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OPTIMIZATION OF BIODIESEL PRODUCTION USING CARBON BASED SULPHONATED CATALYST (CBSC)

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Abstract

In this study, carbon based sulphonated catalyst (CBSC) was developed from coconut shell biomass material by direct sulphonation method using concentrated sulphuric acid. The CBSC was characterized with Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Total acid density, energy dispersive X-ray Spectrometer (EDX) and Bruneuer-Emmet-Teller (BET) surface area. The catalytic activity of the catalyst was evaluated in esterification reactions using oleic acid and methanol. The optimum percentage conversion of 96.78% using coconut sulphonated catalyst (CSC), was obtained at a temperature of 45^{O}C, catalyst dosage of 1.75g and reaction time of 270min. The results obtained showed that the CSC from coconut shell biomass was active in catalyzing the esterification reaction process and this makes it a promising heterogeneous catalyst in biodiesel production.

Keywords: Carbon based sulphonated catalyst, coconut shell, oleic acid, esterification

Introduction

The emerging concept of green chemistry and utilization of green materials for chemical transformation, has gained significant attention, enabling several research groups to develop a catalyst, using inexpensive precursors such as biomass and waste materials [1]. Recent development of eco-friendly chemical processes has boosted the use of solid acid catalyst, due to its convenience in separation and recyclability [2]. Among the various renewable source based catalyst, the sulphonated carbons have attracted a great deal of attention from researchers in recent years [3, 4]. These carbon based sulphonated catalyst are versatile, diverse and a promising class of new solid acid catalyst. This catalyst are reported to be highly active in a range of acid catalyzed reactions, including the reactions associated with the production of biofuels [5-7, 3]. The carbon based sulphonated catalyst have lower production cost, compared to other solid acid catalyst such as a strong acidic cation – exchangeable resins [8, 9]. These carbon based solid acids are environmentally benign catalysts and have shown excellent efficiency in biodiesel production and other esterification reactions [10]. These catalysts are usually prepared by the sulphonation of an incompletely pyrolysed cheap carbon, obtained from sources such as sucrose [11], glucose [9, 11, 12].

RSM, also known as Box-Wilson methodology, is an optimization method, applying statistical techniques based upon the factorial designs of Central composite Design (CCD) and Box-Behnken Design (BBD). It is a set of mathematical technique that describes the relationship of several individual variables with one or more response [13]. RSM is able to evaluate the interaction of two or more variables to the response that allows better understanding of the process. Apart from that, RSM allows the determination of the best level of factors to optimize the desired output [14].

These carbon based sulphonated catalyst resembles sulphuric acid (H_2SO_4) in terms of its acidity and catalytic activity and also offer high operational stability (>240^{o}C and reusability) which makes them versatile acid catalyst for acid catalyzed reactions, included in biomass transformation [4, 15].

Biomass has a large potential to create a sustainable framework in biodiesel market. Catalysts derived from biomass have several advantages over conventional catalysts, as they are biodegradable, non-toxic and have higher surface area [11]. For biomass derived CBSC, the – SO_3H groups are considered as the key active acidic site [16], but the existence of the -OH and –COOH groups would provide the hydrophilic reactant an access to the –SO_3H groups, which will be in favour of the effective catalytic performance. The utilization of biomass as carbon material to prepare solid acid catalyst has become a cutting-edge technology in the production of the catalysts [17]. Coconut shell is abundantly available in Nigeria and comes from renewable resources [18, 19]. Besides, coconut shell is rich in carbon, low ash content, high in strength and hardness make it suitable for catalyst development [20].

In this study, coconut shell biomass material was used as the precursor carbon for solid acid catalyst development. Evaluation of the catalytic activity of carbon based sulphonated catalyst synthesized from coconut shell using Response Surface Methodology (RSM), have received little attention in solid acid catalyzed esterification reaction. Developing a catalyst from coconut biomass waste material will have an added advantage of value addition to the low cost coconut biomass material in carrying out esterification reaction involving biodiesel production.

Materials and Methods

Sample Collection and Reagents

The coconut shell used in this research for the preparation of carbon based sulphonated catalyst was purchased from Oba market, in Benin City. Edo State, Nigeria. All the chemicals used in this research were of analytical grade and supplied by Pyrex-IG chemicals.

Synthesis of Coconut CBSC (CSC)

The dried coconut biomass (coconut shell) was carbonized at a temperature of 400^{o}C in a muffle furnace, over a period of 4hr with continuous supply of nitrogen gas [20]. The carbonized coconut char was ground with a mortar and pestle and sieved with a mess size of 600µm to obtain biochar of uniform particle size. The biochar was mixed with concentrated sulphuric acid as a functionalizing agent in a mass ratio of 10:1 (acid : biochar) and was sulphonated at a temperature of 100^{o}C for 12hr under the inflow of nitrogen gas [21, 8]. The resultant coconut CBSC was washed repeatedly with hot distilled water and dried overnight in an oven at a temperature of 110^{o}C. The

coconut CBSC was then stored in a desiccators until it was further utilized.

Catalyst Characterization

The surface morphology of the catalyst was determined using SEM Model PHENOM PROX by Phenom-world Eindhoven, (The Netherland). In addition, the elemental compositions of the samples were carried out by using EDX (Energy Dispersive X-ray Spectrometer) coupled with the SEM. A BRUKER FTIR (USA) Spectrometer was used to identify the functional groups present in the structure of the catalyst. The surface analysis of the catalyst was determined, using the surface analyzer, Quantachrome, NOVA 4200e (USA). Surface area of the samples was obtained by the Bruneuer-Emmet-Teller (BET) methodology while pore size distribution and pore volume of catalyst were determined using Density Functional Theory (DFT) method. The thermogravimetric analysis (TGA) was carried out to study the weight loss profile and the thermal stability of the catalyst synthesized using the PERKIN ELMER 4000 (Netherland) thermal analyzer. The total acid density of the catalyst was determined by the back titration method, according to the method described by Benak *et al.* [21]. In this method, 0.5 g of catalyst was mixed with 100ml (excess) of 0.1M aqueous NaOH solution in a beaker. The mixture was agitated for a period of 4hr to ensure the solution attains equilibrium. The mixture was filtered to recover the filtrate and the filtrate was back titrated with a standard 0.1M HCl, using phenolphthalein as indicator. The $_{p}$H of the catalyst was determine by immersing 2.0g of the catalyst in 20ml distilled water and stirred for 15min. The bulk density of the catalyst was determined by the method described by Ahmedna *et al.* [23]. In this method, a weighed amount of the catalyst was measured into a 10ml graduated cylinder. The cylinder was tapped constantly, until there was no significant change in volume.

Esterification Reaction

The esterification process between the oleic acid and methanol was carried out in a three-necked round bottom flask of 250ml capacity, operating in a batch mode. A temperature controlled magnetic stirrer was used to carry out the reaction process at a temperature range of 30 – 60^0C, and a stirring speed of 500rpm, in which a reflux condenser was used to avoid the loss of volatile compounds. During all experiments, a known amount of oleic acid and methanol in a molar ratio of 1:10 and catalyst was charged into the reactor and heated to a desired temperature, where the temperature of the reaction mixture was controlled within the range of $\pm 1.0^0$C.

After completion of the reaction, the reaction mass was withdrawn and filtered through a Whatman filter paper to recover the catalyst. Then the liquid phase was subjected to evaporation for 20min in a rotary evaporator, to eliminate methanol and water that might be present in the biodiesel. Furthermore, the final product was analyzed for acid value of unconverted fatty acid.

The fatty acid conversion was determined by titrimetric method, based on the differences in the initial acid value of the feedstock (oleic acid) and the final acid value of the product (fatty acid methyl ester) according to the AOCS 5a-40 standard method. The fatty acid conversion was determined according to equation 1.

$$\left[FFA\ Conversion\,(\%) = \frac{AVi - AVf}{AVi} \times \frac{100\%}{1} \right] \qquad (1)$$

Where AV_i is the initial acid value and AV_f is the final acid value of the product after the fatty acid esterification process.

Experimental Design of Oleic Acid Esterification Reactions

A three-variable-five-levels central composite design of response surface methodology, was employed for the design of the esterification reaction. A total of 20 experimental trials that included 8 trials for factorial design, 6 trials for axial points (two for each variable) and 6 trials for replication of the central points were performed, using the experimental designed generated by the Design Expert software (Version 11.1.2.0, Stat-ease, Minneapolis, USA). The esterification process variables considered and their range of values (with α levels design) are given in Table 1**.** Biodiesel conversion from oleic acid in percentage (Y), was taken as the dependent variable (response) for CSC catalyzed esterification reactions.

Table 1: Range of Values for Esterification Experimental Design

Independent variable (unit)	Symbol	Level				
		$-\alpha$	-1	0	$+1$	$+\alpha$
Temperature (℃)	A	30	36.08	45	53.92	60
Catalyst dosage (g)	B	0.5	1.01	1.75	2.49	3
Reaction time (mins)	C	60	145.13	270	394.87	480

Statistical Analysis

The experimental data was analyzed according to the response surface regression procedure, to fit the second-order polynomial equation in which the level of significance (p-value) of all coefficients was ≤ 0.05. Regression analysis was carried out to predict the process response, as a function of independent variables and their interactions were used to understand the system behaviour. The coded values of the process parameters were determined by equation 2.

$$i = \frac{X_i - X_0}{\Delta X} \qquad (2)$$

where x_i = coded value of the ith variable, X_i – uncoded value of the ith test variable and X_o = uncoded value of the ith test variable at centre point. The mathematical relationship between the process variables and response was calculated by the quadratic polynomial expression (equation 3).

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} \beta_{ij} x_i x_j \qquad (3)$$

where *Y* is the response, i.e. the fatty acid conversion (%), X_i and X_j represent the independent variables, β_0 is constant, β_i is linear term coefficient, β_{ii} is the quadratic term coefficient, β_{ij} is cross-term coefficient and '*n*' is the number of process variables studied and optimized during the study. ANOVA was carried out to estimate the effects of process variables and their possible interaction effects on the maximum percentage conversion of oleic acid to biodiesel in the response surface regression procedure.

Optimization studies of Esterification Reaction

A numerical optimization technique using desirability functions was employed in optimizing the response (percentage conversion of oleic acid to biodiesel). The

objective of the optimization was to find the best settings that maximize the percentage conversion of oleic acid from the esterification process reactions using a desirability value, where $0 \leq d \leq 1$. The value of d increases as the desirability of the corresponding response increases. The variable settings with maximum desirability (close to unity) are considered to be the optimal parameters/conditions.

Results and Discussion

Catalyst Characterization

The SEM images of the coconut biochar and CSC are presented in Figs. 1 and 2. The coconut biochar showed a relatively rough surface with rough edges and exhibited an irregular shape with a developed porous structure. The SEM micrograph of the CSC in Fig. 2 indicates a decrease in porosity. This can be attributed to occasional small cracks, partial oxidation, condensation and partial destruction of the porous structure, brought about by the strong sulphonating agent after the biochar functionalization process [24, 25].

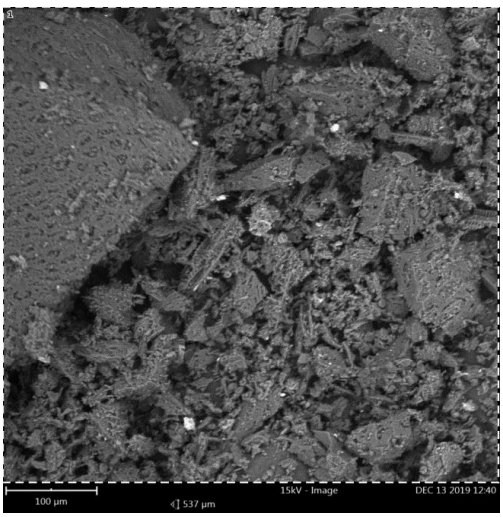


Fig. 1: Surface Morphology of Coconut Biochar

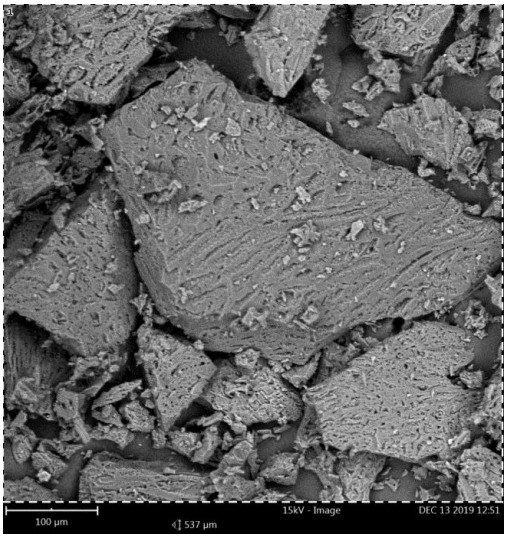


Fig. 2: Surface Morphology of CSC

Tables 2 and 3 presented EDX analysis of coconut biochar and CSC respectively, the percentage of carbon is high due to the carbonization of the coconut biomass. There was a slight reduction in the carbon content (77.49 to 70.10%) with an increase in the oxygen (0.98 to 1.41%) which is attributed to the incorporation of the SO_3H group. After sulphonation, the CSC has a sulphur content of 17.33%.

Table 2: EDX Analysis of Coconut Biochar

Element Symbol	Element Name	Weight Conc.
C	Carbon	77.49
K	Potassium	7.59
Ca	Calcium	2.45
P	Phosphorus	2.23
H	Hydrogen	2.14
S	Sulfur	2.13
Si	Silicon	1.81
Cl	Chlorine	1.28
Al	Aluminium	1.11
O	Oxygen	0.98
Mg	Magnesium	0.46
Na	Sodium	0.33

The FTIR spectra of CSC is presented in Fig. 3. The band at 1024.79 cm^{-1} is the characteristic absorption band of sulphonic (SO_3H) group. The absorption band peak is attributable to O=S=O stretching vibrations. This is similar to the band of 1026cm^{-1} reported by Dawodu *et al.* [26] and Hara [27]. The band peak at 1693.18 cm^{-1} is attributed to C=O stretching mode of –

Table 3: EDX Analysis of CSC

Element Symbol	Element Name	Weight Conc.
C	Carbon	70.10
S	Sulfur	17.33
H	Hydrogen	4.48
O	Oxygen	1.41
Cl	Chlorine	1.37
Ca	Calcium	1.23
Si	Silicon	1.00
P	Phosphorus	0.91
K	Potassium	0.87
Al	Aluminium	0.82
Mg	Magnesium	0.27
Na	Sodium	0.20

COOH group. The aromatic ring of the biochar was also retained after sulphonation which is indicated by the band at 1581.02cm^{-1}. The band is attributed to C=C stretching due to cyclic alkene [28, 29].

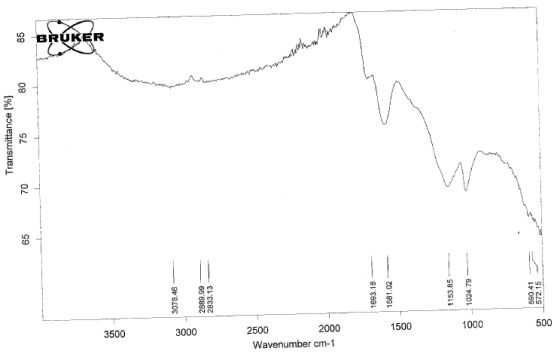


Fig. 3: FTIR Spectra of CSC

The FTIR spectra of coconut biochar is presented in Fig. 4. The band at 1587.371cm^{-1} shows the presence of aromatic ring stretch. Hence the existence of one or more aromatic rings due to the carbonization of the coconut shell. This is consistent with what was reported by Da Luz Correaa *et al.* [28] of a typical bands of a carbonized material from a lignocellulose raw material. The weak broad peak at 2874.28cm^{-1} is attributed to OH stretching vibration.

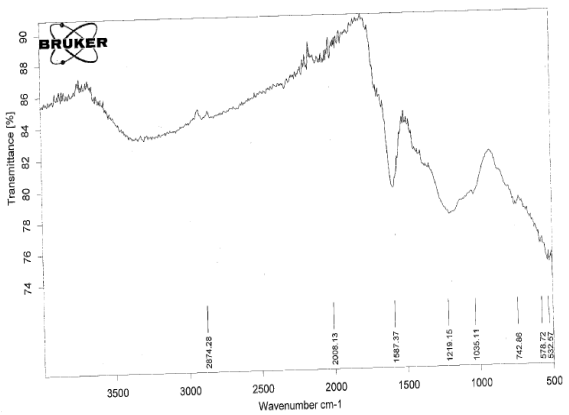


Fig. 4: FTIR Spectra of Coconut Biochar

Thermal Stability

The thermal stability of CSC occurred in three degradation stages as observed in the TG curves presented in Fig. 5. The first degradation step occurred between 28 - 280^oC, which is attributed to the loss of water molecules and sulphonic groups [30]. The second degradation step occurred between 280 - 480^oC which is likely due to the loss of cellulose, hemicellulose and lignin degradation [31]. The third degradation step occurred above 480^oC and this is attributed to the decomposition of the carbon structure [32].

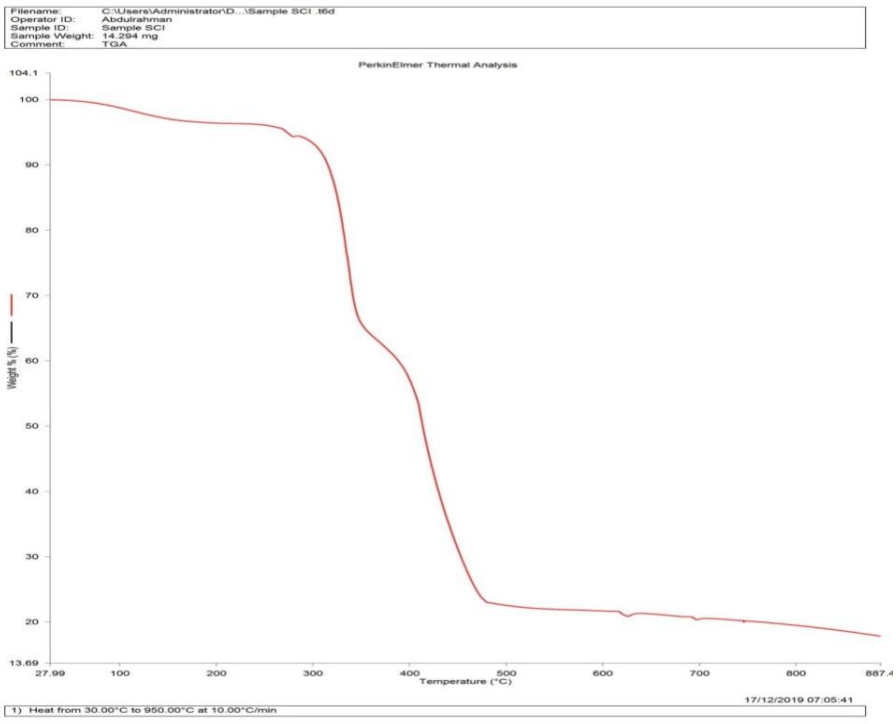


Fig. 5: TGA Curve of CSC

The synthesized CSC was found to exhibit a total acid density of 4.5mmol/g with a BET surface area of 636.30m^2/g and a pore size and pore volume of 2.647nm and 0.2599cc/g respectively. In addition, the CSC was also found to be mesoporous (2 – 50nm) in nature. According to IUPAC classification, mesoporous materials are useful in reactions involving heavy molecules like triglycerides (5.8nm), glycerin (0.6nm) and methyl- oleate. [33]. The CSC has a bulk density of 0.78g/ml. The bulk density is useful in determining the packing volume and it is influenced by the size, shape and particle density of the individual particles.

Esterification of Oleic Acid

Table 4 gives the combination of the values of the esterification process variables considered and the percentage conversion of the oleic acid to biodiesel using the CSC heterogeneous catalysts.

Table 4 shows the percentage conversion of oleic acid to biodiesel for CSC ranges from 13.00 - 96.78% for the esterification. The observed maximum value of the percentage conversion of oleic acid of 96.78% for CSC esterification reaction of oleic acid was obtained at temperature of 45℃ (0), catalyst dosage of 1.75 g (0) and reaction time of 270 mins (0) while the minimum value of 13.00% was obtained at a temperature of 36.08℃ (-1), catalyst dosage of 1.01 g (-1) and reaction time of 145.13 mins (-1). This is an indication that increases in temperature, catalyst dosage and reaction time lead to an increase in the percentage conversion of oleic acid to biodiesel for CSC and esterification reactions.

Table 4: Experimental Design Matrix with Responses

Run	Coded variables			Actual variables			CSC	
	A	B	C	Temp. (℃)	Catalyst dosage (g)	Reaction time (min)	Actual	Predicted
1	0	0	0	45	1.75	270	93.01	90.97
2	-1	1	-1	36.08	2.49	145.13	94.11	92.58
3	0	0	0	45	1.75	270	84.00	90.97
4	-1	-1	-1	36.08	1.01	145.13	13.00	2.98
5	1	-1	1	53.92	1.01	394.87	92.00	91.88
6	1	1	-1	53.92	2.49	145.13	72.62	65.70
7	0	0	-1.68	45	1.75	60	35.40	41.06
8	0	0	0	45	1.75	270	96.78	90.97
9	-1	-1	1	36.08	1.01	394.87	20.00	25.27
10	0	0	0	45	1.75	270	87.44	90.97
11	0	0	0	45	1.75	270	89.20	90.97
12	0	0	1.68	45	1.75	480	91.00	87.67
13	1	-1	-1	53.92	1.01	145.13	20.00	27.61
14	0	-1.68	0	45	0.5	270	20.00	17.57
15	-1	1	1	36.08	2.49	394.87	93.00	83.74
16	1	1	1	53.92	2.49	394.87	90.48	98.85
17	0	1.68	0	45	3	270	94.00	98.76
18	0	0	0	45	1.75	270	95.77	90.97
19	-1.68	0	0	30	1.75	270	40.67	49.12
20	1.68	0	0	60	1.75	270	88.65	82.53

Actual vs. Predicted Plot

Fig. 6 shows the predicted vs. actual plots of oleic acid conversion to biodiesel from the esterification reactions using CSC as catalysts.

The closeness of all values to the regression line indicate that experimental values are in reasonable agreement with the predicted values i.e. there is strong positive correlation between the actual and predicted values of percentage conversion for CSC catalyzed esterification reactions (Fig. 6). The model summary statistics of the biodiesel preparation from the esterification reactions of oleic acid CSC catalyzed reactions is given in Table 5.

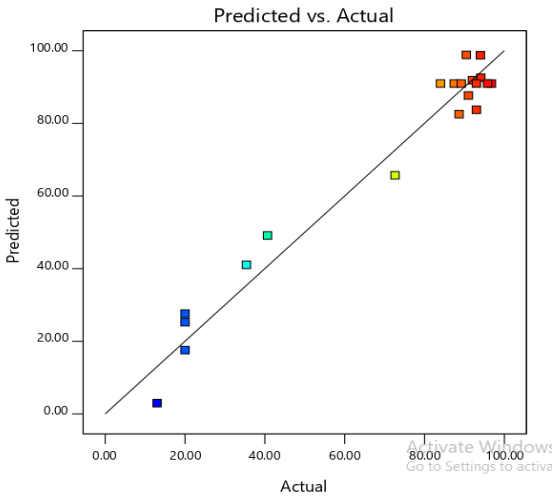


Fig. 6: Predicted vs. Actual Plot of Oleic Acid Conversion to Biodiesel by CSC.

Table 5: Model Summary Statistics for CSC Biodiesel Production

Source	Std. dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	20.97	0.6290	0.5594	0.4135	11122.35	
2FI	18.28	0.7709	0.6652	0.3654	12035.67	
Quadratic	**8.35**	**0.9632**	**0.9301**	**0.7392**	**4945.79**	**Suggested**
Cubic	4.81	0.9927	0.9768	0.8321	3183.43	Aliased

The R^2 value provides a measure of how variability in the observed response values could be explained by the experimental factors and their interactions [34]. The close correlation observed in Fig. 6 can be described by the closeness (the difference is less than 0.2 in all cases) of the adjusted and predicted R^2 values of 0.9301 and 0.7392 for CSC catalyzed esterification. In addition, higher R^2 values were observed in the cubic model than other models. For response surface analysis, the cubic model is assumed to be aliased and hence cannot be used to describe a process. The quadratic model gave better R^2 values than the 2FI (two factor interaction) and linear sources of model, making the quadratic model the best model to describes the esterification reactions by the (CSC) heterogeneous catalysts.

Analysis of variance

Table 6 gives the analysis of variance of oleic acid esterification process reaction to biodiesel, and the significance of the process variables considered on the percentage conversion of oleic acid to biodiesel using the CSC. The ANOVA was done based at a significant level of 5% i.e. the probability value of 0.05 ($\alpha = 0.05$). P-values less than 0.05 indicate model terms/factors are significant i.e. change in the factors leads to a corresponding change in the response at a significant level of 5%. From Tables 6, high model F-values of 29.09 and very low corresponding p-values of <0.0001 indicate that the model terms are highly significant for CSC catalyzed oleic acid esterification reactions. The p-values of main factors (A, B and C), interaction factors (AB, AC and BC) and quadratic factors (A^2, B^2 and C^2) were also found to be less than 0.05 for the CSC esterification reactions indicating that all the factors have a high significant effects on the percentage conversion of oleic acid to biodiesel employing the (CSC) heterogeneous catalyst. The lack of fit p-values were also found to be higher than 0.05 which indicate insignificant lack of fit for the esterification reactions by the CSC which is desirable.

Table 6: Analysis of Variance of Oleic Acid Conversion to Biodiesel by CSC

Source	Sum of squares	df	Mean square	F-value	p-value
Model	18267.44	9	2029.72	29.09	< 0.0001*
A – Temperature	1348.02	1	1348.02	19.32	0.0013*
B – Catalyst dosage	7957.72	1	7957.72	114.06	< 0.0001*
C – Reaction time	2622.75	1	2622.75	37.59	0.0001*
AB	1326.38	1	1326.38	19.01	0.0014*
AC	881.37	1	881.37	12.63	0.0052*
BC	484.38	1	484.38	6.94	0.0250*
A^2	1138.57	1	1138.57	16.32	0.0024*
B^2	1938.09	1	1938.09	27.78	0.0004*
C^2	1274.66	1	1274.66	18.27	0.0016*
Residual	697.70	10	69.77		
Lack of fit	572.59	5	114.52	4.58	0.0603
Pure error	125.11	5	25.02		
Cor. total	18965.14	19			

**=significant*

Model Deduction

The empirical relationships between the esterification process variables considered and the percentage conversion of oleic acid

to biodiesel is given by equation 4 for CSC catalyzed reactions in the coded form.

$$Y_{CSC} = 90.97 + 9.94A + 24.14B + 13.86C - 12.88AB + 10.50AC - 7.78BC - 8.89A^2 - 11.60B^2 - 12.68C^2 \quad (4)$$

In a regression equation, when an independent variable has a positive sign, it means that an increase in the variable will cause an increase in the response while a negative sign will result in a decrease in the response [35, 36]. Equation 4 gives the relationship between the variables of CSC catalyzed esterification reactions. From the equations, all main factors; A, B and C (temperature, catalyst dosage and reaction time) have positive effects on the percentage conversion of oleic acid to biodiesel. That is, increase or decrease in the values of these factors will lead to a corresponding increase or decrease in the values of the percentage conversion of the esterification of oleic acid to biodiesel while the other factors; interaction factors (AB, AC and BC) and quadratic factors (A^2, B^2 and C^2) have negative effects on the percentage conversion of oleic acid to biodiesel. Therefore, increase or decrease in the values of these factors will lead to decrease or increase in the percentage conversion of oleic acid to biodiesel. The models (equation 4) can further be described using the fit statistics given in Table 7 for CSC catalyzed esterification processes.

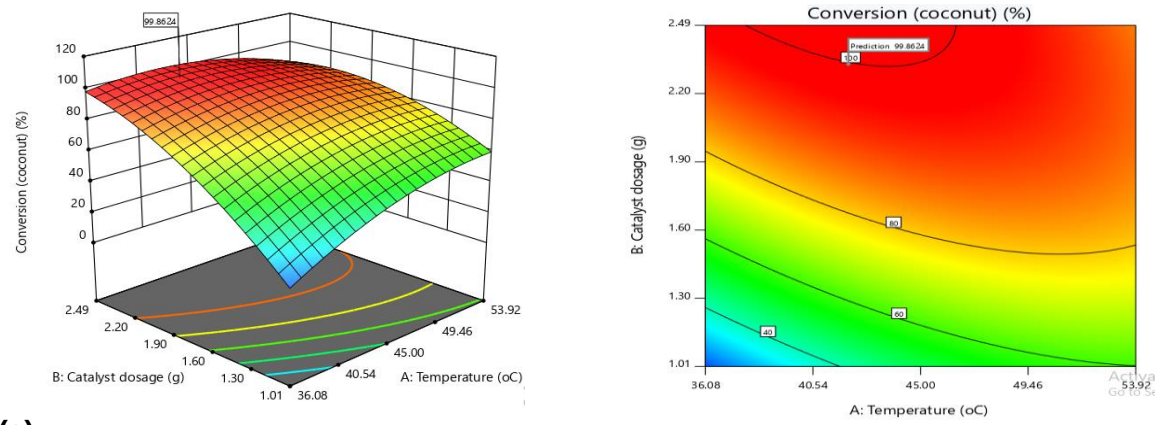
The coefficient of variation (C.V) of 11.84 CSC esterification reactions are within the acceptable range, since CV is a measure of expressing standard deviation as a percentage of the mean; smaller values of CV gives better reproducibility. In general, a high CV indicates that variation in the mean value is high and does not satisfactorily develop an adequate response model [37].The coefficient of regression R^2 was used to validate the fitness of the model equation. Table 7 gives high R^2 value of 0.9632 for CSC esterification reactions indicating that about 96% of the variability in the percentage conversion of oleic acid to biodiesel by the variables considered can be explained by the models. There is also a reasonable agreement between the adjusted R^2 and predicted R^2 values, which shows that the model, equation 1 reasonably predicted the oleic acid esterification reactions by the (CSC) heterogeneous catalysts using quadratic polynomials. Adequate precision measures the signal to noise ratio and a ratio greater than 4 is desirable [36]. The ratio of 16.2308 observed gives adequate signals which imply that the models can be used to navigate the design space.

Table 7: Fit Statistics of Esterification reactions of Heterogeneous Catalysts

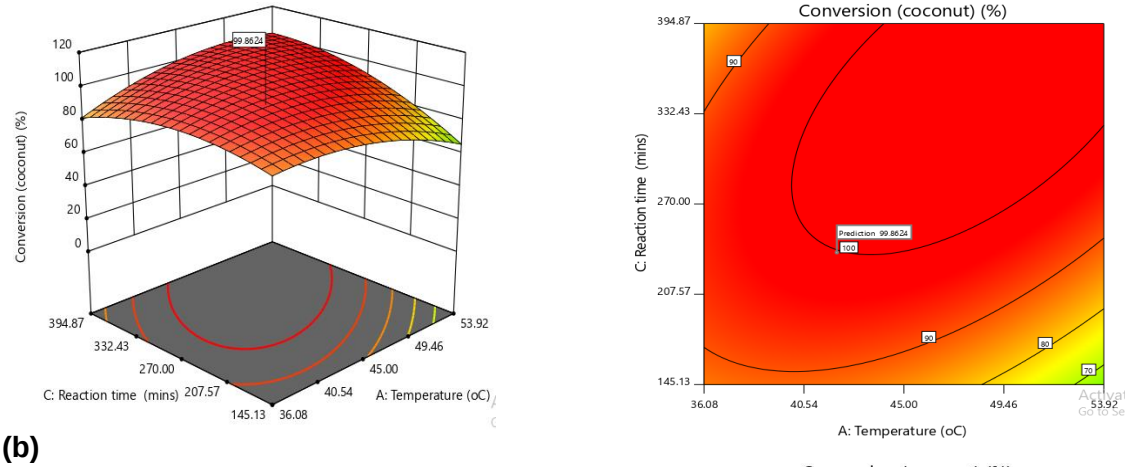
Parameters	CSC
Standard deviation (%)	8.35
Mean (%)	70.56
Coefficient of variation, C.V (%)	11.84
R^2	0.9632
Adjusted R^2	0.9301
Predicted R^2	0.7392
Adequate precision	16.2308

Effect of Interaction of Process Variables on Biodiesel Conversion

The effects of interaction of esterification process variables on the percentage conversion of oleic acid to biodiesel by CSC is presented in Fig. 7(a-c).



(a)



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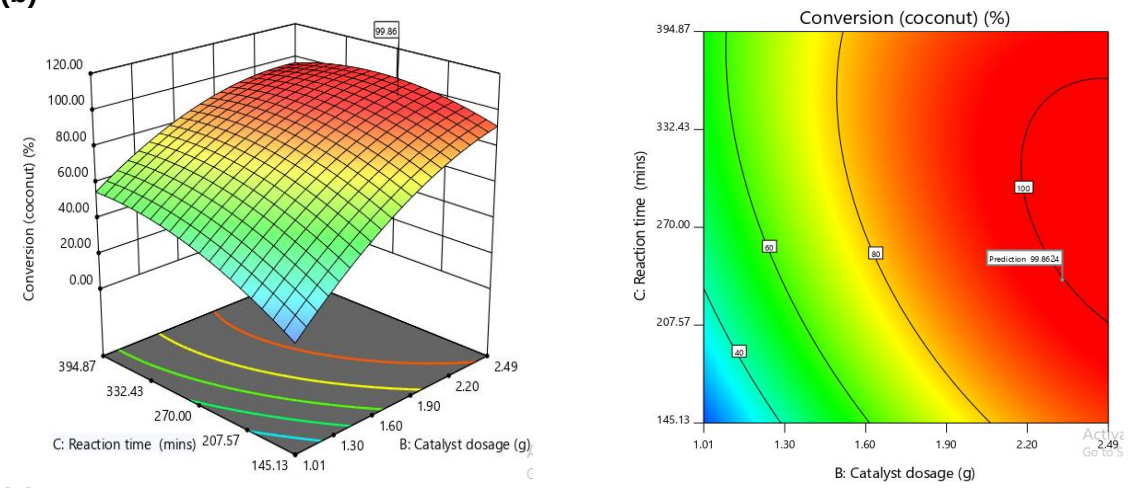

(c)

Fig. 8: Effect of Interaction of Variables on Biodiesel Conversion with CSC (a) Temperature and Catalyst Dosage (b) Temperature and Reaction Time and (c) Catalyst

Dosage and Reaction Time

The effects of interaction of variables on the percentage conversion of oleic acid to biodiesel by coconut shell derived catalyst (CSC) are shown in Fig. 8(a-c). Fig. 8(a) shows the effect of interaction of temperature and catalyst dosage (AB) on the percentage conversion of oleic acid to biodiesel by CSC. From the plot, at constant catalyst dosage, increase in temperature will lead to a corresponding increase in the percentage conversion of oleic acid to biodiesel by CSC and vice versa. Catalyst dosage had a more dominant effect than the temperature in the esterification reaction. The concurrent increase in the temperature and catalyst dosage (AB) at constant reaction time leads to decrease in the percentage conversion of oleic acid to biodiesel. Fig. 8(b) shows the effect of temperature and reaction time (AC) on the percentage conversion of oleic acid to biodiesel by CSC. In the same vein, at constant temperature, increase in reaction time lead to increase in the percentage conversion of oleic acid to biodiesel and vice versa.. Temperature had a more dominant effect than reaction time on percentage conversion of oleic acid to biodiesel. The concurrent increase in temperature and reaction time lead to increase in the percentage conversion of oleic acid to biodiesel at constant catalyst dosage. Fig. 8 (c) shows the effect of interaction of catalyst dosage and reaction time on the percentage conversion of oleic acid to biodiesel by CSC and this follows the same trend as in Fig. 8a and b.

Optimization studies

A numerical optimization technique using desirability functions was employed in optimizing the response (percentage conversion of oleic acid to biodiesel). The objective of the optimization was to find the best settings that maximize the percentage conversion of oleic acid to biodiesel from the esterification process reactions using a desirability value; $0 \leq d \leq 1$. The value of d increases as the desirability of the corresponding response increases. The variable settings with maximum desirability are considered to be the optimal parameter conditions. The maximum desirability of 1.00 for all the CSC catalyst considered for the esterification of oleic acid means that it is possible to reach maximum percentage conversion. The maximum percentage conversion of oleic acid to biodiesel (99.86%) for CSC catalyzed esterification reactions was obtained at temperature, catalyst dosage and reaction time of 42.01℃, 2.32 g and 236.52 min.

Conclusion

The CBSC (CSC) prepared from coconut biomass material was effective in evaluating the catalytic properties in esterification reaction using Response Surface Methodology. The optimum percentage conversion obtain for CSC from the esterification reaction process was 96.78%. The BET surface area and acid density was found to be 636.30m^2/g and 4.5mmol/g. The FT-IR results shows that the sulphonation process of the coconut biochar was successful and the sulphonic (-SO_3H) group was grafted onto the structure of the coconut biochar. The CSC has shown it is a promising class of heterogeneous catalyst in esterification reactions with respect to biodiesel production.

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