Research Article

Journal of Environmental Nanotechnology

Optimized Neem – Karanja Hybrid Biodiesel Production Using Karanja Seed Shells/CuO–NaOH Nanocatalyst and Analysis of their Physico-chemical Properties

V. Hariram[1*], J. Allen Jeffrey[2], C. Sarath Chandran[1], K. Barathiraja[2], G. Suryavel[1], L. Santhosh[2], S. Sidharth[1], E. Albert[2] and K. Balu[2]

[1]Department of Mechanical Engineering, Hindustan Institute of Technology and Science, Padur, Chennai, TN, India
[2]Department of Mechanical Engineering, Loyola Institute of Technology, Chennai, TN, India
Received: 09.08.2025 Accepted: 12.09.2025 Published: 30.09.2025
*connect2hariram@gmail.com

ABSTRACT

The main aim of the present investigation is to prepare biodiesel from neem and karanja bio oil through base-catalysed esterification process using heterogeneous Karanja Seed Shells (KSS)/CuO-NaOH nanocatalyst and methanol. The KSS/CuO-NaOH nanocatalyst was prepared by employing deposition precipitation method. A central rotatable composite design was developed using response surface methodology with the operating influential parameters like methanol to oil molar ratio, KSS/CuO nanocatalyst concentration, reaction duration, reaction temperature and agitation speed. Volumetric fractions of derived neem and karanja biodiesel were prepared by using ultrasonication technique and their physicochemical properties like density, specific gravity, kinematic viscosity, acid value, calorific value, cetane number, Free Fatty Acid (FFA) content, moisture content, iodine value, flash point and fire point were determined using ASTM methods. The hybrid blend N40:K60 (Neem biodiesel 40% and Karanja biodiesel 60%) showed an optimized kinematic viscosity of 4.652 mm^2/sec at 40°C and a density of 860 kg/m^3 at 15°C. The calorific value and cetane number were also found to be higher with improved flash and fire points. Therefore, the derived (N40:K60) hybrid blend was found to be suitable for its usage in compression ignition engine without any modifications.

Keywords: Hybrid biodiesel; Nanocatalyst; Ultrasonication; Base-catalysed esterification; Neem; Karanja.

1. INTRODUCTION

Economy and industrial revolution of any nation mainly depends on its energy reserves. Conventional fossil fuels are depleted day by day and cannot be replenished, once they are exhausted. Also, burning of conventional fossil fuels releases a large amount of harmful gases mainly through automotive and industrial sources into the atmosphere leading to global warming and deteriorated life of flora, fauna and humans. The combustion phenomenon also emits a large quantity of carbon dioxide into the earth's atmosphere resulting in dilution of the greenhouse gases. Globally, as reported 937 million metric tons of petro diesel are used by the industrial and automotive sector which were the derivatives of conventional fossil fuels. The above factors led to the escalated interest in searching for a renewable source of energy in liquid form to mitigate the usage of conventional petro diesel. Biodiesel from edible and non-edible feed stocks shows a sustainable and promising future in this scenario, due to their comparable energy content. Biodiesels are oils basically derived from vegetable sources and are eco-friendly, non-toxic, bio-degradable, renewable and more sustainable. The higher cetane number of biodiesel shortens the ignition delay period and enhances its lubricating properties. Nearly, 12 - 14% oxygen content is present in the vegetable-based biodiesel which in turn releases a comparatively lower fraction of HC, CO and smoke leading to enhanced engine life. As an agricultural output, biodiesel also place a major role in uplifting the communities in rural region of any country.

Non-edible feed stocks for the biodiesel production maybe from seeds of cotton, jatropha, castor, madhuca indica and many more. The present investigation focuses on deriving bio oil from seeds of neem and karanja due to their superior oil content which is between 35 - 57 %. Generally, vegetable-based biodiesel is derived through various techniques like thermal cracking, pyrolysis, heating and transesterification. As widely reported, multistage transesterification process yields better results in deriving the biodiesel in the presence of a catalyst. Multistage transesterification process has two steps, one is the acid pre-treatment and the other is the base-catalysed esterification in the presence of a homogeneous or heterogeneous catalyst which transforms the triglycerides in the bio oil to their respective mono-alkyl fatty acid esters.

Sabri *et al.* (2025) produced hybrid biodiesel blend with waste cooking oil and neem oil using stirring and ultrasound techniques. Waste cooking oil and neem oil were blended in raw form and subjected to ultrasound-based transesterification process with a molar ratio of 12:1, KOH catalyst concentration of 2% w/w, reaction time of 75 minutes at 60°C. About 98.7 % of hybrid biodiesel was derived with reduced cloud/ pour point and higher oxidative stability. The physicochemical properties of waste cooking oil-neem oil blends were found to be within ASTMD6751 standards. Adepoju (2020) optimised the biodiesel production process of neem and animal fat oil blend using solid residue catalyst. Raw neem oil and rendered pig fat oil were blended in multiple concentrations and was subjected to two stage transesterification process using CaO as heterogeneous catalyst. A Central Rotatable Composite Design (CRCD) using Response Surface Methodology (RSM) technique with 30 experimental trials predicted a 60:40 oil blend of neem and pig fat to have low viscosity and further with a CaO catalyst, reaction time, molar ratio, and reaction temperature of 2.179 g, 57.45 min, 5.9: 1 v/v and 59. 91°C, respectively, resulted in a higher biodiesel yield of 98.03 %. Mallah and Sahito, (2020) prepared an optimised biodiesel blend of neem and castor oil and further predicted their characteristics with an empirical model. They have used NaOH and KOH as the reaction catalyst for neem and castor oil, respectively. The physicochemical properties like kinematic viscosity, specific gravity, density, fire point, flash point, pour point and cloud point were found to be within limits. The blends of castor and neem biodiesel at ratios of 90:10, 80:20, 70:30 and 60:40 were found to be within the ASTM limits but higher blending ratios i.e., 50: 50 and 40: 60 of neem and castor oil biodiesel did not satisfy the limits.

Gurunathan and Ravi, (2015) developed the kinetics and process optimisation strategies for producing neem oil biodiesel in the presence of a heterogeneous nanocatalyst. They have employed a non-uniform surface structure and highly porous copper-doped zinc oxide nanocatalyst. A higher yield of neem oil biodiesel (97. 18 %) was obtained when the methanol to oil molar ratio, Cu-ZnO nanocatalyst concentration, reaction duration and reaction temperature of 1:10 v/v 10 % w/w, 60 minutes and 55°C, respectively, were effected. The presence of fatty acid methyl esters (FAMEs) in the obtained biodiesel was confirmed by NMR and GCMS analysis. A kinetic model of first order with R^2 value of 0. 9452 was found to have a better fit. Anwar *et al.* (2023) adopted a two stage transesterification process to derive biodiesel from karanja seed oil. The free fatty acid (FFA) content was reduced using sulphuric acid in the pre-treatment process followed by methanol and KOH in the base-catalysed esterification process to obtain the karanja biodiesel. Optimized reaction parameters were noticed as 1 % of KOH catalyst concentration, 6:1 methanol to oil molar ratio, 60°C reaction temperature, 120 minutes reaction time and 750 rpm agitation rate for a maximum yield (95.4 %) of karanja biodiesel. Further, the characterization studies were performed using GCMS and FTIR analysis on the derived karanja biodiesel. Prajapati *et al.* (2023) used Karanja Seed Shells (KSS) as a heterogeneous catalyst in the biodiesel production process from soya bean. The KSS nanocatalyst was characterized using FTIR, XRD, SEM and TGA techniques for its standardization. The KSS catalyst quantity of 2 % w/w with reaction temperature, reaction time and methanol to oil molar ratio of 60 minutes, 65°C and 1:10, respectively, were found to be optimum. The obtained biodiesel was characterized using FTIR and GCMS analysis followed by determining their physicochemical properties. A comparative study on the production of biodiesel using multiple biomass ash-based heterogeneous catalyst along with their cost analysis was also reported (Rao *et al.* 2015). Anwar *et al*. (2023) produced biodiesel from okra seed oil using optimized esterification conditions. About 96.8% of biodiesel was obtained.

Chung *et al. (*2009) used NaOH catalyst and methanol to produce biodiesel from duck tallow with a transesterification efficiency of 81.3% whereas, a hybrid biodiesel from combinations of pork and chicken fat was produced by Kwon *et al.* (2014) employing potassium hydroxide as the catalyst. Anwar *et al.* (2010) produced biodiesel from pongamia seed oil employing two step transesterification process and their physicochemical properties were found to be comparable with EU and ASTM standards. Raman *et al.* (2015) employed the methanolysis process to derive biodiesel from karanja oil using both the alkaline and acid catalysts. The methanol to oil molar ratio of 10:1 at 60°C reaction temperature yield at 92% of Karanja biodiesel.

The present experimental investigation aims at deriving an optimized hybrid biodiesel blend of neem and karanja biodiesel for its usage in CI engine without any engine modification. Base-catalysed transesterification process with KSS/CuO NaOH nano catalyst produced the biodiesel of neem and karanja bio-oil. The optimal ratios of operating influential parameters during the transesterification process were identified by adopting CCRD design.

2. METHODS AND MATERIALS

Seeds of neem and karanja (10 kg each) were procured from Saara products, Pattibaram, Chennai, Tamil Nadu. Laboratory grade sodium hydroxide and methanol were purchased from Antares Chem Pvt Ltd. Rajawadi Mumbai, India and Sumisons Scientific Pvt Ltd. Chennai, Tamil Nadu, India respectively. The KSS nanocatalyst was derived from the karanja seeds purchased. Double distilled water was purchased from Astrra Chemicals, Chennai.

2.1 Nanocatalyst Preparation

The karanja seed shells were separated from the karanja plant and washed thoroughly in flowing water. Further, distilled water was used for rinsing the washed shells for the removal of impurities and sun dried for 7 days. The dried shells were then broken into small pieces in a mortar and pestle grinder arrangement. The powdered karanja seed shells were burnt in a hot air oven at 250°C for 3 hours during which the powdered shells were converted into an ash like substance. Further, muffle furnace was used to calcinate the processed shell ash at 425°C for 2 hours in a closed desiccator. Deposition-precipitation method was employed for the preparation of KSS/CuO NaOH nanocatalyst. The preparation method started with a base aqueous solution as copper(II) nitrite in liquid form. About 3 g of KSS was dissolved in 50 mL of copper(II) nitrite solution and ultrasonicated at 300 rpm for 15 minutes. Further, 0.3 mol/L of NaOH solution was mixed with the above solution progressively till the pH is stabilized between 9 and 9.2. The mixture was again stirred for 2 hours and further allowed to settle. The white precipitate formed was filtered and washed with double distilled water. The sediment powder was dried in hot air oven at 70°C for 3 hours for the removal of moisture content. The resultant mixture was then calcinated at 375°C in a muffle furnace in the presence of air to produce KSS/CuO nanocatalyst. The synthesized nanocatalyst was subjected to AFM analysis. The surface morphology of the nanocatalyst was also studied to understand its physical appearance. Fourier transform infrared spectroscopy was employed to study the functional groups present in it.



Fig. 1: KSS/CuO NaOH nano catalyst

Thermo scientific Nicolet iS50 FTIR spectrometer was employed to identify the molecular structure of the various chemical components through the absorption capability of infrared light. The instrument has a spectral range of 80 cm^{-1} to 8000 cm^{-1} at a resolution of 0.125 cm^{-1}.

2.2 Production of Neem and Karanja Bio-oil

Neem oil and karanja oil were derived separately through mechanical expeller method. Initially, 2 kg of oil seeds were placed in the expeller and screwed, during which the shell walls were broken expelling the oil content separately. The oil extracting efficiency was calculated based on equation 1.

$$Oil\ Extraction\ Efficiency = \frac{Obtained\ Bio\text{-}oil}{Weight\ of\ oil\ seed} x\,100 \quad \ldots (1)$$

2.3 Production of Neem and Karanja Biodiesel

Like the bio-oil neem and karanja biodiesel were also prepared separately. The free fatty acid content in neem oil and karanja oil was determined using titration method with phenolphthalein and iso-propyl alcohol. It was found to be 7.19 % and 7.06 %, respectively. Higher free fatty acid content pronounced the two stage transesterification process to be more suitable in reducing the kinematic viscosity by breaking down the triglycerides into mono alkyl fatty acid esters. The acid pre-treatment was started as a batch process in a 200-mL conical flask fitted with a magnetic stirrer, thermometer and heating arrangement. The methanol to oil molar ratio of 1:3 was maintained. About 1.75 – 2 ml of sulphuric acid was also added into it. The mixture was maintained at 60°C for 120 minutes during which the neutralization reaction took place in breaking down the free fatty acid. The titration process was repeated on the resultant mixture to ensure the FFA content is less than 2 % (Kulkarni and Dalai, 2006).

The base-catalysed esterification process was initiated with the acid pre-treated neem and karanja oil separately. A 500-mL conical flask fitted with a magnetic stirrer, thermometer and heating arrangement was used. A CCRD design was developed considering the operating variable parameters like methanol to oil molar ratio, KSS/CuO nanocatalyst concentration, reaction duration and reaction temperature as given in Table 1. The esterification reaction was initiated by thoroughly mixing the methanol and KSS/CuO NaOH nanocatalyst initially at 45°C for 30 minutes. A nanosolution of sodium methoxide was prepared using a magnetic stirrer at 200 rpm. The acid pre-treated oil (100 mL) was allowed to gradually mix thoroughly with the sodium methoxide solution with desired values of reaction time and agitation speed as given in Table 2. After the completion of transesterification process, the mixture was transferred into a separating funnel and allowed to cool and settle down. A distinct ring shaped structure formation occurred separating the biodiesel as the upper layer and glycerol as the lower layer. The glycerol layer containing the nanocatalyst and excess methanol as residual sediments was removed by the knob arrangement in the lower portion of the separating funnel. These sediments were dried and methanol was recovered and further used for the successive batch cycles. The biodiesel thus

obtained was washed with double distilled water and heated for up to 75℃ for the removal of impurities and moisture.

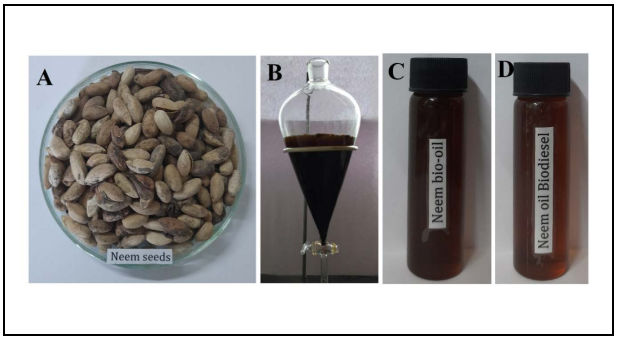


Fig. 2: Feedstock and biodiesel preparation – neem biodiesel



Fig. 3: Feedstock and biodiesel preparation – karanja biodiesel

Table 1. Influential operating parameters in biodiesel production

Factor	Name	Units	Type	SubType	Min	Max	Coded Low	Coded High	Mean	Std. Dev.
A	Methanol to oil Molar ratio	v/v	Numeric	Continuous	6.00	12.00	-1 ↔ 6.00	+1 ↔ 12.00	9.00	2.36
B	KSS/CuO NaOH catalyst	w/w	Numeric	Continuous	0.5000	2.50	-1 ↔ 0.50	+1 ↔ 2.50	1.50	0.7878
C	Agitation speed	rpm	Numeric	Continuous	150.00	600.00	-1 ↔ 300.00	+1 ↔ 600.00	445.00	127.54
D	Reaction Temperature	℃	Numeric	Continuous	45.00	90.00	-1 ↔ 60.00	+1 ↔ 90.00	74.50	12.75

Table 2. Comparison of biodiesel production – actual and predicted - neem and karanja biodiesel

Std	Run	F1 – Methanol to Oil Molar ratio (v/v)	F2 – KSS/CuO NaOH Nano Catalyst(w/w)	F3 – Agitation Speed (rpm)	F4 – Reaction Temperature (℃)	Actual Neem Biodiesel Yield (%)	Predicted Neem Biodiesel Yield (%)	Actual Karanja Biodiesel Yield (%)	Predicted Karanja Biodiesel Yield (%)
23	1	9	1.5	450	45	81.5	84.04	81.6	84.28
2	2	12	0.5	300	60	80.7	81.78	81.78	84.70
1	3	6	0.5	300	60	82.9	81.56	83.7	82.02
17	4	6	1.5	450	75	88.4	94.20	89.7	95.27
25	5	9	1.5	450	75	92.4	93.08	91.75	93.39
7	6	6	2.5	600	60	93.7	91.27	94.7	93.68
28	7	9	1.5	450	75	92.6	93.08	93.7	93.39
3	8	6	2.5	300	60	89.4	85.95	88.7	84.96
21	9	9	1.5	150	75	86.4	88.23	86.7	88.13
22	10	9	1.5	600	75	94.2	92.16	94.6	93.48
15	11	6	2.5	600	90	82.7	81.19	93	88.61
27	12	9	1.5	450	75	95.4	93.08	95	93.39
19	13	9	0.5	450	75	90.4	85.91	91	85.75
18	14	12	1.5	450	75	95.3	94.79	95.7	94.75
12	15	12	2.5	300	90	91.8	89.54	90.9	88.63
26	16	9	1.5	450	75	96.5	93.08	95.7	96.10
24	17	9	1.5	450	90	95	90.11	97.4	97.21
4	18	12	2.5	300	60	83.7	82.17	82.7	80.19
13	19	6	0.5	600	90	79.8	80.45	78.7	81.53

20	20	9	2.5	450	75	76.7	86.48	77.16	87.03
29	21	9	1.5	450	75	92.7	93.08	93	93.39
6	22	12	0.5	600	60	84.7	82.89	85.7	83.43
5	23	6	0.5	600	60	87.9	89.72	88.7	89.50
10	24	12	0.5	300	90	88.4	89.95	88.9	90.24
9	25	6	0.5	300	90	78.4	77.93	78.7	77.76
8	26	12	2.5	600	60	80.4	80.43	80.7	80.17
30	27	9	1.5	450	75	91.6	93.08	92.7	93.39
16	28	12	2.5	600	90	81.7	82.15	82.9	84.90
14	29	12	0.5	600	90	82.4	85.41	83	85.27
11	30	6	2.5	300	90	80.6	81.53	81	83.59

Table 3. ANOVA for neem biodiesel prediction model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	776.89	14	55.49	3.23	0.0156	significant
A-Methanol to oil Molar ratio	1.56	1	1.56	0.0907	0.7674	
B-KSS/CuO NaOH catalyst	1.44	1	1.44	0.0840	0.7759	
C-Agitation speed	0.6867	1	0.6867	0.0399	0.8443	
D-Reaction Temperature	4.13	1	4.13	0.2403	0.6311	
AB	16.00	1	16.00	0.9304	0.3500	
AC	49.70	1	49.70	2.89	0.1097	
AD	139.24	1	139.24	8.10	0.0123	
BC	8.12	1	8.12	0.4723	0.5024	
BD	0.6400	1	0.6400	0.0372	0.8496	
CD	31.92	1	31.92	1.86	0.1932	
A^2	6.61	1	6.61	0.3842	0.5447	
B^2	156.79	1	156.79	9.12	0.0086	
C^2	17.80	1	17.80	1.03	0.3251	
D^2	89.26	1	89.26	5.19	0.0378	
Residual	257.94	15	17.20			
Lack of Fit	239.07	10	23.91	6.33	0.0275	Not significant
Pure Error	18.87	5	3.77			
Cor Total	1034.83	29				

Table 4. ANOVA for karanja biodiesel prediction model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	756.21	14	54.02	2.65	0.0356	significant
A-Methanol to oil Molar ratio	1.19	1	1.19	0.0581	0.8127	
B-KSS/CuO NaOH catalyst	7.45	1	7.45	0.3653	0.5546	
C-Agitation speed	16.04	1	16.04	0.7864	0.3892	
D-Reaction Temperature	0.2555	1	0.2555	0.0125	0.9124	
AB	55.43	1	55.43	2.72	0.1200	
AC	76.48	1	76.48	3.75	0.0719	
AD	96.14	1	96.14	4.71	0.0464	
BC	1.55	1	1.55	0.0760	0.7865	
BD	8.38	1	8.38	0.4110	0.5311	
CD	13.73	1	13.73	0.6731	0.4248	
A^2	8.68	1	8.68	0.4255	0.5241	
B^2	162.00	1	162.00	7.94	0.0130	
C^2	10.22	1	10.22	0.5014	0.4898	

D^2	70.43	1	70.43	3.45	0.0828	
Residual	305.90	15	20.39			
Lack of Fit	294.93	10	29.49	13.45	0.0051	Not significant
Pure Error	10.96	5	2.19			
Cor Total	1062.11	29				

As discussed in the above sections, the optimized biodiesel yield was derived by employing variations in the operating influential parameters like methanol to oil molar ratio, KSS/CuO NaOH nanocatalyst concentration, agitation speed and reaction temperature with the limits as shown in Table 1. A CCRD was developed with a set of 30 experimental trails using RSM technique as given in Table 2. The experiments were conducted at aseptic laboratory conditions as per the CCRD design and the corresponding actual biodiesel yields with respect to neem and karanja biodiesel are tabulated in Table 2. The developed biodiesel prediction model was assisted using analysis of variance (ANOVA) to understand its efficacy. Table 3 and 4 detail the ANOVA factors for neem and karanja biodiesels, respectively. Table 3 depicts details about the model for neem biodiesel in which the model was found to be significant with the "Lack of fit" to be non-significant. The residual value of the mean square data was 17.20. The prediction model showed the p value and F value to be 0.0156 and 3.23, respectively, with the mean square value of 55.49 making the model significant.

Similarly, the ANOVA for karanja biodiesel showed the p value and F value as 0.0356 and 2.65, respectively, with a mean square value of 54.02 as given in Table 4, making the model to be significant. It is to be noted that methanol to oil molar ratio of 1:12, KSS/CuO NaOH nanocatalyst concentration of 1.5 w/w, agitation speed 450 rpm and reaction temperature of 75°C produced an actual yield of 95.3% neem biodiesel and was very close to the predicted value of 94.79%. Similarly, the actual karanja biodiesel was 97.4 % with methanol to oil molar ratio of 1:9, KSS/CuO NaOH nanocatalyst concentration of 1.5 w/w, agitation speed of 450 rpm and reaction temperature of 90°C. The prediction model also was in line with the karanja biodiesel of 97.21 % with the same combinations of influential operating parameters (Dhanya *et al.* 2022).

2.4 Hybrid Fuel Blends

Biodiesels were derived from neem and karanja bio oil separately employing two stage transesterification processes with KSS/CuO NaOH nanocatalyst and methanol. As discussed earlier, hybrid fuel blends were prepared in various ratios of neem and karanja biodiesels, respectively, such as N10:K90, N20:K80, N30:K70, N40:K60, N50:K50, N60:K40, N70:K30, N80:K20 and N90:K10, through ultrasonic technique at 450 Hz for 60 minutes.

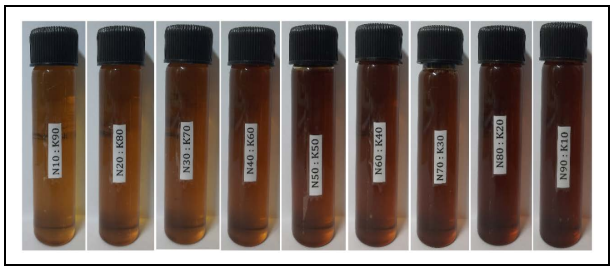


Fig. 4: Hybrid fuel blends of neem and karanja biodiesel

Table 5. Physio-chemical properties of neem – karanja bio-oil and its biodiesel

	Units	ASTM Methods	Diesel	Biodiesel Standards	Neem Oil	Neem Biodiesel	Karanja Oil	Karanja Biodiesel
Density @ 15°C	kg/m³	D7052	836	860-900	941	887	913	824
Specific gravity @ 30°C		D1298	0.836		0.938	0.886	0.911	0.825
Kinematic viscosity @ 40°C	mm^2/s	D6079	3.03	2.5-6	13.58	5.57	15.78	4.04
Acid value	mg/NaOH	D664	0	0.85	5.2	0.97	4.4	0.76
FFA	%	D664	0		7.3	1.92	7.21	1.56
Moisture content	%	--	0		0.9	0	1.2	0
Calorific value	MJ/kg	D240	42.3		36.5	42.35	37.6	43.78
Cetane number		D4737	46	51	36	42	41	45
Iodine value	g I_2/100g	--	1.35		71		73	
Flash point	°C	D93	50	120	160	138	172	127
Fire point	°C	D93	56		215	154	191	143

Table 6. Physio-chemical properties of neem – karanja hybrid biodiesel blends

	N10:K90	N20:K80	N30:K70	N40:K60	N50:K50	N60:K40	N70:K30	N80:K20	N90:K10
Density @ 15°C	830.3	836.6	849	860	859	861.8	868.1	874.4	880.7
Specific gravity @ 30°C	0.8311	0.8372	0.8433	0.8494	0.8555	0.8616	0.8677	0.8738	0.8799
Kinematic viscosity @ 40°C	4.193	4.346	4.499	4.652	4.805	4.958	5.111	5.878	6.243
Acid value	0.781	0.802	0.812	0.805	0.879	0.886	0.907	0.928	0.949
FFA	1.596	1.632	1.668	1.704	1.74	1.776	1.812	1.848	1.884
Moisture content	0	0	0	0	0	0	0	0	0
Calorific value	43.637	43.494	43.351	44.78	43.065	42.922	42.779	42.636	42.493
Cetane number	44.7	44.4	44.1	45.7	43.5	43.2	42.9	41.78	39.7
Iodine value	0	0	0	0	0	0	0	0	0
Flash point	128.1	129.2	130.3	130.7	129.5	129.1	130.1	132.5	136.9
Fire point	144.1	145.2	146.3	147.4	146.9	145.9	144.2	146.7	146.9

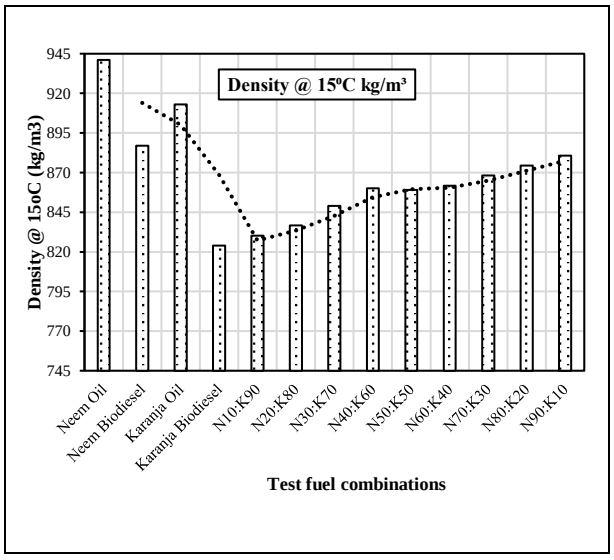


Fig. 5: Variation in fuel density

3. RESULTS AND DISCUSSION

3.1 Effect of Density

Density deeply impacts on the transportation of fuel, its energy content and storage with reference to its volume at ambient temperature. Bio-diesel generally exhibits relatively higher density. Here, the densities of neem oil, karanja oil and their biodiesels at 15°C were tested ASTMD7052 method using hydrometer. The density of neem and karanja bio oil was found to be 941 kg/m^3 and 913 kg/m^3, respectively, whereas, their biodiesel represented 887 kg/m^3 and 824 kg/m^3. Ultra-sonicated hybrid blend of neem and karanja biodiesels at 10:90 showed 830.3 kg/m^3 of density. Increasing the neem biodiesel content volumetrically by 10% and decreasing the karanja bio-diesel content in a similar way escalated the fuel density at 15°C. The hybrid blend N40:K60 represented 860 kg/m^3 of density value beyond which there was a slight dip in fuel density as given in Table 5 and 6. Further, increase in the neem bio-diesel concentration up to 90% significantly increased the fuel density up to 880.7 kg/m^3. This may be due to higher molecular interaction between neem and karanja biodiesels. The blend N10:K90 recorded a lowest density of 830.3 kg/m^3 at 15°C (Kulkarni and Dalai, 2006; Gouran *et al.* 2021).

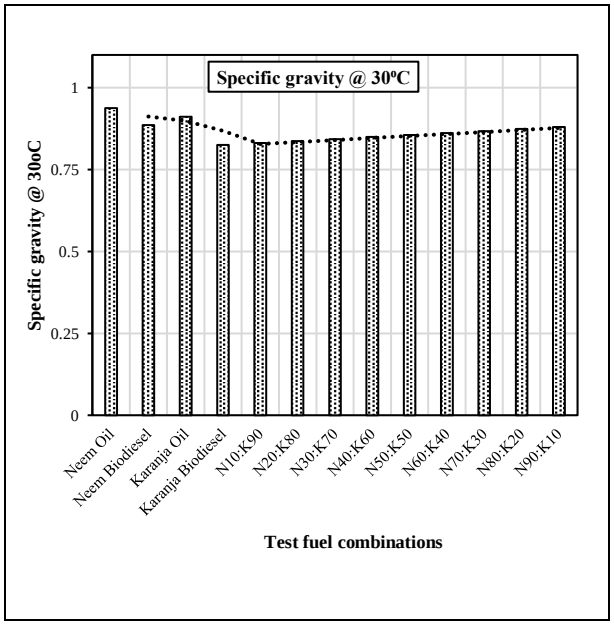


Fig. 6: Variation in specific gravity

3.2 Effect of Specific Gravity

ASTMD1298 method was employed to determine the specific gravity of bio oil, bio-diesel and

their hybrid blends with reference to diesel. It could be noted that neem and karanja bio oils represented specific gravities of 0.938 and 0.911 at 30°C. The transesterification process reduced their specific gravity up to 0.886 and 0.825, respectively. Ultra-sonicated blending of neem and karanja biodiesels in incremental volumetric fractions elevated their specific gravity significantly (Farooq *et al.* 2018; Munir *et al.* 2021). The lower and higher volumetric fraction of neem and karanja biodiesel represented specific gravities between 0.311 and 0.879, respectively. The detailed variations of the test fuels are tabulated in Table 5 and 6.

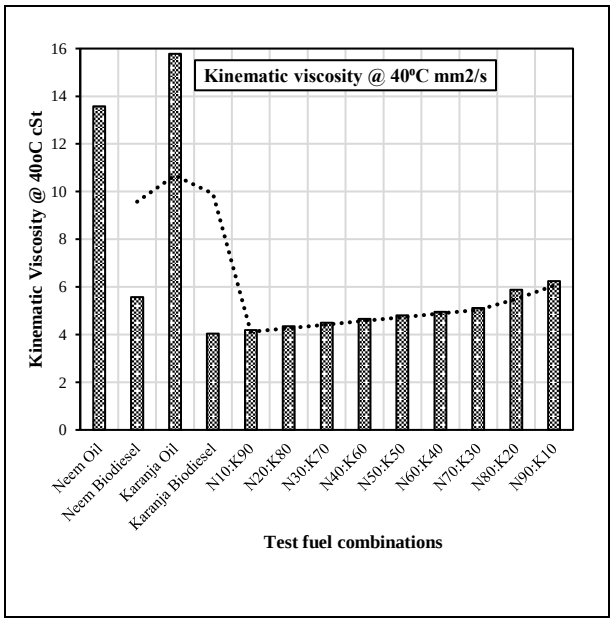


Fig. 7: Variation in kinematic viscosity

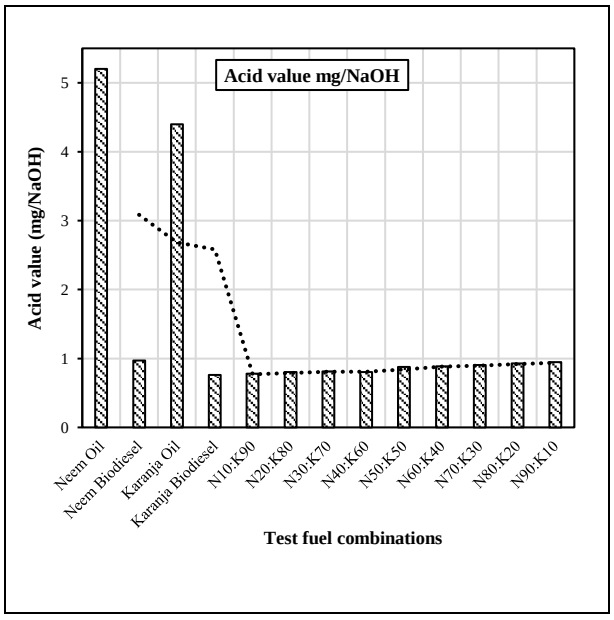


Fig. 8: Variation in acid value

3.3 Effect of Kinematic Viscosity

ASTMD6079 method was used to determine the kinematic viscosity of neem, karanja bio oil, neem, karanja biodiesel and their volumetric fractions with reference to diesel whose kinematic viscosity is 3.03 m^2/s at 40°C. Neem and karanja biodiesels represented 58.9% and 74.39% reduction in kinematic viscosity when compared with their corresponding bio oils. The kinematic viscosity of volumetric fractions of neem and karanja biodiesels ranged from 4.346-6.243 m^2/s. It could also be noticed that neem biodiesel fractions of 80 and 90% in the hybrid fuel blend witnessed a sudden increase in kinematic viscosity by 6.34% (Beyene *et al.* 2024; Karme *et al.* 2005).

3.4 Effect of Acid Value

The acid value of neem and karanja bio oils and their biodiesels was determined by neutralization with sodium hydroxide. Higher acid value indicates increased acidity which should be counteracted to make it suitable for its usage in CI engine. ASTMD664 method was used to estimate the acid values. Neem and karanja bio oils showed higher acid value of 5.2 mg/NaOH and 4.4 mg/NaOH, respectively. The esterification process neutralized the acid value up to 0.97 mg/NaOH and 0.76 mg /NaOH, respectively. The fractional hybrid biodiesel blends of neem and karanja exhibited increasing trend between 0.781 mg mg/NaOH and 9.49 mg/NaOH when neem oil biodiesel concentration was increased (Kodgire *et al.* 2022; Rashid *et al.* 2019). The hybrid fractional blend N40: K60 represented a slight dip in acid value up to 0.805 mg/NaOH during the neutralization process. Further increase in neem biodiesel significantly increased the acid value beyond 0.85 mg/NaOH which is undesirable for the test engine (Miladinovic *et al.* 2022).

3.5 Effect of Calorific Value

Calorific value gives the measure of energy content per unit volume of the fuel. Higher calorific value of the fuel indicates its suitability for combusting in CI engines. ASTMD240 test method was adopted to determine the calorific value of neem and karanja-based fuels. It can be noticed that neem and karanja oils exhibited a relatively lower calorific value of 43.78 MJ/kg and 37.60 MJ/kg, respectively. The thermally cracked esterification process increased their calorific value by 11.21% and 16.62 %, respectively. Hybrid fractional blends with neem and karanja biodiesels indicated a decreasing trend with increasing fractions of neem biodiesel. The blend N10:K90 recorded a calorific value of 47.637 MJ/kg, while, N90:K10 represented 42.493 MJ/kg. The calorific value of N40:K60 blend was 44.78 MJ/kg, which was relatively higher than that of diesel fuel and was within the ASTM limits (Nisar *et al.* 2022; Nath *et al*. 2020).

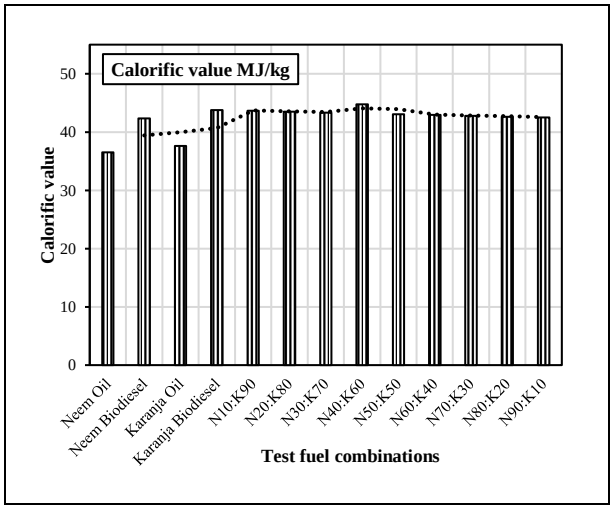


Fig. 9: Variation in calorific value

3.6 Effect of Cetane Number

The fuel ignition speed and its quality are revealed by the cetane number. Higher cetane number brings shorter ignition delay leading to better ignition resulting in efficient and smoother combustion process. ASTMD4737 method was used to determine the cetane number of all the fuels in the study and the reference fuel diesel represented a cetane number of 46. Neem and karanja bio oils represented a lower cetane number of 36 and 41, respectively, whereas, their corresponding biodiesels exhibited cetane number of 42 and 45. The hybrid biodiesel fractional blends exhibited a decreasing trend of cetane number with increasing concentration of neem oil biodiesel. A sharp reduction in the cetane number was seen for N80:K20 and N90:K10 fuel blends as 41.78 and 37.9. Highest cetane number was recorded for the biodiesel fraction N40:K60 (44.78). This indicates that N40:K60 blend is a better hybrid test to be used in CI engines (Patel *et al.* 2017).

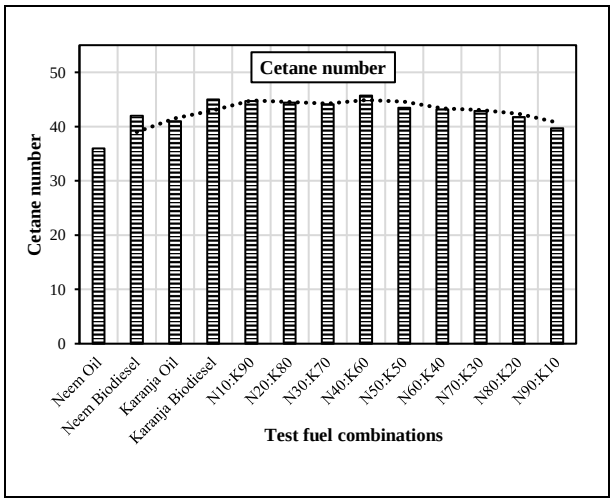


Fig. 10: Variation in cetane number

3.7 Effect of Flash Point

Flash point is the temperature at which the liquid fuel supplies sufficient amount of vaporized fuel particles for the start of ignition in terms of a spark. Flash point is an important phenomenon in the biodiesel characterization, since it directly affects the ignition of the air-fuel mixture. Lower the flash point of a fuel may result in instantaneous ignition at multiple points in the combustion chamber leading to detonation and invariably affects the pre-mixed combustion phase. ASTMD93 testing method was adopted to estimate the flash point of all the samples. The transesterification process significantly reduced the flash point from 160°C to 138°C for neem biodiesel and similarly from 172°C to 127°C for karanja biodiesel. Blending of neem biodiesel and karanja biodiesel in the ratio N10:K90 showed a higher flash point of 128.1°C. Further increase in concentration of neem increased the flash point up to 130.7°C with N40:K60 fuel blend. A sudden decrease of flash point between 2.4 to 5.3 % was noticed in the hybrid blends of N50:K50, N60:K40 and N70:K30. Fuels with higher fraction of neem biodiesel like N80:K20 and N90:K10 showed much higher values of flash point than the nominal i.e.132.5°Cand 136.9°C, respectively (Rao *et al.* 2015).

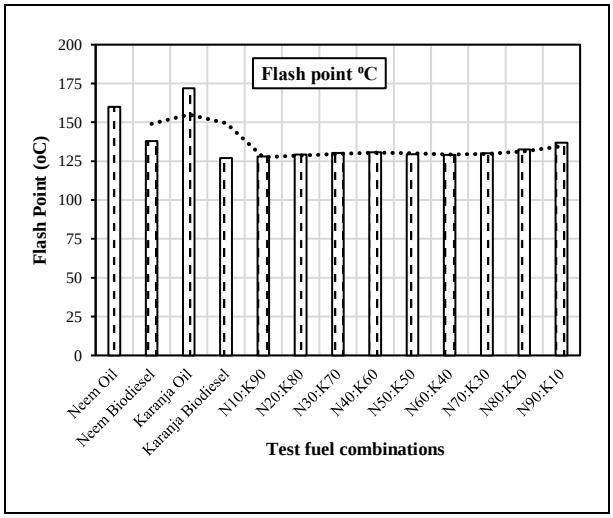


Fig. 11: Variation in flash point

3.8 Effect of Fire Point

It is the minimal temperature of a liquid fuel during which the ignited flame will sustain to burn for a minimum period of 5 seconds after the removal of heating source. Higher the fire point will result in complete combustion process especially in the progressive combustion phase ensuring complete oxidation process resulting in the production of carbon di oxide. Like flash point, the fire point was also determined using ASTMD93 methodology. The fire point of neem and karanja bio oils was found to be 215°C and 191°C,

respectively, whereas, for their biodiesels, it was reduced to 154℃ and 143℃respectively. The fire point of the hybrid fuel blend fractions was very similar to the flash point with the highest amount of fire point by N40:K60 test fuel as 147.4℃ (Suherman *et al.* 2025; Zhou *et al.* 2021).

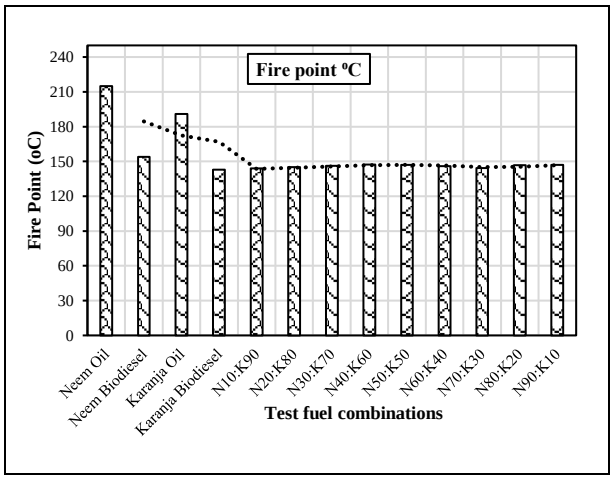


Fig. 12: Variation in fire point

The free fatty acid content was determined using ASTMD664 method. Neem and karanja bio oils contain 7.3% and 7.21 % FFA, respectively, which was reduced to 1.92 % and 1.56 % through acid esterification process. Among all the hybrid fuel fractions, N40:K60 test fuel recorded a lower quantity of FFA content (1.74%), favorable for the combustion process. Both of the bio oils possessed moisture before initiating the esterification process. As moisture is an undesirable component which directly affects the combustion process it was removed by heating the fuel samples up to 100℃ for 15 minutes. Iodine value is an important parameter which shows the unsaturation degree of fatty acid composition in the biodiesel content. The iodine value of Neem and Karanja bio oil was found to be 71 g I_2/100 g and 73 g I_2/100 g.

4. CONCLUSION

The current study successfully optimized biodiesel production from neem and karanja bio-oil using a KSS/CuO–NaOH nano-catalyst through a two-stage transesterification process. The catalyst, synthesized via deposition–precipitation and ultrasonication, enabled high biodiesel yields of 95.3% (neem) and 97.4% (karanja) under CCRD–RSM optimized conditions (methanol-to-oil ratios of 1:12 and 1:9, catalyst concentration 1.5 w/w, agitation 450 rpm, and temperatures of 75 ℃ and 90 ℃). Hybrid blends were prepared through ultrasonication, and the N40:K60 blend demonstrated superior physicochemical properties, including appropriate density, viscosity, calorific value, cetane number, flash point, and fire point, aligning with fuel standards. Overall, the neem–karanja 40:60 biodiesel blend shows strong potential as a sustainable CI engine fuel without requiring engine modifications.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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