Journal of Energy Research and Reviews

11(4): 33-47, 2022; Article no.JENRR.88797
ISSN: 2581-8368

Kariya Biodiesel Process Optimization Using Kariya Pod-husks Bio-catalyzed

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JENRR/2022/v11i430285

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/88797

Original Research Article

Received 15 April 2022
Accepted 25 June 2022
Published 30 June 2022

ABSTRACT

In this study, biodiesel was produced from underutilized kariya oilseed using ethanol in the presence of kariya pod-husks bio-catalyst. The oil used was extracted through the soxhlet solvent extraction approach. Transesterification of kariya seed oil was investigated using Central Composite Design (CCD) of Response surface methodology. Process factors such as reaction temperature (65, 70, and 85^{o}C), reaction time (2, 3, and 4 h), and ethanol/kariya oil molar ratio (8:1, 10:1, and 12:1) were modeled based on CCD experimental design. The fuel properties of biodiesel produced, and its blends with petrol-diesel were determined. The average yield of extracted kariya oil was 32.55 wt. %. Based on the results, biodiesel yield of 94.41 wt.% was obtained at optimal conditions; a temperature of 75^{o}C, time of 2 h, and ethanol: oil mole ratio of 10:1 at catalyst loading of 5 wt.%. The physicochemical and fuel properties of produced biodiesel and its blend were well within American Society for Testing and Materials (ASTM D6751) standard and compared favorably with petrol-diesel.

Keywords: Kariya oil biodiesel; heterogeneous catalyst; transesterification; bio-catalyst.

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1. INTRODUCTION

The gradual diminution of fossil fuels around the world with its unstable price in global market, and attendant environmental pollution such as greenhouse gas emissions have made the utilization of environmental-friendly and renewable energy an increasing interest in the modern world [1,2]. Biodiesel is a renewable energy which has the good physiochemical properties to supplement petroleum diesel due to its environmental benefits. Blending sustainable energy conservation with environmental preservation is a goal that is crucial to the stability of the ecological system. Therefore, the use of biodegradable waste materials is a cost effective means for the production of carbon-free energy [3]. Biofuels present a better supplement to fossil fuels due to its environmental-friendliness, performance, and low carbon emission properties in diesel engines [3]. Biodiesel is a product of a transesterification reaction between vegetable oil or animal fat and simple alcohols with a base catalyst [4,5].

Africa, especially Nigeria, has a great potential for biodiesel utilization as fuel given a vast range of underutilized oil-bearing forest products that may be explored as feedstock for biodiesel production [6]. Kariya seed (*Hildergadia barteri*) is a reddish-gold seed produced by a tropical tree which has visible sunny-red flowers on leafless branches all through the dry season. This seed oftentimes ends as a refuse. However, it contains nearly 40% oil which has yielded 55.7wt.% and 97wt.% oil through cold pressing and solvent extraction, respectively [7,8]. Okeleye and Betiku [9] evaluated the effect of solvent type on Kariya seed oil yield, and among the three solvents of extraction investigated, acetone has the highest oil yield of 32.52wt.%, while hexane has 25.11wt.% and ethyl acetate has the lowest oil yield of 19.20wt.%. Adebayo et al. [8] reported kariya seed oil specific gravity and viscosity to be 0.73-0.91, and 4.05-4.45mm^2/sec, respectively. Besides, the acid value of cold pressed and solvent-extracted kariya seed oil is 2.12 and 2.09mgKOH/g oil respectively which indicates its potential as a biodiesel feedstock. However, the physicochemical properties of the extracted oil depend largely on the solvent of extraction as presented in Okeleye and Betiku [9] study. Betiku et al. [10] produced biodiesel from Kariya seed oil using a base heterogeneous catalyst prepared from Kola nut pod husks. The yield of Kariya biodiesel was 98.67 wt.% at the optimal condition; methanol/oil molar ratio of 6:1, a reaction time of 75 mins, and at 65 ˚C temperature using 3wt.% catalyst amount.

To date, large biodiesel production is carried out using homogeneous base acid. However, the challenges posed by this mineral catalyst in biodiesel production such as product stream separation and intolerability of the extreme operating conditions. These challenges have led several researchers toward the development of green heterogeneous catalysts. In producing Kariya oil biodiesel, Betiku et al. [10] utilized a base catalyst developed from kola nut pod husk, and resulted in an optimal reaction condition of methanol/K_2SO_4 molar ratio of 6:1, catalyst loading level of 3wt%, for 75 min at 65 °C to produce maximum yield of 98.67 ± 0.01wt%. Towards maximal utilization of waste biomass in improving chemical processes in terms of cost-saving, every component of the biomass can be converted into usable raw material to optimize raw material utilization. Hence, this study investigated and optimized Kariya oil biodiesel production process using a solid base catalyst synthesized from Kariya pod. Furthermore, the produced biodiesel was blended at various ratios with petroleum diesel to compare their physicochemical properties using American standards for biodiesel. This is to explore the possibility of maximizing the utilization of the non-edible seed for large biodiesel production.

2. MATERIALS AND METHODS

2.1 Materials

Kariya seeds used for this study were gathered from Obafemi Awolowo University campus Ile-Ife, Nigeria. The chemicals and reagents used for this research were of analytical grade and were obtained from a local supplier. The calcined kariya pod-husks were used as a bio-catalyst which was investigated by a Ph.D. research, was obtained from the Agricultural and Environmental Engineering Department, Obafemi Awolowo University, Ile-Ife, Nigeria.

2.2 Methods

2.2.1 Sample preparation

Kariya nuts were manually removed from the harvested kariya dry pods and dehulled to remove the seeds which were later separated and cleaned from all extraneous materials such as nutshell, dirt, and sand. The seeds were sun-dried for three days to 7.8% moisture content. The kernels were ground into powder of 75µm particle size using a blender.

(A) **(B)** **(C)**

Plate 1: (A) Matured dried *kariya* pod-husks **(B)** Kariya seeds **(C)** *Kariya* kernels.

2.2.2 Procedure for oil extraction and determination of oil yield

Kariya seed oil was extracted from the milled powder using the solvent extraction method. Four liters of N-hexane were used as an extraction solvent for 5.6 kg of powdered kariya seeds under reflux for 2h using a Soxhlet apparatus. The solvent in the extract was recovered using vacuum distillation.

The percentage yield (Y_o) of the extracted oil was determined using Eq. (1).

$$Y_0 = \frac{M_o}{M_k} \times 100\% \quad (1)$$

Where, Y_o= Yield of the extracted oil, %; M_o= Mass of oil extracted in gram; M_k= Mass of kariya powder used (g). The physical and chemical properties of the extracted oil were determined using AOAC [11].

2.2.3 Determination of kariya oil physiochemical characteristics

The physicochemical properties of extracted Kariya oil were determined after gravimetric quantification. Properties such as specific gravity, refractive index, viscosity, peroxide value, saponification value, iodine value, and acid value were carried out using ASTM [12] and AOAC [11].

2.2.4 Procedure for oil pre-treatment

The extracted kariya seed oil has high Free Fatty Acid (FFA) which makes it unsuitable for biodiesel production without pretreatment. The oil was esterified to reduce the extracted oil FFA below 1. A known-volume of extracted kariya oil was measured, and a known volume of ethanol was added to the oil in a 250 ml round bottom flask, hence, the ethanol to oil ratio used was 10:1. Then, a known amount of anhydrous ferrous sulphate as a catalyst was added to the reaction mixture on a hotplate with a magnetic stirrer. The reaction mixture was heated and maintained at 80 ^{o}C temperature for 90 mins. The esterified oil and alcohol were separated using a separating funnel. The FFA of the pretreated oil was again determined using AOAC [11].

2.3 Biodiesel Production

2.3.1 Transesterification of kariya seed oil

The pretreated Kariya oil of known volume was discharged into the reactor placed on a hotplate with a magnetic stirrer and heated up to the specified temperature by the modeling. Then, a known volume of ethanol was added to the heated kariya oil in the reactor, followed by 5wt.% of calcined Kariya pod ash as a catalyst. The mixture was stirred at 150 rpm and the transesterification reaction continued until the fixed time specified in the modeling. On completion of this process, the resulting mixture was transferred into a separating funnel to allow biodiesel separation from the product mixture by gravity after which two layers was formed (biodiesel layer and glycerol layer). The biodiesel layer (lower layer) was decanted and washed with warmed water till the residual glycerol (upper layer) was removed. The glycerol is totally removed when no layer is observed in the biodiesel. Then, the washed biodiesel sample was dried over anhydrous calcium chloride to remove the residual water in the biodiesel. In this study, the production was carried out in triplicate and the average biodiesel yield was calculated. The biodiesel yield was determined according to Eq. (2)

$$\text{Biodiesel yield (wt.\%)} = \frac{\text{Weight of biodiesel produced}}{\text{Weight of Kariya oil used}} \times 100\% \quad (2)$$

2.3.2 Experimental design of kariya seed oil transesterification

The transesterification process of kariya seed oil was modeled using fractional factorial design (three-factor-three-level) of Central Composite Design (CCD) thereby giving 15 experimental runs as depicted in Table 1. Response surface method (RSM) was used in optimizing the biodiesel production process and in evaluating the influence of process parameters on the model response [13].

The biodiesel yield was the response in this study. A 3^3 CCD design of the experiment was used (three factors each at three levels). The process factors chosen are temperatures (65, 75, and 85^{o}C), time (2, 3, and 4 hrs.), and ethanol: oil molar ratio (8:1, 10:1, and 12:1). The experiments conducted in the laboratory are presented in Table 2.

2.3.3 Determination of fuel properties

The physicochemical and fuel properties of produced biodiesel were carried out according to the methods outlined in the American Society for Testing Materials (ASTM D40, D93, D97, D445, D1298, D2500, and A6584) standards. The fuel properties of kariya biodiesel blends with petroleum diesel were also determined. These properties include flash point, pour point, cloud point, heating value, carbon content, and cetane number. The viscosity of biodiesel and blended fuel was determined by using Capillary U-tube viscometer while the specific gravity was determined using a pycnometer according to the method described in ASTM D1298.

Table 1. Experimental range of process factors for biodiesel production process

Factor	Name	Unit	Type	Low Actual	High Actual	Low Coded	High Coded
A	Temperature	^{o}C	Numeric	65	85	-1	1
B	Reaction Time	Hours	Numeric	2	4	-1	1
C	Ethanol:Oil Molar ratio	%w/w	Numeric	8	12	-1	1

Table 2. Full central composite design for kariya oil transesterification process

Std	Run	Factors		
		Temperature	Time	Ethanol-Oil Molar ratio
		X_1 (^{o}C)	X_2(hrs)	X_3 (mol/mol)
8	1	85.00	4.00	12.00
4	2	85.00	4.00	8.00
11	3	75.00	1.32	10.00
1	4	65.00	2.00	8.00
7	5	65.00	4.00	12.00
9	6	58.18	3.00	10.00
12	7	75.00	4.68	10.00
13	8	75.00	3.00	6.64
2	9	85.00	2.00	8.00
14	10	75.00	3.00	13.36
6	11	85.00	2.00	12.00
10	12	91.82	3.00	10.00
5	13	65.00	2.00	12.00
15	14	75.00	3.00	10.00
3	15	65.00	4.00	8.00

3. RESULTS AND DISCUSSION

3.1 Kariya Oil Yield from Extraction

The results of the oil yield obtained from kariya seeds using the soxhlet apparatus method are shown in Table 3. Physical observation of extracted kariya oil showed that the oil is light yellow. The average oil yield obtained in this study was 32.55%. The average oil yield in this study was more than the values (23.15-30.53%) reported by Oluwadare and Adeniyi [14] using the same solvent for kariya oilseed, and more than 25.11 % reported by Okeleye and Betiku [9]. It was observed that Kariya seed has higher oil content than some oilseeds used in producing biodiesel when the same extraction method and solvent were used. The oil yield of a few common oilseeds; Chrysophyllum albidum (21.57%), Luffa cylindrical (14.08%), Groundnut (45%), Cotton (18.28%), and Soya bean (11 - 25%) [15,16] indicates that Kariya seed could be a better alternative to other oilseeds used in producing biodiesel owning to its high oil yield.

3.2 Physicochemical Properties of Extracted Kariya Oil

The physicochemical properties of kariya seed oil are presented in Table 4. From the results, it was observed that the average pH value of the extracted oil was 3.35, which means that the oil is highly acidic. Moreover, vital to the resistance of the flow of oil is the specific gravity and kinematic viscosity [17]. The specific gravity of extracted oil is 0.88 which is within the range specified for biodiesel standard. In this study, the viscosity of the extracted kariya oil was 2.29 which is low compared to the value obtained in Okeleye and Betiku [9]. Similarly, the extracted oil has lower specific gravity and viscosity compared with the results (viscosity of 4.45 and specific gravity of 0.91) reported by Oluwadare and Adeniyi [14] on the same oil. This difference could be attributed to the source from which the seeds were collected [17]. The heating value of kariya oil was 4090.6 2 KJ/kg which is an indication that the extracted oil has abundant energy to burn. The iodine value which measures the degree of unsaturation in the vegetable oil was 91 g I2/100g in this study, and this oil is therefore considered nondrying since its iodine value was less than 110 [18].

In comparison with other non-edible seed oils, extracted kariya seed oil seems like a good feedstock for biodiesel since its iodine value was within the range of value reported for oils earlier used in producing biodiesel. Non-edible oils such as Chrysophyllum, luffa cylindrical, and jatropha have iodine values of 33.18, 82.56, and 90.8, respectively [19]. The free fatty acid of the extracted kariya oil was marginally higher than the stipulated amount (FFA<1%) when carrying out transesterification [20]. In this case, different factors could have led to the high FFA ranging from the handling of seeds to the processing of the oil. Besides, the origin of the oilseeds, exposure to sunlight, and the presence of moisture could be the cause of the high FFA. Therefore, the extracted oil has to be pretreated before its usage in biodiesel production to reduce its acid value. In comparison with Okeleye and Betiku [9] who reported peroxide value to be within 5.2 – 6.53 meq/kg, the value obtained in this study was 90.80 meq/kg and far greater than the value earlier reported. This is an indication that the extracted oil has a high tendency to absorb oxygen from the air if not properly handled. The pour point of the extracted kariya oil was 0.59^{o}C, the value is far lower than loofah oil pour point of 3^{o}C, and higher than pour point of rapeseed oil (-15^{o}C), sunflower oil (-15^{o}C), safflower oil (-6.7^{o}C), and linseed oil (-15^{o}C) [19]. This result implies that the biodiesel from these oils could form crystal wax as their temperature will reduce faster than the temperature of biodiesel from kariya seed oil. Hence, kariya oil could be more suited in producing biodiesel in the cold climatic regions due to its favorable properties which could favor engine performance and emission under cold climatic conditions [21]. Also, the saponification value of the extracted kariya oil was lower than some non-edible oilseeds earlier used in biodiesel production such as luffa cylindrical (148.50) and Chrysophyllum albidum (193.7 and 246.84) [7]. It should be noted that high saponification value oil tends to form soap during the production of biodiesel and this results in the reduction of yield [22].

Table 5 shows the fatty acid composition and their percentage amount in the extracted kariya seed oil. The total saturated fatty acid composition was 60.95% while the total unsaturated fatty acid was 39.05%. Although the fatty acid profile observed in this study is at variance with the fatty acid composition of the non-edible oils display in Table 5, the result is consistent with the fatty acid profile reported for kariya seed oil by other authors. The percentage composition of saturated and unsaturated fatty acids in kariya seed oil was reported to be 77.11-79% and 21.01-22.73%, respectively [8].

Table 3. *Kariya* oil extraction

Experimental run	Mass of *Kariya* seed sample, M_g, (g)	Mass of oil extracted, M_o, (g)	Percentage oil yield, $M_o/M_g * 100$ (%)
1	1000	327	32.7
2	1000	335	33.5
3	1000	330	33.0
4	1000	322	32.2
5	854	266	31.15
Average	**970.8**	**316**	**32.55 %**

Table 4. Physiochemical properties of *kariya* oil

Parameters	Value
pH	3.35 ± 0.09
Specific gravity @ 20 ^oC	0.88 ± 0.01
Viscosity @ 20^oC	2.29 ± 0.05
Heating value (KJ/kg)	4090.62 ± 13.7
Cloud point (^oC)	2.91 ± 0.23
Pour point (^oC)	0.59 ± 0.10
Iodine value (g I2/100g)	91.0 ± 7.02
Peroxide value (meq/kg)	90.8 ± 4.89
Saponification value (mg KOH/g)	110.3 ± 3.3
Acid value (mgKOH.g^{-1})	5.61 ± 0.05
Free fatty acid (%)	2.82 ± 0.02

Table 5. Fatty acid composition (%) of *kariya* seed oil compared with other oils

Fatty Acid	Type	*Kariya* Oil	[1]Sun-flower Oil	[1]Jatropha Curcas Oil	[2]Neem Oil	[3]Castor Oil	[3]Lin Seed Oil	[4]Rubber Seed Oil	[5]Rice Brain Seed Oil
Palmitic	Saturated	16.13	-	14.2	18.1	1.10	5.10	10.20	17.70
Stearic	Saturated	19.65	4.5	7.0	18.1	3.10	2.50	8.70	2.20
Oleic	Unsaturated	18.05	21.1	44.7	44.5	4.90	18.90	24.60	40.60
Linoleic	Unsaturated	8.12	66.2	32.8	18.3	1.30	18.10	39.60	35.60
Arachidic	Saturated	17.98	0.3	0.2	0.8	NR	NR	NR	0.30
Arachdidoleic	Unsaturated	12.88	NR	NR	NR	NR	NR	NR	NR
Beheric	Saturated	7.19	NR	-	-	NR	NR	NR	NR

NR (No Record). Ref.: [1]Akbar et al.*, [24]; [3] Encinar* et al.*, [25], [3]Demirbas, [1]; [4]Ramadhas, [26]; [5] Ju and Vali, [27]*

Similarly, Ogunsina et al. [23] observed 77.02% and 22.73% of saturated and unsaturated fatty acids, respectively in Kariya seed oil. However, Okeleye and Betiku [9] observed different fatty acid compositions using three different solvents. The authors reported saturated and unsaturated fatty acids to be 35.72-38.42% and 54.73-57.99%, respectively. Factors such as growth condition, quality of feedstock, and location of the oil plant influenced the composition. Generally, biodiesel with a high level of unsaturation components is prone to autoxidation [9], thereby oils with high unsaturated fatty acids are less suitable for biodiesel production.

3.3 Results and Statistical Analysis of Kariya Seed Oil transesterification Process

A total of 15 experimental runs generated using three factors and three levels were conducted to model the transesterification process of kariya seed oil. The process models (temperature, reaction time, and oil: ethanol molar ratio) employed and the biodiesel yields obtained in this study ranged between 86-94wt.% as presented in Table 6. The results from regression analysis of the developed process model and response are presented in Table 7. The process model is significant at a 95% confidence level since p-value ≤ 0.05. Among the linear terms in the model, only the ethanol:oil molar ratio is significant while the other two parameters are insignificant to the response. All the quadratic terms and one cross-product term are significant since their p-value ≤ 0.05. The fitness of the regression model was checked with the coefficient of determination having an R^2 of 0.9449. This means that 94.49% variation observed in the response of this model has been accounted for experimentally.

The quadratic regression equation in terms of coded factors describing the transesterification process of kariya seed oil is given in Eq. (3).

$$\text{Biodiesel yield} = 93.90 - 0.07A - 0.32B + 1.57C - 0.21A^2 - 1.98B^2 - 1.80C^2 + 1.37AB - 0.12AC - 0.12BC \quad (3)$$

Where A is reaction temperature (^oC); B is reaction time (h); C is Ethanol:Oil molar ratio.

Fig. 1 shows the plot of the predicted value of biodiesel yields against the actual yields obtained from the experiments. It can be observed that the data points lie close to the line of fitness, indicating that the experimental values of biodiesel yield are closer to the predicted values by the model. The good agreement between the predicted values and the actual value of biodiesel yield further explains why the obtained R2 in this study is close to unity. Therefore, the regression model adequately estimates the model response (Kariya biodiesel yield) to the variation in ethanol:oil molar ratio, reaction time, and reaction temperature.

Table 6. Process factors and biodiesel yields using CCD

Std	Run	Factors			Response
		Temperature	Time	Ethanol-Oil Molar Ratio	Yield wt.%
		A (^oC)	B(hrs)	C (mol/mol)	
8	1	85.00	4.00	12.00	90
4	2	85.00	4.00	8.00	87
11	3	75.00	1.32	10.00	89
1	4	65.00	2.00	8.00	87
7	5	65.00	4.00	12.00	93
9	6	58.18	3.00	10.00	93
12	7	75.00	4.68	10.00	87
13	8	75.00	3.00	6.64	86
2	9	85.00	2.00	8.00	90
14	10	75.00	3.00	13.36	91
6	11	85.00	2.00	12.00	93
10	12	91.82	3.00	10.00	93
5	13	65.00	2.00	12.00	91
15	14	75.00	3.00	10.00	94
3	15	65.00	4.00	8.00	90

Table 7. Analysis of variance (ANOVA) of Kariya seed oil transesterification process

Source	Sum of Squares	DF	Mean Square	F Value	Prob. > F
*Model	95.02	9	10.56	27.66	0.0010
A	0.073	1	0.073	0.19	0.6797
B	1.39	1	1.39	3.65	0.1142
C	33.56	1	33.56	87.93	0.0002
A^2	0.26	1	0.26	0.69	0.4432
B^2	23.65	1	23.65	61.97	0.0005*
C^2	19.61	1	19.61	51.38	0.0008*
AB	15.12	1	15.12	39.63	0.0015
AC	0.12	1	0.12	0.33	0.5919
BC	0.12	1	0.12	0.33	0.5919
Residual	1.91	5	0.38		
Cor Total	96.93	14			

Significant at P<0.05

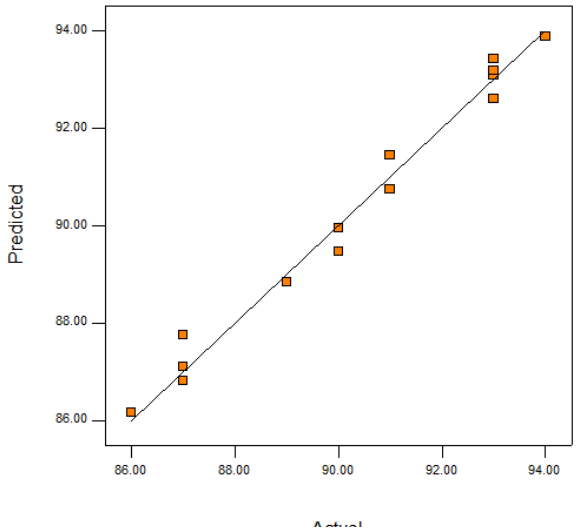

Fig. 1. Plot of predicted values against the actual value of biodiesel yields

3.3.1 Effect of temperature and time interaction

The contour and response surface plot of temperature and time on biodiesel yield is shown in Fig. 2(a). In this study, the reaction temperature was varied between 65-85^{o}C while reaction time was varied between 2-4 h. Although, the effect of the individual parameter was insignificant to biodiesel yield as revealed in (Analysis of variance) ANOVA results and the interactive effect of reaction time and reaction temperature cannot be overlooked. Visual observation reveals that biodiesel yield increases with an increase in reaction temperature and time. The surface plot shows that biodiesel yield marginally increased as the reaction temperature increased, though the effect of temperature at the high value on biodiesel yield can hardly be distinguished. The relationship between reaction time and biodiesel yield was at first linear until the biodiesel yield started to decrease at high reaction time. Increasing reaction temperature and time from 75 to 91.82^{o}C and 1.32 to 3 h respectively, led to an increase in biodiesel yield from 89 to 93 wt.%.

3.3.2 Effect of ethanol-oil molar ratio and temperature interaction

Fig. 2(b) shows the contour plot and 3D surface plot of ethanol-oil molar ratio and temperature on biodiesel yield. The interaction between temperature and ethanol-oil molar ratio favored biodiesel yield to a lesser degree. The impact of the reaction temperature is marginal compared to the ethanol-oil molar ratio that had a dominant effect on the transesterification process. Generally, excess alcohol is expected to favor forward reaction thereby leading to a high

biodiesel yield [28]. However, at high temperatures, biodiesel yield gradually decreases as the ethanol-oil molar ratio increases.

3.3.3 Effect of ethanol-oil molar ratio and time interaction

The contour plot and 3D surface plot of the ethanol-oil molar ratio against reaction time on biodiesel production yield are depicted in Fig. 2(c). The combined effect of ethanol-oil molar ratio and reaction time on biodiesel yield is similar to the observation noted for the interactive effect of ethanol-oil molar ratio and temperature on biodiesel yield. A visual inspection of the surface plot reveals that the ethanol-oil molar ratio greatly influenced the biodiesel yield out of the two process variables. At first, biodiesel yield increased as both ethanol-oil molar ratio and reaction time increased from 10:1 to 13.36:1 and 1.32 hr to 3 hr respectively. However, increasing the reaction time beyond 3 hrs as the ethanol-oil molar ratio keep increasing had a negative effect on the biodiesel yield. At the highest level of reaction time and ethanol-oil molar ratio, biodiesel yield declines and this could be attributed to the hydrolysis of alkyl ester since the transesterification process is a reversible reaction [10].

3.4 Process Optimization of Kariya Biodiesel and Validation

The optimization condition for the kariya biodiesel yield as predicted by the regression model in this study was ethanol:oil molar ratio of 10:1, the reaction time of 2 hrs, and the reaction temperature of 75^{o}C. The transesterification process of kariya oil was validated at the optimal process condition to obtain an average biodiesel yield of 94. 41 wt.% against the 95.2 wt.% predicted by the model. Hence, the regression model obtained gives a good estimate of the biodiesel yield to the process variables investigated in this study. Biodiesel yield from kariya oil is comparable to the biodiesel yield obtained from other non-edible oils. Sharma et al. [29] reported a biodiesel yield of 95 wt.% from the karaja oil using calcined chicken eggshell at the methanol to oil molar ratio of 9:1 and time of 2 h. However, Betiku et al, [10] reported a higher biodiesel yield of 98.67 wt.% from kariya seed oil at the methanol:oil molar ratio of 6:1, time of 75 min, and temperature of 65^{o}C.

3.5 Fuel Properties of Kariya Biodiesel

Biodiesel produced in this study was blended at different volumetric ratios with diesel fuel to compare the physicochemical properties at that ratio to diesel fuel. Besides, blending biodiesel and diesel could help to determine a suitable ratio that this mixture can be used to maximize the utilization of individual components in the blend. The fuel properties of Kariya oil, Kariya biodiesel, Kariya biodiesel-diesel blends, and Petroleum diesel are shown in Table 8. Biodiesel produced in this study is within the limit specified by ASTM D6751 standards.

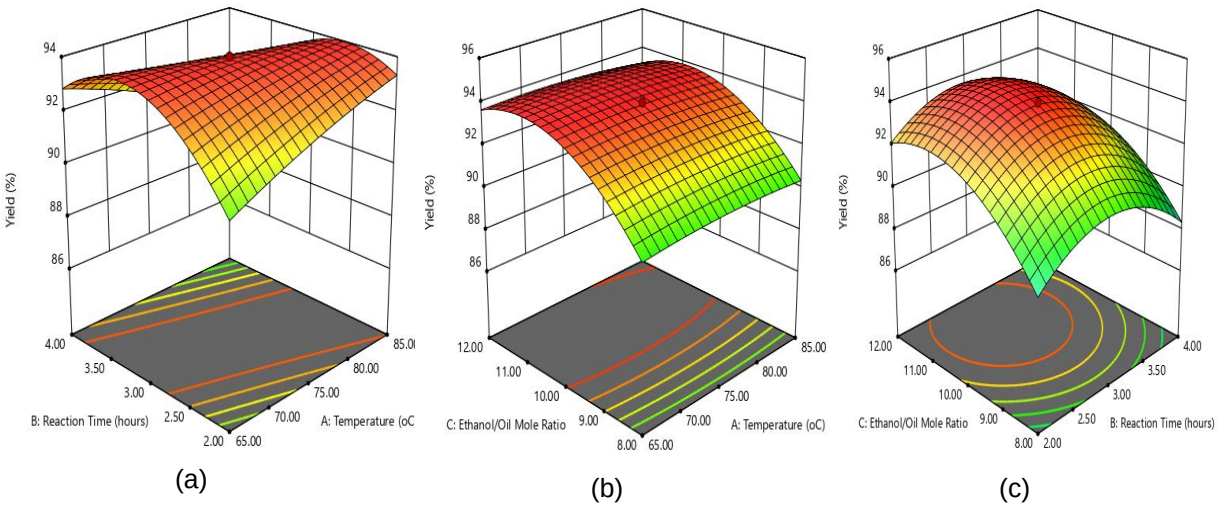

Fig. 2. (a) Surface plot of the reaction temperature and time on biodiesel yield. (b) Surface plot of the ethanol-oil mole ratio and reaction temperature on biodiesel yield. (c) Surface plot of the ethanol-oil mole ratio and reaction time on biodiesel yield

Table 8. Fuel properties of kariya oil, kariya biodiesel blends, produced biodiesel, and petroleum diesel

Fuel Properties	*Kariya* Oil	*Kariya* Biodiesel Blends					*Kariya* Biodiesel Produced	Petroleum Diesel	*ASTM D6751
		B10	B30	B50	B70	B90			
Flash Point (^{o}C)	-	87	96	113	118	127	128	75	93-130
Pour Point (^{o}C)	0.59	-12	-8	-6	-2	-2	-3	-18	-15 to 1
Cloud Point (^{o}C)	2.91	-9	-3	1	2	3	2	-13	-12 to -3
Specific Gravity at 20^{o}C (Kg/L)	0.88	0.865	0.870	0.870	0.880	0.890	0.89	0.860	0.80-0.90
Viscosity at 20^{o}C (mm^{2}/s)	2.29	2.98	3.22	3.29	3.57	3.95	3.85	3.01	1.9-6.0
Heating Value (MJ/kg)	40.90	43.58	41.05	43.21	40.86	38.21	37.85	44.21	37.10-41.55
Cetane Number	-	46	51	59	63	74	75	49	48-65

**Each value represents the mean of three replicates.*

B10 – 10% biodiesel and 90% Petroleum diesel. B30 – 30% biodiesel and 70% Petroleum diesel.

B50 – 50% biodiesel and 50% Petroleum diesel. B70 – 70% biodiesel and 30% Petroleum diesel.

B90 – 90% biodiesel and 10% Petroleum diesel

3.5.1 Flashpoint of kariya biodiesel and its blends

The flashpoint of biodiesel produced and various biodiesel-diesel blends are presented in Table 8. The biodiesel produced has a flashpoint of 128˚C which is within the ASTM specification for biodiesel. Moreover, it is observed that flashpoint increases with increase in biodiesel amount in the biodiesel-diesel blends. However, B10 does not meet up with the ASTM biodiesel flash point standard even though it has a higher flash point than petroleum diesel. Flashpoint is the temperature at which fuel ignites on exposure to flame [30]. Biodiesel-diesel blends in this study compared with petro-diesel would be less volatile since they have flashpoints higher than fossil diesel. According to Sanjay, [31] and Vuppaladadiyam et al., [32], biodiesel produced and biodiesel blends are less flammable and can be safely transported without fire explosion.

3.5.2 Pour and cloud point of kariya biodiesel

The pour points obtained for B10, B30, B50, B70 and B90 are -12^{o}C, -8^{o}C, -6^{o}C, -2^{o}C and -2^{o}C, respectively while the cloud points are -9^{o}C, -3^{o}C, 1^{o}C, 2^{o}C, 3^{o}C, respectively. These results show that the obtained value is an intermediate between the original value of pour point and cloud point for biodiesel and petrol-diesel. It can be observed that the value depends on the proportion of individual components in the biodiesel blend. In the case of cloud point, B10 and B30 blends fall within the specified ASTM D6751 standard, while the rest of the blend and Kariya biodiesel are slightly higher. The cloud point is the temperature at which solid wax in the fuel starts to form a cloudy appearance. Meanwhile, the increasing pour point in the blends means that the temperature at which the fuel becomes semi-solid and loses its flow characteristics also increases [30]. According to Antony Raja et al., [21], these results reveal that the biodiesel blends (B10, B30, and B50) will perform satisfactorily in cold climatic regions due to their low cloud point and pour point.

3.5.3 Viscosity and specific gravity of kariya biodiesel

The viscosity of fuel is a vital property that affects the operation of injection equipment particularly at high viscosity [30]. The viscosity of Kariya oil, biodiesel blends, and Kariya biodiesel are within the standard specified. In comparison to biodiesel produced from Kariya seed oil, Betiku et al. [10] reported kinematic viscosity of 5.6113mm2 /s, a value higher than all values observed for both Kariya oil and biodiesel in this study. Meanwhile, the viscosity of biodiesel-diesel blends increases with an increase in biodiesel amount in the blend. Similarly, the specific gravity values of the biodiesel and its blends follow the trend observed for the viscosity in this study. Here, the viscosity and specific gravity of biodiesel-diesel blends exhibit a similar pattern to loofah oil biodiesel and its blends (B10 to B100) and jatropha methyl ester and its blends (B25 to B100) earlier reported [15,33]. High viscosity above recommended value is not desirable in biodiesel or its blends because it results in poor fuel atomization, poor incomplete combustion, and carbon deposition on the injectors [34].

3.5.4 Heating value

The heating value (also known as calorific value) is essential in the selection of fuel, and biodiesel heating value is generally lower than diesel heating value due to the presence of oxygen [30]. The heating value of petro-diesel and biodiesel is 44.21 MJ/kg and 37.85MJ/kg, respectively. It is not clear why the heating value of kariya oil (40.90 MJ/kg) decreases significantly after transesterification. Moreover, the heating value decreases proportionately with an increase in biodiesel amount in the blend from 43.58 – 38.21 MJ/L for B10 to B90. However, the B50 blend heating value (43.21 MJ/kg) shows slight variation by not following this trend.

A calorific value of 39.05 MJ/kg was reported for Kariya biodiesel using methanol and solid biowaste catalyst [10]. The decrease in the heating value of the blend can be attributed to the decrease in the carbon content of the biodiesel-diesel blends as the biodiesel amount increased. A similar trend was reported by Rao et al. [38] for jatropha methyl ester blends. These results are consistent with the report of biodiesel blends produced from mustard, rapeseed, and sunflower oils (c).

3.5.5 Cetane number

Cetane number is an important parameter that describes the ignition quality of any fuel in a diesel engine and it varies between 48 – 67 depending on the oil processing method and climatic region of the collected oilseeds [35,36]. The cetane number obtained in this study is more than the minimum specified by ASTM

D6751 standard as it increases with an increase in biodiesel amount in the blend. In this study, the cetane number was 75 which is slightly higher than the value recommended for biodiesel and equally higher than the value reported in Betiku et al. [10]. It has been reported that the cetane number of biodiesels depends on the fatty acid composition of the parent oil [10]. As a result, biodiesel-diesel blends (B10, B30, and B50) would produce a better ignition effect in the combustion engine compared to pure Kariya biodiesel.

4. CONCLUSION

Based on the average oil yield (32.55wt.%) obtained in this study, Kariya seed oil could be a better alternative feedstock in producing biodiesel than other non-edible oils, in addition to its better physicochemical properties such as low specific gravity and viscosity. The optimum biodiesel yield of 94.41 wt.% was obtained at the optimal condition; reaction temperature 75^{o}C, time 2 hrs., and the ethanol-oil molar ratio of 10:1 using 5 wt.% of calcined Kariya pod as the catalyst. Kariya biodiesel produced in this study has fuel properties that are within the ASTM D6751 standard for biodiesel. Also, the fuel properties of the kariya biodiesel blends showed that not all blends provide suitable value that is within the standard specified by ASTM D6751 fuel. The Kariya biodiesel-diesel blends (B30, B50, and B70) would produce satisfactory output when used in an internal combustion engine compared to all other blends. In particular, kariya biodiesel-diesel blend (B50) is a good fuel that could be used in diesel engine without modifying the engine and excessive environmental pollution.

ACKNOWLEDGEMENTS

The authors appreciate the technical staff in the Biochemical Engineering Laboratory, Department of Chemical Engineering, Obafemi Awolowo University, Ile-Ife.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/88797