



Research Article

Methyl-Esters from Ternary Oil Blend Using Catalyst Synthesized from Mixed Agro-Wastes

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ABSTRACT

This study used ternary substrates consisting of honne, neem, and yellow oleander (HONOYO) oil blend to produce methyl-esters for sustainability of raw materials for biodiesel synthesis. A biomass-based catalyst from calcined mixed agro-wastes consisting of kolanut pod, cocoa pod, and plantain peel ash was employed to transesterify the blend. A two-step method was adopted to convert HONOYO into methyl-esters. Taguchi L9 experimental design tool was used to ascertain the interactive effects of microwave irradiation power (W), Methanol/oil ratio (MeOH), time (min), and agro-wastes synthesized catalyst ASC (wt %) on the yield of methyl-esters from HONOYO. Results demonstrated that at 3:1 MeOH, microwave power of 150 W, ASC of 1.5 wt %, and reaction time of 1 minute, a yield of 80.96 % was achieved. HONOYOB satisfied ASTM D6751 and EN 14214 standards. Performance evaluation of the process input variables suggests weight of ASC as the most significant process parameters for HONOYOB yield. This work authenticates that biomass catalyst from agricultural wastes can adequately be applied to synthesis biodiesel effectively from blends of non-edible oils to supplement fossil diesel.

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1. INTRODUCTION

There is a continuous demand for low-cost and eco-friendly fuel both for domestic and industrial purposes in the developed and developing countries. The quest for sustainable energy source is a main concern for the present and future needs. Efforts made by various research works suggest that renewable energies from biomass, hydropower, wind, geothermal, solar, and tidal waves are among the suggested alternatives to combustion of fossil-diesel, although these choices suffer one form of disadvantage or others ranging from initial costs (solar) to restriction of efficiency due to geographical location (geothermal) and need for appropriate head and water conservation during drought (hydropower) [1]. Despite the suggested alternatives, it has been projected that fossil fuel would still supply almost 80 % of the world's energy requirement for more than the next three decades [2]. One major alternative fuel suggested as a supplement for the transportation industry is biofuel, which a non-petroleum natural recyclable liquid fuel. This fuel type is obtained by the combined chemical activity of catalyst and alcohol on oil from plant origin or fats from animals via transesterification. Biofuels possess properties suitable to be applied in the

automotive gas engine directly or mixed with automotive gas oil to obtain a blend [3]. The consideration of biofuel as a supplement or supernumerary for fossil fuel is directly concomitant with some benefits, including energy safety, biological advantage, direct application in diesel engines, and related socio-economic reasons [4]. Among several existing biofuel alternatives, bioethanol and biodiesel are the most extensively renowned biofuels appropriate for transportation purposes, especially biodiesel [5]. This is because biodiesel is characterized by additional advantages including non-toxicity, low level of polycyclic aromatic hydrocarbons and their nitrate derivatives, its direct use in unmodified diesel engines as fuel, and its miscibility with automotive gas oil in different proportions [6]. It is nearly sulfur-free and possesses the ability to cut down on the amount of SO_x, besides other products of combustion [7]. However, the production cost is directly related to feedstock, that is, a major concern that hinders its commercialization [2]. There is an indication that biofuels may eventually become a globally recognized substitute for fossil diesel both in unindustrialized and developed countries if low-cost and accessible feedstock can be adopted. Furthermore, synthesis of biodiesel from edible oil is discouraged due to other applications including contest with food as well as pharmaceutical and cosmetic purposes that these oils serve [8, 9].

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Transesterification is a catalyzed chemical interaction between molecules of triglycerides and alcohol. Such catalysts could be acid, base or both, and the reactions could be done either in a single step or two steps depending on the acid value of the substrates which is directly linked to the percentage of free fatty acid [10, 11]. At present, the two forms of catalyst used for transesterification are homogeneous and heterogeneous catalysts. Heterogeneous catalyst types have been found to be containing more than one active element and they are used for the transesterification process successfully [11, 12].

The key element in producing biodiesel is feedstock, which is vegetable oil. A major hitch in adopting biodiesel as fuel in the transportation industry is the need for sustainable feedstock, which will not hamper food, drug, pharmaceutical, or other purposes. Current research has shifted to the use of nonedible and waste oils as well as catalysts made from biowastes for producing biodiesel to prevent the crisis of edible vegetable oil shortage in the future and possibly reduce the cost of production [13, 14]. Waste from the agro and bio sectors, threatening the environment, can be used in a single or mixed fashion and used to produce catalysts capable of transesterifying vegetable oil. Heterogeneous catalysts were processed from different biowaste materials such as peels of plantain peel [15], kolanut pud [16], egg shell [17], banana trunk [18], bagasse from sugarcane, and oil palm trunk [19].

Agro-wastes can also be mixed to investigate the possibility of improving its elemental composition potency for transesterification of a combination of oils at different volumetric ratios. As shown earlier, when a biowaste-based catalyst is used for transesterification, the yield is comparable to that of the homogeneous catalyst and the time of reaction is very short, meaning that this method could be more cost-effective [20]. In addition, the application of catalysts synthesized from agrowastes in synthesizing oils is an emerging technology. Nonedible oil types can be blended based on types or volumetric ratios to alter physicochemical properties to facilitate applicability to transesterification. Similarly, previous research studies have revealed that the time required for transesterification when microwave irradiation is adopted is quite shorter than that when the hot plate is used (Table 1). Thus, there is still a wider gap in exploration in biodiesel synthesis from different oil blends to be breached in terms of the characteristic feature of oil, volumetric ratio and whether the transesterification process is aided or not.

An important issue which cannot be overlooked is that no research has discovered any seed with hundred percent oil yield so far, thereby putting a limit on the quantity of oil that can be extracted per given species of oil seed. It has also been found that there are nonedible oils having a substantial oil percentage but cannot be used alone due to the limited and peculiar characteristics of such oils [21]. There is a need for research interest in the combination of different nonedible oil samples to discover the combinations, which will have substantial yield, especially when transesterified using different blends of biowaste catalysts.

1.1. Objectives and novelty

This study explored the effect of blend of ternary oil samples including honne (*Calophyllum inophyllum*), neem (*Azadirachta indica*), and yellow oleander (*Thevetia peruviana*) in equal proportion using ASC as an agrowaste synthesized catalyst on the yield of biodiesel via microwave irradiation assisted transesterification process. Times for reaction, weight of ASC, MeOH, and irradiation power were optimized using the L9 Taguchi tool for experimental design to obtain optimum yield. The process parameter with premier effect on biodiesel yield was also determined and the biodiesel produced was analyzed for fuel properties. The experiment was carried out to:

- i. determine the physiochemical properties of the oil mixture (HONOYO) to ascertain suitability for biodiesel production;
- ii. use agro-waste materials plantain peel, cocoa, and kolanut husk to make catalysts (ASC), thus finding a useful purpose for the waste materials;
- iii. investigate the influence of microwave irradiation on the time required for completion of the transesterification process;
- iv. study the effect of four process parameters namely microwave irradiation power, MeOH, ASC, and time on biodiesel yield using the Taguchi L9 design tool; and
- v. characterize the biodiesel produced code named HIONOYOB to verify its properties with ASTM D6751 and EN 14214 standards and ascertain its suitability as fuel.

Table 1. Biodiesel synthesized from oil blends via homogeneous and bio-based catalysts

Oil blend	Volumetric ratio	Method	Time	Catalyst type	Optimum yield (wt %)	Reference
Soybean and rape seed	50:50	Hot plate	2 h	Homogeneous	94.00	[22]
Pongamia and Neem	70:30	Hot plate	77 min	Homogeneous	86.3	[23]
Waste cooking/Honne	70:30	Microwave	7.15 min	Homogeneous	97.65	[24]
Pongamia, Jatropha, and honne	Equal	Hot plate	95 min	Homogeneous	98.00	[25]
Rubber seed and Neem	40:60	Microwave	5.88 min	Heterogeneous	98.77	[26]
Castor oil and waste fish	50:50	Hot plate	39 min	Homogeneous	95.2+2.5	[27]
Soybean/castor	25:75			Homogeneous	87.00	
Palmoil/Rubber seed	50:50	Hot plate	1 h	Homogeneous	97.00	[28]
Honne rubber seed and yellow oleander	20:20:60	Microwave	6 min	Heterogeneous	98.45	[20]

2. MATERIALS AND METHODS

2.1. Material procurement

The honne and yellow oleander seeds were collected from Obafemi Awolowo University Ile-Ife Nigeria compound, processed, and taken to the Faculty of Pharmacy, Obafemi Awolowo University, Ile-Ife for oil extraction via Soxhlet apparatus using n-hexane to obtain Honne Oil (HO) and yellow oleander oil (YO) oils, while Neem Oil (NO) was purchased from National Research Institute of Chemical Technology (NARICT) Zaria, Nigeria. The three oils were blended at equal volumetric ratios to obtain HONOYO. Reagents and chemicals including di-ethyl ether, ethanol, methanol, potassium iodide, starch solution, cyclohexane, sulphuric acid, sodium sulphate, phenolphthalein, potassium hydroxide, and Wij's solution of analytical grade were used for the study.

2.2. Blended agro-wastes synthesized catalyst (ASC) preparation

The obtained agro-wastes were cut into tiny pieces, washed 3 times with distilled water and sundried for 2 weeks, and then dried in the oven at 80 °C until constant weight was achieved. These wastes were separately charred into ashes in the open air, after which each ash was manually minced to a fine powder using porcelain mortar and pestle. The resulting powdered samples were weighed in equal proportion, mixed, and calcined in a muffle furnace at 300, 500, 700, 900, and 1100 °C for four hours to determine the best calcination temperature. The produced calcined ASC ash was then stored in corked plastic vessels.

2.3. Determination of characteristic features of ASC

The ASC was characterized using Energy Dispersive X-ray Spectroscopy (EDX), Fourier Transform Infrared (FT-IR), XRD chromatograms, and Scanning Electron Microscopy (SEM). The Cambridge S200 SEM equipped with an energy dispersive X-ray analyzer system was employed to investigate the surface morphology of ASC, as represented in Figure 1. The EDX was used to analyze the elemental composition of the ASC sample. The active surface functional groups of the ash sample were also determined by FT-IR spectral studies using Perkin Elmer Spectrum 100 FT-IR spectrophotometer in the wavelength range of 4000-400 cm^{-1} (Figure 2). XRD chromatograms reveal the crystalline compounds present in ASC at 500 °C (Figure 3). In addition, the residual gases in the ASC were eliminated at 150 °C for 16 h to eliminate moisture and atmospheric vapor by heating and evacuation.

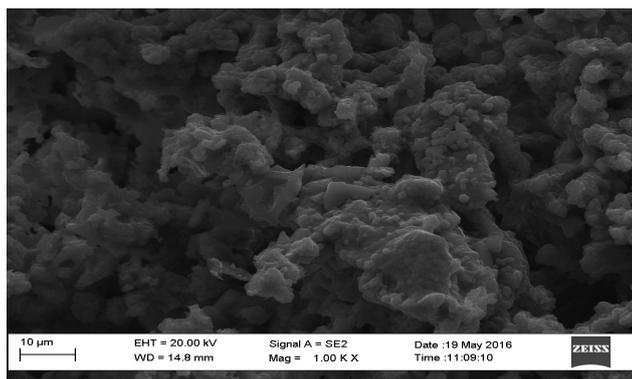


Figure 1. SEM image of calcined ASC

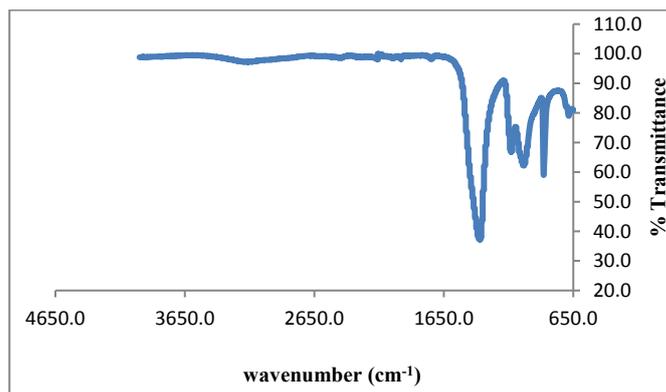


Figure 2. FTIR spectra of calcined ASC at 500 °C

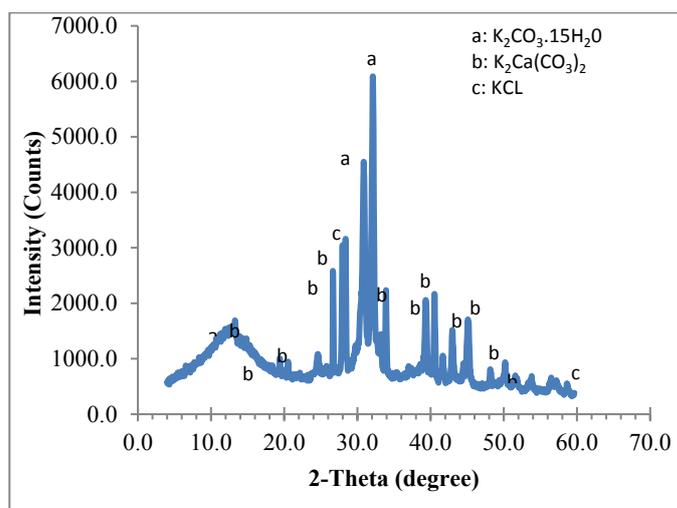


Figure 3. XRD chromatogram calcined ASC at 500 °C

2.4. Blending of honne, neem, and yellow oleander (HONOYO) oils

This study mixed an equal volume of honne, neem, and yellow oleander seed oils by first heating them separately in a 500 ml conical flask at 60 °C for 15 minutes and then, decanted one after the other into a 1000 ml flat bottom flask placed on a hot plate equipped with a stirrer having magnetic property for agitation and proper fraternization at 60 °C for another 30 minutes to obtain HONOYO.

2.5. Experimental design for transesterification

The acid value of HONOYO was determined to be 37.5 mg of KOH/g of oil, corresponding to FFA of 18.84. This was reduced to < 2 mg KOH/g oil via sulphuric acid pretreatment to prevent the formation of soap during transesterification.

2.5.1. Acid catalyzed esterification of HONOYO

A known amount of HONOYO was measured into a 500 ml two-necked glass reactor. The esterification process was carried out using MeOH 25:1, H₂SO₄ 1 wt %, microwave power 300 w, and reaction time of 15 minutes. The reaction took place in a glass reactor placed in the microwave oven. Following the completion of the reaction, the mixture was allowed to be separated by gravity and the residual methanol was removed by heating off on the hot plate before determining the acid value of the esterified oil.

A known quantity of esterified HONOYO was measured into a two-necked glass reactor. A known volume of methanol

was added to a certain amount of ASC. This was placed in a pre-timed microwave and the reaction was stopped based on the time specified by the experimental design, as given in Table 3. MeOH, reaction time, microwave irradiation power, and weight of ASC were combined at three levels to generate an orthogonal array of nine experimental conditions using the

Taguchi L9 experimental design tool to model the production of HONOYO methyl-esters, as depicted in Table 2. The genera of process parameters considered for the transesterification process of pretreated HONOYO are presented in Table 3.

Table 2. Factors and levels for design of experiment for transesterification of pretreated HONOYO

Factors	Unit	Level for factors		
		-1	0	1
MeOH	v/v	3	9	15
Catalyst amount	wt %	1.5	3.0	4.5
Microwavw power	Watt	150	300	450
Reaction time	Mins	1	3	5

Table 3. Transesterification of the pretreated HONOYO

Run	MeOH	ASC (wt.%)	Power (W)	Time (min)	Actual yield (wt%)	Predicted yield (wt%)	Residuals (wt %)
1	9	3	450	1	62.70	61.20	1.50
2	15	1.5	450	3	75.71	77.22	-1.51
3	15	3	150	5	65.20	65.19	0.013
4	3	3	300	3	42.36	43.87	-1.51
5	9	4.5	150	3	81.86	83.37	-1.51
6	3	1.5	150	1	80.96	79.46	1.50
7	9	1.5	300	5	90.30	90.29	0.013
8	3	4.5	450	5	49.00	48.99	0.013
9	15	4.5	300	1	65.29	63.79	1.50

Upon the completion of the reaction, the resulting product was allowed to separate; glycerol was tapped off; and the HONOYOB was washed with distilled water at 50 °C to get rid of residual catalyst, glycerol, methanol, and soap. The washed HONOYOB was dried over heated anhydrous sodium sulphate powder and the HONOYOB yield was determined gravimetrically according to Equation 1.

$$\text{HONOYOB yield (wt. \%)} = \frac{\text{weight of oil sample}}{\text{weight of biodiesel sample}} \times 100 \quad (1)$$

The most significant factor was evaluated using Equation 2 where SS_f is the sum of the square of the individual parameters and SS_T is the total sum of squares of all the parameters obtained for the model (Dhawane et al., 2016b).

$$\text{C. F. (\%)} = \frac{\text{SS}_f}{\text{SS}_T} \times 100 \quad (2)$$

2.6. Determination of HONOYOB properties

The physicochemical properties of the produced HONOYOB considered. The determined properties include kinematic viscosity, density, moisture content, acid value, saponification value (sv), iodine value, higher heating value, cetane number diesel, and index AOAC (Chemists and Horwitz, 1990) [22, 23].

3. RESULTS AND DISCUSSION

3.1. Characterization of ASC

It was revealed by the EDS study that the active elemental compositions of ASC were significantly affected by the

temperature of calcination (Table 4). The result shows Magnesium (Mg), phosphorous (P), calcium (Ca), and potassium (K) as the metallic element in ASC and that K has the highest mass fraction (47.67 wt % and 47.93 wt %) at 500 °C and 700 °C, respectively, suggesting that it is the main active element responsible for transesterification of HONOYO. Similar results were found in the research finding in which cocoa pod husk was used to produce CCPHA bio-based catalyst [2]. The SEM image at a resolution of 1000X reveals that the morphology of ASC is composed of disjointed clusters of granules that are glossy, porous, and spongy, suggesting better permeability to moisture as well as improved surface area. This property is preferred for conversion of pretreated oil or feedstock which may likely contain traces of moisture to methyl-esters. The XRD pattern of ASC shows peaks in the plot, corresponding to various components such as KCl (Sylvite), K₂Ca(CO₃)₂ (Fairchildite), and K₂CO₃·5H₂O (potassium carbonate) as the prominent crystalline compounds present in the calcined ASC. It was equally observed that increase in calcination temperature results in decomposition of CaCO₃ to CaO and quartz to SiO₂. Similar peaks were observed for ash samples of waste rubber seed shell [30] and banana peel [31, 20]. The elemental analysis data and the XRD studies establish that a significant amount of potassium present in the characterized calcined ASC ash exists in its chloride form. The FT-IR results for the ASC ash reveal various adsorption bands, as shown in (Figure 2). The IR spectrum consists of 673, 876, 1020, 1410, 2160, 3120, and 3640 per cm bands. The bands from 3134-673 per cm indicate the expanse hydrogen-bonded vibration of O-H functional group and unseparated water molecules forming the

surface hydrated layer. This correlates with the report by [33] and [34]. Characteristic bands between the regions of 1410–3120 cm^{-1} indicate the symmetric and asymmetric elongation and vibration of the CH_3 group [35]. The elongation and vibrations of the $\text{C}-\text{O}$ bond are observed near 1020–876 cm^{-1} , indicating the presence of CO_3 . This band is peculiar to K_2CO_3 and prominent in the XRD spectral.

3.2. Transformation of HONOYO to HONOYOB

The biodiesel production-related properties were determined for HO, NO, and YO as well as HONOYO (Table 5). The acid values were found to be 40.28, 14.57, 61.49, and 37.5 mg KOH/g oil, respectively. This corresponds to an FFA of 18.84 % for the HONOYO. The acid value of HONOYO shows a need to reduce the acid value to prevent saponification.

3.2.1. Pretreatment of HONOYO

The acid value of HOMOYO was reduced from 37.5 to < 2 % via acid esterification. Thus, the tendency of soap formation was eliminated.

3.2.2. Modeling and parameter optimization for transesterification of pretreated HONOYO

The result of predicted and experimental yields of HONOYOB via ASC catalyzed methanolysis of HONOYO to HONOYOB using an orthogonal array of nine experiments is

shown in Table 3. The mathematical expression for the reaction is represented by Equation 3.

$$N = +68.15 - 10.71A1 + 10.13A2 + 14.17B1 - 11.40B2 + 7.85C1 - 2.17C2 \quad (3)$$

The terms A, B, and C are the molar ratio of methanol to pretreated HONOYO (MeOH), amount of agrowastes synthesized catalyst (ASC), and microwave irradiation power, respectively, and N is the biodiesel (HONOYOB) yield. The yield varied between 42.36 wt % and 90.30 wt %. The minimum and maximum yields were obtained at fourth and seventh experimental runs, respectively. These correspond to 3 min, 3 wt %, 300 W, 3:1 and 5 min, 1.5 wt %, 300 W, 9:1, respectively. The fuel properties of HONOYOB are presented in Table 6. HONOYOB improved cetane number, implying better fuel strength; the iodine value is very low, signifying good cold flow properties. The viscosity is a tad higher than specified; therefore, HONOYOB may require blending with AGO to be fit for use in an unmodified IC engine to secure engine life for long-term usage. The regression analysis for this study tested by means of ANOVA shows that $p < 0.05$ as revealed in Table 7 for all model terms, meaning that the result is statistically significant at a 95 % level of confidence and that the most influential parameter affecting the yield of HONOYOB is ASC. The F value of 48.29 and p-value of 0.0204 of the models confirm that all the model terms are significant, as shown in Table 7.

Table 4. Elemental composition of ASC

Temperature (°C)	Elements (mass %)											
	O	Mg	Si	P	S	Cl	K	Ca	Fe	Zn	Na	Al
300	40.43	4.06	0.90	1.74	1.41	1.97	43.99	5.50	0.00	0.00	0.00	0.00
500	37.21	4.21	0.56	1.65	1.26	1.88	47.67	5.56	0.00	0.00	0.00	0.00
700	41.20	3.05	0.79	1.61	0.92	1.88	47.93	3.93	0.00	0.00	0.00	0.00
900	41.59	1.85	1.41	1.77	1.29	1.43	45.55	4.68	0.64	0.00	0.00	0.00
1100	45.30	0.81	2.82	5.20	1.17	1.03	43.90	0.00	0.00	0.00	0.00	0.75

Table 5. Properties of oil samples

Parameters	Values			
	HO	NO	YO	HONOYO
Physical state at 25 °C	Liquid/dark green	Liquid/dark brown	Liquid/golden yellow	Liquid/dark brown
Moisture content (%)	0.640 ± 0.001	0.050 ± 0.001	0.342 ± 0.001	ND
Specific gravity	0.901 ± 0.005	0.961 ± 0.001	0.908 ± 0.017	0.967 ± 0.00
Kinematic viscosity (mm^2/s) at 40 °C	37.01 ± 0.76	124.43 ± 0.04	35.47 ± 0.27	72.22 ± 0.00
Refractive index at 25 °C	1.475 ± 0.00	1.4764 ± 0.001	1.464 ± 0.00	1.47 ± 0.00
Density (kg/m^3) at 25 °C	901 ± 0.014	964 ± 0.001	909 ± 0.001	967 ± 0.00
% FFA (as oleic acid)	20.24 ± 0.35	7.32 ± 0.91	30.90 ± 0.35	18.84 ± 0.53
Acid value (mg KOH/g oil)	40.28 ± 0.00	14.57 ± 0.00	61.49 ± 0.00	37.5 ± 0.00
Iodine value ($\text{g I}_2/100 \text{ g oil}$)	80.44 ± 0.65	84.53 ± 0.74	87.37 ± 0.96	ND
Saponification value (mg KOH/g oil)	226.5 ± 0.94	178.86 ± 0.81	174.74 ± 0.61	ND
Higher heating value (MJ/kg)	51.69 ± 0.00	49.39 ± 0.00	57.04 ± 0.00	50.71 ± 0.00
Cetane number	52.29 ± 0.00	58.00 ± 0.00	57.87 ± 0.00	56.05 ± 0.00

ND: means not done

Table 6. Fuel properties of HONYOYOB

Properties	HONYOYOB	ASTM D6751	EN 14214
Physical state and colour	Liquid/golden yellow	NS	NS
Kinematic viscosity(mm ² /s) at 40 °C	6.83	1.9 - 6.0	3.5 - 5.0
Density at 25 °C (kg/m ³)	868.	NS	860 – 900
Moisture content (%)	0.025	<0.03	0.02 max
Acid value (mg KOH/g oil)	0.20	0.50 max	0.50 max
SV (mg KOH/g oil)	212	-	-
Iodine value (g I ₂ /100 g oil)	33. 18	NS	120 max
Higher heating value (MJ/kg)	40.00	NS	NS
Flash point	ND	130 minimum	120 minimum
Pour point	ND	NS	NS
API gravity (deg.)	ND	39.95	NS
Diesel index	72.6	331.00	NS
Aniline point	ND	NS	NS
Cloud point	ND	NS	NS
Cetane number	62.57	47 mi	51 min
aNS = not specified bNS = not specified			

Table 7. Significance result for modeling of methanolysis of HONYOYO

Source of variance	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	1964.71	6	327.45	48.29	0.0204
A- MeOH:HONYOYO	653.39	2	326.69	48.18	0.0203
B - ASC	1015.27	2	507.63	74.87	0.0132
C - Power	296.05	2	148.03	21.83	0.0438
Standard Deviation	2.60				
Mean of response	68. 15				
Coefficient of Variation (%)	3.82				
R ²	0.9931				
Adequate Precision	20.212				

The model terms were developed by eliminating the term that is not significant in the response. Only the reaction time is insignificant on the yield of HONYOYOB being the reason why it was not contained in the model terms. ASC catalyst has the most prominent effect on HONYOYOB yield when placed side by side with other significant factors. From the value of the R² (0.9931), the model can explicate 99.31 % of the changeability of the process [2] (Table7). For the signal of the design process to be strong enough, the adequate precision must be > 4. Thus, 20.212 denotes a strong signal of the design of this study. Similarly, the adeptness of the model is reflected in its percentage Coefficient of Variation (CV), which is required to be less than ten. The CV for this study is 3.82 %. This substantiates the finding that the model is fit to describe this process adequately. The lack-of-fit F-value of 0.0204 implies that the model is 99.97 % fit to predict this process. The model predicted data by equation and the data

obtained from the experiment were plotted to obtain Figure 4. Plot 4a reflects the adequacy of the model equation in predicting the yield of HONYOYOB. The closeness to the linearity of both the model-predicted and experimental values is proof that the untainted error is minimal and that there is agreement between the model predicted and experimental data. Thus, the model is adequate for predicting this process [36]. Figure 4b shows the normal distribution pattern for the plot of the studentized residuals, showing that the experimental errors were random. The scattering of data points in Figure 4c plot which is a plot of studentized residuals against the data predicted by the model implies evenness in variation for response values, thus confirming that the model is suitable. The outlier t plot for all studentized residuals is depicted in Figure 4d. The plot reveals that all data values lie within ± 3.0 . This further establishes the fitness of the model [37, 20].

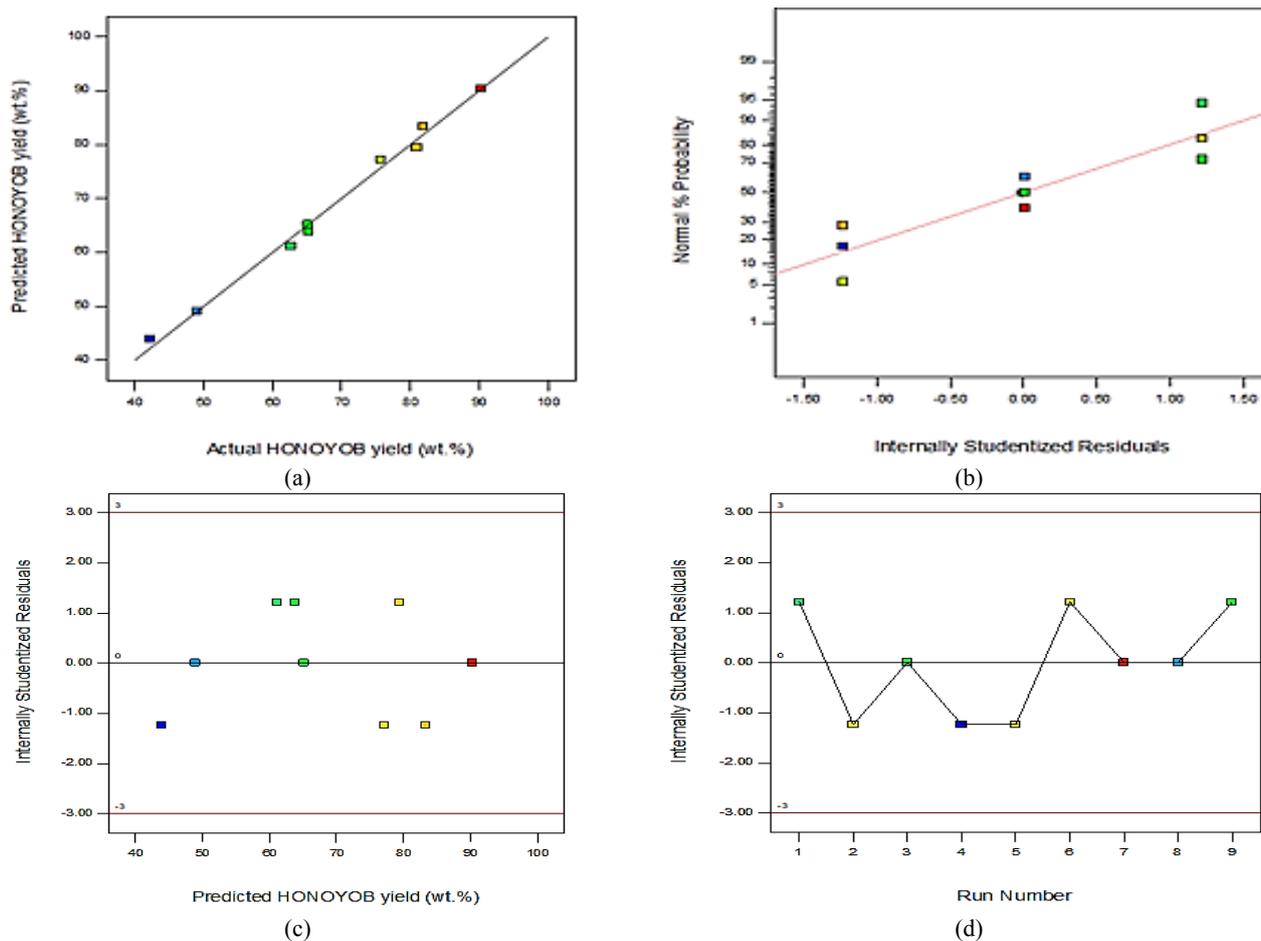


Figure 4. Analytical plot of the surface model for HONOYOB formation

3.3.1. Effect of MeOH on HONOYOB yield

Transesterification is a reversible reaction. As reported by various researchers, 1 mole of oil is to be reacted with 3 mole of alcohol stoichiometrically for transesterification. The equilibrium of the reaction can be driven to the product side if the excess amount of alcohol is present in the reaction [13, 32, 38, 39]. However, caution should be exercised in the quantity of alcohol used to prevent dilution; otherwise, there will be a reduction in the expected yield of the methyl-esters [32]. In this study, the molar proportion of methanol to oil at three levels i.e., 3:1, 9:1, and 15:1, was adopted to investigate its influence on HONOYOB yield while keeping other parameters constant (Table 2). The effect of these ratios is represented in Figure 5a. HONOYOB yield increased from 3:1 and reached the peak at 9:1. The ratio that favoured HONOYOB yield most was 9:1 with a significant yield of 90.30 wt %.

3.3.2. Effect of microwave power on HONOYOB yield

Microwave power is one of the key factors that facilitates biodiesel production. The raised temperature at the reaction sites may favor the antiphon rate [40]. Microwave powers at 150 W, 300 W, and 450 W were investigated to study their effect on the yield of HONOYOB while keeping other parameters constant (Table 2). This is represented in Figure 5b. The yield was significantly higher for 150 W. The reduction in the yield at the other investigated power may result from the possibility of drying-off of the alcohol in the reaction mixture because of the intensity of heat generated in the microwave.

3.3.3. Effect of ASC loading on HONOYOB Yield

Catalyst loading at three levels, 1.5, 3, and 5 wt %, were investigated to study the influence of the amount of catalyst on HONOYOB yield while keeping other parameters constant (Table 2). The graph obtained by plotting HONOYOB yield against catalyst amount in weight percentage is shown in Figure 5c. At the methanol-to-oil molar ratio of 9:1, 1.5 wt % catalyst loading, microwave power of 150 W, and reaction time of 1-minute, maximum HONOYOB yield was observed to be 80.96 wt %. Further increase in the amount of catalyst in the reaction does not favor the yield of HONOYOB. This is an advantage for the ASC catalyst used because a small quantity of it is required for transesterification, thus lowering the production cost of HONOYOB. Researchers also reported similar observations on the amount of biowastes catalyst required for transesterification in their study [2].

3.4. Model validation

The optimization of each parameter was performed to determine the best combination to give the optimum HONOYOB yield based on the mathematical model developed. The optimum values of the process parameters and the biodiesel yield obtained from this study for the conversion of HONOYO into HONOYOB using ASC catalyst were methanol to oil molar ratio of 9:1, catalyst loading of 1.5 wt %, microwave power of 150 W, and reaction time of 1 minute. The optimum HONOYOB yield projected in this condition was 100 wt % with desirability of one. The optimum condition forecast by the regression model equation was validated through experimentation in triplicates. It was

observed that the results of the experimental and predicted were close, implying that the chosen model was appropriate for predicting the optimum condition for HONOYOB

production. The average HONOYOB yield observed was 98.57 ± 0.58 wt % (Figure 5 a, b, and c).

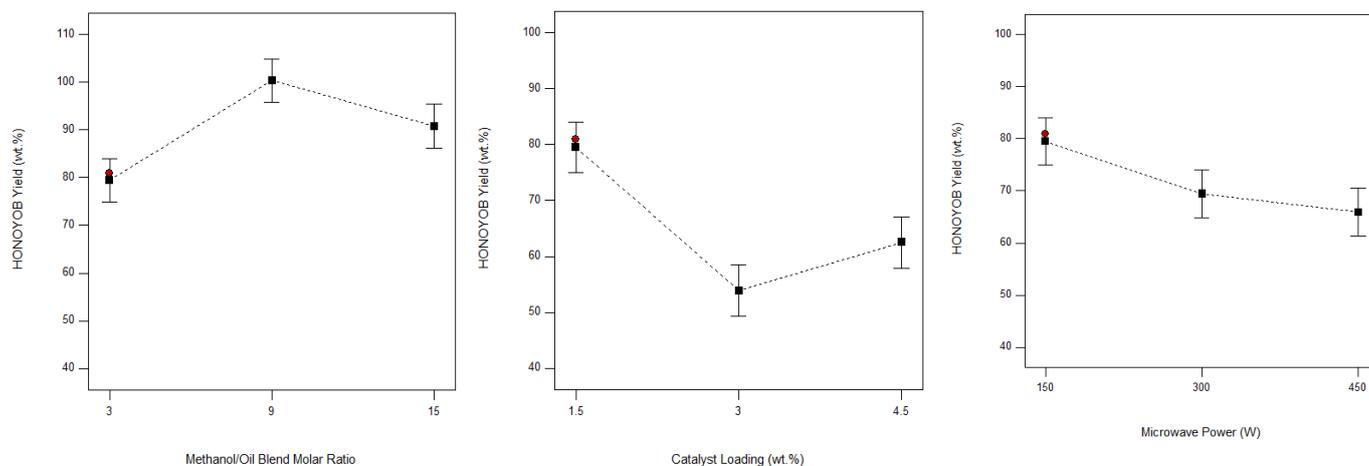


Figure 5. Plot of model validation

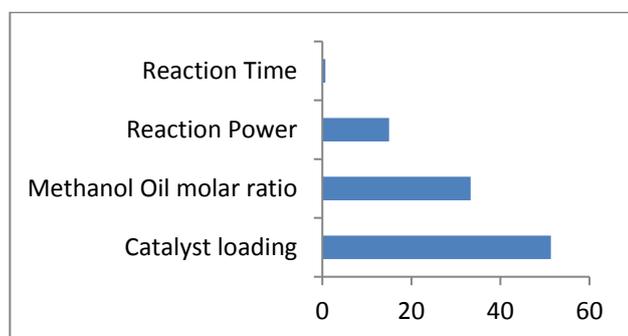


Figure 6. Level of contribution of process parameters in transesterification process

4. CONCLUSIONS

This work investigated the combination of three oil types in equal proportion to obtain HONOYO. The HONOYO was used to synthesize biodiesel by two steps. Calcined agrowastes ash ASC was used as a catalyst for the transesterification process. Microwave irradiation was employed to aid the production process. The physicochemical properties of HONOYO demonstrated that it was a feasible feedstock for biodiesel production, but required acid pre-treatment prior to transesterification. ASC catalyst was heterogeneous in nature containing potassium, calcium, Magnesium, and Phosphorus as active metallic elements. The optimal condition for synthesizing biodiesel from pretreated HONOYO was MeOH of 3:1, microwave power of 150 W, ASC of 1.5 wt %, and reaction time of 1 minute. An optimum yield of 80.96 % was achieved. ASC was found to be the process parameter with peak effect on the yield (Figure 6). The application of microwave irradiation to the transesterification process reduced the production time drastically. The produced biodiesel (HONOYOB) is of high quality since most of its properties are considered to be satisfactory in line with biodiesel standard specifications (ASTM D6751 and EN 14214).

5. ACKNOWLEDGEMENT

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NOMENCLATURE

ASC	Agro-waste Catalyst
HONOYO	Honne, Neem and Yello Oleander Blend
HONOYOB	Methyl esters from HONOYO
ASTM D	American
EN14214	European
MeOH	Methanol to oil ratio
CV	coefficient of Variation
SV	Saponification Value
FFA	Free Fatty Acid
ANOVA	Analysis of Variance
AGO	Automotive Gas Oil

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