Utilization of *Alpinia nigra* leaves as a sustainable source of highly efficient heterogeneous catalyst for biodiesel production from waste cooking oil

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Introduction

Biodiesel

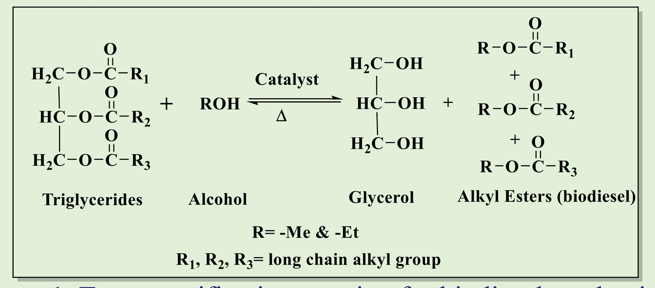
- Biodiesel is a renewable, biodegradable and non toxic green energy alternative
- Emits less amount of green house gas, have high cetane number, low viscosity, high flash point etc.
- It can be used in diesel engine by blending it with conventional diesel with different proportion (e.g. 5%, 10%, 20%, etc.)
- It contains different fatty acid alkyl esters
- It can be prepared through different method from various triglyceride sources (i.e. edible/non edible oil, animal fats, algae oils, etc.)

Dilution or blending | **Pyrolysis** | **Micro emulsification**

Transesterification (widely used method)

Transesterification

- It may be catalytic or non catalytic
- Catalysts enhance the rate of the reaction, need milder reaction conditions
- Catalysts are basically three types – acidic, basic and enzymatic. These can be of homogeneous and heterogeneous in nature.



Scheme 1: Transesterification reaction for biodiesel production

- Acid catalysts are suitable for feedstocks with high acid value (> 2 mg KOH/g) and base catalyst are suitable for feedstocks with low acid value (< 2 mg KOH/g)
- Enzyme catalyst are costly and take prolong reaction time
- Heterogenous catalysts have many advantages e.g. easy separation, remarkable catalytic activity, good stability and reusability

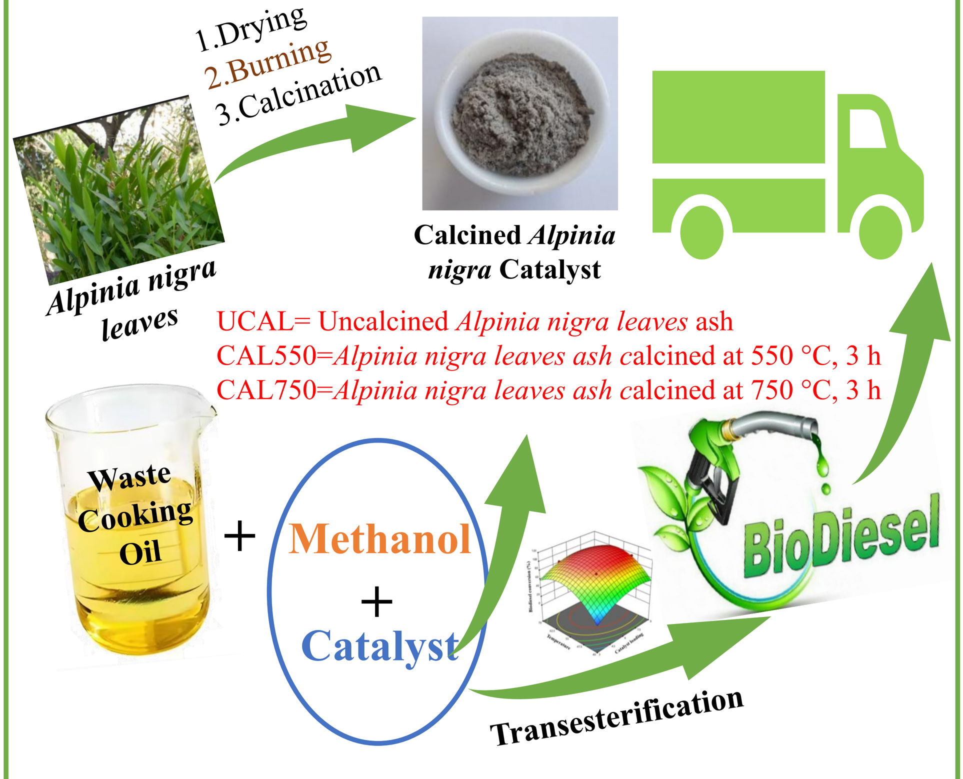
Heterogeneous catalyst

Derive from chemical source	**Derive from biomass source**
• Preparation steps are sometimes difficult • Involve toxic chemical, non renewable • Comparatively less effective	• Easy preparation steps • Non toxic, renewable and affordable • Highly efficient • Help to reduce the cost of biodiesel

Objective

- To synthesize a highly efficient solid base catalyst from easily available renewable *Alpina nigra* (Tora) leaves
- Application of this catalyst on biodiesel production from **waste cooking oil (WCO)**

Experimental section



UCAL= Uncalcined *Alpinia nigra leaves* ash
CAL550=*Alpinia nigra leaves ash* calcined at 550 °C, 3 h
CAL750=*Alpinia nigra leaves ash* calcined at 750 °C, 3 h

Result and Discussions

Characterization of catalyst

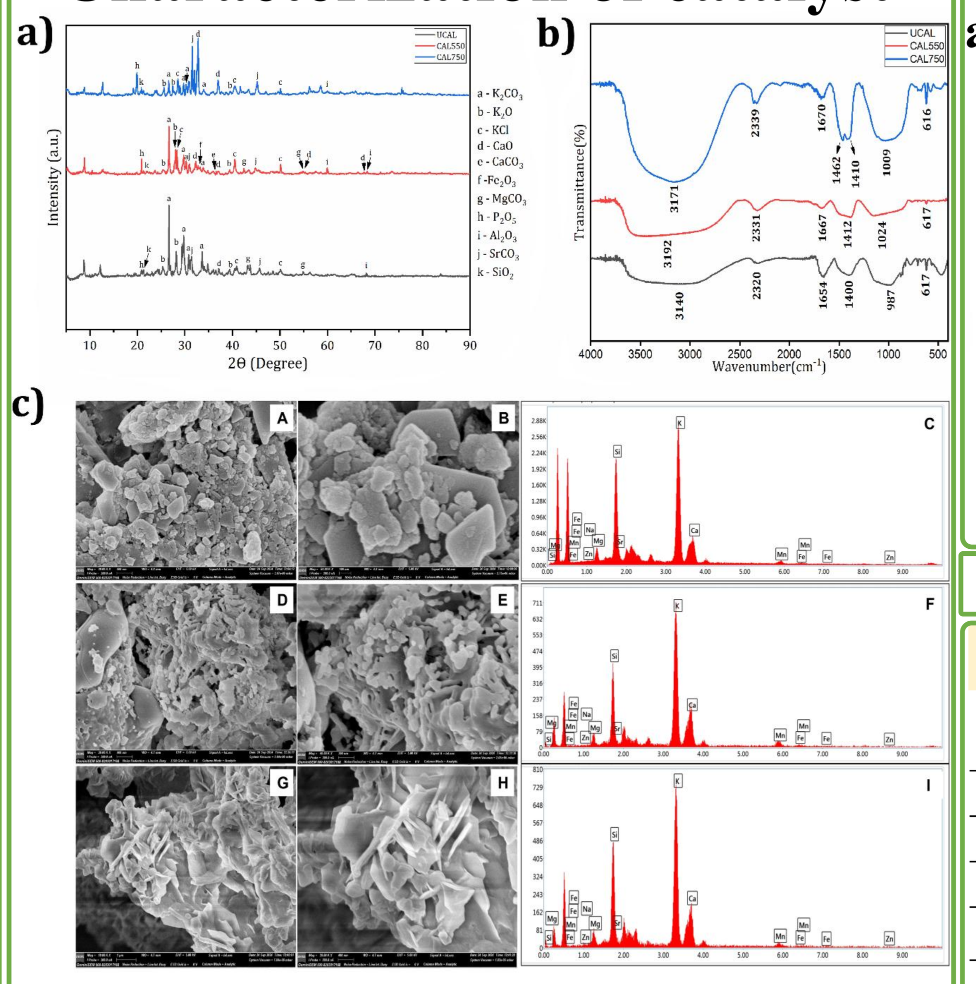


Fig. 1: Powder XRD pattern of *Alpinia nigra* catalyst (**a**); FT-IR spectra of uncalcined *Alpinia nigra* leaves ash, CAL550, CAL750 (**b**); FESEM image and EDX-spectra of UCAL (A, B, C); CAL550 (D, E, F); and CAL750 (G, H, I) (**c**)

Table 1: Elemental composition of *Alpinia nigra* catalyst by EDX analysis

Elements	UCAL	CAL550	CAL750
	Atomic %	Atomic %	Atomic %
Na	0.2	0.0	0.0
Mg	4.0	5.7	6.0
Si	19.7	16.1	19.2
K	53.5	48.6	47.7
Ca	15.1	19.6	17.0
Mn	2.8	4.2	3.1
Fe	1.0	1.4	1.2
Zn	1.0	2.1	2.5
Sr	2.6	2.3	3.2

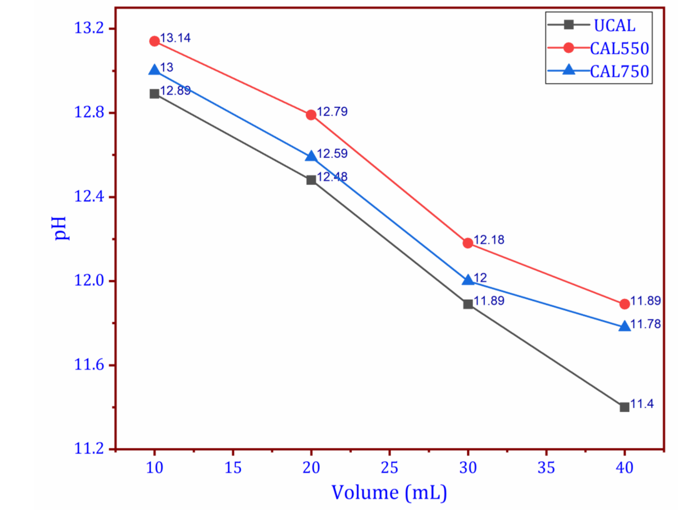


Fig. 2: pH value of **UCAL, CAL550** and **CAL750** with respect to volume of water

Table 2: Determination of basic strength using Hammet indicator method

UCAL	CAL550	CAL750
1.56 mmol/g	1.67 mmol/g	1.60 mmol/g

Characterization of catalyst

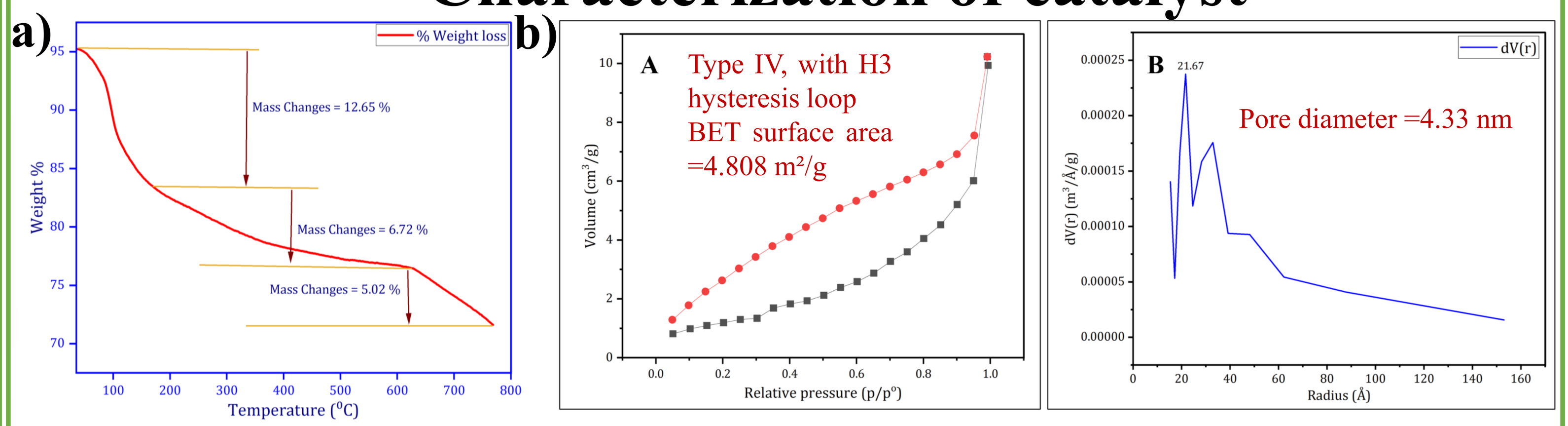


Fig. 3: TGA analysis of *Alpinia nigra* leaves ash (**a**); N_2 adsorption desorption curve of CAL550 (**bA**); and pore size distribution curve of CAL550 (**bB**)

Application of catalyst towards transesterification reaction

WCO pretreatment

Table 3: Properties of WCO

Sl. No.	Properties	Results
1	Acid value (mg KOH/g)	1.6257
2	Density (g/cm³ at 15 °C)	0.920
3	Kinematic viscosity (mm²/s at 40 °C)	80.35
4	Cloud Point (°C)	-3
5	Pour Point (°C)	-8
6	Calorific Value (MJ/Kg)	40.82

Catalyst screening

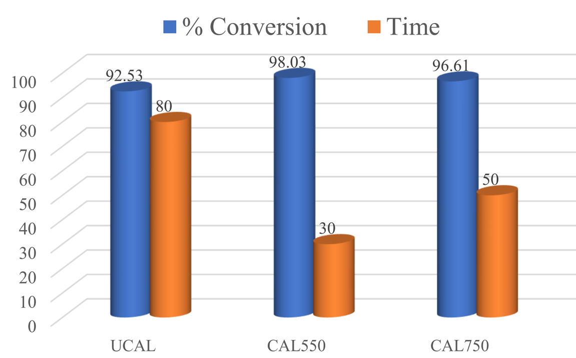


Fig. 4: Effect of calcination temperature

FAME conversion was calculated using [1]H NMR method using Eq. 1

$$\text{Conversion (\%)} = \frac{2A_{Me}}{3A_{CH_2}} \times 100 \qquad \text{Eq. 1}$$

Gelbard et al. 1995 JAOCS

Where X and Y are the area of the methoxy (OCH_3) proton at 3.6 ppm and the methylene (–CH_2-) protons at 2.3 ppm.

Process optimization using Response surface methodology (RSM)

$$\text{Biodiesel conversion} = 88.86 + 2.84\,A + 17.79\,B + 25.59\,C + 17.19\,D - 1.90\,AB - 0.21AC - 1.77\,AD - 1.34\,BC - 11.52\,BD - 2.99\,CD - 5.17\,A^2 - 7.86\,B^2 - 14.75\,C^2 - 8.57\,D^2 \qquad \textbf{Eq. 1}$$

Table 4: Optimization of biodiesel conversion using RSM

Std	Run	Space Type	MTOR (A)	Catalyst loading (B)	Temperature (C)	Time (D)	Actual conversion (%)	Predicted conversion (%)
14	1	Factorial	12	3	60	40	88.71	90.13
30	2	Center	9	5	50	30	90.06	88.86
23	3	Axial	9	5	50	10	20.46	20.20
5	4	Factorial	6	3	60	20	28.89	29.62
15	5	Factorial	6	7	60	40	98.03	98.27
8	6	Factorial	12	7	60	20	93.23	94.38
28	7	Center	9	5	50	30	88.28	88.86
4	8	Factorial	12	7	40	20	38.86	40.30
7	9	Factorial	6	7	60	20	88.88	89.36
26	10	Center	9	5	50	30	87.68	88.86
18	11	Axial	15	5	50	30	75.28	73.87
1	12	Factorial	6	3	40	20	~~6.8~~	
16	13	Factorial	12	7	60	40	95.23	96.18
17	14	Axial	3	5	50	30	62.28	62.50
24	15	Axial	9	5	50	50	89.89	88.96
29	16	Center	9	5	50	30	88.37	88.86
12	17	Factorial	12	7	40	40	54.58	54.08
20	18	Axial	9	9	50	30	94.61	92.98
19	19	Axial	9	1	50	30	21.39	21.83
21	20	Axial	9	5	25	30	~~1.97~~	
25	21	Center	9	5	50	30	90.23	88.86
6	22	Factorial	12	3	60	20	43.16	42.24
11	23	Factorial	6	7	40	40	53.46	55.33
9	24	Factorial	6	3	40	40	37.23	36.32
3	25	Factorial	6	7	40	20	35.63	34.45
22	26	Axial	9	5	70	30	82.23	81.04
10	27	Factorial	12	3	40	40	42.21	42.68
2	28	Factorial	12	3	40	20	~~15.87~~	
27	29	Center	9	5	50	30	88.57	88.86
13	30	Factorial	6	3	60	40	85.09	84.60

Application of catalyst towards transesterification reaction

Table 5: Statistical outcome of the CCD model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	17956.20	14	1282.59	570.10	< 0.0001	significant
A-MTOR	168.08	1	168.08	74.71	< 0.0001	
B-Catalyst loading	5483.39	1	5483.39	2437.31	< 0.0001	
C-Temperature	6590.96	1	6590.96	2929.61	< 0.0001	
D-Time	5122.16	1	5122.16	2276.74	< 0.0001	
AB	47.01	1	47.01	20.89	0.0006	
AC	0.5681	1	0.5681	0.2525	0.6244	
AD	40.91	1	40.91	18.19	0.0011	
BC	18.13	1	18.13	8.06	0.0149	
BD	1346.37	1	1346.37	598.45	< 0.0001	
CD	90.97	1	90.97	40.44	< 0.0001	
A²	709.70	1	709.70	315.45	< 0.0001	
B²	1642.48	1	1642.48	730.06	< 0.0001	
C²	2771.05	1	2771.05	1231.70	< 0.0001	
D²	1950.71	1	1950.71	867.07	< 0.0001	
Residual	27.00	12	2.25			
Lack of Fit	21.63	7	3.09	2.88	0.1313	not significant
Pure Error	5.37	5	1.07			
Cor Total	17983.20	26				

Std. Dev.	**1.50**	**R²**	**0.9985**
Mean	68.98	Adjusted R²	0.9967
C.V. %	2.17	Predicted R²	0.9887
		Adeq Precision	69.8284

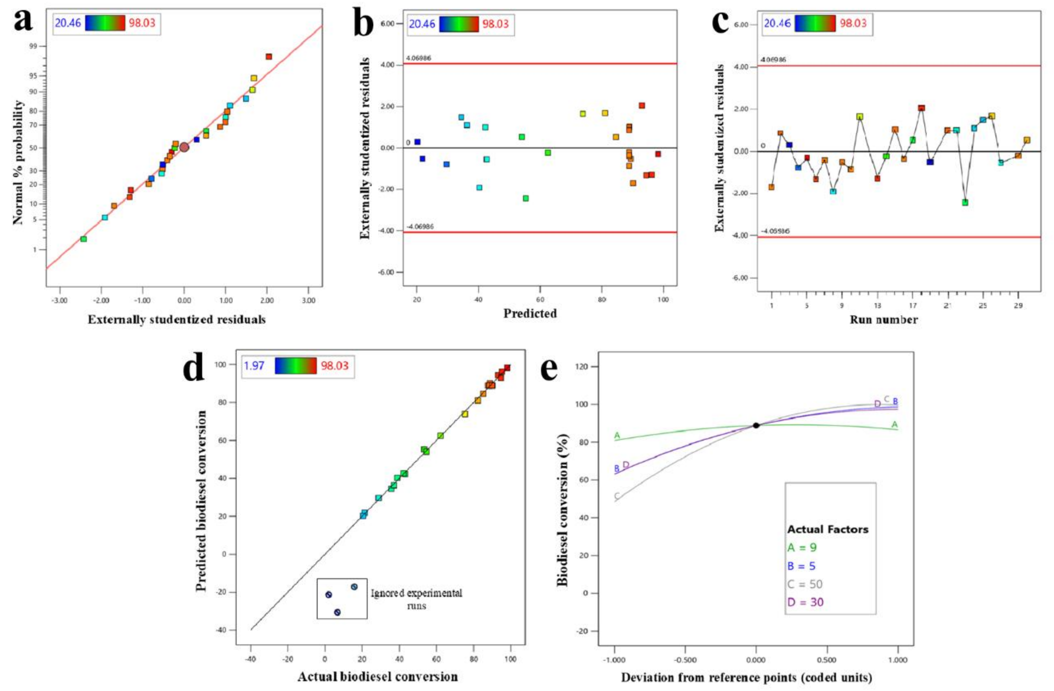


Fig. 5: Normal plot of residuals (a), residual vs. predicted (b), residuals vs. run number (c), actual vs predicted biodiesel conversion (d) and perturbation plot (e)

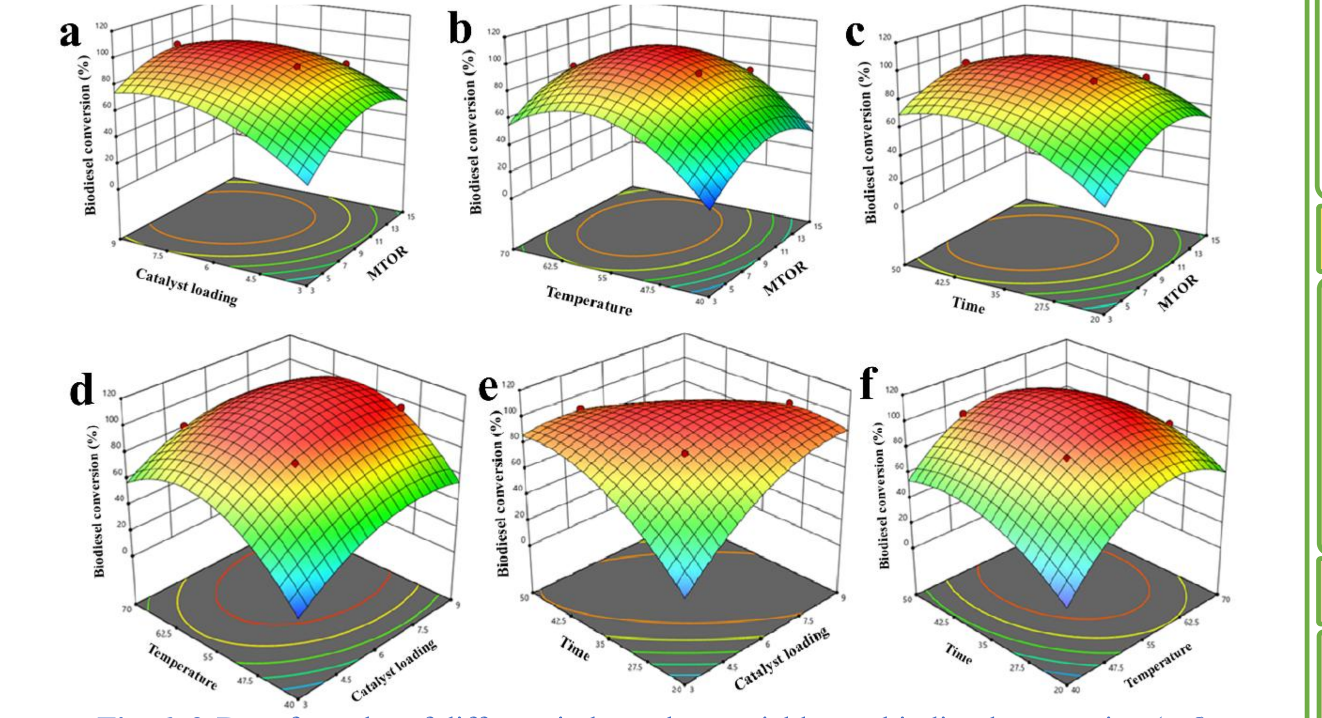


Fig. 6: 3-D surface plot of different independent variables on biodiesel conversion (**a-f**)

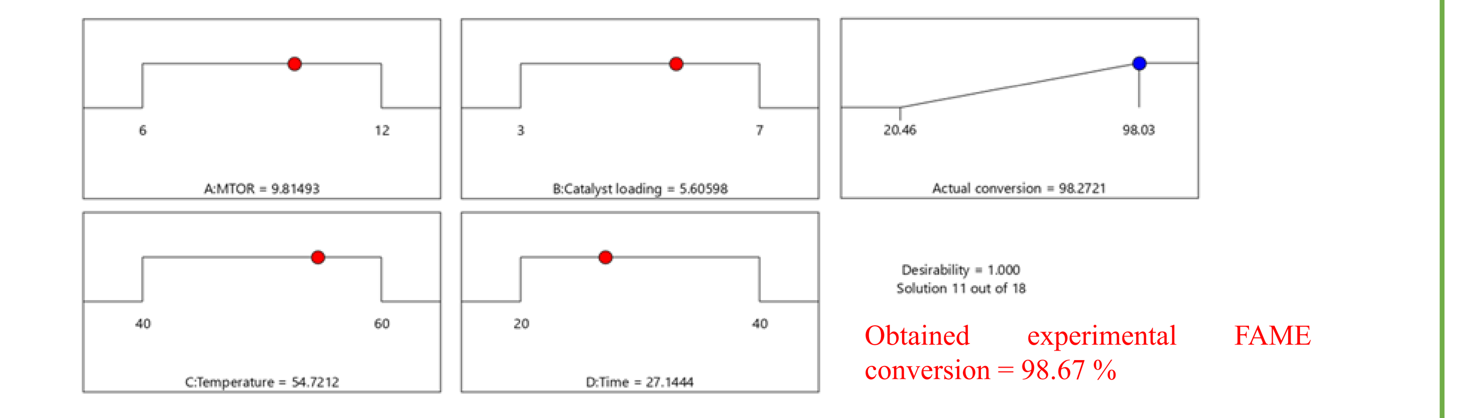


Fig. 7: Numerical optimization process of RSM for biodiesel production

Table 6: Kinetic and thermodynamic study result

Activation Energy (Ea)	Enthalpy (ΔH°)	Entropy (ΔS°)	Gibb's free energy (ΔG°)
62.85 kJmol[-1]	60.23 kJmol[-1]	-0.104 kJK[-1]mol[-1]	95.382 kJmol[-1]

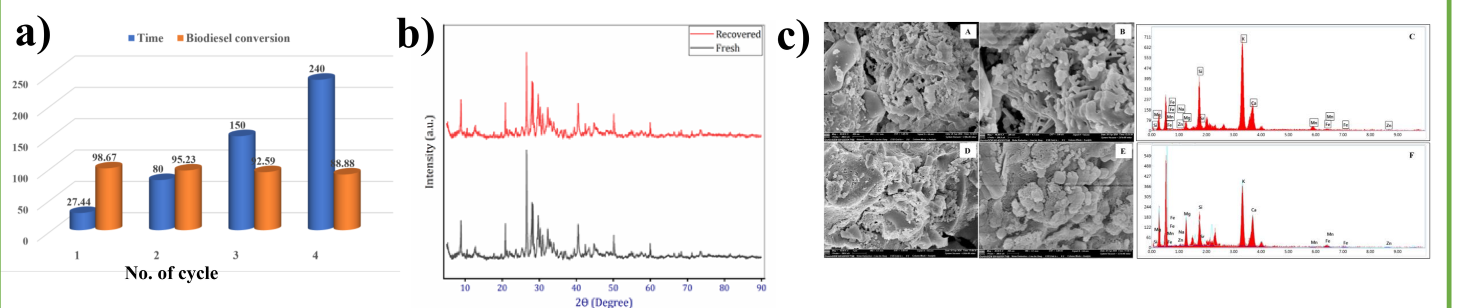


Fig. 8: Reusability study of CAL550 catalyst (a), and XRD spectra of CAL550 and 4[th] recycled CAL550 catalyst (**b**), FESEM images and EDX spectra of CAL550 (A, B and C) and 4[th] recycled CAL550 catalyst (D, E and F) (c)

Characterization of biodiesel

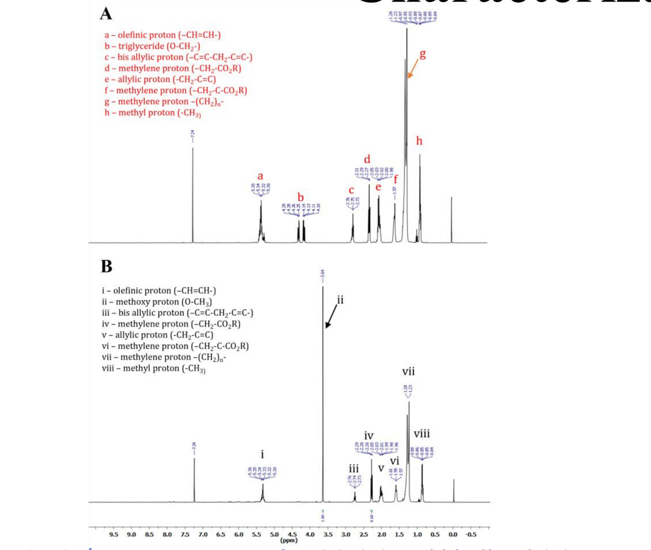


Fig. 9: [1]H NMR spectra of WCO (A) and biodiesel (B)

Table 7: FAME composition from GCMS data

Sl. No.	Retention time (mins)	Area (%)	Name
1	10.747	0.91	Methyl hexadec-9-enoate
2	10.881	19.23	Methyl 14-methylpentadecanoate
3	12.120	55.29	Methyl acetyl ricinoleate
4	12.223	12.32	Methyl stearate
5	13.365	2.39	11-Eicosenoic acid, methyl ester
6	13.507	2.31	Methyl 18-methylnonadecanoate
7	14.898	5.45	13-Docosenoic acid, methyl ester
8	15.067	2.10	Methyl 20-methyl-heneicosanoate

Table 8: Fuel properties of WCO biodiesel

Sl. No.	Properties	Results	ASTM D6751	EN14214
1	Cloud Point (°C)	6	NS	
2	Pour Point (°C)	−4	NS	
3	Flash Point (°C)	137	93 (min)	120 (min)
4	Carbon residue (wt%)	0.06	0.05 (max)	0.3
5	Kinematic viscosity (mm²/s at 40 °C)	3.8	1.9-6.0	3.5-5.0
6	Calorific Value (MJ/Kg)	40.5	NS	35 (min)
7	Density (g/cm³ at 15 °C)	0.875	0.86-0.90	0.85

Table 9: Cost assessment of the catalyst

Catalyst preparation	Description	Expenses (Rs.)
Raw materials collection (a)	Collection + transportation + labor cost	100
Drying and burning (b)	Sun dried followed by open air burning	0
Calcination (c)	Expenses = Time (h) × unit consumption × cost per unit	5 × 3.6 × 5.65 = 101.7
Net expenses (d) = a + b + c		201.7
Total expenses of the catalyst (in 1 kg) US dollars ($)		2.37 $

Conclusion

- Synthesized a solid base catalyst from *Alpinia nigra* leaves
- Catalyst contains K in the highest amount, exhibits BET surface area of 4.808 m²/g
- Biodiesel was successfully produced from waste cooking oil
- Using RSM-CCD model and taking CAL550 as model catalyst, a maximum FAME conversion of 98.67 % was achieved under the optimized condition given by the model (i.e. MTOR = 9.81:1, catalyst dose = 5.6 wt.%, reaction temperature = 54.27 °C and reaction time = 27 min)
- Catalyst was reusable upto 4[th] reaction cycle

References

1. Bhuyan, P., Star, R., Rokhum, S. L., & Saikia, L. (2026). Utilization of Alpinia nigra leaves as a sustainable source of highly efficient heterogeneous catalyst for biodiesel production from waste cooking oil. *Biomass and Bioenergy*, *206*, 108593.