D. Singh, D. Sharma, S.L. Soni, S. Sharma, D. Kumari, “Chemical compositions, properties, and standards for different generation biodiesels: A review “. Fuel 253, 60–71, 2019. https://doi.org/10.1016/j.fuel.2019.04.174