

# Methanolysis Optimization of Cottonseed Oil to Biodiesel Using Heterogeneous Catalysts

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**ABSTRACT:** *This paper presented the process optimization for heterogeneous catalysts transesterification of refined cottonseed oil catalyzed by calcium oxide (CaO) and magnesium oxide (MgO) impregnated on Saw Dust Ash (SDA) using Response Surface Methodology Central Composite Design (RSMCCD). The five transesterification process variables studied were: catalyst concentration (4-8 wt% oil), methanol/oil molar ratio (4:1-8:1), reaction temperature (45-85°C), reaction time (3-5h), and agitation speed (200-300rpm). It was revealed that the reaction temperature gave the most significant effect on the yield of Fatty Acid Methyl Ester (FAME), followed by methanol/oil molar ratio. There were also significant interaction effects between catalyst concentration and methanol/oil molar ratio, catalyst concentration and agitation speed, methanol/oil molar ratio and reaction temperature, methanol/oil molar ratio and reaction time, methanol/oil molar ratio and agitation speed, reaction time and agitation speed for CaO/SDA transesterified reaction while for MgO/SDA transesterified reaction the significant interaction effect between variable is methanol/oil molar ratio and reaction time. Based on the optimized conditions, the highest yield of 90% for CaO/SDA transesterified reaction and 77% for MgO/SDA transesterified reaction were predicted using the following variables catalyst concentration, CaO/SDA = 6wt% and MgO/SDA = 8wt%, methanol/oil molar ratio = 6:1(CaO/SDA) and 8:1 (MgO/SDA), reaction*

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temperature = 65°C, reaction time = 4h and agitation speed = 250rpm. Experimental validation of the predicted optimum conditions gave an actual yield of 86% (CaO/SDA) and 73.3% (MgO/SDA). The small errors between the predicted and actual optimum yield (4.7% (CaO/SDA) and 5.2% (MgO/SDA)) indicated that the model were valid and accurate in representing the actual experimental values and also in predicting yield at any conditions within the range studied. The results proved the efficacy of saw dust ash impregnated with CaO and MgO in transesterification reaction.

**KEYWORDS:** Refined cottonseed oil; Saw dust ash; Free fatty acid methyl ester; Response surface methodology; Central composite design; Heterogeneous catalysts.

## INTRODUCTION

Centuries ago the world energy demand had relied on non-renewable crude oil derived (fossil) liquid fuels out of which 90% is estimated to be consumed for energy generation, transportation and industrial applications. It is also known that gaseous emissions from the combustion of these fuels are the principal causes of global warming and many countries have passed legislation to arrest their adverse environmental consequences [1].

The depletion of world petroleum reserves and the increasing environmental hazards associated with the use of fossil fuels have stimulated the search for an alternative and efficient fuels by many researchers in recent years. One of the most promising alternative fuels is biodiesel, which has attracted attention worldwide [2]. This is primarily due to its outstanding benefits over the conventional petro diesel. It is renewable, biodegradable, non-toxic, has a high flash point and good reduction in greenhouse emissions [3-6].

Biodiesel is the free fatty acid methyl esters, popularly referred to as FAME, derived from fats and vegetable oil sources. There are various processes that have been adopted in production of biodiesel from vegetable oils and animal fats namely; micro-emulsification with alcohols, catalytic cracking, Pyrolysis, transesterification and ultrasonic assisted transesterification [4, 6-9]. Among these methods, transesterification is the key and foremost important process to produce the cleaner and environmentally safe fuel [10,11].

The transesterification is usually carried out using primary or secondary alcohols. Fukuda et al. [12] reported that methanol and ethanol are most frequently used in the production of biodiesel but methanol is more

preferred due to their low cost. Biodiesel has been produced through transesterification of edible oils [2] and non-edible oils [13-15]. The production of biodiesel from non-edible oils may not meet energy demand. Therefore, there is need to augment the non edible feed stocks with some of edible feed stocks such as cotton seed that are not of significant value. In recent years, research interests have shifted towards biodiesel production from cottonseed oil [16-22], of which conversions between 72% and 94% were obtained by enzyme catalyzed transesterification of cottonseed oil with short-chain primary and secondary alcohols. The application of solid acid catalysts on the cottonseed oil transesterification was investigated by Chen et al. [19]. He reported that the yield of methyl ester was above 90% after 8hours of reaction. In a related research, transesterifying cottonseed oil by microwave irradiation produced a biodiesel yield in the range of 89.5%-92.7% [20]. Also, Ramachadran et al. [23] studied production of biodiesel from mixed waste vegetable oil using an Aluminium hydrogen sulphate as a heterogeneous acid catalyst and obtained a good yield.

Many materials have been used as heterogeneous catalysts for the biodiesel synthesis. Alkaline earth oxides, in particular magnesium oxide (MgO) [21, 22, 24] and calcium oxide (CaO) [25, 26] are potential heterogeneous catalysts for use in biodiesel production research and have attracted attention in recent years. Di Serio et al. [24] reported that MgO exhibited very low catalytic performance in transesterification of soybean oil at reaction temperature of 100°C. Sivakumar et al., [27] studied sonochemical biodiesel production using smoke deposited nano MgO catalyst and reported a good yield.

Refaat [28] reported that calcium oxide as a heterogeneous base catalyst has been used both as single and supported in production of biodiesel from different vegetable oils. Bharathi *et al.* [29] studied biodiesel production from waste vegetable oil using calcium oxide as a heterogenous catalyst.

Nevertheless, very little studies have focused on the utilization of CaO impregnated onto wastes sources like ash. Chakraborty *et al.* [30], developed a heterogeneous coal fly ash-based CaO catalyst using waste eggshell as raw materials for the transesterification of soybean oil to produce biodiesel. In addition, many research studies on the application of ash-based catalyst for synthesis of biodiesel have been published (such as palm oil boiler ash [31], cocoa pod husks ash [32], palm empty fruit bunch ash [33] and wood ash [34]). Those ash-based catalysts not only showed good catalytic performance but also were environmentally friendly and renewable for biodiesel production. To the best of our knowledge, few or no investigations have been made by using saw dust impregnated with alkaline earth oxides for biodiesel synthesis.

There are some factors that affect the yield of biodiesel through transesterification of vegetable oils. They are alcohol/oil molar ratio, catalyst concentration, reaction temperature, reaction time and agitation speed. The optimization of transesterification reaction requires a large number of experiments and mathematical tool that can predict the effect of each process parameter of the reaction and their interactions. Response surface methodology has been successfully applied to the optimization of biodiesel production from different raw materials and different types of catalysts. Several researchers have applied it in optimization of various production processes. Suganya and Renganathan [35] applied it in optimization of algal oil extraction from marine macroalgae *Ulva lactuca* for biodiesel production. Also, Sivakumar *et al.*, [36] employed response surface methodology in extraction of oil from *Sterculia foetida* seed oil and its process augmentation for biodiesel production. Sivakumar *et al.*, [37] employed it in Optimization of biodiesel production from underutilized *Ceiba Pentandra* oil. In this study, response surface methodology in combination with CCD was applied to optimize the transesterification of refined cottonseed oil with methanol in presence of calcium oxide and magnesium oxide to produce biodiesel.

## EXPERIMENTAL SECTION

### Materials

The commercial refined, edible grade cottonseed oil was purchased from Shoprite Mall Enugu, Nigeria. While the saw dust was collected from, Timber Market, Trans-Ekulu, Enugu, Enugu State, Nigeria. The methanol, CaO and MgO were purchased from De-Cliff Integrated Services Ltd Enugu, Nigeria and they were of analytical grade.

### Preparation of Catalyst

The method used by Guan-Yin *et al.* [38] was adopted in the preparation of the catalysts. Dry raw Saw Dust (SD) was sieved to eliminate clay particles. After thorough washing with deionized water, the SD was filtered and oven-dried at 105°C until constant weight was attained. Then, the SD was calcined at a temperature of 800°C for 4 h to prepare saw dust ash, SDA. This ash was used as support for the active catalyst.

2 g each of CaO and MgO powder were added slowly to 100 mL of water to prepare aqueous solutions of Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>. These solutions were subsequently added to 10 g of dried SDA differently and mixed with constant magnetic stirring at 500 rpm for 4 h. The solutions were aged for 24 h for formation of the Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> precipitate on SDA carrier. Excess water in the samples was removed by oven-drying them at 120°C for 8 h. The catalysts were then calcined in a muffle furnace at temperature of 550 °C for 5h. They were stored in a desiccator in the presence of silica and KOH pellets in order to avoid water and CO<sub>2</sub> contact with the catalysts.

### Characterisation of the catalysts

The catalysts were characterized using a powder X-ray diffractometer (Rigaku, Japan) coupled with Cu K $\alpha$  radiation to determine their crystalline phase. The BET surface area was measured by N<sub>2</sub> adsorption–desorption isotherm apparatus (BEL; BELSORP-max). The FTIR spectra were recorded on a Shimadzu IR-Prestige21 spectrometer in the range of 500–4000 cm<sup>-1</sup>. The KBr pellet method was used for the sample preparation. The SEM images were recorded on a Quanta 200 SEM system equipped (FEI Company, Netherlands).

### Characterisation of refined cottonseed oil

The physiochemical properties; relative density, moisture content, melting point, free fatty acids content, iodine values, peroxide value, saponification value and viscosity of the oil were determined using the American Oil Chemists Society methods [39].

### Transesterification reaction

Transesterification reactions were carried out according to each design points (Tables 1 and 3) and the results of the methyl ester yield of refined cottonseed oil were used as the response values in order to optimize the reaction conditions for both catalysts. The transesterification was carried out in a batch reactor using a 200ml round-bottom flask was equipped with a reflux condenser, set up on a hot plate magnetic stirrer to control the temperature and the speed. The refined cottonseed oil was precisely quantitatively transferred into the reactor. Then specific amount of each catalyst, CaO/SDA and MgO/SDA (by weight of refined cottonseed oil) dissolved in the required amount of methanol was added. The reaction flask was kept on a hot magnetic stirrer at a particular temperature and an agitation speed throughout the reaction. At the defined time, sample was taken out, cooled, and the biodiesel (i.e. the methyl ester in the upper layer) was separated from the by-product (i.e. the glycerol in the lower layer) by settlement overnight under ambient condition. The percentage of the biodiesel yield was determined by comparing the weight of the biodiesel layer with the weight of refined cottonseed oil used.

$$\text{Biodiesel Yield (\%)} = \quad (1)$$

$$\frac{\text{weight of fatty acid methylester}}{\text{weight of oil used}} \times 100$$

### Statistical Analysis

Design Expert software (version 8.0.7.1) was used in this study to design the experiment and to optimize the reaction conditions. The experimental design employed in this work was a Central Composite Design (CCD) a two-level- five –factor ( $2^{5-1} + 2*5 + 6$ ), including 32 experiments. Catalyst concentration, A, methanol/oil molar ratio, B, reaction temperature, C reaction time, D and agitation speed, E were selected as independent factors for the optimization study. The response chosen was the methyl ester yields obtained from

transesterification of refined cottonseed oil. Six replications of centre points were used in order to predict a good estimation of errors and experiments were performed in a randomized order. The actual and coded levels of each factor are shown in Table 1. The coded values were designated by  $-1$  (minimum),  $0$  (centre),  $+1$  (maximum),  $-\alpha$  and  $+\alpha$ . Alpha is defined as a distance from the centre point which can be either inside or outside the range, with the maximum value of  $2n/4$ , where  $n$  is the number of factors [40]. Hereby the value of alpha is set at  $0.5$ . It is noteworthy to point out that the software uses the concept of the coded values for the investigation of the significant terms, thus equation in coded values is used to study the effect of the variables on the response. Each response of the transesterification process was used to develop a mathematical model that correlates the yield of refined cottonseed oil into FAME (response) to the transesterification process variable studied through first, second order and interaction terms according to the following second order polynomial equation.

$$Y = \beta_0 + \sum_{i=1}^5 \beta_i X_i + \sum_{i=1}^5 \sum_{j=i+1}^5 \beta_{ij} X_i X_j + \sum_{i=1}^5 \beta_{ii} X_i^2 \quad (2)$$

Where  $Y$  is the predicted yield of FAME (%),  $X_i$  and  $X_j$  represent the transesterification process variables,  $\beta_0$  is the offset term,  $\beta_i$  is the linear effect,  $\beta_{ij}$  is the first order interaction effect,  $\beta_{ii}$  is the squared effect.

Selection of levels for each factor was based on the experiments performed to study the effects of process variables on the application of solid base catalysts for transesterification reaction of refined cottonseed oil.

## RESULTS AND DISCUSSION

### Characterization of the synthesized catalysts

#### Scanning electron microscope (SEM)

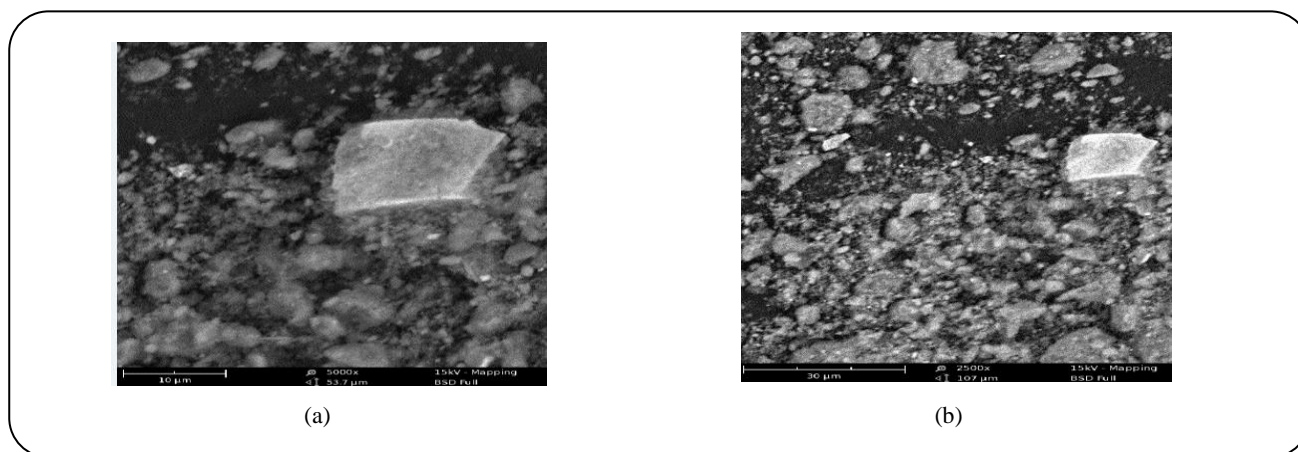
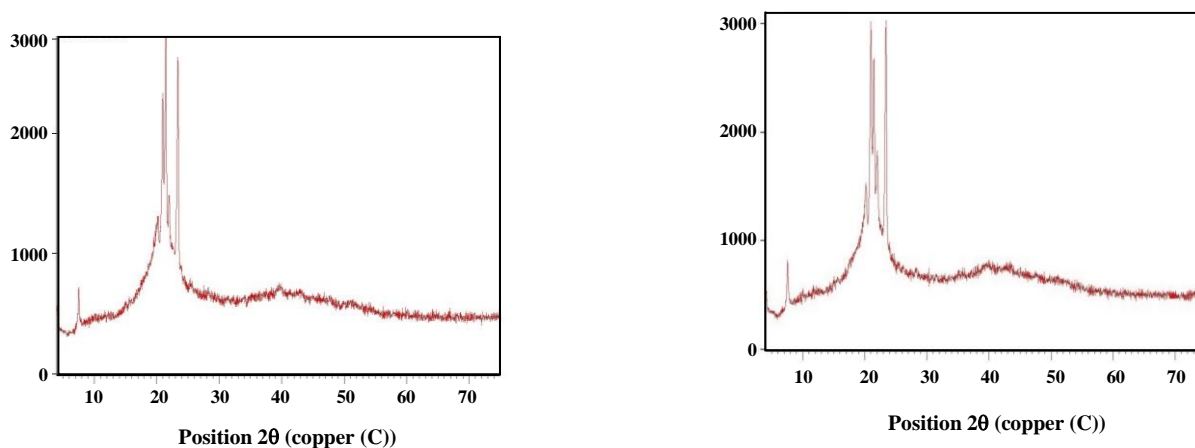
The morphology of the modified catalysts are shown in Figs. 1a & 1b, the modified CaO and MgO exhibited an aggregation of numerous nanoparticles and it also showed that after calcination CaO and MgO were well distributed on the SDA800.

#### X-ray diffraction (XRD)

The crystalline phases of the modified catalysts are shown in Figs. 2a & 2b. The XRD profiles of catalysts exhibited the characteristic peaks of crystalline phases,

**Table 1: Studied range of each factor in actual and coded form for CaO/SDA and MgO/SDA.**

Factor	Coding	Units	Low level	High level	- $\alpha$	+ $\alpha$	Centre
Catalyst conc.	A	Wt %	4(-1)	8(+1)	2(-2)	10(+2)	6(0)
Methanol/oil ratio	B	mol/mol	4(-1)	8(+1)	2(-2)	10(+2)	6(0)
Temperature	C	°C	45(-1)	85(+1)	25(-2)	105(+2)	65(0)
Reaction Time	D	Hours	3(-1)	5(+1)	2(-2)	6(+2)	4(0)
Agitation Speed	E	Rpm	200(-1)	300(+1)	150(-2)	350(+2)	250(0)

**Fig. 1: a) SEM of CaO/SDA. b) SEM of MgO/SDA.****Fig. 2: a) XRD pattern of CaO/SDA. b) XRD pattern of MgO/SDA.**

namely CaO, MgO and SiO<sub>2</sub>. The CaO, MgO and SiO<sub>2</sub> (quartz) peaks could be observed for all catalysts.

#### BET surface area

The physical properties of the catalysts are shown in Table 2. It could be observed that the pore size decreased which consequently increased the BET surface area

with SDA treatment at temperature of 800°C. The increased in surface area signified more concentration of pores/active sites.

#### Fourier Transform Infrared Spectrometer.

Fourier Transform Infrared spectrometer (FT-IR) was used to probe the surface characteristics. The presence of OH and SiO<sub>2</sub> functional group were confirmed by FT-IR

Table 2: Physiochemical properties synthesized catalysts.

Parameters	Raw SDA	CaO/SDA	MgO/SDA
Surface area (m <sup>2</sup> /g)	240	450	448
Pore size (nm)	4.3	2.1	1.99
Total pore volume (cm <sup>3</sup> /g)	14.1	24.1	23.8

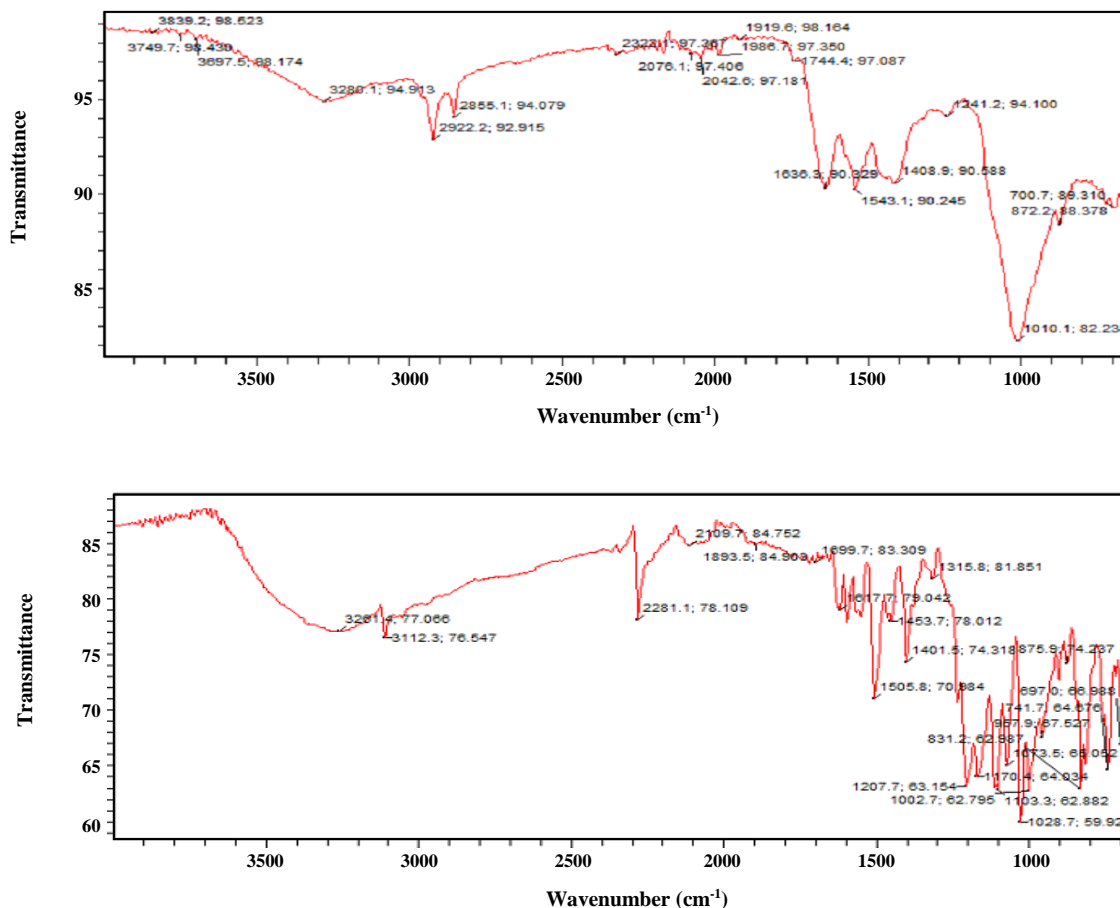


Fig. 3: a) FT-IR spectra of CaO/SDA. b) FT-IR spectra of MgO/SDA.

spectra. The peak appearing was assigned to various functional group according to their respective wave numbers. In Figs. 3a, and 3b the presence of OH and SiO<sub>2</sub> functional group were confirmed by FT-IR spectra. The peaks and their intensities at 700.7-1636.3 and 697-1028.7cm<sup>-1</sup> for CaO/SDA and MgO/SDA respectively were attributed to the SiO<sub>2</sub> group, while the peaks and intensity at 2922.2 -3112.3 and 3339.7-3369.5cm<sup>-1</sup> for CaO/SDA and MgO/SDA respectively were attributed to the OH group.

#### Characterization of the refined cottonseed oil

The summary of the characterization is shown in the Table 3. From the table, it was observed that the FFA value of the refined cottonseed oil is less than 1%. This is an acceptable level for transesterification reaction. The density and high viscosity of the oil will make it difficult to be atomised in internal combustion engine, hence it cannot be used directly as bio-fuel. The acid value, iodine value, and saponification value show that the oil will form less soap and improve separation of the biodiesel

Table 3: The summary of characterization of refined cottonseed oil.

Properties	Units	Values
Specific gravity		0.912
Kinematics viscosity at 40°C	Centistokes	63.9
Acid value	mgKOH/Oil	0.29
Iodine	g I <sub>2</sub> /100g oil	22.1
Saponification value	mgKOH/g oil	63.19
Free fatty acid	%	0.145
Pour point	°C	-4.9
Refractive index		1.467
pH		3.64

from the glycerol, thus increase the yield. The low pour point shows that the oil will hardly solidify at room temperature hence can be stored for a long time.

#### Transesterification process

The complete design matrix for the heterogeneous transesterification of refined cottonseed oil with results is given in Table 4. From the table, it was observed that the yield ranged from 14% to 86% for CaO/SDA and from 4% to 83% for MgO/SDA, indicating that the conversion of refined cottonseed oil into FAME using heterogeneous catalysts was highly successful. The highest yield was obtained at catalyst concentration of 6wt% (CaO/SDA) and 8wt% (MgO/SDA), molar ratio of oil to methanol of 1:6 (CaO/SDA) and 1:8 (MgO/SDA), reaction temperature 65°C, reaction time of 4h and agitation speed of 250rpm where as the lowest yield was obtained at catalyst concentration of 6wt% (CaO/SDA) and 8wt% (MgO/SDA), molar ratio of oil to methanol of 1:6 (CaO/SDA) and 1:8 (MgO/SDA), reaction temperature 25°C, reaction time of 4h and agitation speed of 250rpm.

#### Development of regression model equation

The responses (yields) in Table 4 were analyzed using multiple regression analysis to develop a polynomial expression as in equation (2). The final equations in terms of coded factors after excluding some of the insignificant terms (identified using Fisher's test) for CaO/SDA and MgO/SDA transesterified reactions are shown in Eqs. (3) and (4) respectively.

$$\begin{aligned} \text{Yield, } Y = & 85.55 - 0.67A + 2.75B + 7.25C + \quad (3) \\ & 2.25D + 5.58E - 1.12AB + 1.25AC - 0.75AD - \\ & 0.87BC + 2.63BD + BE - 1.38CE - 0.38DE - 5.30A^2 - \\ & 4.80B^2 - 14.17C^2 - 4.92D^2 - 6.05E^2 \end{aligned}$$

$$\begin{aligned} \text{Yield, } Y = & 77.13 + 3.13B + 6.79C + 4.96E + \quad (4) \\ & 2.81BD - 4.87A^2 - 4.37B^2 - 13.12C^2 - 4.50D^2 - 6.25E^2 \end{aligned}$$

The positive signs in front of the terms in both equations (Eqs. (3) and (4)) indicate synergistic effect whereas the negative sign indicates antagonistic effect. Both equations 3 and 4 suggested that the yield of FAME has linear and quadratic effects on five variables studied. The qualities of the models developed were evaluated from the coefficients of determination, R<sup>2</sup>. From the ANOVA (Tables 5 and 6), the values of R<sup>2</sup> for CaO/SDA and MgO/SDA transesterified reaction were found to be 0.9996 and 0.9745 respectively. These high values of R<sup>2</sup> (very close to 1) indicate that there are good agreements between the experimental (actual) and predicted values.

Based on 95% confidence level, the developed regression models were tested to be highly significant since their computed F-values (1247.71) (CaO/SDA) and 21.04 (MgO/SDA) were much higher than the theoretical F<sub>0.05</sub> (20, 11) value that is 2.65. This indicates that the regression models are highly reliable. Most terms in the regression model equations (Eq. (3) and (4)) were also shown to be significant as their computed F values in Tables 5 and 6 are much higher than the theoretical

**Table 4: Experimental Design Matrix For the Factorial Design of Biodiesel Production from Cotton Seed Oil using CaO/SDA and MgO/SDA.**

Runs	A:Catalyst conc.(wt%)	B:Methanol/oil ratio	C:Temperature (Deg.celcius)	D:Time (Hour)	E:Agitation speed (rpm)	Yield (%) (CaO/SDA)	Yield (%) (MgO/SDA)
1	4(-1)	4(-1)	45(-1)	3(-1)	300(+1)	47	48
2	8(+1)	4(-1)	45(-1)	3(-1)	200(-1)	34	30
3	4(-1)	8(+1)	45(-1)	3(-1)	200(-1)	36	38
4	8(+1)	8(+1)	45(-1)	3(-1)	300(+1)	48	40
5	4(-1)	4(-1)	85(+1)	3(-1)	200(-1)	50	40
6	8(+1)	4(-1)	85(+1)	3(-1)	300(+1)	62	52
7	4(-1)	8(+1)	85(+1)	3(-1)	300(+1)	60	55
8	8(+1)	8(+1)	85(+1)	3(-1)	200(-1)	49	45
9	4(-1)	4(-1)	45(-1)	5(+1)	200(-1)	35	25
10	8(+1)	4(-1)	45(-1)	5(+1)	300(+1)	43	33
11	4(-1)	8(+1)	45(-1)	5(+1)	300(+1)	63	60
12	8(+1)	8(+1)	45(-1)	5(+1)	200(-1)	40	40
13	4(-1)	4(-1)	85(+1)	5(+1)	300(+1)	58	48
14	8(+1)	4(-1)	85(+1)	5(+1)	200(-1)	54	50
15	4(-1)	8(+1)	85(+1)	5(+1)	200(-1)	61	51
16	8(+1)	8(+1)	85(+1)	5(+1)	300(+1)	68	58
17	2(-2)	6(0)	65(0)	4(0)	250(0)	65	60
18	10(+2)	6(0)	65(0)	4(0)	250(0)	63	53
19	6(0)	2(-2)	65(0)	4(0)	250(0)	60	55
20	6(0)	10(+2)	65(0)	4(0)	250(0)	72	62
21	6(0)	6(0)	25(-2)	4(0)	250(0)	14	4
22	6(0)	6(0)	105(+2)	4(0)	250(0)	43	43
23	6(0)	6(0)	65(0)	2(-2)	250(0)	61	51
24	6(0)	6(0)	65(0)	6(+2)	250(0)	70	65
25	6(0)	6(0)	65(0)	4(0)	150(-2)	50	40
26	6(0)	6(0)	65(0)	4(0)	350(+2)	72	62
27	6(0)	6(0)	65(0)	4(0)	250(0)	85	75
28	6(0)	6(0)	65(0)	4(0)	250(0)	86	80
29	6(0)	6(0)	65(0)	4(0)	250(0)	86	76
30	6(0)	6(0)	65(0)	4(0)	250(0)	85	75
31	6(0)	6(0)	65(0)	4(0)	250(0)	86	76
32	6(0)	6(0)	65(0)	4(0)	250(0)	86	80



**Table 5: Significance of regression coefficients the yield of biodiesel catalyzed by CaO/SDA using the design-expert version 8.0.7.1 trial version.**

Source	Coefficient estimate	Degree of freedom	Sum of square	F-value	P-value (Prob>F)
Model	85.55	20	503.55	1247.71	<0.0001
A	-0.67	1	10.67	26.43	0.0003
B	2.75	1	181.50	449.72	<0.0001
C	7.25	1	1261.50	3125.76	<0.0001
D	2.25	1	121.50	301.05	<0.0001
E	5.58	1	748.17	1853.82	<0.0001
AB	-1.12	1	20.25	50.18	<0.0001
AC	1.25	1	25.00	61.95	<0.0001
AD	-0.75	1	9.00	22.30	0.0006
AE	-0.13	1	0.25	0.62	0.4479
BC	-0.87	1	12.25	30.35	0.0002
BD	2.63	1	110.25	273.18	<0.0001
BE	1	1	16.00	39.65	<0.0001
CD	0.25	1	1.00	2.48	0.1438
CE	-1.38	1	30.25	74.95	<0.0001
DE	-0.38	1	2.25	5.58	0.0377
<b>A<sup>2</sup></b>	-5.30	1	822.56	2038.15	<0.0001
<b>B<sup>2</sup></b>	-4.80	1	674.56	1671.44	<0.0001
<b>C<sup>2</sup></b>	-14.17	1	5890.19	14594.79	<0.0001
<b>D<sup>2</sup></b>	-4.92	1	710.19	1759.71	<0.0001
<b>E<sup>2</sup></b>	-6.05	1	1072.06	2656.37	<0.0001
Residual	4.44	11	0.4		
Cor. Total			10075.50		

Std. Dev.=0.64; Mean = 59.13; C.V.% = 1.07; PRESS = 77.51;  $R^2 = 0.9996$ ; Adj.  $R^2 = 0.9988$ ; Pred.  $R^2 = 0.9923$ ; Adeq. Precision = 138.3

**Table 6: Significance of regression coefficients the yield of biodiesel catalyzed by MgO./SDA using the Design-Expert version 8.0.7.1 trial version**

Source	Coefficient estimate	Degree of freedom	Sum of square	F-value	P-value (Prob>F)
Model	77.13	20	454.25	21.04	<0.0001
A	-1.29	1	40.04	1.85	0.2005
B	3.13	1	234.38	10.86	0.0071
C	6.79	1	1107.04	51.27	<0.0001
D	1.87	1	84.38	3.91	0.0737
E	4.96	1	590.04	27.33	0.0003
AB	-1.56	1	39.06	1.81	0.2057
AC	2.44	1	95.06	4.40	0.0598
AD	0.69	1	7.56	0.35	0.5659
AE	-2.44	1	95.06	4.40	0.0598
BC	-1.44	1	33.06	1.53	0.2417
BD	2.81	1	126.56	5.86	0.0339
BE	0.19	1	0.56	0.026	0.8747
CD	0.81	1	10.56	0.49	0.4988
CE	-1.31	1	27.56	1.28	0.2826
DE	-0.56	1	5.06	0.23	0.6377
<b>A<sup>2</sup></b>	-4.87	1	697.13	32.29	<0.0001
<b>B<sup>2</sup></b>	-4.37	1	561.46	26	0.0003
<b>C<sup>2</sup></b>	-13.12	1	5053.13	234.04	<0.0001
<b>D<sup>2</sup></b>	-4.50	1	594	27.51	<0.0001
<b>E<sup>2</sup></b>	-6.25	1	1145.83	53.07	<0.0001
Residual	237.50	11	21.59		
Cor. Total			9322.47		

Std. Dev. = 4.65; Mean = 52.23; C.V.% = 8.89; PRESS = 4937.42;  $R^2 = 0.9745$ ; Adj.  $R^2 = 0.9282$ ; Pred.  $R^2 = 0.9235$ ; Adeq. Precision = 17.556

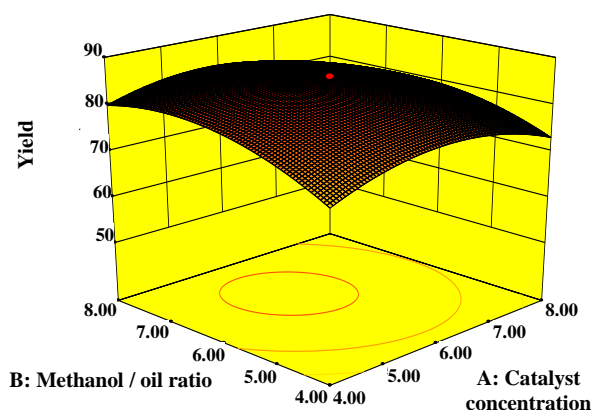


Fig. 4: 3D Plot showing the effect of methanol/oil ratio and catalyst concentration on the biodiesel yield using CaO/SDA.

$F_{0.05}(1, 11)$  value that is 4.84. From these statistical tests, it can be concluded that the developed regression models are thoroughly adequate in representing the experimental (actual) data and therefore reliable in predicting the yield of FAME from refined cottonseed oil using CaO/SDA and MgO/SDA at any given condition (variables), within the ranges studied.

#### Effects of transesterification process variables

From Tables 5 and 6, it was clearly shown that among the five variables studied, reaction temperature (C) has the largest effect on the yield of FAME as it has the highest F-test value (3125.76) and (51.27) respectively followed by the agitation speed (E) F-test values (1853.82 and 27.33 respectively). Catalyst concentration (A) showed the most insignificant effect as it has the lowest F-test values (26.43 and 1.85 respectively). There were also significant interaction effects between variables; as shown by those between catalyst concentration and methanol/oil molar ratio, catalyst concentration and reaction temperature, catalyst concentration and agitation speed, methanol/oil molar ratio and reaction temperature, methanol/oil molar ratio and reaction time, methanol/oil molar ratio and agitation speed for CaO/SDA transesterified reaction while for MgO/SDA transesterified reaction, the significant interaction effect between variables is methanol/oil molar ratio and reaction time.

Fig. 4 is the surface plot of the predicted FAME yield which can be generated by Eq.(3). The figure depicts

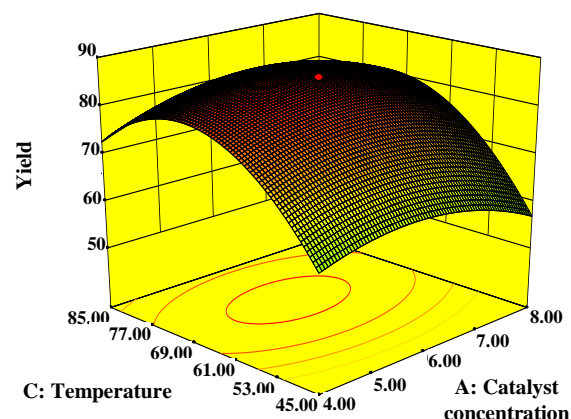


Fig. 5: 3D Plot showing the effect of temperature and catalyst concentration on the biodiesel yield using CaO/SDA.

the interaction effect between methanol/oil molar ratio and catalyst concentration (CaO/SDA) on the yield of FAME for. The figures have similar trend and show that the amount of methyl ester yield increases with methanol/oil molar ratio and catalyst concentration. However, at higher catalyst concentrations and methanol/oil molar ratio, a reduction in the yield can be observed due to the fact that the quadratic terms of the two factors are more significant with a negative effect (Eq.(3)).

Fig. 5 shows the interaction effect between reaction temperature (C) and catalyst concentration (A) on FAME for CaO/SDA. The figure indicates that the yield of FAME increases with reaction temperature and catalyst concentration. This is as a result of a positive significant effect of catalyst concentration and temperature interaction, AC. However, at higher catalyst concentration and reaction temperature, a decrease in the yield can be observed due to evaporation of methanol at higher temperature and the fact that the quadratic terms of the two factors are more significant with a negative effect (Eq.(3)).

Fig. 6 shows the interaction effect between reaction time (D) and catalyst concentration (A) on FAME yield for CaO/SDA. This figure indicates that increase in reaction time and catalyst concentration increases the yield of FAME. However, at higher reaction time and catalyst concentration, reduction in the yield can be observed due to the fact that the interaction term and quadratic terms of the two factors are more significant with negative effects (Eq.(3)).

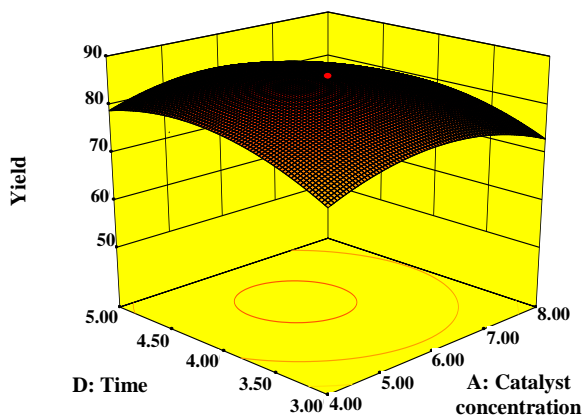


Fig. 6: 3D Plot showing the effect of time and catalyst concentration on the biodiesel yield using CaO/SDA..

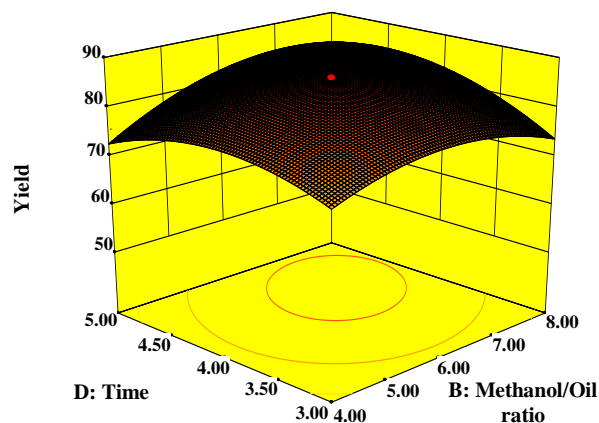


Fig. 8: 3D Plot showing the effect of time and methanol/oil ratio on the biodiesel yield using CaO/SDA.

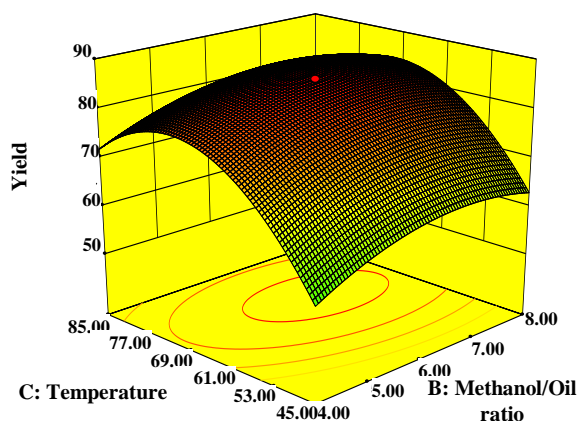


Fig. 7: 3D Plot showing the effect of temperature and methanol/oil ratio on the biodiesel yield using CaO/SDA.

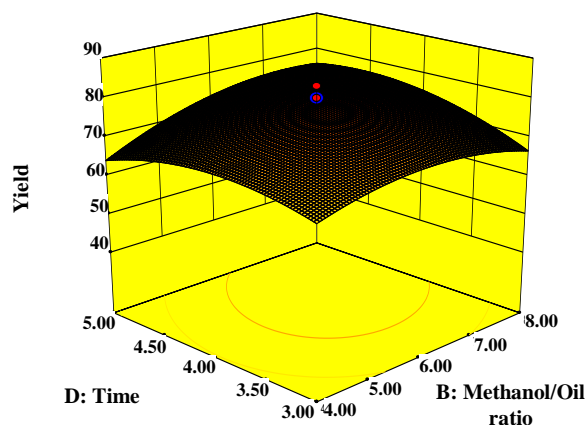


Fig. 9: 3D Plot showing the effect of methanol/oil ratio and time on the biodiesel yield using MgO/SDA..

Fig. 7 shows the interaction effect between reaction temperature (C) and methanol/oil ratio (B) on FAME yield for CaO/SDA. At lower temperature, below 65°C, the yield increase with methanol/oil molar ratio. However, at a temperature above 65°C, there was reduction in yield. This could be as a result of evaporation of methanol which inhibits the reaction on the three-phase interface.

Figs. 8 and 9 show the interaction effect between methanol/oil molar ratio (B) and reaction time (D) for CaO/SDA and MgO/SDA respectively. The figures indicate that the amount of FAME yields increase with methanol/oil molar ratio and reaction time. This is as a result of positive significant effect methanol/oil molar ratiion-reaction time interaction, BD on the response

(Fig. 8,12 and Eq. 3 and 4). At higher methanol/oil molar ratio and reaction time, a reduction in FAME yield can be observed due to the fact that the quadratic terms of the two factors are more significant with a negative effect (Eq.(3) and Eq.(4)).

Fig. 10 shows the interaction effect between methanol/oil molar ratio (B) and agitation speed (E) on FAME yield for CaO/SDA. The figure shows that the FAME yield increases with methanol/oil molar ratio and agitation speed as a result of a positive significant effect of methanol/oil molar ratiion-agitation speed interaction term, BE on response. However, at higher methanol/oil molar ratio and agitation speed a reduction in the yield can be observed due to the fact that the quadratic terms of the two factors are more significant with a negative effect (Eq.(3)).

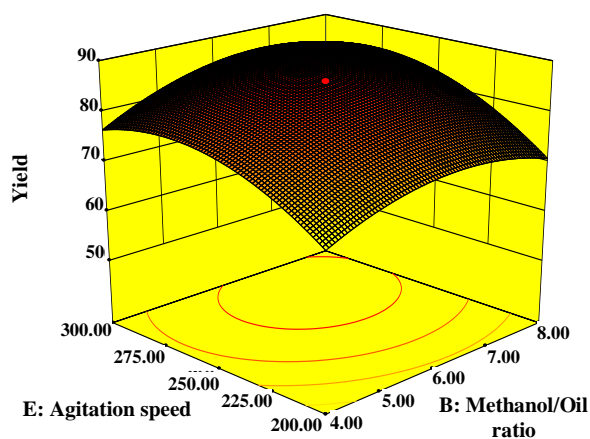


Fig. 10: 3D Plot showing the effect of Agitation speed and methanol/oil ratio on the biodiesel yield using CaO/SDA.

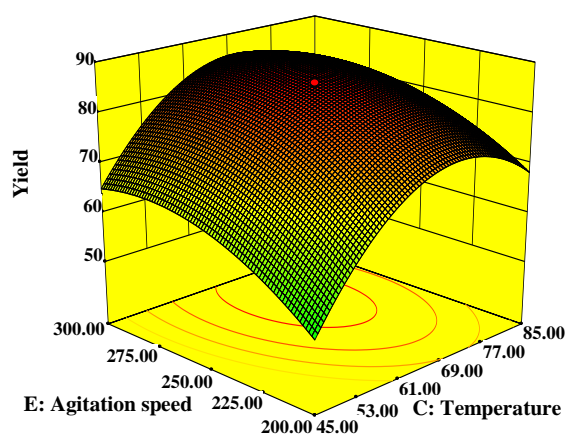


Fig. 11: 3D Plot showing the effect of temperature and Agitation speed on the biodiesel yield using CaO/SDA.

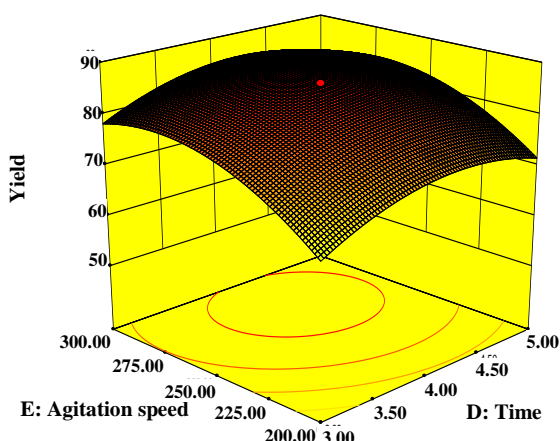


Fig. 12: 3D Plot showing the effect of Agitation speed and time on the biodiesel yield using CaO/SDA.

Fig. 11 shows the interaction effect between reaction temperature (C) and agitation speed (E) for CaO/SDA. The figure indicates that the yield of FAME increases with reaction temperature and agitation speed. However, at higher reaction temperature and agitation speed, there was a decreased in FAME yield because there is a negative significant effect of reaction temperature-agitation speed interaction term, (CE) on response (Eq. (3)).

Fig. 12 shows the interaction effect between reaction time (D) and agitation speed (E) for CaO/SDA. The figure indicates that the yield of FAME increases with reaction time and agitation speed. However, at higher reaction time and agitation speed, there was a reduction in FAME yield because reversible reaction of transesterification resulting in loss of esters. This is shown by the negative significant effect of reaction time-agitation speed interaction term, DE on the response (Eq.(3)).

#### Optimization process

The results in Table 4 and ANOVA in Tables 5 and 6 suggested that there is a great possibility of improving the yield of FAME from refined cottonseed oil by optimizing the variables studied. The optimization of variables in the study was carried out using the same software. The optimum conditions suggested by the software to produce maximum yield of FAME 90% (CaO/SDA) and 77% (MgO/SDA) within the ranges studied were: catalyst concentration 6% wt (CaO/SDA) and 8% wt (MgO/SDA), methanol/oil molar ratio 6:1 (CaO/SDA) and 8:1 (MgO/SDA), reaction temperature 65°C and reaction time 4h and agitation speed 250rpm. Actual experiment based on the optimum conditions produced 89% (CaO/SDA) and 76.3% (MgO/SDA) yield of FAME with small percent errors of 1.1% and 0.52% respectively. This percent errors of actual values compared to the predicted values indicate that the regression model developed in this study was accurate in representing the overall data and reliable in predicting the yield at any given conditions within the range studied.

#### CONCLUSIONS

This study has demonstrated the feasibility of converting refined cottonseed oil to FAME successfully using heterogeneous catalysts, CaO and MgO impregnated on saw dust ash. The investigations have

shown that reaction temperature gives the most significant effect on the yield followed by agitation speed whereas catalyst concentration gives insignificant effect for both catalysts. The variables were also shown to have significant interaction effect, particularly between catalyst concentration and methanol/oil molar ratio, catalyst concentration and agitation speed, methanol/oil molar ratio and reaction temperature, methanol/oil molar ratio and reaction time, methanol/oil molar ratio and agitation speed, reaction time and agitation speed for CaO/SDA transesterified reaction while for MgO/SDA transesterified reaction the significant interaction effect between variable is methanol/oil molar ratio and reaction time. The optimization of the process gave good optimum value for each process parameter for production of biodiesel using both catalysts with CaO/SDA having best performance.

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