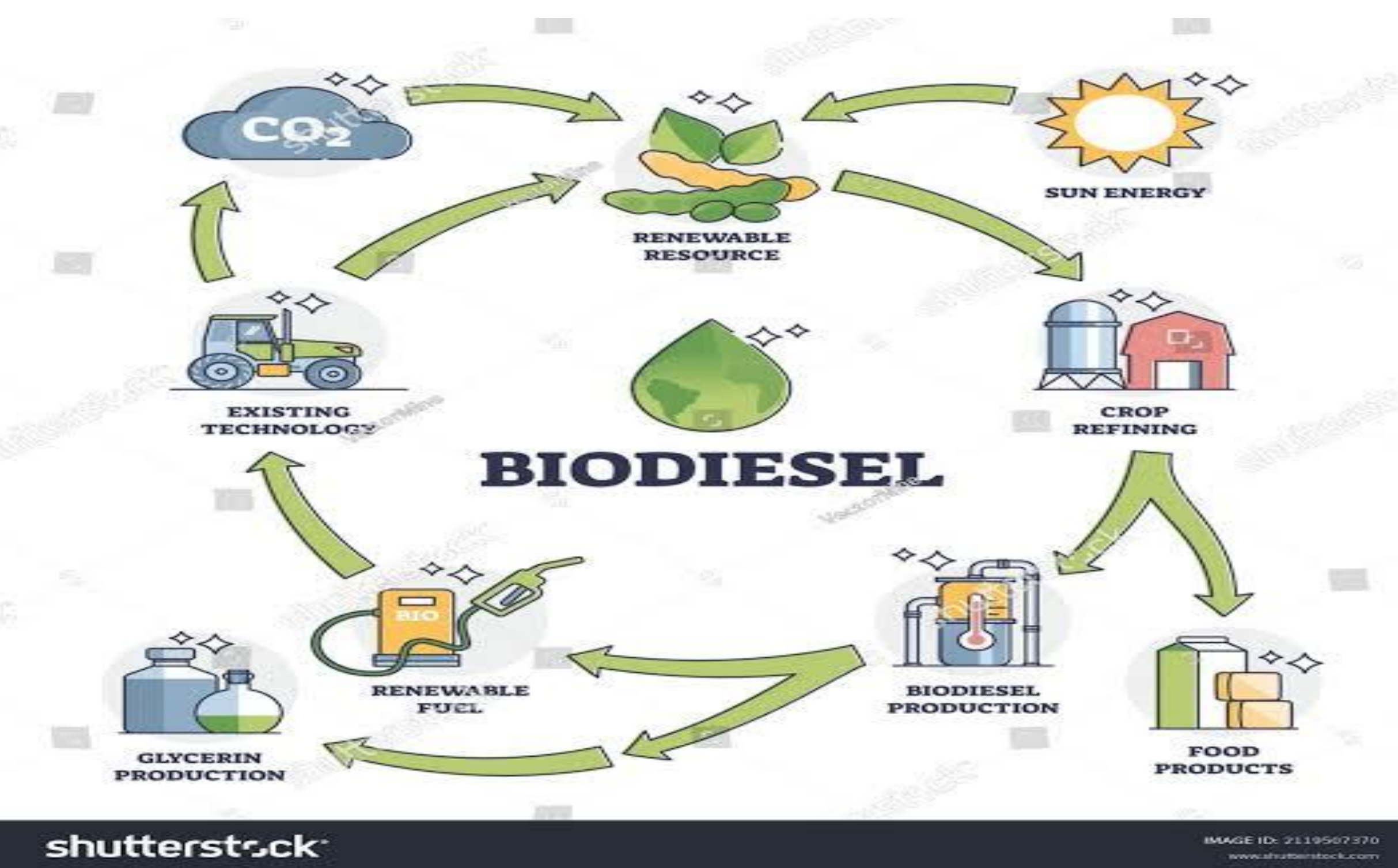




INTRODUCTION

In the past decade, much research has focused on the production of biodiesel, a renewable and sustainable alternative to conventional fossil fuels. Biodiesel is derived from organic sources such as vegetable oils, animal fats, and recycled cooking grease, making it an environmentally friendly option for reducing greenhouse gas emissions and mitigating the impacts of climate change (Benjamin *et al.*, 2017; Jabbar *et al.*, 2019). The exploration of biodiesel production methods has been driven by the growing demand for cleaner energy solutions, as well as the need to reduce dependence on fossil fuels.



METHODOLOGY

The data used for this study were collected by the use of;

- ✓ Association of Official Analytical Chemists (AOAC) methods for the physico-chemical characterization of the waste cooking oil (WCO) and palm kernel oil (PKO)
- ✓ AOAC methods and American Society of Testing and Material (ASTM) standards for the physico-chemical characterization of the biodiesel produced, that is, waste cooking oil methyl ester (WCOME) and palm kernel oil methyl ester (PKOME)
- ✓ Scanning Electron Microscopy (SEM) for the characterization of the Calcium Oxide (CaO) catalyst (uncalcined and calcined)
- ✓ Central Composite Design (CCD) with Response Surface Methodology (RSM) for the design of experiment and optimization process on the biodiesel production
 - ✓ Transesterification process for the biodiesel production
- ✓ Fourier's Infra-red Spectroscopy (FTIR) and Gas Chromatography-Mass Spectroscopy (GC-MS) for the spectroscopic and chromatographic analysis of the WCOME and PKOME produced.

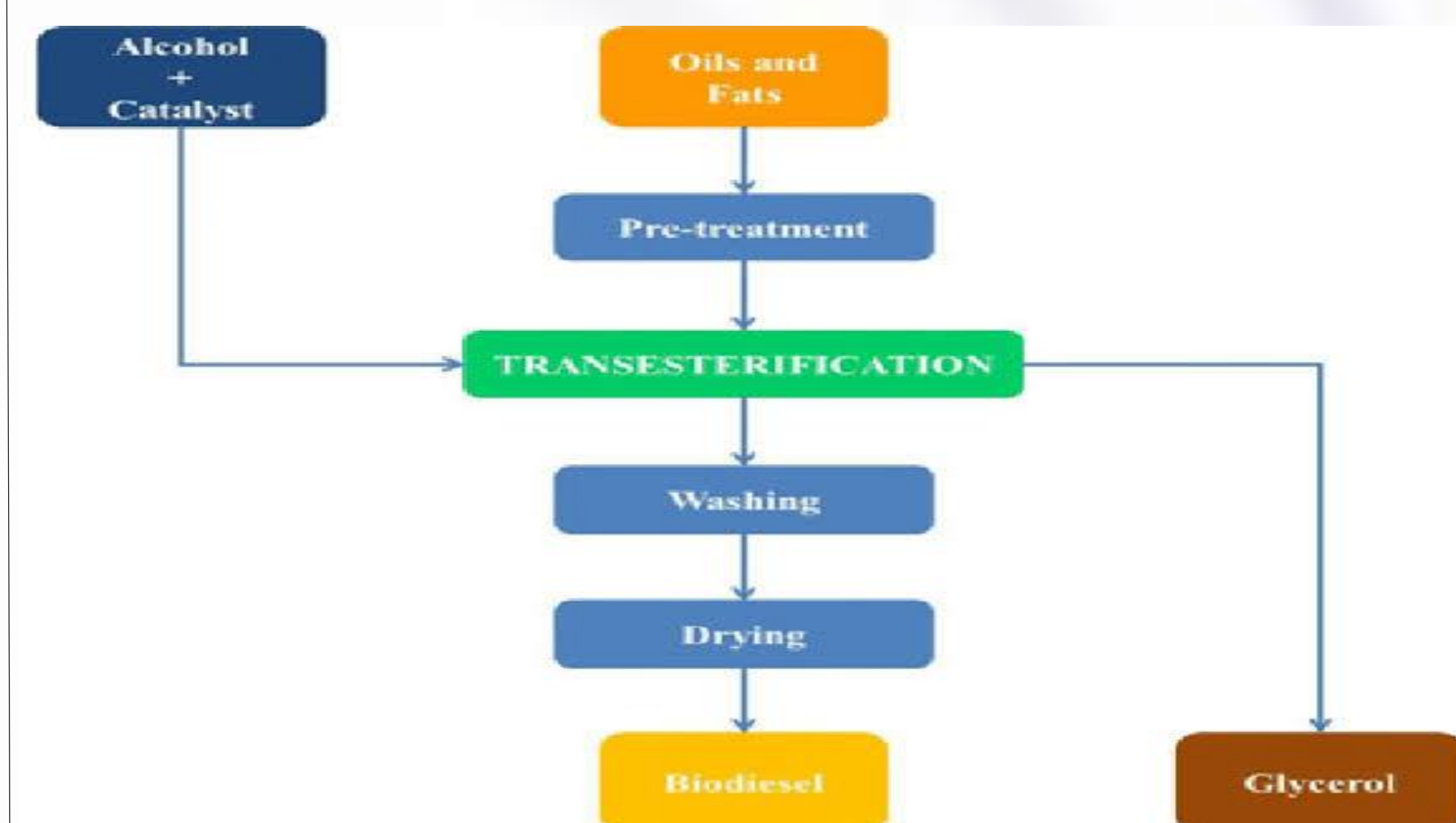
DESIGN OF EXPERIMENT

The factors and their levels of Central Composite Design for the CaO -catalyzed transesterification process

Variable	Symbols	Coded levels				
		-2	-1	0	1	2
Calcination temperature (°C)	A	400	500	600	700	800
Calcination time (min)	B	60	120	180	240	300
Reaction temperature (°C)	C	50	55	60	65	70
Reaction time (min)	D	50	60	70	80	90

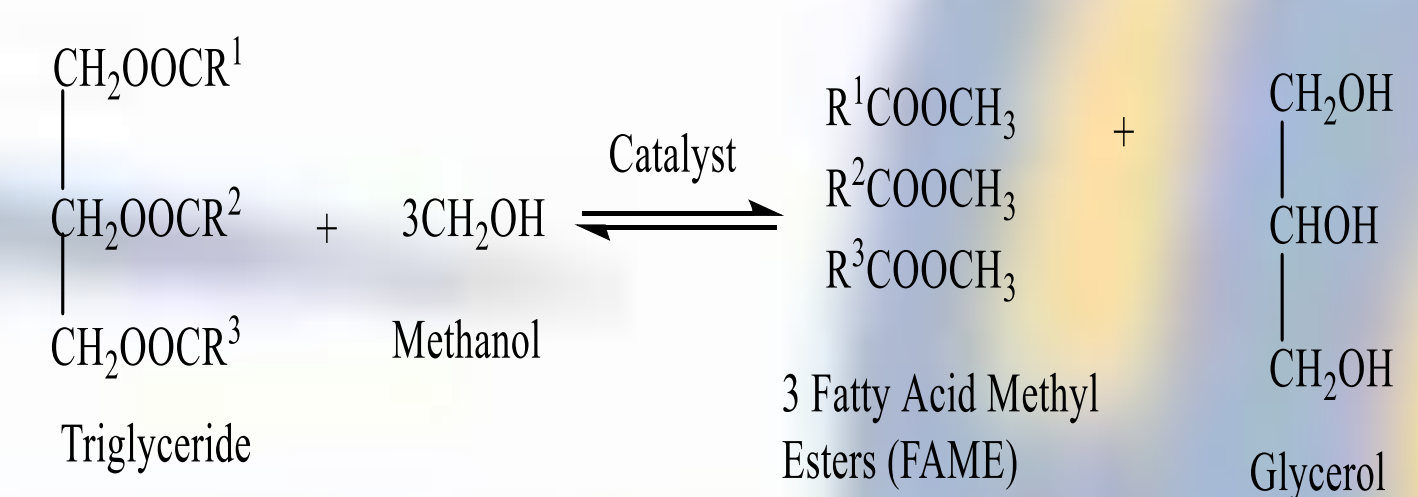
Experimental runs were 30, that is, (2^k + 2k + 6) for each catalysts

Flow chat of the production process



The biodiesel yield was calculated as shown below.
Yield of biodiesel (Y) = $\frac{\text{liters of biodiesel produced}}{\text{liters of oil used}}$ × 100

Transesterification reaction



Experimental set-up of the batch reaction

Production WCOME (CaO-catalyzed)

Run	Calcination Temp (°C)	Calcination Time (min)	Reaction Temp (°C)	Reaction Time (min)	Biodiesel yield(%wt) WCO EXP.	Biodiesel yield(%wt) WCO PRED.
13	2(800)	0(180)	0(60)	0(70)	86.46	83.12
17	1(700)	-1(120)	1(65)	-1(60)	43.58	49.25

Production of PKOME (CaO-catalyzed)

Run	Calcination Temp (°C)	Calcination Time (min)	Reaction Temp (°C)	Reaction Time (min)	Biodiesel yield(%wt) PKO EXP.	Biodiesel yield(%wt) PKO PRED.
16	0(600)	2(300)	0(60)	0(70)	76.73	76.63
20	-1(500)	-1(120)	-1(55)	1(80)	37.73	40.82

The chosen fitted quadratic model equations for the biodiesel in terms of coded and actual terms (factors)

WCOME (CaO) yield (%wt) =

$$-953.28381 + 0.39217 \times A - 1.20346 \times B + 32.69625 \times C + 1.25683 \times D - 9.17490E - 005 \times AB - 0.018475 \times AC + 6.40386E - 003 \times AD + 0.010159 \times BC + 9.16986E - 003 \times BD - 0.11510 \times CD + 1.96434E - 004 \times A - 9.17374E - 005 \times B^2 - 0.11886 \times C^2 - 2.37157E - 003 \times D^2$$

PKOME (CaO) yield (%wt) =

$$-124.58329 + 0.88811 \times A + 0.52442 \times B - 14.54950 \times C + 8.52023 \times D - 2.36355E - 004 \times AB - 1.02722E - 003 \times AC - 7.31920E - 003 \times AD - 4.87428E - 003 \times BC - 5.29774E - 003 \times BD + 0.045626 \times CD - 1.82579E - 004 \times A^2 + 9.69952E - 004 \times B^2 + 0.10166 \times C^2 - 0.038821 \times D^2$$

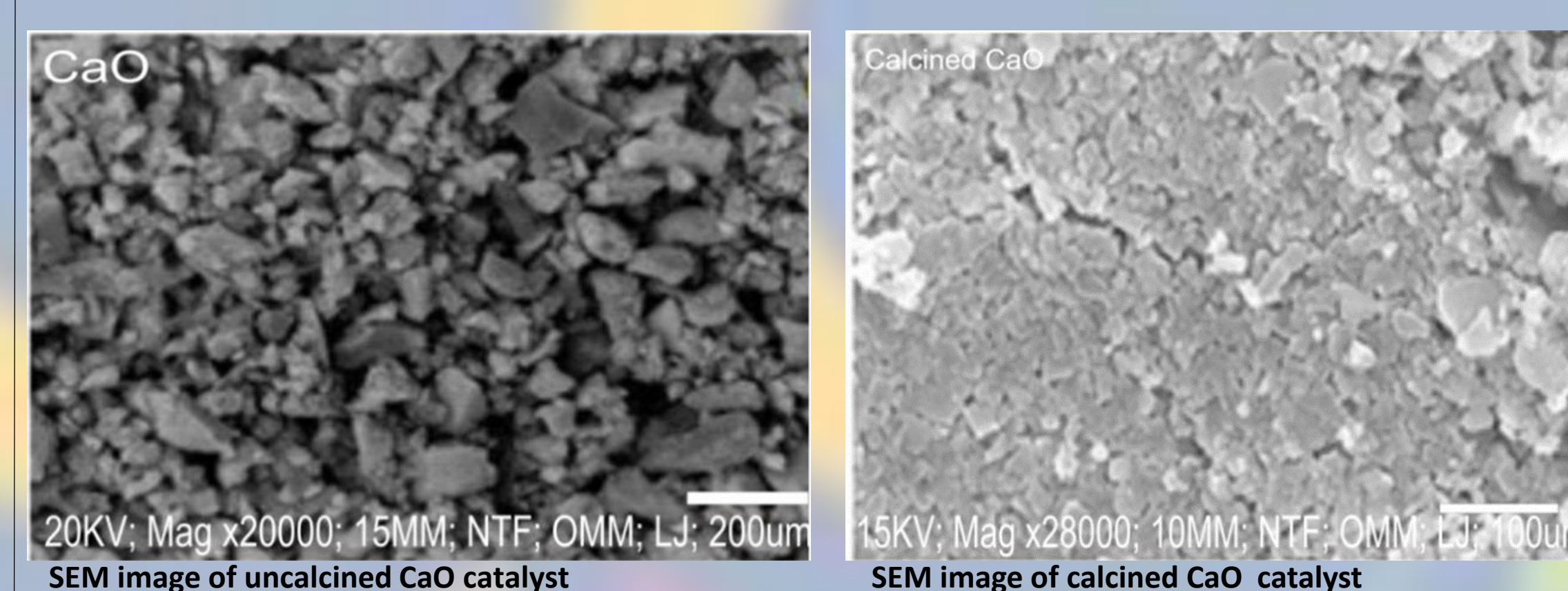
Where, A is calcination temperature (°C), B is calcination time (min), C is reaction temperature (°C) and D is reaction time (min).

RESULTS AND DISCUSSIONS

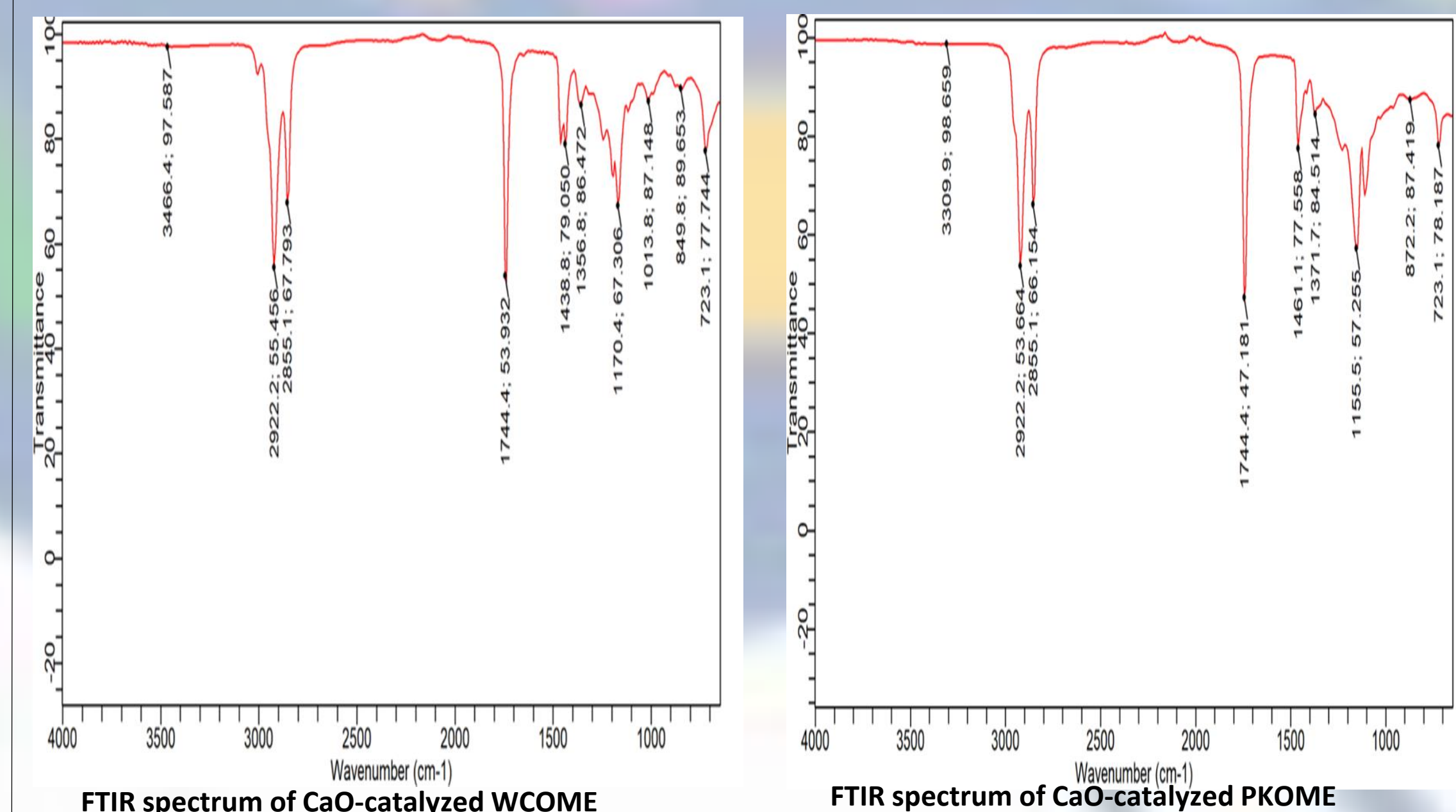
Physico-chemical characterization of the oils and biodiesel produced with CaO catalyst in comparison with ASTM standard

Properties	Waste cooking oil (WCO)	Palm kernel oil (PKO)	CaO-catalyzed WCOME	CaO-catalyzed PKOME	ASTM D-6751 Range
Density (g/ml)	0.9096	0.9109	0.8750	0.893	0.8600-0.8940
Kinematic viscosity at 40°C (mm ² s ⁻¹)	53.6581	44.7798	8.8790	6.371	1.9-6.0
Refractive index at 29°C	1.4641	1.4553	1.4512	1.4555	-
Acid value (mgKOH/kg)	2.2087	3.3065	0.9840	0.499	0.5000
Free fatty acid value (mgKOH/kg)	1.6533	1.1044	0.4920	0.249	≤ 0.5000
Moisture content (%)	0.099	0.1990	-	-	-
Saponification (mgKOH/kg)	235.58	255.99	-	-	-
Peroxide value (mg/kg)	7.4656	0.7677	-	-	-
Iodine value (mg/100g)	9.3346	7.7745	-	-	-
Molecular weight (g/mol)	721.168	666.051	-	-	-
Ester value (%)	99.0624	98.7083	-	-	-
Flash point (°C)	-	-	220	152	>120
Smoke point (°C)	-	-	92	68	-
API gravity	-	-	30.21	26.95	-
Aniline value (°F)	-	-	181	176	-
Diesel index	-	-	54.68	47.43	-
Cetane number	-	-	51	44	40-55

Characterization of uncalcined and calcined Calcium Oxide (CaO) catalyst using SEM



FTIR Characterization of the Biodiesels



FTIR spectrum of CaO-catalyzed WCOME

FTIR spectrum of CaO-catalyzed PKOME

REFERENCES

- [1] Benjamin *et al.* (2017). *Energy Conversion and Management*, 132, 231-240.
- [2] Jabbar *et al.* (2019). *Journal of Environmental Management*, 249, 109316.
- [3] Ofoefule *et al.* (2019). *Industrial Crops and Products*, 140: 111706, 1-16.
- [4] Sridevi *et al.* (2020). *Materials Science and Engineering*, 872 (1): 012166.

GC-MS characterization of the optimal yield of the CaO-catalyzed biodiesels

Composition of CaO-catalyzed WCOME

RT	Systematic Name	Formula	Molecular weight (g/mol)
16.31	10,13-Octadecadienoic acid, methyl ester	C ₁₉ H ₃₄ O ₂	294.50
13.86	Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	270.50
16.53	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C ₁₉ H ₃₄ O ₂	294.47
17.76	11-Octadecenoic acid, methyl ester	C ₁₉ H ₃₆ O ₂	296.50
34.72	Dodecanoic acid, ethenyl ester	C ₁₄ H ₂₆ O ₂	226.36
31.52	Dodecanoic acid, 1,2,3-propanetriyl ester	C ₃₉ H ₇₄ O ₆	639.00
23.65	Docosanoic acid, methyl ester	C ₂₃ H ₄₆ O ₂	354.61
21.67	cis-11-Eicosenoic acid	C ₂₀ H ₃₈ O ₂	310.51
20.81	Eicosanoic acid, methyl ester	C ₂₁ H ₄₂ O ₂	326.56
28.54	Dodecanoic acid, 2,3-dihydroxypropyl ester	C ₁₅ H ₃₀ O ₄	274.40
10.02	Dodecanoic acid, methyl ester	C ₁₃ H ₂₆ O ₂	214.34
25.95	Tetracosanoic acid, methyl ester	C ₂₅ H ₅₀ O ₂	382.66
9.06	Nonanoic acid, 9-oxo-, methyl ester	C ₁₀ H ₁₈ O ₃	186.25
15.31	Hexadecanoic acid, 14-methyl-, methyl ester	C ₁₈ H ₃₆ O ₂	284.48

Composition of PKOME CaO-catalyzed

RT	Systematic Name	Formula	Molecular weight (g/mol)
16.68	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	C ₁₉ H ₃₄ O ₂	294.47
17.58	13-Octadecenoic acid, methyl ester	C ₁₈ H ₃₄ O ₂	296.50
13.90	Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	270.50
17.12	10,13-Octadecadienoic acid, methyl ester	C ₁₉ H ₃₄ O ₂	294.50
17.78	Methyl stearate	C ₁₉ H ₃₈ O ₂	298.50
10.05	Dodecanoic acid, methyl ester	C ₁₃ H ₂₆ O ₂	214.34
27.73	Docosanoic acid nonyl ester	C ₃₃ H ₆₀ O ₂	466.80
18.21	9,12-Octadecadienoic acid, methyl ester, (E,E)-	C ₁₉ H ₃₄ O ₂	294.47
20.22	Methyl 9-eicosenoate	C ₂₁ H ₄₀ O ₂	324.54
12.45	Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	228.37
24.88	Tricosanoic acid, methyl ester	C ₂₄ H ₄₈ O ₂	368.60
11.70	Methyl tetradecanoate	C ₁₅ H ₃₀ O ₂	242.40
6.16	Octanoic acid, methyl ester	C ₉ H ₁₈ O ₂	158.24
15.58	Heptadecanoic acid, methyl ester	C ₁₈ H ₃₆ O ₂	284.50
23.68	Docosanoic acid, methyl ester	C ₂₃ H ₄₆ O ₂	354.61

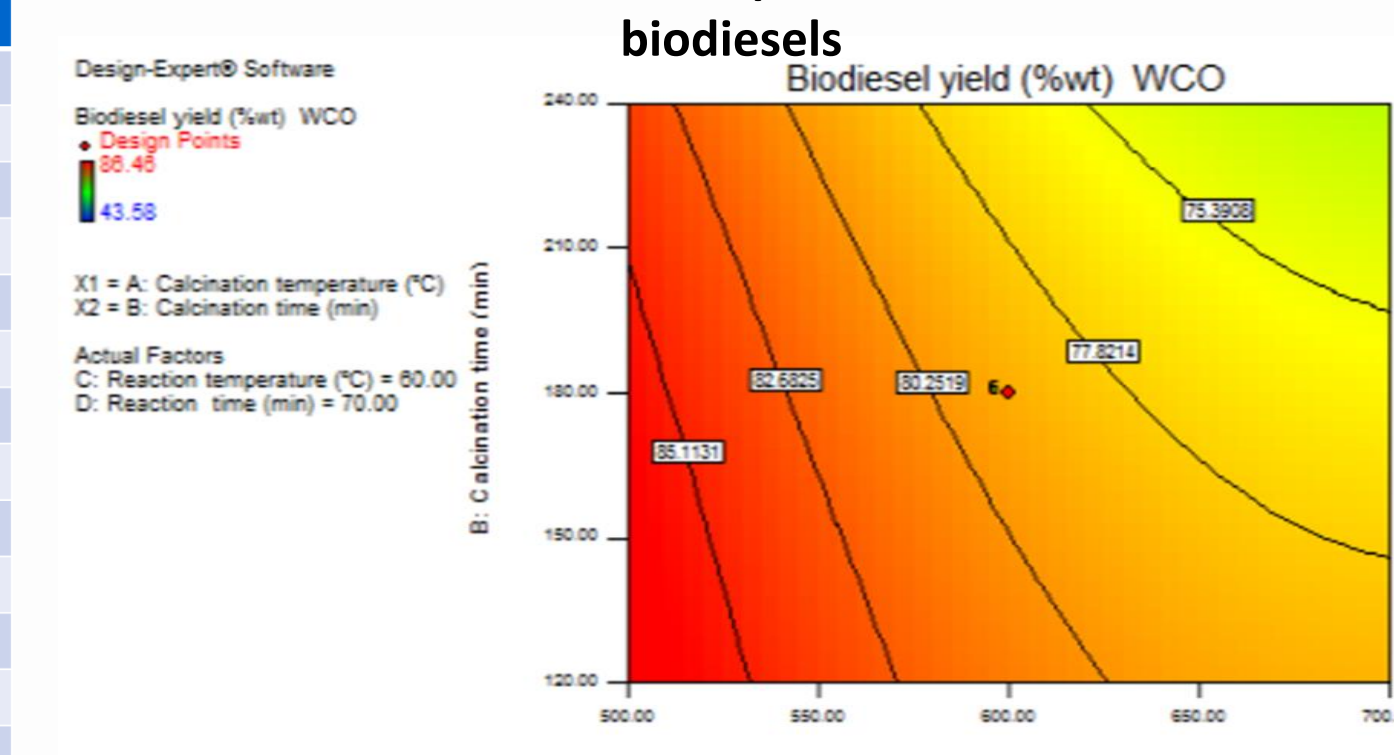
ANOVA for Response Surface Quadratic Polynomial Regression Model for WCOME (CaO-catalyzed)

Source	Squares	df	Square	Value	Prob > F
Model	2211.16	14	157.94	1.72	0.0047
A- Calcination temperature (°C)	68.97	1	68.97	0.75	0.0399
B- Calcination time (min)	18.77	1	18.77	0.20	0.0577
C- Reaction temperature (°C)	232.73	1	232.73	2.53	0.0123
D- Reaction time (min)	426.02	1	426.02	4.64	0.048
AB	2.03	1	2.03	0.022	0.8837
AC	455.09	1	455.09	4.95	0.0418
AD	170.89	1	170.89	1.86	0.1927
BC	60.18	1	60.18	0.66	0.0031
BD	185.05	1	185.05	2.01	0.1763
CD	198.25	1	198.25	2.16	0.0125
A²	34.47	1	34.47	0.38	0.5493
B²	0.82	1	0.82	8.97E-03	0.9258
C²	143.72	1	143.72	1.56	0.0002
D²	1.73	1	1.73	0.019	0.8927
Residual	1378.1	15	91.87		
Lack of Fit	233.88	2	116.94	1.33	0.2985
Pure Error	1144.22	13	88.02		
Cor Total	3589.27	29			
Std. Dev.	9.59	R-Squared		0.9166	
Mean	75.8	Adj R-Squared		0.9077	
C.V. %	12.65	Pred R-Squared		0.8842	
PRESS	201.6	Adeq Precision		14.24	

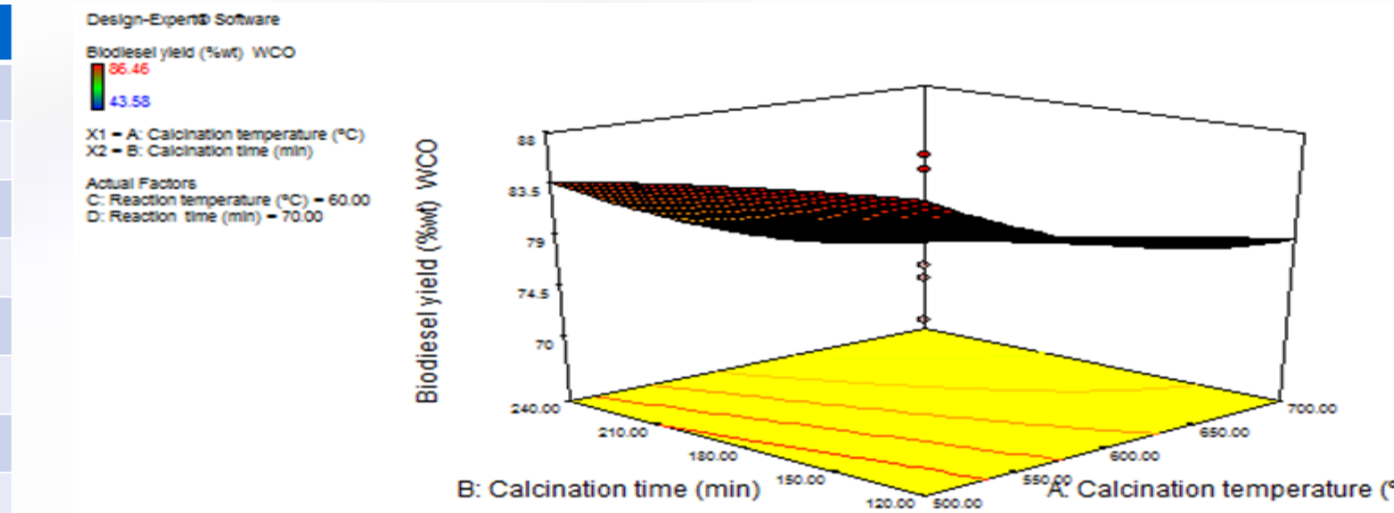
ANOVA for Response Surface Quadratic Polynomial Regression Model for PKOME (CaO-catalyzed)

Source	Sum of Squares	df	Mean Square	F	p-value
Model	1699.71	14	121.41	5.63	0.0010
A- Calcination Temperature (°C)	79.66	1	79.66	3.69	0.0039
B- Calcination Time (min)	54.73	1	54.73	2.54	0.0021
C- Reaction Temperature (°C)	78.47	1	78.47	3.64	0.0758
D- Reaction Time (min)	407.89	1	407.89	18.9	0.0006
AB	13.49	1	13.49	0.63	0.4415
AC	1.41	1	1.41	0.065	0.8019
AD	223.24	1	223.24	10.35	0.0058
BC	13.86	1	13.86	0.64	0.4354
BD	61.77	1	61.77	2.86	0.1113
CD	31.15	1	31.15	1.44	0.2481
A²	29.78	1	29.78	1.38	0.2584
B²	92.11	1	92.11	4.27	0.0565
C²	105.13	1	105.13	4.87	0.0433
D²	463.66	1	463.66	21.49	0.0003
Residual	323.65	15	21.58		
Lack of Fit	214.33	2	107.17	12.74	10.09
Pure Error	109.32	13	8.41		
Cor Total	2023.36	29			
Std. Dev.	4.65	R-Squared		0.940	
Mean	70.57	Adj R-Squared		0.8907	
C.V. %	6.58	Pred R-Squared		0.8477	
PRESS	131.43	Adeq Precision		11.12	

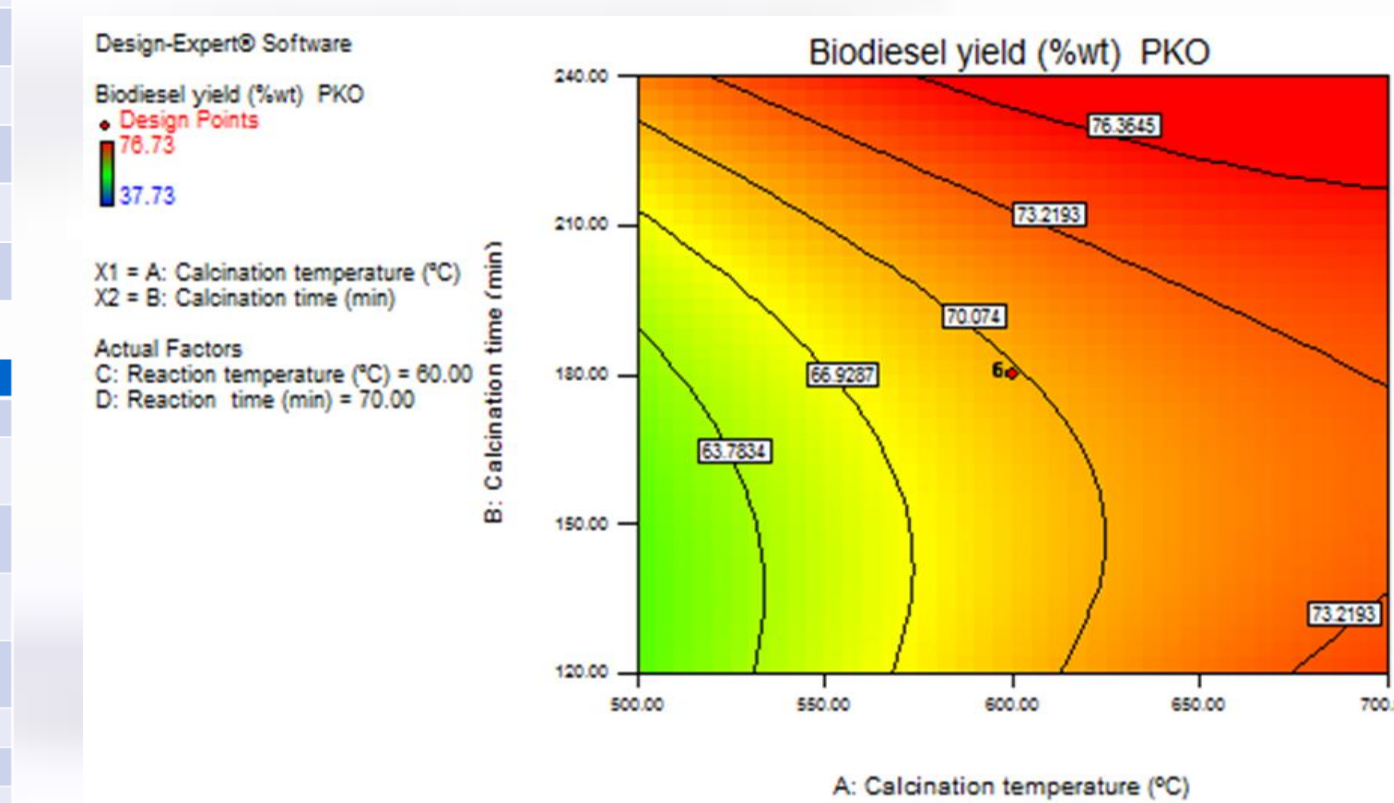
2D contour plot and 3D surface graph showing the interactions between independent variables of the biodiesels



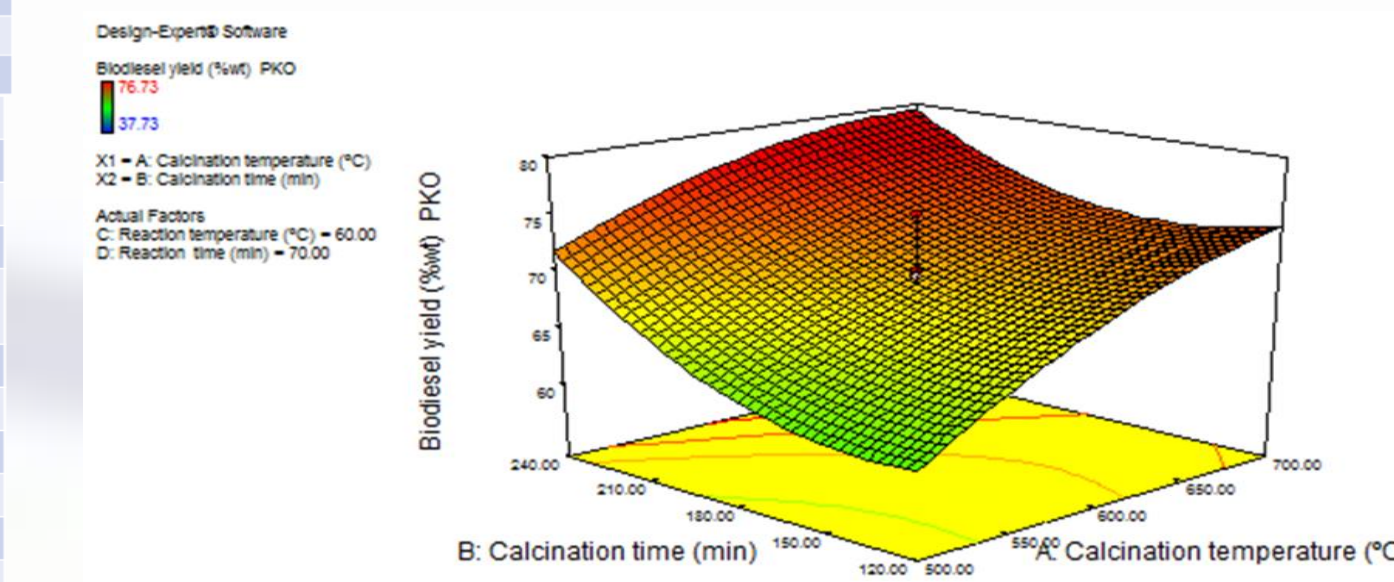
2D interactive contour plot of the effect of calcination time and calcination temperature on WCOME yield



3D interactive surface graph of the effect of calcination time and calcination temperature on WCOME yield



2D interactive contour plot of the effect of calcination time and calcination temperature on PKOME yield



3D interactive surface graph of the effect of calcination time and calcination temperature on PKOME yield

Experimental system selected yield versus experimental validated yield of the optimum process parameters to produce the highest yield of biodiesel

Optimization data for the production of biodiesel	Calcination Temp. (°C)	Calcination Time (min)	Reaction Temp. (°C)	Reaction Time (min)	Experimental system selected values/ Experimental validated values of biodiesel yield (%wt)
CaO-catalyzed WCOME	505.84	218.94	61.02	65.02	91.51/ 94.85
CaO-catalyzed PKOME	652.11	203.77	55.59	69.27	79.76/ 79.66

CONCLUSION

- ✓ The production of biodiesel of better optimization yield and quality from WCO and PKO respectively using CaO catalyst has been achieved.
- ✓ The biodiesel yields were significantly influenced by the calcination time and temperature of the catalyst and the reaction temperature and time according to the Response Surface Quadratic Polynomial Regression Model.
- ✓ The study provided up-to-date information on the optimum reaction conditions in the transesterification of PKO and WCO with CaO as catalyst.