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Hydrogen-enriched Compression Ignition Performance of RSM-optimized Neem–Karanja Hybrid Biodiesel Using Eggshell-derived Nano-catalyst

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ABSTRACT

Increasing demand of fossil is a big issue due to their finite abundance in nature. The present investigation explores the development of a hybrid biodiesel which refers to a fuel produced by blending Neem and Karanja non-edible oils and converting them into biodiesel via transesterification i.e., derived from vegetable feedstock (i.e.) neem and karanja seeds using Eggshell / CuO-NaOH nano catalyst through transesterification process thereby combining the complementary physicochemical properties of both feedstock into a single optimized fuel. The effects of this fuel on a 6.2 kW compression ignition engine were evaluated under hydrogen enrichment at flow rates of 2, 4, and 6 LPM (liters per minute). The main focus is on performance, combustion, and emission characteristics. The production process was optimized using a central composite rotatable design within a Response Surface Methodology (RSM) framework, considering molar ratio, catalyst concentration, agitation speed, and reaction temperature as input variables. The developed regression model was validated using analysis of variance (ANOVA) and showed statistical significance. An approximately 97% Bio-diesel yield can be achieved by optimizing the processes. The physicochemical properties, including calorific value, kinematic viscosity, and flash/fire point, showed improved performance compared to individual neem and karanja biodiesel. The engine study showed an BTE (Brake Thermal Efficiency) increase upto 38.27% when D80HyBD20 was fueled along with 6 LPM of hydrogen with relatively lower BSFC (Brake-specific fuel consumption) at part and full load operation. CO (Carbon monoxide) and UBHC (Unburned Hydrocarbon) emissions increased at partial and full load conditions; however, hydrogen injection significantly reduced CO emissions compared to baseline fuel operation. Nitrogen oxides (NO_x) emissions were increase at all loads but significantly under full load. Enhanced in-cylinder pressure and heat release rate were observed at 4 LPM hydrogen supplementation for the D80HyBD20 (Diesel 80% and Hybrid biodiesel 20%) blend. Thus, the study presents a novel integration of hybrid neem–karanja biodiesel with hydrogen enrichment in order to achieve a significant BTE improvement so that it portrays the potential as a high-efficiency alternative fuel.

Keywords: Hydrogen; Nano catalyst; Emission; Performance; Response surface methodology.

1. INTRODUCTION

The dependency on fossil fuel is reducing day-by-day due to enormous release of green- house gases into the atmosphere through power generation and transportation sector worldwide (Anwar *et al.* 2023). Global warming, air and water pollution, climatic change and other factor too have impacted human life along with the ill-effects of flora-fauna on the earth's surface. Deep concerns about environmental hazards and rapid fossil fuel depletion have urged the researchers in search of clean energy feedstocks in which vegetable-based biodiesel has emerged as a promising alternate to fossil fuel. Non-edible vegetable-based bio-oil like Karanja, Neem, Cotton seed oil, and Jatropha in neat or hybrid form possess higher kinematic viscosity which prohibits its usage directly in compression ignition engine like petro-diesel (Sruthi *et al.* 2025). It is also to be noted that hybrid biodiesel blends possess superior cetane number, calorific value with considerably lower kinematic viscosity which supports the combustion process favorably. Thermal cracking, pyrolysis, super heating and transesterification are few techniques through which their viscosity can be reduced considerably, thereby enabling them to be amalgamated with diesel fuel and subjected to compression engine to produce energy.

Based on the literatures, it can be understood that the efficacy of transesterification reaction solely depends on the characteristics of catalyzed used (Shankar *et al.* 2017). Improper selection of catalyst may lead to corrosiveness, downstream separation, moisture content,

soapy formation and environmental hazards. Heterogeneous catalyst can overcome the above limitations notably and can be reused and easily recovered. Few common types of heterogeneous catalyst include bi-functional material, nano catalyst, metal oxides, hydrotalcite based and solid acids. Nano based catalyst are advantageous due to their improved catalytic activity, higher surface area ratio and its durability. Specifically, calcium based nano catalyst derived from processed egg shells were effective in catalyzing the transesterification process in-spite of its phase leaching and low intrinsic capability.

Aytav *et al.* (2024) optimized a biodiesel–hydrogen dual-fuel CI engine with EGR (Exhaust Gas Recirculation) using RSM analysis and reported improved combustion and engine performance at 7.68% EGR and 6.93% hydrogen enrichment under varying engine load conditions. Sen, (2024) optimized the performance and emission characteristics of a diesel engine fueled with isopropyl alcohol blends by comparing ANN–genetic algorithm and RSM–hill climbing optimization approaches. The ANN-based optimization method demonstrated superior prediction capability for identifying emission-focused optimal operating conditions. Dubey *et al.* (2022) reported approximately 10.07% improvement in brake thermal efficiency, 21.68% reduction in CO emissions, and nearly 27.81% increase in heat release rate during hydrogen–biodiesel dual-fuel RCCI (Reactivity Controlled Compression Ignition) operation with only marginal increase in NO_x emissions.

Despite extensive studies on biodiesel and hydrogen-enriched dual-fuel engines, limited research has focused on hybrid biodiesel derived from multiple non-edible feedstocks with hydrogen supplementation. There is also a lack of integrated studies combining RSM-based nano-catalyst optimization with engine performance and emission analysis under hydrogen enrichment. Furthermore, the interaction between hydrogen flow rate and hybrid biodiesel combustion characteristics across varying engine loads remains insufficiently explored.

This study presents a novel integration of hybrid Neem–Karanja biodiesel (a blend of neem and karanja non-edible oils using an eggshell/CuO–NaOH nano-catalyst to obtain a fuel with enhanced physicochemical properties) with hydrogen enrichment in order to achieve a significant BTE improvement so that it can demonstrate its potential as a high-efficiency alternative fuel. The work advances existing research by combining nano-catalyzed fuel optimization (RSM-based) with dual-fuel engine operation, bridging fuel synthesis and engine application. From an academic perspective, it provides new insights into the interaction between hydrogen flow rate and hybrid biodiesel combustion behaviour under varying loads. From a societal standpoint, the approach supports sustainable energy transition by reducing fossil fuel dependency while improving engine performance with cleaner fuel blends.

2. MATERIALS AND METHODS

This section details about the production of oil, transesterification process, design of experiments method and ANOVA analysis clearly.

2.1 Feedstock Preparation

Neem and Karanja seeds (15 kgs each) were procured from S R neem agro product Tamil Nadu, India. Laboratory grade sodium hydroxide and methanol were purchased from Hans-Chem enterprises and Nice chemical, Chennai, Tamil Nadu, India. The purchased neem and karanja were deshelled and thoroughly cleaned with flowing water. The derived seeds were then sundried for 48 hours separately.

2.2 Oil Extraction

Mechanical expeller method with screw expeller technique was applied to extract oil from Neem and Karanja respectively. The free fatty acid content in the derived oil was evaluated through titration method using phenolphthalein and isopropyl alcohol which showcase 7.19% and 7.06% respectively. Since the FFA (Free Fatty Acid) content was more than 2% two stage transesterification process was adopted to significantly reduce its kinematic viscosity in the acid pretreatment stage 1.8 ml of sulphuric acid was mixed with 250 ml of neem oil and agitated at 200 rpm for 40 minutes at 45°C. This process neutralizes the FFA content from 7.06% to 1.92%. Similarly, the obtained karanja oil was also subjected to acid pretreatment process which neutralize the FFA content to 1.87% the neutralized oils were then blended in the ration of neem 40% and karanja 60% based on their improved physiochemical properties like kinematic viscosity, calorific value, acid number and flash point.

2.3 Catalyst Synthesis and Transesterification Process

The secondary stage involved a base-catalyzed transesterification process using a hybrid blend of neem and karanja bio-oil with an eggshell/CuO–NaOH nano-catalyst and methanol. The nano-catalyst was synthesized from waste eggshells through a deposition–precipitation method. Initially, collected eggshells were cleaned thoroughly with double-distilled water to remove impurities and membranes, followed by sun drying for 48 h. The dried shells were ground into fine powder using a mortar–pestle and subsequently heated in a hot air oven at 200°C for 3 hrs. This was followed by calcination in a muffle furnace at 500°C to obtain processed eggshell ash. For catalyst preparation, 5 g of the processed eggshell ash was dispersed in 50 mL of copper (II) nitrate solution and

ultra-sonicated at 300 rpm for 15 min to ensure uniform mixing. A sodium hydroxide solution (0.32 mol/L) was then added gradually under continuous stirring to maintain controlled precipitation, ensuring the pH remained below 9.5 throughout the process (Jamil *et al.* 2024). The resulting mixture was allowed to cool and settle for 60 min to facilitate complete sedimentation. The precipitate was separated using Whatman filter paper, washed, and dried in a hot air oven at 80°C for 2 h to remove residual moisture. Finally, the dried material was calcined at 400°C in a muffle furnace to obtain the eggshell/CuO–NaOH nano-catalyst (John *et al.* 2017). The synthesized catalyst was further characterized using surface morphology analysis, Atomic Force Microscopy (AFM), and Fourier Transform Infrared Spectroscopy (FTIR) to identify its structural and functional properties. Figure 1 and Figure 2 depicts the bio-oil preparation and nano catalyst production respectively.



Fig. 1: Preparation of hybrid biodiesel blend



Fig. 2: Transesterification process with eggshell / CuO-NaOH nano catalyst

2.4 Design of Experiments (DOE)

This sub section of DOE deals with RSM approach and regression model.

2.4.1 Base Catalyzed Transesterification-An RSM Approach

A central rotatable composite design (CCRD) in RSM approach developed a 29 run experimental model to understand the optimal conditions for deriving neem-karanja hybrid biodiesel. Design of experiments (DOE) is an optimization tool which output response in the present investigation. The independent input variable was methanol to oil molar ratio, eggshell/CuO-NaOH nano-catalyst, agitation speed and reaction temperature with output response as hybrid biodiesel yield (Hariram and Bharathwaaj, 2015). The maximum and minimal value of input independent variable are tabulated along with its mean and standard deviation values. A quadratic function order polynomial as indicated in the equation (1) represents a sequential P value 0.0009 with a lack fit as 0.3331. The adjusted and predicted R^2 value of the polynomial equation was found as 0.6268 and 0.5321 respectively. The predicted R^2 value was found to be in close agreement with the adjusted R^2 value, indicating acceptable predictive capability and demonstrating that the developed regression model can be considered statistically valid for optimization and interpretation within the selected experimental range (Gugulothu *et al.* 2025). The transformation of hybrid blended Neem-Karanja bio-oil into its biodiesel was chosen as the response factor suggested by RSM-CCRD design and their interaction between the independent input variable and output response was validated.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad \ldots (1)$$

Where Y represents the responses, k is the total number of independent variables, β is the intercept, i, ii, and ij with β represents, linear coefficient, quadratic coefficient, and interaction coefficient, respectively, and xi and xj shows the coded levels for independent variables and ε is the statistical error.

The base catalysed transesterification process was initiated by a procedural step involved primary mixing of eggshell/CuO-NaOH catalyst and methanol in a round bottomed conical glass at elevated temperature and agitated speed as per the experimental design further the pre-treated hybrid neem-karanja bio-oil was thoroughly mixed with the primary solution in a separating flask. Table 1 details the input variables for each of the experimental trial and the completion of transesterification reaction was ensured by identifying a ring formation which separates the hybrid biodiesel from glycerol. The recovery of methanol and eggshell/CuO-NaOH nano-catalyst was carried out for its subsequent usage in the further trial experiments (Naik *et al.* 2008). The derived hybrid biodiesel was washed with distilled

water and heated up to 75ºC to remove the moisture, it was observed that among the 29 experimental trials the standard 26 with methanol to oil molar ratio as 9:1 v/v, eggshell/CuO-NaOH nano-catalyst as 1.55 w/w, agitation speed as 375 RPM and reaction temperature as 67.5°C yielded the hybrid biodiesel of 97.8% as shown in experiment trials in table 2.

2.4.2 Development of Regression Model

The present study was focused to maximize the yield of hybrid biodiesel by developing a regression model using CCRD design using RSM. The experimental design was developed by RSM tool in version 11 of the design expert software the regression model analysis. The effect of input variable like methanol to its molar ratio (6:1 – 12;1 v/v), eggshell/CuO-NaOH nano-catalyst (0.5 – 2.6 w/w), agitation speed (150-600 rpm) and reaction temperature (45ºC-90ºC) against the output response as hybrid biodiesel yield table 2 details as randomised 29 experimental design along with their actual and predicted yield it can be further noted that standard 0.26 and 15 exhibited a higher and lower hybrid biodiesel yield of 97.8% and 89.2% respectively.

2.4.3 ANOVA Analysis

The efficacy of the developed regressive model is illustrated by analysis of variance (ANOVA). Table 3 depicts the inter relationship between independent input variable with output response through empirical and statistical data for confirming its suitability. The probability value (P) of the developed model was found as 0.0156 which is less, thereby making the model to be significant along with the larger fisher test (F value). The F value and P value for all the individual input parameter and their inter-relationship are tabulated in table 3. it can also be noted that the lack of fit value was also found to net significant in the table 3.

2.4.4 Interaction Between Input Process Parameter

A three-dimensional plot represents the interaction between two independent input variables on hybrid biodiesel are shown in Figure 3 the effect of varying the methanol to oil molar ratio of 6:1-12:1 v/v with eggshell/CuO-NaOH nano-catalyst concentration between 0.5-2.6 w/w on the yield of hybrid biodiesel at constant reaction temperature and agitation speed is shown in the surface plot of Figure 3. The pattern shows that 1.55w/w of catalyst concentration and 9:1 methanol to oil molar ratio, 375 rpm of agitation speed and 67.5°C reaction temperature produces higher biodiesel yield of 97.8% increasing the catalyst concentration beyond and 1.55 w/w deteriorates the biodiesel yield greatly due to soapy sludge up to 6:1 v/v also shows the reduced yield of hybrid biodiesel (Sharma *et al.* 2010).

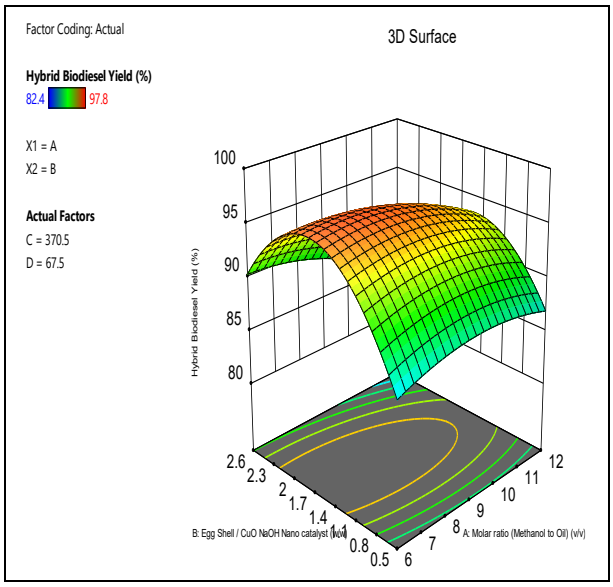


Fig. 3: Surface plot – effect of catalyst concentration and molar ratio on hybrid biodiesel yield

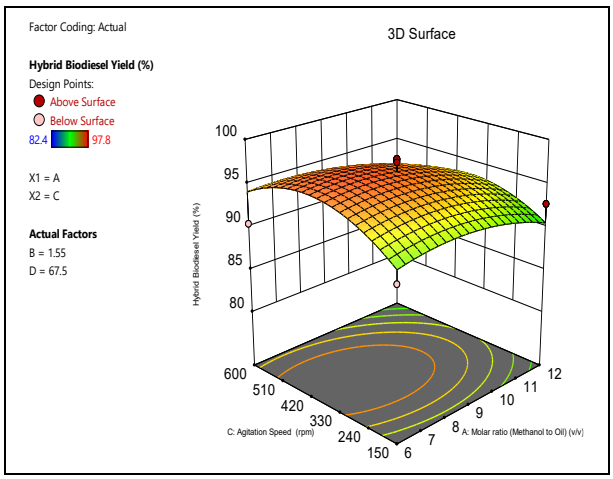


Fig. 4: Surface plot – effect of agitation speed and molar ratio on hybrid biodiesel yield

Table 1. Experimental design for optimized biodiesel production

Factor	Name	Units	Type	Sub Type	Min	Max	Coded Low	Coded High	Mean	Std. Dev.
A	Molar ratio (Methanol to Oil)	v/v	Numeric	Continuous	6.00	12.00	-1 ↔ 6.00	+1 ↔ 12.00	9.00	1.96
B	Egg Shell / CuO NaOH Nano-catalyst	w/w	Numeric	Continuous	0.5000	2.60	-1 ↔ 0.50	+1 ↔ 2.60	1.55	0.6874
C	Agitation Speed	rpm	Numeric	Continuous	150.00	600.00	-1 ↔ 150.00	+1 ↔ 600.00	375.00	147.30
D	Reaction Temperature	ºC	Numeric	Continuous	45.00	90.00	-1 ↔ 45.00	+1 ↔ 90.00	67.50	14.73

Table 2. Experimental trials

Standard	Run	Methanol to Oil Molar Ratio (v/v)	Egg Shell / CuO NaOH Nano Catalyst (w/w)	Agitation Speed (rpm)	Reaction Temperature (ºC)	Predicted Yield	Actual Yield
13	1	9	0.5	150	67.5	86.53	82.28
28	2	9	1.55	375	67.5	96.26	97.68
1	3	6	0.5	375	67.5	86.25	86.58
26	4	9	1.55	375	67.5	96.38	97.8
3	5	6	2.6	375	67.5	90.33	89.28
25	6	9	1.55	375	67.5	96.26	97.48
7	7	9	1.55	150	90	92.71	92.58
17	8	6	1.55	150	67.5	91.99	90.48
8	9	9	1.55	600	90	91.44	89.58
6	10	9	1.55	600	45	90.28	90.58
14	11	9	2.6	150	67.5	83.09	84.78
11	12	6	1.55	375	90	95.19	96.58
27	13	9	1.55	375	67.5	96.26	91.18
21	14	9	0.5	375	45	82.29	83.34
18	15	12	1.55	150	67.5	90.41	92.58
24	16	9	2.6	375	90	86.16	83.58
4	17	12	2.6	375	67.5	84.14	83.98
19	18	6	1.55	600	67.5	93.98	90.28
22	19	9	2.6	375	45	86.17	82.67
10	20	12	1.55	375	45	89.2	84.78
29	21	9	1.55	375	67.5	96.26	97.28
16	22	9	2.6	600	67.5	87.97	93.58
2	23	12	0.5	375	67.5	86.79	88.01
20	24	12	1.55	600	67.5	89.88	89.86
5	25	9	1.55	150	45	87.55	89.58
15	26	9	0.5	600	67.5	83.23	82.9
9	27	6	1.55	375	45	92.04	96.58
12	28	12	1.55	375	90	92.36	93.58
23	29	9	0.5	375	90	88.61	90.58

Table 3. Analysis of variance

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	528.77	13	41.05	3.31	0.0156	significant
A-Molar ratio (Methanol to Oil)	24.06	1	24.06	1.97	0.1810	
B-Egg Shell / CuO NaOH Nano catalyst	1.54	1	1.54	0.1260	0.7275	
C-Agitation Speed	1.60	1	1.60	0.1308	0.7227	
D-Reaction Temperature	29.93	1	29.93	2.45	0.1385	
AB	11.32	1	11.32	0.9263	0.3511	
AC	1.59	1	1.59	0.1299	0.7236	
BC	17.22	1	17.22	1.41	0.2537	
BD	10.02	1	10.02	0.8195	0.3796	
CD	4.00	1	4.00	0.3272	0.5758	
A^2	14.51	1	14.51	1.19	0.2932	
B^2	403.46	1	403.46	33.00	< 0.0001	
C^2	66.39	1	66.39	5.43	0.0342	
D^2	42.69	1	42.69	3.49	0.0813	
Residual	183.36	15	12.22			
Lack of Fit	150.99	11	13.73	1.70	0.3228	
Pure Error	32.37	4	8.09			
Cor Total	713.14	28				

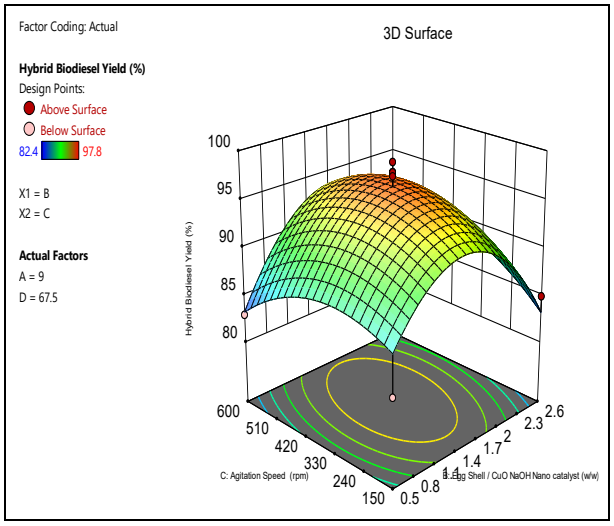


Fig. 5: Surface plot – effect of agitation speed and catalyst concentration on hybrid biodiesel yield

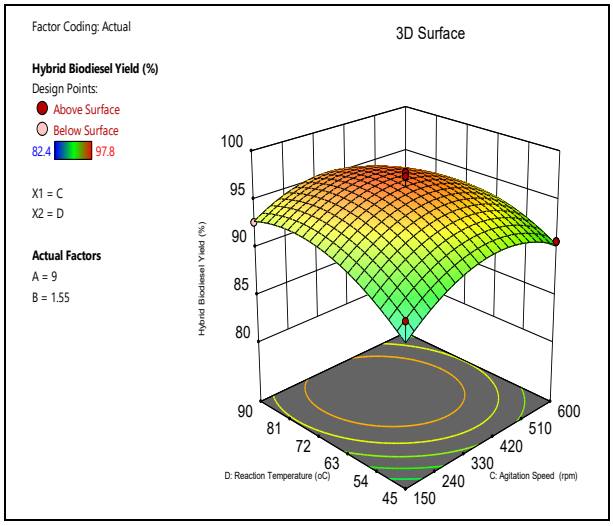


Fig. 6: Surface plot – effect of agitation speed and reaction temperature on hybrid biodiesel yield

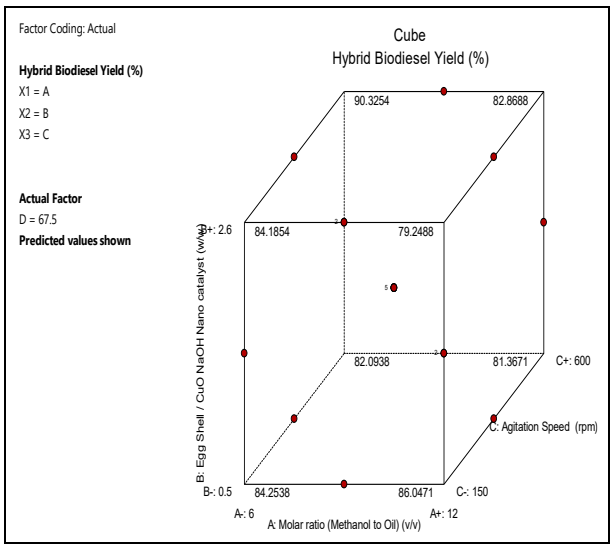


Fig. 7: Cube plot – effect of agitation speed, reaction temperature, molar ratio and eggshell / CuO-NaOH nano catalyst on hybrid biodiesel yield

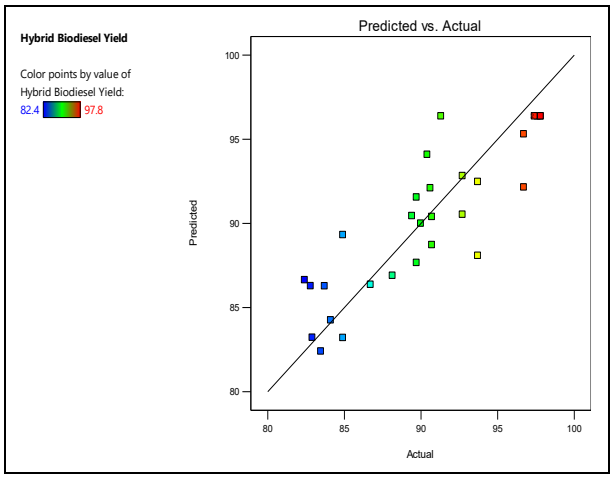


Fig. 8: Predicted vs actual hybrid biodiesel yield

Figure 4 shows that the inter relationship between agitation speed and methanol to oil molar ratio on the hybrid biodiesel yield. It can be observed that these input variable parameters had minimal effects on the yield of hybrid biodiesel which varied between 91.2% and 94.34% respectively. Increasing the agitation speed up to 600 rpm showcased a marginal increment in the biodiesel yield. This may be due enhanced catalytic activity during the conversion of tri-glycerides into its respective fatty acid methyl ester (Rashid *et al.* 2011).

Figure 5 shows an interaction between agitation speed and eggshell/CuO-NaOH nano-catalyst at constant reaction temperature f The catalyst concentration between 1.4 and 1.7 w/w showcased incremental yield of hybrid biodiesel at 400 rpm agitation speed lower concentration of catalyst nullified the FAME conversion reaction resulting the transesterification efficacy on the other hand increasing the catalyst beyond 2% at relatively higher reaction temperature interfered the glycerol formation leading to lowering the rate of conversion.

Figure 6 shows the inter relationship between reaction temperature and agitation speed at relatively higher molar ratio increment in reaction temperature from 72-90°C increased the biodiesel yield with minimal effect on agitation speed. Excessive methanol concentration in molar ratio leads to higher solubility with escalation in agitation speed resulting in enhanced higher biodiesel production. However, reduced agitation speed at 150 rpm with 45°C lower reaction temperature showcased the poor yield of higher biodiesel as 81.48%. Figure 7 details the cube plot towards the effect of agitation speed, reaction temperature, molar ratio and eggshell / CuO-NaOH nano catalyst on hybrid biodiesel yield. Figure 8 details the Predicted Vs Actual hybrid biodiesel yield (Garugubilli *et al.* 2024).

2.5 Physiochemical Properties

This section focuses on analysing the physiochemical properties hybrid biodiesel blends (neem 40-karanja 60). The kinematic viscosity which is the resistance offered against the gravitation force was found to be 4.652 mm²/s for the hybrid biodiesel blend the floatability of a liquid substance the measure of specific gravity at 30°C. Hybrid biodiesel shows a reduced specific gravity of 0.8494. The release of complete heat energy by combusting a unit quantity of hybrid biodiesel is designated as calorific value hybrid biodiesel blend showcase the superior calorific value of 44.78 MJ/kg. The density of hybrid biodiesel blend at 15°C was found to be 860 kg/m³ with relatively lower acid value of 0.805 mg/NaOH. The flashpoint and fire point of the hybrid biodiesel blend was found to be very much favourable during combustion process with 130.7°C and 147.4°C respectively. All the properties were tested under standard laboratory condition and was found to be within ASTM limits. The detailed physiochemical properties of the hybrid biodiesel in comparison with neem and karanja biodiesel are shown in table 4.

2.6 Experimental Setup

Kirloskar TV1 test engine was employed in present investigation. It is a single cylinder water cooled diesel engine with a rated speed and power of 1500 rpm and 6.2 kW respectively. The stroke length and bore diameter of engine cylinder measured about 110 and 87.5 mm respectively.

Table 4. Physio-chemical properties of hybrid biodiesel blends

	Units	ASTM Methods	Diesel	Biodiesel Standards	Karanja Biodiesel	Neem Biodiesel	Hybrid Biodiesel Blend (N40:K60)
Kinematic viscosity @ 40ºC	mm^2/s	D6079	3.03	2.5-6	4.04	5.57	4.652
Specific gravity @ 30ºC		D1298	0.836		0.825	0.886	0.8494
Calorific value	MJ/kg	D240	42.3		43.78	42.35	44.78
Cetane number		D4737	46	51	45	42	45.7
Density @ 15ºC	kg/m^3	D7052	836	860-900	824	887	860
Fire point	ºC	D93	56		143	154	147.4
Flash point	ºC	D93	50	120	127	138	130.7
Moisture content	%	--	0		0	0	0
Acid value	mg/NaOH	D664	0	0.85	0.76	0.97	0.805
FFA	%	D664	0		1.56	1.92	1.704
Iodine value	g I2/100g	--	1.35				0

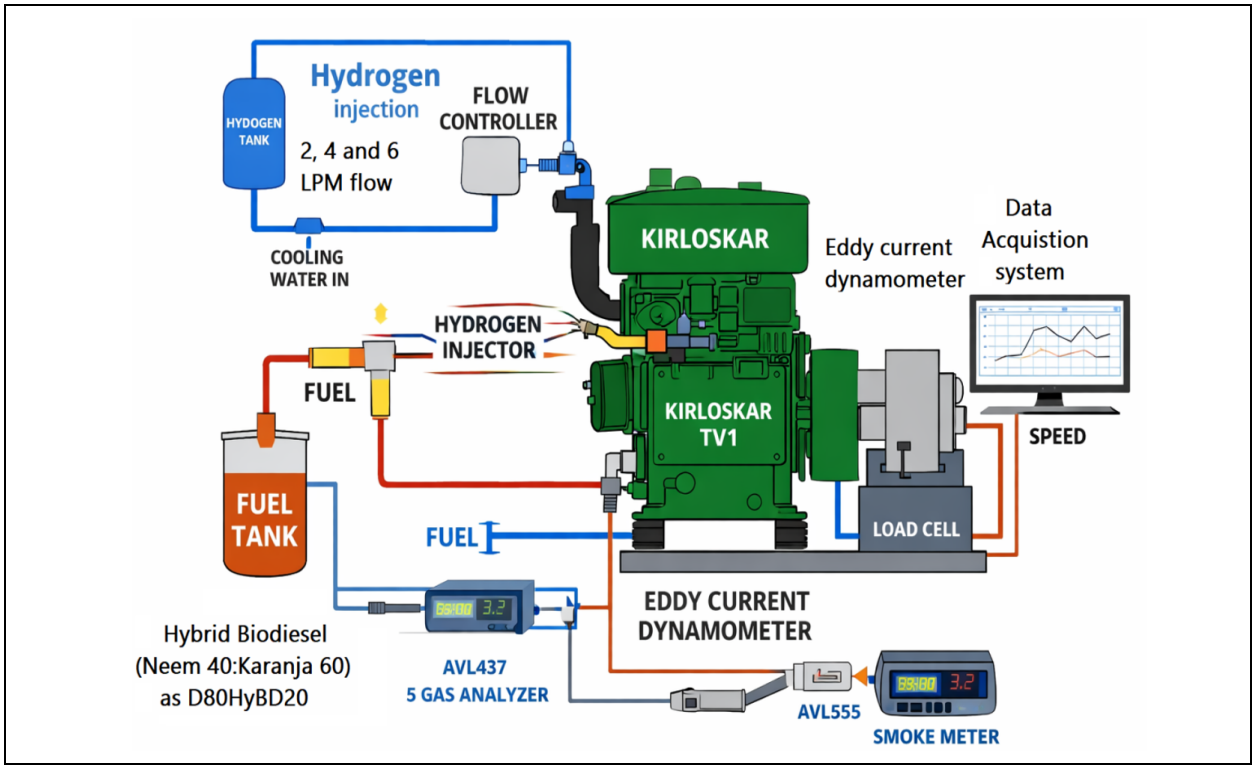


Fig. 9: Schematic image of the Test engine

The engine operates at factor set compression ratio of 17.5:1 loading of the engine is accomplished using Technomech made eddy current dynamometer (TMEC10). The maximum power produced by eddy current dynamometer was 7.5 kW between 1500 rpm and 600 rpm range. Pipe in pipe type of calorimeter was used in study and air-box encompassed on manometer and orifice meter. The combustion study was made by employing a kristler made piezo sensor which has a range of 500 psi possessing a low noise cable the crack angle sensor is attached in the system it senses a rotating speed of 5500 rpm with a TDC (Top Dead Centre) pulse NIUSB6210 type of data acquisition along with AX409 piezo powering unit was also employed. PT100 and RTD type of temperature sensor along with temperature transmitter was also used in the engine. Figure 9 details the test engine schematic diagram.

3. RESULTS AND DISCUSSION

This section focuses on the performance, emission and combustion characteristics of Kirloskar TV1 test engine fueled with diesel and hybrid biodiesel along with supplementing hydrogen.

3.1 Brake Thermal Efficiency (BTE)

Brake Thermal Efficiency is the ratio between useful power at the crank shaft and complete energy released during the fuel combustion process. Figure 10 shows the variation between brake thermal efficiency and BMEP (Brake Mean Effective Pressure) of a CI engine fueled with diesel and hybrid biodiesel blends with hydrogen fraction at 2, 4 and 6 LPM respectively. It can be noted that a maximum brake thermal efficiency of 34.79% was exhibited by diesel fuel at full load condition supplementing hydrogen fractions at 2, 4 and 6 LPM with diesel fuel exhibited marginal escalation between 2.5% and 3.4% across all loads. This increase in brake thermal efficiency maybe due to improved combustion process as a result of faster flame propagation. Hybrid biodiesel blend exhibited comparatively lower BTE of 20.05%, 27.16% and 32.33% during low, part and full load operations. Supplementing hydrogen fraction at 2 LPM with HyBD20 (Hybrid Biodiesel 20% blend) fuel marginally increased BTE up to 33.63% at full load condition increasing the hydrogen fraction up to 6 LPM in the diesel, hydrogen biodiesel blend sharply escalated BTE up to 38.27% reduction in kinematic viscosity with increase in calorific value loading to enhanced fuel automation maybe a reason for higher BTE increasing the hydrogen fraction up to 6 LPM also attributed for the increase in BTE considerably. BTE increased from 34.79% (diesel) to 38.27% (D80HyBD20 + 6 LPM H_2), showing an approximate 9.99% improvement at full load. The hybrid blend alone exhibited lower BTE (32.33%), indicating that hydrogen supplementation plays a dominant role. The incremental rise between 2–6 LPM confirms a strong dependence of efficiency on hydrogen flow rate.

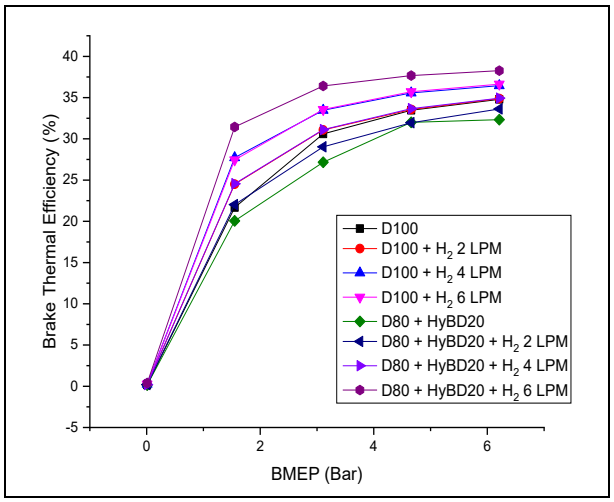


Fig. 10: Variation in BTE

The increase in BTE (up to 38.27%) is attributed to hydrogen's high flame speed and enhanced premixed combustion, improving thermal efficiency by approximately 8–15% as reported in recent studies. Hydrogen enrichment improves combustion completeness and reduces diffusion burning losses. Similar improvements in efficiency for hydrogen–diesel dual-fuel systems are widely reported (Sanatha *et al.* 2021).

3.2 Brake Specific Fuel Consumption (BSFC)

Figure 11 shows the variation in brake specific fuel consumption of a CI engine fueled with diesel, hybrid biodiesel along with fractions of hydrogen respectively on the whole a decreasing trend of brake specific fuel consumption was witnessed in the present study. Diesel fuel represented a maximum BSFC of 0.241 kg/kWhr at full load condition were as diesel, hybrid biodiesel blend (D80+HyBD20) representing 0.273 kg/kWhr respectively supplementing hydrogen fraction between 2 LPM and 6 LPM with diesel marginally reduced the BSFC by 5.52% at full load condition. Similarly throttling hydrogen fractions with diesel, hybrid biodiesel blend significantly reduced the BSFC between 4.6% and 8.9% across all loads. This may be due to increment in calorific value of hybrid fuel blends. BSFC reduced from 0.273 kg/kWh (D80HyBD20) to nearly 0.249–0.248 kg/kWh with hydrogen enrichment (approximately 4.6–8.9% reduction). Diesel fuel also showed a 5.52% decrease with hydrogen addition. This indicates improved fuel utilization efficiency with increasing hydrogen fraction across all loads. Similar improvements in efficiency for hydrogen diesel dual-fuel systems were widely reported by Saravanan *et al.* (2007).

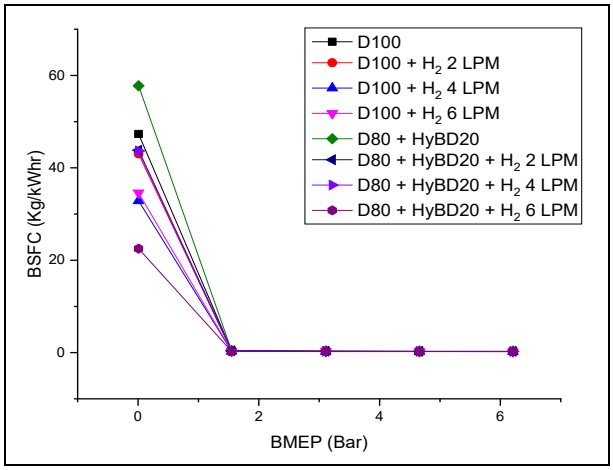


Fig. 11: Variation in BSFC

3.3 Exhaust emission

3.3.1 Carbon Monoxide (CO)

Carbon monoxide is generated mainly due to lack of oxygen atom and low temperature during the combustion reaction. The unavailability of oxygen atom required to oxidize C to CO_2 results in the formation of carbon monoxide. Figure 12 depicts variation in carbon monoxide formation against BMEP when the CI engine

is fueled with diesel, hybrid biodiesel blends with different fractions of hydrogen. It could be seen that carbon monoxide emission was considerably lower during part load operation especially with hybrid biodiesel blends. Diesel fuel released the carbon monoxide emission of 0.034%, 0.031% and 0.102% at low, part and full load operations. Addition of hydrogen with diesel reduced the carbon monoxide formation at all loads with escalation on the hydrogen concentration up to 6 LPM considerably increase CO emission up to 0.081% which was 19.81% lower than straight diesel. Hybrid biodiesel blend with diesel (D80HyBD20) showcased a marginal increment in carbon monoxide emission as 0.018% and 0.102% at part and full load condition. Injecting hydrogen in the throttle body up to 4 LPM considerably reduced carbon monoxide emission up to 0.082% at full load condition which may be due to enhanced oxidation reaction towards the formation of CO_2. Increasing the hydrogen concentration further 6 LPM slightly increased the carbon monoxide formation as 0.005% and 0.087% at part and full load condition respectively which may be due to dilution effect. At full load, CO emission decreased from 0.102% (diesel) to 0.081% with hydrogen (approximately 19.8% reduction). For D80HyBD20, CO dropped to 0.082% at 4 LPM, but slightly increased to 0.087% at 6 LPM, indicating an optimal hydrogen threshold. These highlights diminishing returns at higher hydrogen flow rates. Similar improvements for hydrogen diesel dual-fuel systems were widely reported by Hariram *et al.* (2021).

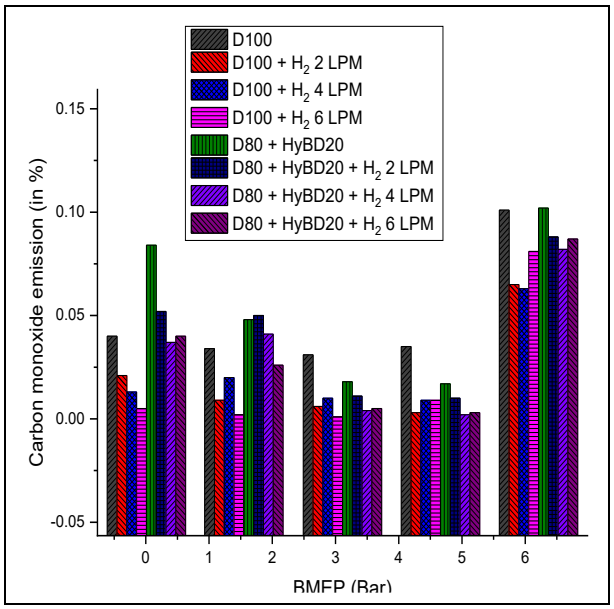


Fig. 12: Variation in CO emission

3.3.2 Unburned Hydrocarbon (UBHC)

Fuel particle sedimented near cylinders' piston crevice area and injector nozzle accounts for the major emission of UBHC. It also allows gives the measure of combustion in-efficiency which may be due to locally lean/rich air fuel mixture, incomplete fuel evaporation and fuel spray impingement. Figure 13 shows the variation of UBHC emission against BMEP when the CI engine is fueled with diesel, hybrid biodiesel blends with hydrogen injection. Generally, it could be seen that UBHC emission escalated with increase in engine load. At part load condition diesel fuel emitted a lowest UBHC emission of 40 ppm adding hydrogen significantly increased UBHC emission by 6-8% as 53 ppm and 61 ppm respectively. Further increment in hydrogen concentration of 6 LPM with diesel showcased a minor decrement up to 49 ppm. At fuel load condition similar trend was seen in which 6 LPM of hydrogen concentration emitted 87 ppm of UBHC. Hybrid biodiesel blend with diesel (D80HyBD20) test fuel showcased lower UBHC emission when compared with straight diesel. Higher concentration of oxygen atom in the hybrid biodiesel may have resulted in lower UBHC emission. At full load condition diesel-biodiesel blends (D80HyBD20) emitted 77 ppm of UBHC. Injecting hydrogen gas at 2 LPM with diesel-biodiesel blend considerably increased UBHC emission especially at full load condition increasing the hydrogen concentration as 2 LPM and 6 LPM showcased the UBHC emission of 85 ppm and 84 ppm respectively. UBHC increased from 40 ppm (diesel) to 53–61 ppm with hydrogen at part load (approximately 30–52% rise), before reducing to 49 ppm at 6 LPM. At full load, D80HyBD20 showed 77 ppm, rising to 85 ppm (2 LPM) and stabilizing at 84 ppm (6 LPM), indicating incomplete combustion at moderate hydrogen levels.

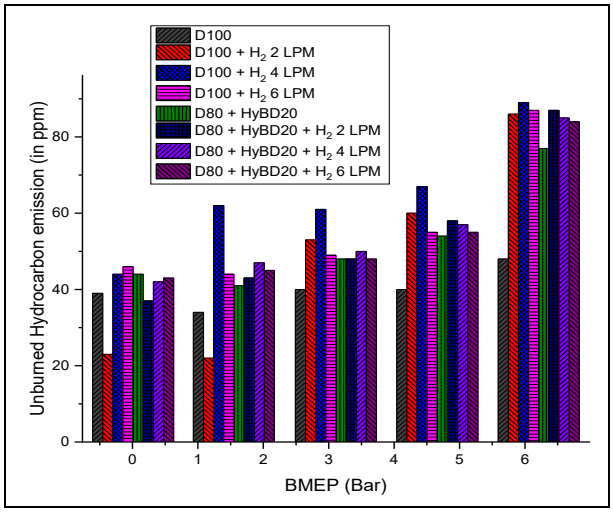


Fig. 13: Variation in UBHC emission

3.3.3 Oxides of Nitrogen (NO_x)

The formation of NO_x mainly depends on the burning temperature inside the combustion chamber. It is directly related to quantity of oxygen atom inside the combustion chamber, residence duration of nitrogen and peak flame temperature. Figure 14 details the variation in NO_x emission against BMEP with diesel, hybrid

biodiesel blends and hydrogen gas as fuel. It can be generally noticed that NO_x emission increases with escalation in engine load. Diesel fuel exhibited 448 ppm, 914 ppm and 1911 ppm of NO_x at low, part and full load operations. Injection of hydrogen with diesel considerably increased NO_x emission especially at pert and full load condition as 894 ppm and 917 ppm respectively. Further increment in hydrogen concentration up to 6 LPM reduced the NO_x considerably at 882 PPM during part load condition on the other hand injecting hydrogen in fractions of 2, 4 and 6 LPM witnessed a continuous increase in NO_x emission as 2214 ppm, 2258 ppm and 2346 ppm respectively. Blending hybrid biodiesel with diesel in ratios of 20 and 80 showed a minor escalation in NO_x at part and full load condition as 996 ppm and 1975 ppm respectively. Introducing hydrogen when fuelling the hybrid biodiesel blends reduced the NOx emission thereby minimizing the catalytic reaction towards the formation of intrinsic oxygen. It can be absorbed that injecting hydrogen at 2, 4 and 6 LPM with D80HyBD20 fuel blend emitted the engine NOx of 892 ppm, 870 ppm, 849 ppm at part load condition and 2115 ppm, 2207 ppm and 2293 ppm at full load condition. NO_x increased from 1911 ppm (diesel) to 2346 ppm at 6 LPM H_2 (approximately 22.7% increase). For D80HyBD20, NOx reached 2293 ppm at full load, showing a gradual rise with hydrogen concentration. However, at part load, NO_x reduced from 996 ppm to 849 ppm, indicating load-dependent behaviour.

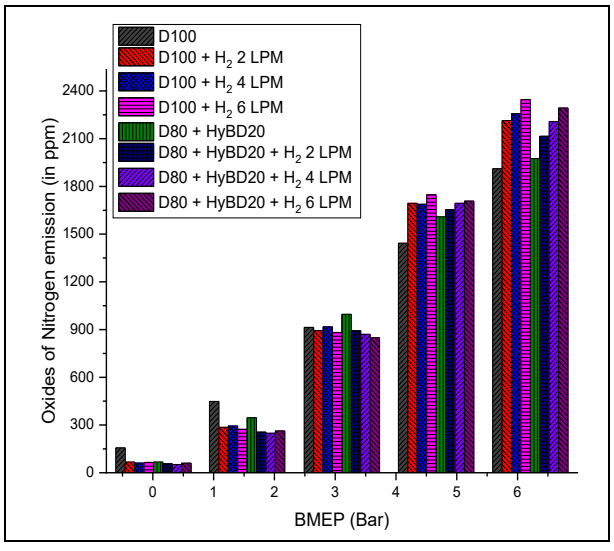


Fig. 14: Variation in NO_x emission

The rise in NO_x emission (up to 2346 ppm) is due to elevated in-cylinder temperature and peak pressure during hydrogen-assisted combustion. Hydrogen increases flame temperature, accelerating thermal NO_x formation, especially at higher loads. This NO_x escalation trend is consistently observed in recent dual-fuel engine studies. Thermodynamically, NO_x formation is governed by the Zeldovich mechanism, where higher in-cylinder temperatures (>1800 K) promote nitrogen oxidation; hydrogen enrichment increases adiabatic flame temperature and reduces ignition delay, thereby enhancing NO_x formation at high loads, while at part load, the charge dilution effect and reduced local equivalence ratio can lower peak temperature, leading to reduced NO_x (Asaad *et al.* 2023)

3.3.4 Smoke Emission

Smoke formation takes place due to insufficiency of oxygen during the combustion process especially in the air fuel rich zone. Diffusive combustion phase in primarily responsible for smoke formation which may also be dependent on improper automation and relatively higher kinematic viscosity of the fuel. It could be generally observed that smoke emission increases with escalation in engine load and injecting oxygen in incremental fraction reduces the formation of smoke considerably. At all loads diesel, hybrid biodiesel (D80HyBD20) exhibited higher smoke formation across all loading condition. At 100% load diesel fuel emitted 44.2% of smoke opacity (Refer Figure 15). Addition of hydrogen gas at 2, 4 and 6 LPM initially escalated the smoke opacity by 27% but was gradually reduced up to 54.6% with escalation of hydrogen fraction up to 6 LPM. Diesel, hybrid biodiesel blend exhibited higher percentage of smoke opacity at part and full load condition as 36.5% and 64.9% respectively. Injecting hydrogen with diesel-biodiesel blend considerably reduced smoke formation by 9.82% across part load and full load condition. Smoke opacity increased from 44.2% (diesel) to 64.9% (D80HyBD20) at full load. However, hydrogen addition reduced smoke by approximately 9.82%, indicating improved combustion quality. The reduction trend becomes more evident at higher hydrogen flow rates.

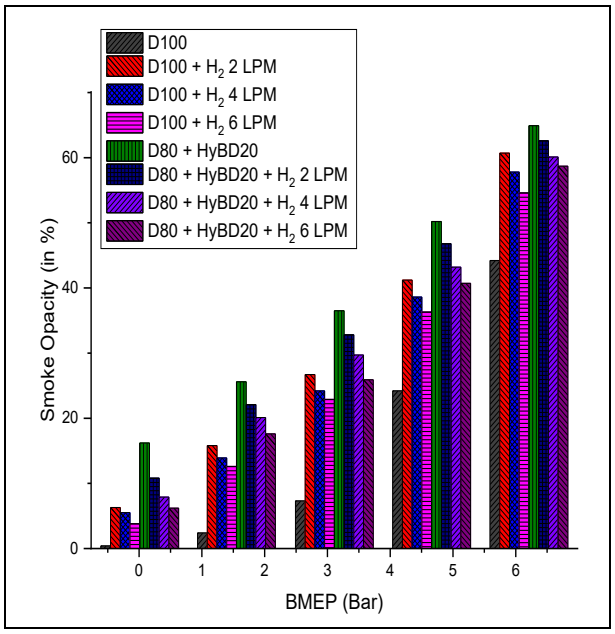


Fig. 15: Variation in smoke emission

3.4 Combustion Analysis

3.4.1 In-cylinder Pressure

The combustion process during the premixed combustion stage is primarily responsible for rise in incylinder pressure increase in cetane number and reduced ignition delay also contributes for the increase in incylinder pressure of the hybrid biodiesel blends infused with hydrogen gas. Injecting hydrogen with straight diesel and hybrid biodiesel blends improves the flame propagation speed. Figure 16 details the variation in incylinder pressure with crank angle when diesel and its hybrid blends are used in CI engine along with incremental hydrogen full load condition injection hydrogen with straight diesel improved the incylinder pressure rise of 2.3%. similarly, addition of hydrogen adds a similar effect when injected with hybrid biodiesel blends up to 42 PPM but increment in hydrogen fraction up to 6 LPM marginally reduced the incylinder pressure to 1.72% which may be due to dissolution of hydrogen gas during the premixed combustion phase. In-cylinder pressure increased by approximately 2.3% with hydrogen in diesel, while hybrid blends reached up to 42 bar peak pressure. However, at 6 LPM, pressure reduced by approximately 1.72%, indicating possible charge dilution at higher hydrogen concentration. Similar improvements were also reported by Venkatesan *et al.* (2017).

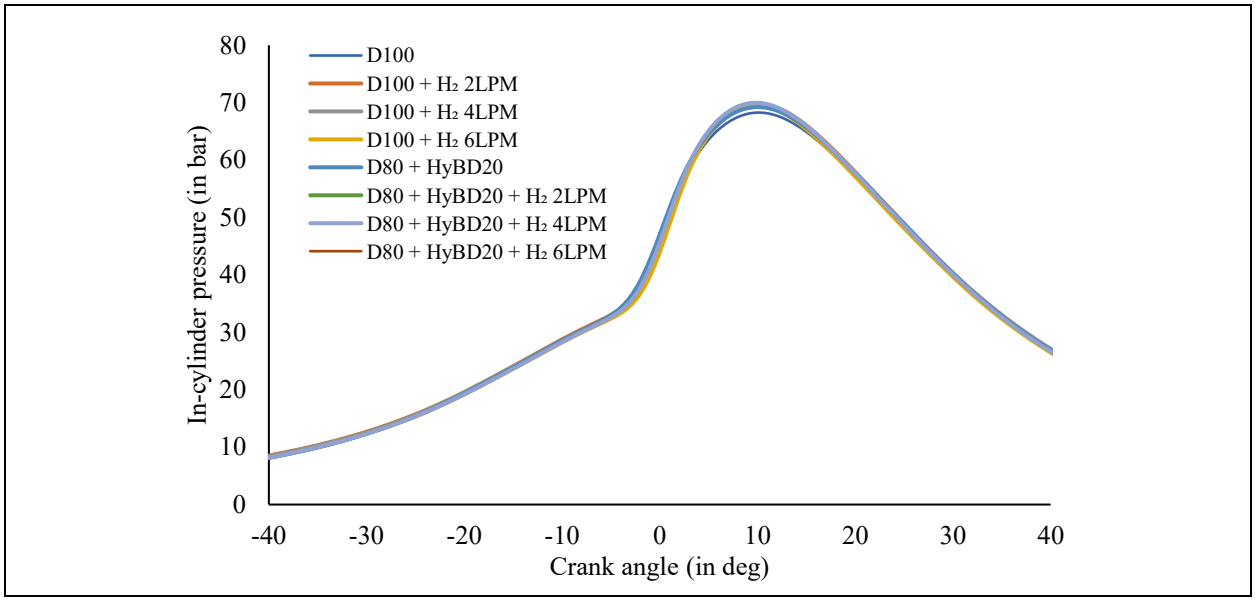


Fig. 16: Variation in incylinder pressure

3.4.2 Rate of Heat Release

The quantity of fuel burnt during the diffusive combustion phase of combustion process is primarily responsible of rate of heat release and contribute to escalation in rate of heat release. Figure 17 depicts the variation in rate of heat release when diesel and hybrid biodiesel are used in CI engine as fuel along with hydrogen injection in variable fractions. The result indicated that diesel and hybrid biodiesel exhibited a least rate of heat release as 43.8 J/CAD and 45.43 J/CAD respectively. Injecting hydrogen with diesel fuel considerably increases rate of heat release up to 48.66 J/CAD, 50.75 J/CAD and 52.96 J/CAD when 2, 4 and 6 LPM of hydrogen fraction were supplemented. On the other hand, hybrid biodiesel and diesel blends with hydrogen fraction showed marginal improvement in rate of heat release (i.e.) 49.15 J/CAD, 50.19 J/CAD and 50.26 J/CAD when hydrogen fraction of 2, 4 and 6 LPM are used during full load condition. It could be generally noticed that increasing the hydrogen fraction in hybrid biodiesel blends showed minimal increase in rate of heat release when compared with diesel fuel. HRR increased from 43.8 J/CAD (diesel) to 52.96 J/CAD at 6 LPM (approximately 20.9% rise). For hybrid blends, HRR increased from 45.43 to 50.26 J/CAD (approximately 10.6%), showing comparatively lower sensitivity. This confirms stronger combustion intensification in diesel–hydrogen mode. Similar improvements were also reported by Sanatha *et al.* (2021).

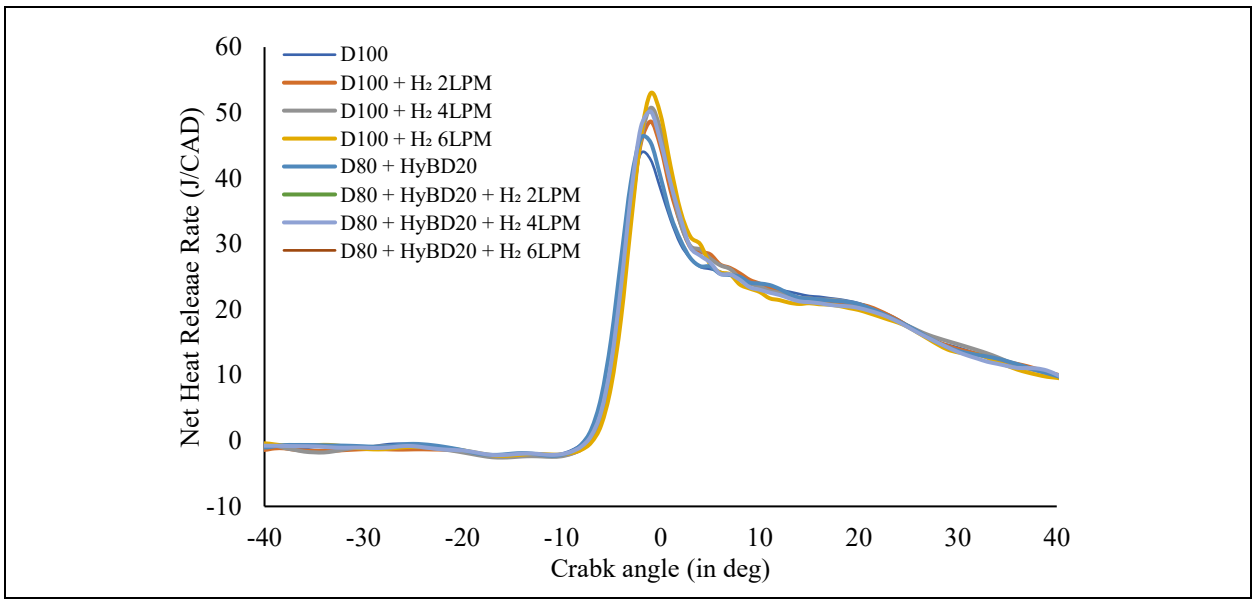


Fig. 17: Variation in net heat release rate

4. CONCLUSION

The present study successfully integrates RSM-based optimization of hybrid neem–karanja biodiesel with hydrogen-assisted CI engine operation, establishing a combined fuel–engine framework for performance enhancement and emission control.

- Hybrid biodiesel (neem 40%: karanja 60%) was produced via a two-stage transesterification process, and RSM–CCD optimization identified the optimum conditions (9:1 molar ratio, 1.55 w/w catalyst, 375 rpm, 67.5°C), achieving a maximum yield of 97.8%, validating the statistical model.

- The produced hybrid biodiesel exhibited improved physicochemical properties, including reduced kinematic viscosity and enhanced calorific value, contributing to better combustion characteristics compared to individual feedstock biodiesel.

- Engine experiments conducted on a 6.2 kW compression ignition engine at 1500 rpm demonstrated that hydrogen enrichment significantly influences combustion behaviour. The maximum BTE of 38.27% was achieved with D80HyBD20 + 6 LPM hydrogen, representing an approximately 10% improvement over diesel operation, along with a reduction in BSFC by up to 8.9%.

- Emission analysis revealed trade-offs: hydrogen enrichment reduced CO emissions by 19.8% and smoke opacity by ~9.8%, indicating improved oxidation and cleaner combustion. However, NO_x emissions increased up to 2346 ppm, attributed to elevated in-cylinder temperature and enhanced combustion intensity. UBHC emissions showed a marginal increase under certain operating conditions, indicating localized incomplete combustion.

- Combustion analysis indicated an increase in in-cylinder pressure (approximately 2.3%) and heat release rate (approximately 20.9%), confirming enhanced premixed combustion with hydrogen supplementation.

- Overall, the study demonstrates that hybrid biodiesel combined with controlled hydrogen enrichment improves engine efficiency and reduces incomplete combustion emissions, but introduces a NO_x penalty, highlighting the need for emission control strategies. This work contributes to the advancement of multi-feedstock biodiesel utilization and hydrogen-assisted combustion systems for sustainable CI engine applications.

AUTHORS' CONTRIBUTIONS

All authors have equally contributed to the manuscript.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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