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Hybrid Response Surface Method-African Buffalo Optimization Technique for Ultrasonic Production of Biodiesel from Waste Cooking Oil using Li doped CaO Nanocatalyst

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Abstract: ***In the current era, there is an increasing emphasis on green fuels for a clean environment. Authors in this work have tried to devise an innovative method to optimize ultrasonic production of biodiesel from used cooking oil, using composite technique combining Response surface Methodology and African Buffalo optimization. In this research work, heterogeneous catalyst Lithium doped CaO has been obtained from a new natural source by high-temperature thermal decomposition of Musa Balbisiana root ash and tested its Conversion efficiency for conversion of waste cooking oil into methyl esters. It was observed that the catalyst is really effective for the production of biodiesel from even high Free Fatty Acid waste cooking oil. For optimization of production parameters authors have used ABO complemented with RSM to maximize the biodiesel production yield. The maximum biodiesel yield of 96.67% was achieved using ABO which is about 15% higher than provided by RSM which is 81.01%. The highest biodiesel yield of 96.67 % is obtained at 15:1 Molar Ratio with 3.5% catalyst wt. percent, 60 Degree C Temp. in 45 Minutes with an error of 2.5 % in yield prediction by ABO. The work may be utilized by industries and researchers to use ultrasonic reactors optimally to extract better biodiesel volume in very short time instead of presently used slow mechanical stirring tank reactors.***

Keywords : African Buffalo Optimization, Biodiesel, Lithium doped CaO, Musa Balbisiana, Response Surface, Waste cooking oil.

I. INTRODUCTION

Now a day, researchers are working on innovative ways to efficiently produce alternate energy sources to fossil fuels to reduce the pollution and dependency on already extinct fossil fuel sources. [1] The fossil fuels have the advantage of being safely stored underground for centuries and can be used when over the ground sources may not be available in future due to any natural catastrophe or man-made destruction of over the ground energy sources. But these fossil fuel sources are limited and are being consumed at a very fast rate which might lead to the extinction of these resources in the next hundred years.

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[2] Also burning of fossil fuel is causing a lot of Air pollution in recent years. Due to all these reasons, scientists have now started to look for some clean renewable alternate for these.

Biodiesel is a viable and renewable alternative to fossil fuels as it can be generated from a variety of renewable plant seed oils in sufficient quantity by all the countries and has almost equal efficacy to fossil fuels with much-reduced pollution through exhaust emissions. [3, 4] In this research the authors have adopted a novel method of composite Response surface and African buffalo optimization technique for the optimization of Ultrasonic production parameters for the conversion of waste cooking oil into its methyl esters. Waste cooking oil is the used frying oils collected from small scale restaurants and hotels in India. The Waste cooking oil is either used for making soaps or is disposed off, for other purposes and is available at cheap rates in the open market. [5] The cost of biodiesel is detrimental to its practical usage and any reduction in the cost of the feedstock may increase the extent of usage many times. [6] It has been observed in the past research work that at least some of the consumables involved in the production of biodiesel are non-renewable in nature and biodiesel production is still not completely renewable although the vegetable oil feedstock can be replenished back other components are still non-renewable. Authors in the present work have tried to use all renewable components for fast and efficient Ultrasonic Transesterification for making the whole biodiesel production process a, fast, completely sustainable and renewable process. [7] In addition to feedstock which is waste cooking oil, a catalyst used is also sourced mainly from the renewable Musa-Balbisiana root obtained from the abundantly available wild banana species of Coastal India. [8] Vegetable oils provide a renewable alternate to depleting fossil fuels. Fossil fuel takes centuries to build up under the earth and it is not possible to create fossil fuels in a short time of a lifetime of a human being. Due to this, these are generally considered non-renewable sources of energy. Vegetable oils, on the other hand, have also various limitations like high viscosity and high fire-point. Vegetable oils can't be used directly in present-day engines without significant modifications. [9] There are many ways suggested by past researchers to make vegetable oils more compatible with conventional I.C. Engine. Fuel properties can be changed by mainly two methods thermal and Chemical. Thermal methods involve the reduction of viscosity of vegetable oils by preheating the oils to make them less viscous or there are chemical means like dilution, pyrolysis, microemulsion, and transesterification.

[10] Transesterification is the most commonly adopted and most efficient method to produce practically usable biofuel for a conventional engine.

Transesterification can be performed by various methods like mechanical stirring based catalytic processing, microwave-assisted process, hydrodynamic cavitation, and ultrasonication. [11, 12] Ultrasonication is a more aggressive and fast process than other processes providing high yield at high production rates.

In addition, to have different process technology alternates, there are also many options for various kinds of catalysts used for the Transesterification. Depending on the characteristic properties of feedstock, various categories of catalysts can be adopted for the production of biodiesel. Homogenous and heterogeneous catalysts are used by various researchers in the past and homogeneous catalysts like NaOH, KOH, etc. have distinct advantages of Acidic Catalysts like TiO_2 /SiO_4^-, ZrO_2-Al_2O_3, and SO_4^{2-}/ZrO; Basic Catalysts like CaO, CaO-MgO, MgO-ZnO, Na/SiO2, and Li-CaO, Acid-Base Catalysts like Bi_2O_3-La_2O_3, CaO–La_2O_3,, Montmorillonite KSF, Biocatalysts like Rhizopus oryzae lipase, Novozyme, Lipozyme, Pseudomonas cepacian, etc. have been successfully used by various authors. [13, 14, 15]

The Biocatalysts are effective in providing high purity biodiesel but the reaction rate is comparatively slow and production time consumed per liter of production is high. Many authors are now working to create a heterogeneous catalyst. [16]The major parameters affecting the Biodiesel production using ultrasonication are the kind of vegetable oil used, the water content in the oil, the Free Fatty acid level in the oil, Amplitude of vibration, Frequency of vibration, Molar Ratio, Catalyst Quantity, Reaction Temperature and Reaction Time. [17, 18]Preliminary screening experiments were performed to shortlist the independent variables and their ranges to minimize the number of experiments with the most significant variables only. It was observed during screening experiments that the probe type ultrasonicator apparatus used has a very small range of variation in frequency which does not lead to any significant impact on the biodiesel yield. The remaining parameters were found to be significant and were considered as the input independent variables for the current research work.

RSM has been used for studying the behavioral impact of process variables on Biodiesel yield and also to get the optimized yield and corresponding values of process parameters. [19] is an International reputed journal that published research articles globally. All accepted papers should be formatted as per Journal Template. Be sure that Each author profile (min 100 word) along with photo should be included in the final paper/camera ready submission. It is be sure that contents of the paper are fine and satisfactory. Author (s) can make rectification in the final paper but after the final submission to the journal, rectification is not possible. In the formatted paper, volume no/ issue no will be in the right top corner of the paper. In the case of failure, the papers will be declined from the database of journal and publishing house. It is noted that: 1. Each author profile along with photo (min 100 word) has been included in the final paper. 2. Final paper is prepared as per journal the template. 3. Contents of the paper are fine and satisfactory. Author (s) can make rectification in the final paper but after the final submission to the journal, rectification is not possible.

II. MATERIALS AND METHODS

Lithium Carbonate Anhydrous (AR), Methanol and Hemmet's indicators are procured from Sigma Aldrich. Isopropanol (AR), H_2SO_4(AR), and Sucrose are procured from High Media. KOH(AR) and silica gel Desiccant Grade were procured from CDH Fine Chemicals India Ltd.

ABB Fourier transform-Infrared spectrophotometer (FT-IR) MB3000 model was used to analyze biodiesel Spectrum equipped with Horizon 3 software for peak analysis and Thermo-Scientific TSQ 8000 Gas Chromatograph - Mass Spectrometer was used to analyze the ester composition and yield. Hammett indicators were used for the qualitative measurement of the basicity of the prepared catalyst as per the Henderson-Hasselbach equation.

X-ray diffraction (XRD) data for calcined Musa Balbisiana root ash and Li-CaO samples were collected on Panalytical's X'Pert Pro. All the above instruments were used at Kurukshetra University, Kurukshetra.

All these instruments were used at Sophisticated Analytical Instrumentation Facility at Punjab University, Chandigarh.

A. Preparation and characterization of Catalyst

It has been observed from the past literature that CaO is an effective catalyst for biodiesel production. [22, 23] In this work a new method of catalyst preparation has been devised in which, first, CaO has been obtained thermal decomposition of Musa Balbisiana plant root ash and later it was doped with Lithium using the sol-gel process to increase the basicity of the catalyst further. [8, 24] Lithium doped CaO has been used for further processing of Waste cooking oil into Biodiesel. It was seen that calcined Li-CaO remained effective for up to 6 cycles.

Step by step methodology:

1. Root of Musa balbisiana tree was extracted and peeled into thin slices.
2. The thin slices of the root were dried in open sun to remove the moisture for 15 days.
3. The dried slices were burnt in open air and ash was filtered and collected.
4. Ash characterization was done using SEM-EDX, FTIR and TEM techniques to evaluate the composition.
5. Ash was calcined at high temperature of 450 Deg C in the muffle furnace.
6. Later, high temperature treatment is given to the calcined ash at 1100 Deg C.

High temperature treatment lead to the thermo-decomposition of the ash content leaving behind the powder with CaO as the most stable constituent at this high temperature.

7. A suspension of 10 g of calcium oxide was prepared in 40 mL of deionized water, and to this 10 mL of aqueous alkali metal salt solution (Li_2CO_3) of appropriate concentration, which is stirred for 2.5 hrs., dried at 120 degree C and later on calcined in furnace at 450 degree C for 4 hrs. The prepared nano-catalyst was stored in vacuum dried for further characterization and further use in the production
7. Characterization of catalyst was done using SEM, XRD and other techniques to analyse the morphology and catalytic behaviour of the prepared catalyst.

7. Ultrasonicator was used for the production of biodiesel using above mentioned catalyst.
8. RSM was used to get the optimized process parameters and to study interactive effects of various variables.
9. Further the regression equation provided by RSM analysis is used as objective function in African Buffalo optimization technique to further enhance the optimum yield of production.
10. After getting the predicted values of various factors, confirmation experiments were performed using both RSM predicted parameters and RSM ABO predicted parameters values. Biodiesel quality was checked with FTIR.

B. SEM analysis:

The SEM JSM 6100 model of JEOL has a resolution of 4 nm at 8 mm working distance and having a maximum magnification capability of X 300,000.

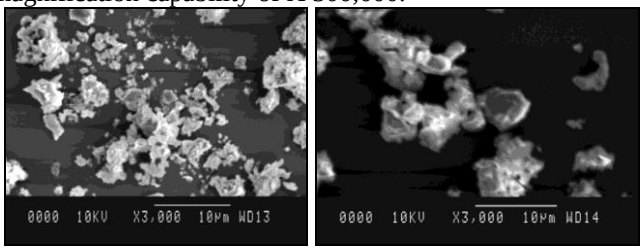

Figure-2 SEM Images of Li-CaO catalyst with 4% and 5% doping at 3000X

The SEM image analysis shows that the mixture of triangular, oval and hexagonal particles of average particle size of 1.2 µm which are actually an agglomeration of much smaller sub-particles of size in less than 100 nanometer range.

C. XRD Analysis:

XRD shows that the powder is crystallite in nature.

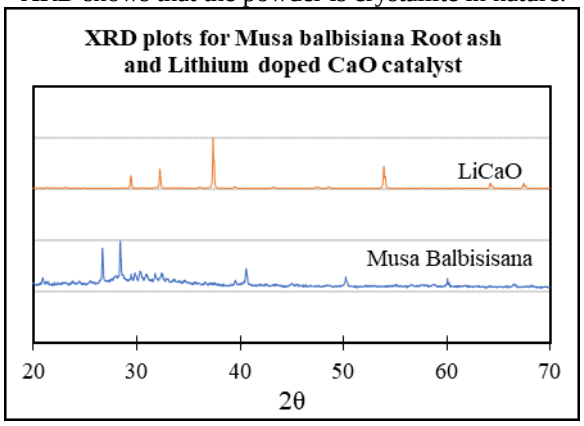

Figure-3 XRD Plots for Musa Balbisiana Root Ash and Lithium doped CaO

Debye Scherrer equation gives the crystal particle size of 60 nm which proves that the particle size shown in SEM is actually an agglomerated form of smaller sub-particles and the actual average particle size is in nano-sized range.

D. Biodiesel Production and optimization of the yield

Another objective of the research work was to optimize biodiesel production parameters using Waste cooking oil. For the production of biodiesel two-stage process of acid esterification-base transesterification was used as the Free Fatty acid content was very high in the waste cooking oil (1.65%). [25] Preheating of waster cooking oil for one hour at 115 Degree C removed traces of moisture and then oil was filtered using 10 µm cloth filter to remove suspended particles. 200 mL of oil was allowed to cool to the desired reaction temperature range and a mixture of H_2SO_4 (catalyst) and methanol was added in an appropriate quantity. [26] The acid value of each withdrawn sample was observed and when the acid value stopped varying then the reactants were further transferred to separating funnel to allow separation in two layers. [27] During this process major quantity of FFAs converts into esters due to the reaction with Acid catalyst and then the second stage transesterification was performed over the upper layer oil and esters of the first stage. In the second stage transesterification first methanol and Li-CaO catalyst. [28] Sample was transferred to a separating funnel and then allowed to settle under gravity for over-night. After the reaction is completed, due to gravity separation, the glycerol layer settles on the bottom and Biodiesel being lighter settles on top and catalyst settles as precipitate inside glycerol. Optimization of production parameters was done using the Central Composite Design (CCD) based RSM method, which was applied using Design-Expert software.

E. Gas Chromatograph Technique (GC-MS) for Biodiesel Yield evaluation

Ester yield was provided by GC-MS analysis and Ester yield has also been calculated using the following equation

Yield = (Total Weight of Biodiesel)/ (Total weight of Vegetable oil).

The most accurate analytical method for determining the quality of biodiesel and ester content in both the ASTM and European standards is Gas Chromatography-Mass Spectrophotometer. GC-MS is widely used to quantify various components in products of transesterification. [20] The GC has its own limitations because of the high time consumed in preparing samples and analyzing the samples but it has the unmatchable advantage of the precision of both Qualitative and quantitative analysis of a sample. [21]

Gas Chromatography was performed on Thermo-Scientific TSQ8000 GCMS equipment equipped with a split injection facility, a detector for flame ionization and Thermo-Scientific Dionex Chromeleon Chromatography Data System (CDS) software for precise evaluation of Ester results. The MS part Uses Selected Reaction Monitoring (SRM) to achieve lower detection limits. This mass spectrometer comes paired with the TRACE 1300 GC Triple Quadrupole for very precise detection capabilities of compounds even in trace quantities also and it comes equipped with automated sample handling.

III. RESULT AND ANALYSIS

A. RSM Analysis

To select the significant parameters Screening design was used using Design expert software and, in this work, five Independent variables Molar Ratio, Amplitude, Reaction Time, Reaction Temperature, Catalyst Quantity were selected out of six investigated and their impact on the Biodiesel yield was studied. The independent variables and their range are shown in Table 1.

Table-1 Factors and their range

Factor	Name	Units	Min.	Max.
A	Molar Ratio	Moles Alcohol /Moles Oil	6	18
B	Catalyst Quantity	% of Oil wt.	0.5	5.0
C	Reaction Temp.	Deg C	45	65
D	Reaction Time	Mins	10	50
E	Amplitude	%	30	70

A table of Experimental design and corresponding actual experimental and predicted yield values are shown in table -2. The randomized run of experiments helps in overcoming biases in Experimental setup and human operator. Planned experimental design with the RSM approach also helps in minimizing the total number of experiments

Table-2 Experimental design with response values

Run	Factors					Actual Yield	Predicted Yield	Residual
	A: Molar Ratio	B: Catalyst Quantity	C: Temp.	D: Time	E: Amplitude			
1	12	2.8	55	30	50	69	69.17	-0.170
2	6	2.8	55	30	50	47	47.41	-0.405
3	9	1.6	60	20	40	50	49.82	0.1818
4	9	3.9	50	20	40	51	50.36	0.6402
5	12	2.8	55	10	50	55	55.24	-0.238
6	9	3.9	60	40	40	65	65.86	-0.859
7	12	2.8	55	30	70	72	72.74	-0.738
8	12	2.8	65	30	50	66	65.74	0.2614
9	15	1.6	60	20	60	62	61.65	0.3485
10	12	2.8	45	30	50	59	60.24	-1.24
11	12	2.8	55	30	30	59	59.24	-0.238
12	9	1.6	60	40	60	65	63.94	1.06
13	12	2.8	55	30	50	70	69.17	0.8295
14	15	3.9	50	40	40	68	67.82	0.1818
15	12	2.8	55	30	50	71	69.17	1.83
16	15	1.6	50	40	60	72	71.15	0.8485
17	18	2.8	55	30	50	54	54.57	-0.572
18	12	2.8	55	30	50	68	69.17	-1.17
19	15	3.9	50	20	60	56	56.44	-0.443
20	12	5.0	55	30	50	72	71.41	0.5947
21	9	3.9	60	20	60	56	56.23	-0.234
22	9	1.6	50	20	60	62	61.94	0.0568
23	15	3.9	60	20	40	65	65.32	-0.318
24	15	1.6	60	40	40	54	54.28	-0.276
25	12	2.8	55	30	50	69	69.17	-0.170
26	9	1.6	50	40	40	63	62.32	0.6818
27	12	0.5	55	30	50	61	62.57	-1.57
28	12	2.8	55	50	50	75	75.74	-0.738
29	15	3.9	60	40	60	81	80.44	0.5568
30	15	1.6	50	20	40	45	43.78	1.22
31	9	3.9	50	40	60	62	61.73	0.2652
32	12	2.8	55	30	50	69	69.17	-0.170

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The Sum of square table-3 shows the variability depending on the corresponding degree of the polynomial. The polynomial level having the least P value should be chosen for the particular model.

Table-3: Sequential Model Sum of Squares

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	1.266E+05	1	1.266E+05			
Linear vs Mean	1143.21	5	228.64	5.33	0.0017	
2FI vs Linear	446.13	10	44.61	1.07	0.4384	
Quadratic vs 2FI	**654.95**	**5**	**130.99**	**99.79**	**< 0.0001**	**Suggested**
Cubic vs Quadratic	5.60	5	1.12	0.7612	0.6089	Aliased
Residual	8.84	6	1.47			
Total	1.289E+05	32	4027.78			

The higher order model is only selected it provides for variation not explained by the lower order model. Also, two-factor interaction model containing additionally It can be observed from the data available in table 3 that the linear model containing Molar Ratio(A), Catalyst Quantity(B), Reaction Temp.(C), Reaction Time(D), Amplitude(E) terms i.e. A, B, C, D, and E may not be suitable. interactions terms like AB, AC, AD, etc. still does not have significantly large p-value. The total variability is best explained by the quadratic model in the current research as a p-value < 0.05. Although the linear model also has a p-value<0.05 the quadratic model has even more significant smaller p-value and higher F-value that's why the quadratic model is recommended in the present case. The cubic terms will not add significance to the model (p value=0.6089>>0.1) and also CCD is not equipped to handle cubic terms.

The table below provides the lack of fit values for various models and it has been observed that the lack of fit value for the quadratic model is higher than 0.1 and all other models have lower P-Value than quadratic. The quadratic model acts as the whole equivalent including lower order linear and 2FI terms too. Table-5 below shows the R2 values and their modified forms Adjusted and Predicted R2. Predicted R2 in the quadratic model (0.8947) clearly stands out largest among all models to suggest the selection of the quadratic model. Higher predicted and adjusted R2 and lowest PRESS value clearly affirm the suitability of the selection of the Quadratic model.

Table-4: Lack of Fit table

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Linear	1110.18	21	52.87	49.56	0.0002	
2FI	664.05	11	60.37	56.60	0.0002	
Quadratic	**9.11**	**6**	**1.52**	**1.42**	**0.3579**	**Suggested**
Cubic	3.50	1	3.50	3.28	0.1298	Aliased
Pure Error	5.33	5	1.07			

Table-5 below shows the R^2 values and their modified forms Adjusted and Predicted R^2. Predicted R^2 in the quadratic model (0.8947) clearly stands out largest among all models to suggest the selection of the quadratic model. Higher predicted and adjusted R^2 and lowest PRESS value clearly affirm the suitability of the selection of the Quadratic model.

Table-5: Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	6.55	0.5061	0.4112	0.2482	1698.10	
2FI	6.47	0.7036	0.4258	-0.7254	3897.21	
Quadratic	**1.15**	**0.9936**	**0.9820**	**0.8947**	**237.90**	**Suggested**
Cubic	1.21	0.9961	0.9798	-0.6861	3808.49	Aliased

Test of significance using ANOVA was performed which predicted the regression equation relation for response and input variables and it was observed that the model is significant and lack of fit is not significant. [29]

As tabulated in Table 6, by comparing the different F-values and P-values of various possible regression equation terms, the quadratic model was observed to be significant for the given response, Biodiesel production yield.

The mathematical regression model for biodiesel yield from experimental data was obtained as The Model F-value of 85.49 implies the model is significant. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AB, AC, AD, AE, BC, BD, BE, CD, A^2, B^2, C^2, D^2, E^2 are significant model terms and there is no significant interaction between CE and DE (C-Reaction Temp. and E-Amplitude; D-Reaction Time and E-Amplitude). The Lack of Fit F-value of 1.42 implies the Lack of Fit is not significant relative to the pure error.

Table-6 ANOVA for Quadratic model for response yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2244.28	20	112.21	85.49	< 0.0001	significant
A-Molar Ratio	77.04	1	77.04	58.69	< 0.0001	
B-Catalyst Quantity	117.04	1	117.04	89.16	< 0.0001	
C-Reaction Temp.	45.38	1	45.38	34.57	0.0001	
D-Reaction Time	630.37	1	630.37	480.22	< 0.0001	
E-Amplitude	273.38	1	273.38	208.26	< 0.0001	
AB	115.56	1	115.56	88.04	< 0.0001	
AC	33.06	1	33.06	25.19	0.0004	
AD	7.56	1	7.56	5.76	0.0352	
AE	33.06	1	33.06	25.19	0.0004	
BC	105.06	1	105.06	80.04	< 0.0001	
BD	10.56	1	10.56	8.05	0.0162	
BE	115.56	1	115.56	88.04	< 0.0001	
CD	22.56	1	22.56	17.19	0.0016	
CE	1.56	1	1.56	1.19	0.2986	
DE	1.56	1	1.56	1.19	0.2986	
A^2	606.06	1	606.06	461.70	< 0.0001	
B^2	8.73	1	8.73	6.65	0.0257	
C^2	70.06	1	70.06	53.37	< 0.0001	
D^2	24.85	1	24.85	18.93	0.0012	
E^2	18.56	1	18.56	14.14	0.0032	
Residual	14.44	11	1.31			
Lack of Fit	9.11	6	1.52	1.42	0.3579	not significant
Pure Error	5.33	5	1.07			
Cor Total	2258.72	31				

Now Backward elimination method was adopted to remove the least-significant terms from the analysis and thus new ANOVA table is obtained as shown in table-7.

The model is still significant with a much lower corrected total value. [30]

The Sum of squares is **Type III – Partial**. The **Model F-value** of the reduced model is 92.15 much higher than the earlier model with an F-value of 85.49. Higher F-value with P-Value less than 0.05 implies the reduced model is more significant.

Predicted R^2 has shown further improvement from 0.8947 to 0.9363 after the backward elimination in the reduced quadratic model as shown in the Fit statistics in Table-8. Adequacy precision increases to 40.9378 from 39.5056.

Table-7: ANOVA for Reduced Quadratic model for Biodiesel yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2241.15	18	124.51	92.15	< 0.0001	significant
A-Molar Ratio	77.04	1	77.04	57.02	< 0.0001	
B-Catalyst Quantity	117.04	1	117.04	86.63	< 0.0001	
C-Reaction Temp.	45.38	1	45.38	33.58	< 0.0001	
D-Reaction Time	630.37	1	630.37	466.56	< 0.0001	
E-Amplitude	273.38	1	273.38	202.33	< 0.0001	
AB	115.56	1	115.56	85.53	< 0.0001	
AC	33.06	1	33.06	24.47	0.0003	
AD	7.56	1	7.56	5.60	0.0342	
AE	33.06	1	33.06	24.47	0.0003	
BC	105.06	1	105.06	77.76	< 0.0001	
BD	10.56	1	10.56	7.82	0.0151	
BE	115.56	1	115.56	85.53	< 0.0001	
CD	22.56	1	22.56	16.70	0.0013	
A^2	606.06	1	606.06	448.57	< 0.0001	
B^2	8.73	1	8.73	6.46	0.0246	
C^2	70.06	1	70.06	51.85	< 0.0001	
D^2	24.85	1	24.85	18.39	0.0009	
E^2	18.56	1	18.56	13.74	0.0026	
Residual	17.56	13	1.35			
Lack of Fit	12.23	8	1.53	1.43	0.3596	not significant
Pure Error	5.33	5	1.07			
Cor Total	2258.72	31				

Table-8: Fit Statistics table

Std. Dev.	1.16	**R^2**	0.9922
Mean	62.91	**Adjusted R^2**	0.9815
C.V. %	1.85	**Predicted R^2**	0.9363
		Adeq. Precision	40.9378

Yield=+69.17+1.79*A+2.21*B+1.37*C+10.25*D+6.75*E+2.69*A*B+1.44*A*C+ 1.38*A*D +2.87*A*E +2.56*B*C +1.63*B*D -5.38*B*E-2.37*C*D+0.6250*C*E +1.25D*D*E -4.55*A*A -0.5455*B*B-1.55*C*C -3.68*D*D-3.18*E*E (1)

The equation-I in terms of coded factors is generally used for making predictions about the response for a given factor value and to assess the relative impact of the various factors based on their coefficients. The equation-II of actual factors can be used for making predictions for given levels of each factor but cannot be used to analyze the relative impact of each factor as the coefficients are adjusted to include the units of each of the factors.

Yield=-130.69718+2.17445*Molar_Ratio-20.50000* Catalyst_Quantity +5.07222* Reaction_Temp. +1.74116*Reaction_Time +0.777399* Amplitude+0.796296*Molar_Ratio*Catalyst_Quantity+0.095833*Molar_Ratio*Reaction_Temp.+0.022917*Molar_Ratio*Reaction_Time+ 0.047917*Molar_Ratio*Amplitude+0.455556* Catalyst_Quantity *Reaction_ Temp.+0.072222* Catalyst_Quantity *Reaction_Time -0.238889* Catalyst_Quantity*Amplitude-0.023750*Reaction_Temp.* Reaction_Time-0.023750*Reaction_Temp.*Amplitude+ 0.003125*Reaction_Time*Amplitude-0.505051 *Molar_Ratio*

Molar_Ratio-0.430976*Catalyst_Quantity* Catalyst_Quantity-0.061818 *Reaction_Temp.* Reaction_Temp.-0.009205*Reaction_Time *Reaction_Time-0.007955*Amplitude *Amplitude –(2)

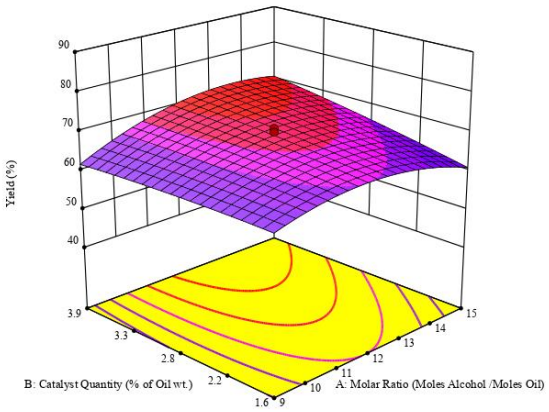

Figure:4 Interaction of Molar Ratio and Catalyst Quantity on the Biodiesel yield

The interaction of yield with Molar ratio and catalyst weight shows that the yield increases with catalyst quantity at a lower molar ratio at a lower rate than at a higher molar ratio. Also, there is no significant increase in the yield with an increase in the molar ratio at lower catalyst weight while there is a very significant increase in the yield obtained with an increase in molar ratio at higher catalyst quantity. This is due to the catalyst gets dissolved easily in higher alcohol quantity and can work more effectively to provide a higher yield.

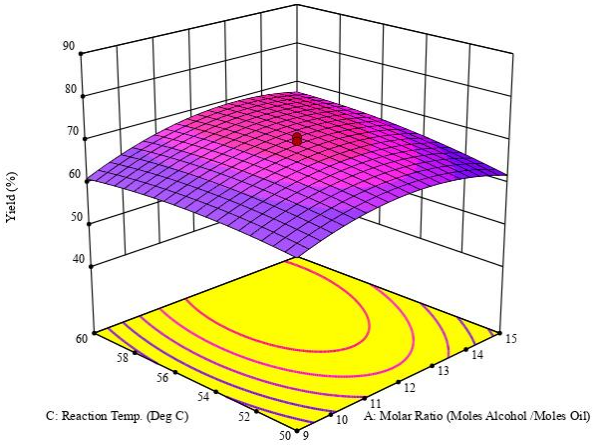

Figure:5 Interaction of Molar Ratio and Reaction Temperature on the Biodiesel yield

Interactive effect of Molar ratio and Reaction temp. with Biodiesel yield are shown above. The biodiesel yield is increased at a higher rate on a higher molar ratio than at a lower molar ratio. Also, the biodiesel yield increase is higher at higher reaction temperature but the yield is not increasing significantly at a lower temperature range.

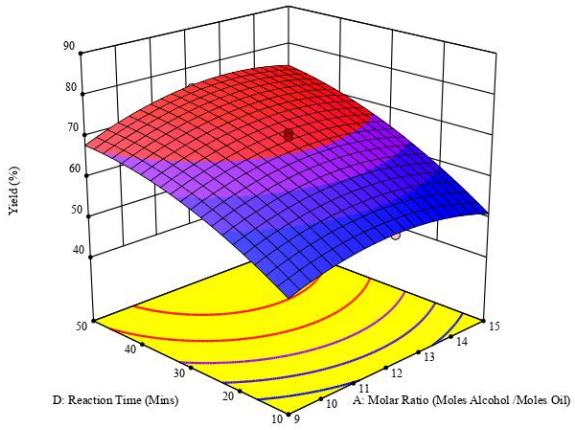

Figure:6 Interaction of Molar Ratio and Reaction Time on the Biodiesel yield

Fig. 6 shows that the yield increases with an increase in reaction temperature at a faster rate when the higher quantity of catalyst is added but there is no significant increase at lower catalyst amount. Similarly, yield increases significantly at higher temperatures but the increase is not significant at lower temperatures.

The increase of molar ratio leads to higher yield increase with higher reaction time but the increase is not significant at a time less than 15 minutes. Yield increases significantly with reaction time both at lower and high molar ratios. Yield increases at a higher rate with the molar ratio at a higher amplitude. Similarly, the yield increase is higher at higher molar ratios with an increase in amplitude. Yield increases with an increase in reaction temperature at a faster rate when the higher quantity of catalyst is added but there is no significant increase at lower catalyst amount.

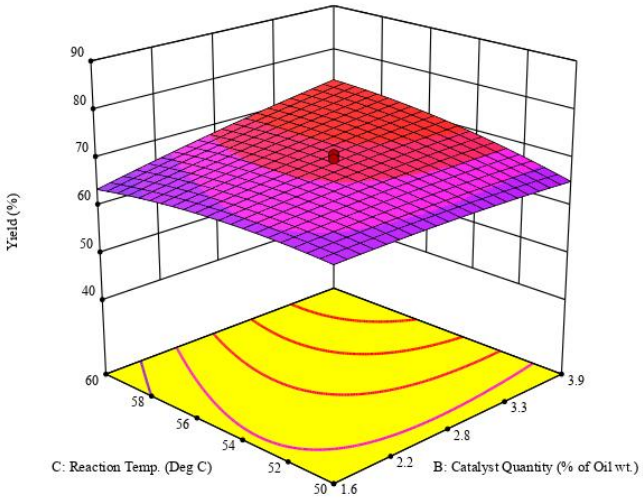

Figure:7 Interaction of Reaction Temp. and Catalyst wt. on the Biodiesel yield

Similarly, yield increases significantly at higher temperatures but the increase is not significant at lower temperatures.

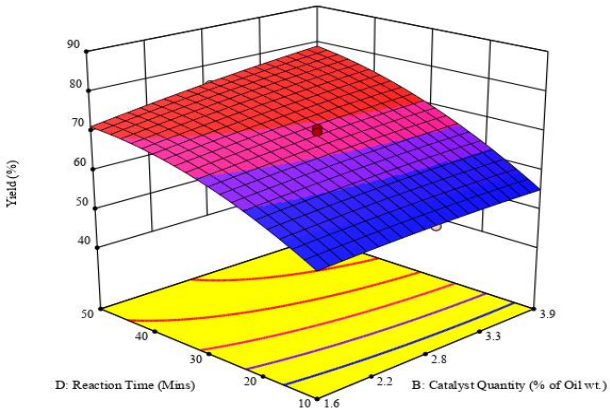

Figure:8 Interaction of Reaction Time and Catalyst Quantity on the Biodiesel yield

There is a sharp rise in yield with reaction time even at lower catalyst amount. The increase further enhances at higher catalyst weights. The biodiesel yield increases with an increase in catalyst quantity but the rate of increase is more at higher reaction time and is lower at smaller reaction time.

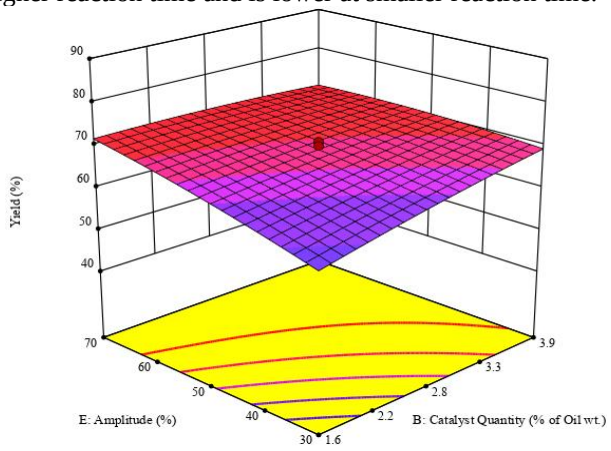

Figure:9 Interaction of Amplitude and Catalyst Quantity on the Biodiesel yield

The yield rises sharply with increasing amplitude at smaller catalyst weights but adding more catalysts at high amplitude actually does not lead to any significant effect on yield. At lower amplitude, the increase rate of yield with the catalyst is higher in comparison to at higher amplitude.

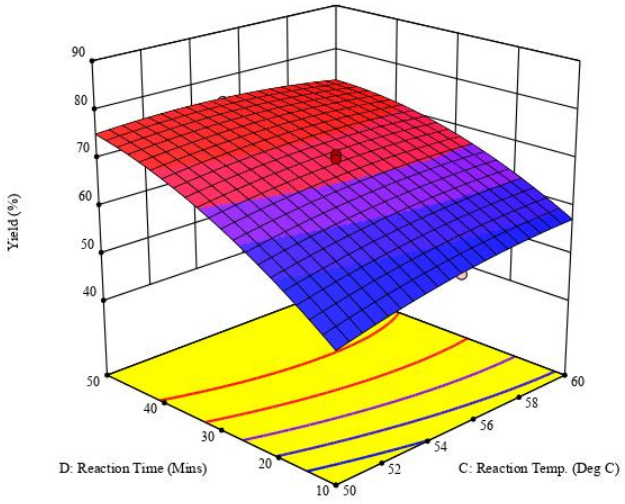

Figure:10 Interaction of Reaction Temp. and Reaction Time on the Biodiesel yield

The increase in reaction temperature and reaction time leads to significant enhancement in biodiesel production yield. The yield increases with reaction temperature but increasing reaction time will not have any significant enhancement in the yield because in the Ultrasonic transesterification due to vigorous stirring the maximum conversion takes place in the first few minutes only and thereafter more time of reaction will not have provided any further improvement in yield.

Table-9: Solution Table Based on Desirability index

No.	Molar Ratio	Catalyst Quantity	Temp.	Time	Amplitude	Yield	Desirability	
1	**14.88**	**3.875**	**59.7**	**50.00**	**69**	**83.13**	**0.719**	**Select**
2	14.79	3.875	59.5	50.00	69	83.12	0.719	
3	14.95	3.875	59.9	50.00	69	83.12	0.719	
4	14.81	3.875	59.4	50.00	69	83.12	0.719	
5	14.96	3.875	59.7	49.97	69	83.12	0.719	
6	14.87	3.871	59.8	49.99	69	83.11	0.719	
7	14.87	3.875	59.1	50.00	69	83.11	0.719	
8	14.86	3.875	59.6	50.00	69	83.10	0.718	
9	14.76	3.875	59.5	49.93	67	83.05	0.718	
10	14.50	3.875	59.9	49.99	70	83.05	0.718	

B. Result Validation

The confirmatory experiments were performed five times to ascertain the legitimacy of the predictions in the model and their average is taken as the actual yield. The confirmatory experiments performed with optimum factor values and predicted and actual yield is shown below in the table.

Table-10 Confirmation experiment parameters and Yield

Response	Yield
Molar Ratio (Alcohol /oil)	14.88
Catalyst (wt. %)	3.875
Temp. (Deg C)	60
Reaction Time(Mins)	50
Amplitude(%)	70
Predicted Yield(%)	83.13
Actual yield (%)	81.01
Error(%)	2.62

C. GC Profile of Biodiesel

Gas Chromatography was performed on Thermo-Scientific TSQ8000 GCMS equipment. The column was TG5MS a 30.0 m × 0.25 mm × 0.25 µm capillary column with highly pure helium gas being used as the carrier gas. Injector and detector temperature were 250°C. Mass Spectrophotometer condition during analysis are; ion source temp: 200°C, interface temp: 240°C, scan range: 40-700 m/z, total run time=57.10 Min. The total ester content found is shown in the table-11.

Table-11-GC Profile of the biodiesel

S. No.	Retention time	Name of the esters	FAME's %	Molecular Formula
1	32.72	Tetradecanoic acid, 12-methyl, methyl ester,	1.34	$C_{16}H_{32}O_2$
2	38.17	Tetradecanoic acid, 10,13-dimethyl, methyl	29.54	$C_{17}H_{34}O_2$
3.	40.43	Heptadecanoic acid, methyl ester	1.13	$C_{18}H_{36}O_2$

4	42.11	9,12-Octadecadienoic acid, methyl ester	11.77	$C_{19}H_{34}O_2$
5	43.26	9-Octadecenoic acid (Z), methyl ester	19.04	$C_{19}H_{36}O_2$
6	43.5	Heptadecanoic acid, 16-methyl-methyl ester	5.19	$C_{19}H_{38}O_2$
7	43.68	9,12-Octadecadienoic acid, methyl ester	3.91	$C_{19}H_{34}O_2$
8	46.45	9-Octadecenoic acid, 12-hydroxy, methyl ester	1.92	$C_{19}H_{36}O_3$
9	46.66	11-Eicosenoic acid, methyl ester	1.33	$C_{21}H_{40}O_2$
10	47.24	Tetradecanoic acid, 12-methyl, methyl ester	2.48	$C_{16}H_{32}O_2$
11	51.35	Docosanoic acid, methyl ester	3.12	$C_{23}H_{46}O_2$
12	56.97	Tetracosanoic acid, methyl ester	1.13	$C_{25}H_{50}O_2$

D. FTIR for Biodiesel

FTIR of Waste cooking oil biodiesel was performed using ABB MBR3000 FTIR before confirmation experiments to evaluate the quality of biodiesel. The Ester group presence was reflected by peaks at 1743 cm^{-1} and 1465 cm^{-1}.

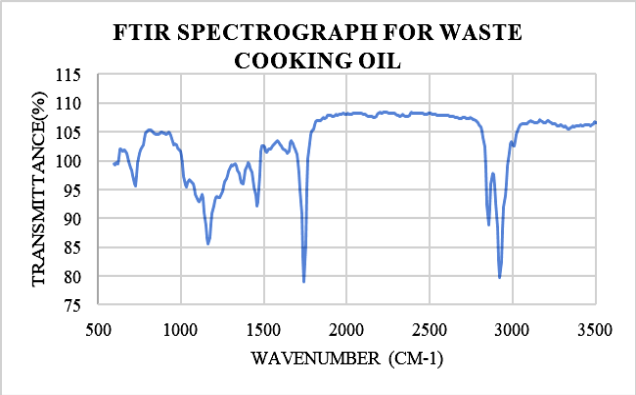

Figure-11 FTIR of WCO biodiesel

E. Biodiesel Production Yield enhancement using African Buffalo Optimization

The optimized yield level of 81.01 % obtained by the RSM approach was economically viable but to make it sustainable in long term we can further improve the yield of production bringing non-required byproducts to their minimum possible level. There are many nature-based algorithmic approaches used by various authors like Neural network, PSO, GA, etc. [31] Most of these techniques have certain limitations like complex fitness function, poor search space exploration, premature convergence, and large computing power requirements. [32, 33]

Also, the precision is dependent on user-dependent parameters. African Buffalo Optimization technique devised by Odili and Kahar in 2015 provides an effective algorithm without all these limitations, still maintaining a real good accuracy level. [34] This algorithm is based on the intelligent behavior of wild buffalo with symbiotic support and grazing area search capabilities of the African buffalos. [35]

The algorithm is based on the three features of wild African buffalo, Good memory, peculiar sounds of 'Waa' and 'Maa' to communicate about danger or safe grazing areas and a sort of voting in a group whenever a dispute arises between the leader and group members.

ABO algorithm used in the present work initializes the Production parameters like Amplitude, Reaction Temperature, catalyst quantity, reaction time and molar ratio to gather the yield at different values of parameters. After getting the yield at different values of production parameters, the predicted values of yield are stored in the memory. This updates the process and this process maintains until the whole of the catalyst and oil is exhausted. In each iteration, it will store the output in the memory and finally, it compares the predicted yield and time and finally produces the optimized output. The principal behavior is used to empower the buffalos to maintain up the track of their courses through a large number of kilometers. These three behaviors are considered as the African buffalo improvement. The 'maaa' sound of buffalo (μ=1,2,3,...N) is represented by m_μ and 'waaa' sound of buffalo is denoted as w_μ. The movement of buffalo is determined using an equation.

$$m_{\mu+1} = m_\mu + l_1 x_1 (r_{gmax.\mu} - w_u) + l_2 x_2 ((r_{pmax.\mu} - w_u) \quad (3)$$

where w_u and m_μ represent the respective exploration and exploitation moves respectively of μ_{th} buffalo (μ =1,2,3...N); l_1 and l_2 are learning parameters, $r_{gmax.\mu}$ denotes the best fitness of the herd and $r_{pmax.\mu}$ denotes the location of the best individual buffalo in the herd, x_1 and x_2 are random numbers from 0 to 1. [36]

Step1. Objective Function is defined by the regression equation provided by RSM analysis.

$$Z = \alpha_o + \sum_{i=1}^{k} \alpha_i Y_i + \sum_{i=1}^{k} \alpha_{ii} Y_i^2 + \sum_{i=1,i<j}^{k-1} \sum_{j=2}^{k} \alpha_{ij} Y_i Y_j \quad (4)$$

Step2. Initialize the Biodiesel production parameters with imposed constraints over their ranges as used in the RSM (equivalent to buffalos) randomly to nodes at the search space

Step2. Update the Production parameters (buffalos' exploitation) using equation (1)

Step3. Refresh the Production parameters (next location of buffalos μ in relation to $r_{gmax.\mu}$ and $r_{pmax.\mu}$ using the following equation

$$w_{\mu+1} = \frac{w_\mu + m_\mu}{\lambda} \quad (5)$$

Where λ is a random number

Step4. If $r_{gmax.\mu}$ is refreshing then go to 6. If Not, then go to step 2.

Step5. Validate stopping criteria. If it is achieved, go to 6, otherwise, return to Step 3

Step6. Output best solution for optimized yield. Perform confirmation experiments using the optimized production parameters. Evaluate the error between Predicted and Experimental yield results. Now compare it with the yield achieved using RSM.

Here, this algorithm initializes the production parameters and also to gather the yield at different values of input variables. After getting the yield at different catalyst amounts, the predicted values like time and yield are stored in the memory. This update process maintains until the whole of the catalyst and oil are exhausted.

In each iteration, it will store the output in the memory and finally, it compares the predicted yield and time and finally produces the optimized output.
The Biodiesel yield actually obtained by the Hybrid approach of RSM with ABO was more precise and near to prediction and was 15.66 percent above the Biodiesel yield obtained by RSM alone.

Table-12 Comparison of predictions and corresponding actual yield by RSM and RSM-ABO

	RSM	RSM-ABO
Molar Ratio	14	15
Catalyst (wt %)	3.8	4
Temp. (°C)	60	65
Time (Mins.)	50	55
Amplitude (%)	70	65
Yield (%)	83.13	98.3
Actual Yield (%)	**81.01**	**96.67**
Error (%)	2.55	1.54

IV. CONCLUSION

The present research work was targeted towards devising a novel way to use heterogeneous catalyst Li Doped CaO from a new source with a new route for Biodiesel production and evaluate the effectiveness of ABO along with RSM for Optimization of Biodiesel production yield. The following conclusions are drawn after completion of the research work:
1. Through this work authors have proved that fast production of active CaO nano-catalyst can be done by the thermo-decomposition of root ash of wild banana species Musa Balbisiana Colla Root ash
2. Lithium doping in CaO improves the basicity of the catalyst resulting in a better catalytic action leading to high yield of biodiesel production up to 96.67 percent even with a High FFA Waste Cooking oil. The catalyst was characterized using various effective analytical techniques and the catalyst could be reused effectively for 6 cycles without losing its catalytic efficiency.
3. Interactions effects of various process variables on the Biodiesel yield have been evaluated between various parameters were analyzed using RSM and it was observed that the process parameters not only significantly affect the Yield of Biodiesel production but also have unique interactive behavior between the independent variables. Analysis of the regression equation did also provide the information that the relatively most impactful independent variables among all these is the Reaction time and Molar Ratio which have larger coefficients of 1.74116 and 2.17445 in comparison to the other independent variables.
4. It was observed that the optimum yield of 96.67 % was obtained at 15:1 Molar ratio, 4% catalyst quantity of oil weight at an amplitude of 65% and Time of 55 minutes. The yield obtained as per the predictions by the ABO algorithm is about 15.66% higher than RSM. It proves that ABO along with RSM could be built as an effective technique to optimize biodiesel production process and similar other processes.
Authors observed that Carbonates are difficult to separate out from Glycerol and biodiesel which are generated due to the use of Lithium carbonates for preparing catalyst. It would be better if some other salt like Lithium hydroxide is used for preparation of Lithium doped CaO catalyst. It is also prudent to mention here that the impact of multiple calcination cycle at different temperatures on each catalyst sample's catalytic efficacy can also be studied.

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