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**OPTIMIZATION OF BIODIESEL FROM ORANGE PEEL USING CALCIUM  
OXIDE CATALYST FROM LIMESTONE VIA *IN-SITU*  
TRANSESTERIFICATION**

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**ABSTRACT**

*Biodiesel is an environmentally friendly alternative fuel to petro-diesel. In-situ transesterification method is an easy method for biodiesel production where the oil was simultaneously extracted and transesterified into biodiesel in one single process. This study was carried out to study the optimization of Biodiesel synthesis from orange peel using Calcium Oxide from Limestone Methanol used was used as the alcohol in the process as it is widely accessible and economically viable. Reaction temperature, catalyst loading, time, and methanol to orange peel ratio were varied from 50 to 120°C, 0.5 to 5 wt %, 40 to 60 minutes, and 3:1 to 12:1 respectively. The process parameters considered for the optimization study of the in-situ transesterification reaction resulted in an optimum biodiesel yield of 70% which was observed at the condition of 85°C, 2.75 wt % catalyst, 100 minutes and 16.5:1 methanol to orange peel ratio. It was observed that a close correlation exists between the experimental and predicted results as confirmed by the validation experiment and the square of the correlation coefficient ( $R^2$ ) for the in-situ transesterification reaction was estimated to be 0.9124.*

**Keywords:** *Biodiesel, Calcium oxide, In-situ Transesterification, Orange peel.*

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## INTRODUCTION

The world today is facing a rise in energy crisis due to increase in population, depletion of fossil fuel, emission of greenhouse gases, and fluctuation in oil prices, and as such led to the search for alternative source of energy (Vlontzos & Pardalo, 2017).

Bio-fuel is considered a suitable alternative source of energy because it is environmentally friendly, more economical, biodegradable, and can be converted from common and abundant biomass sources which contributes to sustainability and the reduction of fossil fuel consumption (Robert, 2013).

Biodiesel is non-toxic, biodegradable, produced from renewable sources, and contributes a negligible amount of net greenhouse gases, such as CO<sub>2</sub> and NO<sub>2</sub> (Tasyurek *et al.*, 2010). It is a combination of mono alkyl esters (C<sub>14</sub> – C<sub>22</sub>) that can be derived from renewable lipid feedstock majorly plant, plant oil, and animal fat (Feddern, *et al.*, 2011).

The advantages of biodiesel compared to petro-diesel include the fact that it has no aromatics; it has higher cetane number, and flash point. Vital issues to be considered in the production of biodiesel include source of oil (animal or plant), type of oil (edible or inedible oil), cost of production, feasible pretreatment and production method (Abdulrahman, *et al.*, 2016). Emphasis is currently placed on using non-edible feed stocks as the demand for these feed stocks is not affected by nutritional needs. The use of orange peel as an example of inedible source of biodiesel feedstock has been considered (Akpan *et al.*, 2014).

There are several methods for the production and application of biodiesel such as direct use of vegetable oils, micro emulsions, thermal cracking (pyrolysis) and transesterification (Lourdes *et al.*, 2016). According to Leung, *et al.*, (2010), transesterification reaction is one of the most successful processes of converting lipid feed stocks into biodiesel.

Typically, transesterification involves the reaction of triglycerides with alcohol in the presence of a suitable catalyst to produce a mixture of biodiesel and glycerol (Poonam & Anoop, 2010). The stoichiometric reaction requires 1 mole of triglycerides and 3 moles of alcohol; it consists of three reversible steps of reaction which yields one methyl ester

molecule from each glyceride at each step. However, excess alcohol is required to drive the reaction close to completion (Borges & Diaz, 2012). A remarkable alternative approach is the *in situ* transesterification without going through a tedious extraction step. Therefore, it would be less stressful to extract and convert the triglycerides from the orange peel into biodiesel in a single step, avoiding the use of large amounts of organic solvents (Chattip *et al.*, 2012).

Primary alcohols such as methanol are widely used for *in situ* transesterification process because they favor rapid and complete reaction (Musa, 2016).

A good catalyst for biodiesel production must be characterized by a high surface area, thermally stability, low deactivation rate, low temperature activation, and high selectivity (Rafaat, *et al.*, 2010). On these bases, the three main classifications of catalyst used in transesterification are acid catalysts, base catalysts and biocatalysts (Tshizanga, 2017; Pathak, 2015). Depending on the phase in which they exists, these catalysts can also be classified as either homogeneous or heterogeneous. The use of heterogeneous catalysts have become more popular in the production of biodiesel because they are insensitive to high FFA, can be removed easily from reaction mixture, are reusable, and readily available (Shu, *et al.*, 2010).

Conversely, heterogeneous catalysts could be acidic or basic. Tshizanga, (2017) reported that heterogeneous basic catalysts have faster reaction rate and higher product yield compared to heterogeneous acid catalyst,

## METHODOLOGY

The major feedstock used in this research work was orange peel, which was obtained from an orange seller in Jebbu Market in Bassa, plateau State. Calcium oxide catalyst from limestone was obtained from Obajana in Kogi State.

### Catalyst Preparation

The calcium oxide catalyst was prepared from raw limestone which was gotten from Obajana in Kogi State. The limestone was crushed and its

Thermo-gravimetric Analysis (TGA) of the limestone sample was carried out. The calcium oxide catalyst was prepared at a temperature 850 ° C while Brunnauer, Emmitt and Teller (BET) analysis was done to determine the surface area, pore size and pore volume of the sample.

### **Catalyst characterization**

The chemical, physical and morphological properties of calcium oxide catalyst was evaluated using Scanning Electronic Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD)

### **Scanning Electron Microscope (SEM) Analysis**

The physical surface morphology of the catalyst sample gotten was tested using LEO S-440 Scanning Electron Microscope. A thin layer of calcium oxide catalyst sample was attached on an aluminum holder by a double-sided tape. The catalyst sample was covered with gold with a thickness of 1.5 to 3 nm in order to avoid poor image resolution and discharge of electrostatics. The experiment was carried out at different magnifications and data generated was recorded.

### **Fourier Transform Infra-Red (FT-IR) Spectroscopy**

The infra-red spectrometer analysis of the catalyst was done using Bruker Alpha II infra-red spectrometer. In conducting the experiment, the spectrometer was powered and allowed to warm up for 5 minutes. For a reliable analysis, the spectrometer sample press tip and the diamond sampling window were cleaned and made clear of any residue from previous sample which was confirmed by the system software. The sample was then placed on the cleaned crystal window and the overhead press tip adjusted until it exerted the desired pressure on the introduced sample. Transmission spectra of composite films were recorded at ambient temperature. Sample was scanned from 4000 to 400  $\text{cm}^{-1}$  with resolution of 0.4  $\text{cm}^{-1}$ .

### **X-ray Diffraction (XRD) Spectrometry**

First, 2 g sample of size 100  $\mu\text{m}$  was pressed in stainless steel holder and then identification of the crystalline phase was conducted by X-ray

diffractor (X'Pert MPD – PAN analytical X-ray B.V.) using Cu-K $\alpha$  radiation operated at 45 kV, 35 mA in which the incidence angle spanned from 5° to 85°2 $\theta$  at 0.02°2 $\theta$  step size with a scan speed of 0.5 s/step. This method was used to obtain a high-quality diffraction data of the sample.

### **X-ray Fluorescence (XRF) Spectrometry**

X-rays fluorescent (XRF) analysis was conducted using PANanalytical XRF spectrometer (MiniPal 4). X-RF analysis was carried out by placing 2 g of 100  $\mu$ m size of the sample on a clean stainless steel lid which was placed in the cubicle of the spectrometer to determine its elemental composition. When the sample was irradiated by X-rays, the system software measures the individual component wavelengths of the fluorescent emission produced by atoms in the sample and compares to standard wavelengths of atoms of known elements.

### **Feedstock preparation**

The orange peel obtained was air dried for a week. The dried orange peel was then crushed into powder form, and filtered in order to obtain fine and uniform size. With the use of a soxhlet extractor, oil was extracted from the powdered orange peels using methanol as solvent. The crude orange peel oil was separated from the methanol by allowing the oil mixture to stand under a fan for the methanol to volatilize to a constant weight of the oil. The oil was then dried in a hot air oven at 60 °C for 1 hr. The fine powder was used as feedstock for biodiesel production.

### **Feedstock characterization**

The orange peel oil was characterized for color, odor, fatty acid content, viscosity, and saponification value to determine its physical and chemical properties. The physical properties determined for the orange peel oil include density, specific gravity, kinematic viscosity, cloud point, and flash point while the chemical properties tested for include pH value, acid value/free fatty acid (FFA), saponification value, ester value, iodine number, and peroxide value. All tests were carried out using ASTM standard.

## IN-SITU TRANSESTERIFICATION OF ORANGE PEEL

*In situ* transesterification experiment was conducted for production of biodiesel using orange peel powder, methanol as alcohol and calcium oxide as heterogeneous catalyst.

### Design of experiment

Response surface methodology (RSM) with five-level-four-factor central composite design (CCD) was applied to optimize the *in-situ* transesterification of orange peel into biodiesel DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA) software was used.

The process parameters considered in the *in-situ* transesterification phase include methanol to oil ratio, catalyst amount, reaction time, and reaction temperature. Table 1 shows the range of independent factors (process parameters) considered in this study.

TABLE 1: INDEPENDENT FACTORS USED FOR CCD IN *IN-SITU* TRANSESTERIFICATION OF ORANGE PEEL

<i>Variables</i>	Low	High
<i>Methanol to orange peel (w/v)</i>	3:1	12:1
<i>Catalyst Loading (% vol)</i>	0.5	5
<i>Reaction Temperature (° C)</i>	50	120
<i>Reaction Time (minutes)</i>	40	160

### Characterization of produced biodiesel

The synthesized biodiesel was characterized and its properties were compared against the ASTM D6751.

## RESULTS AND DISCUSSION

This section presents a comprehensive view of the results obtained from the experimental study. It also contains statistical analysis of the results as well as evaluation of the effect of selected process factors on solid catalyzed *in-situ* transesterification of orange peel to produce biodiesel.

## Catalyst Characterization

### Thermo-gravimetric analysis (TGA)

The TGA analysis of the raw limestone sample was carried out and presented in Figure 1

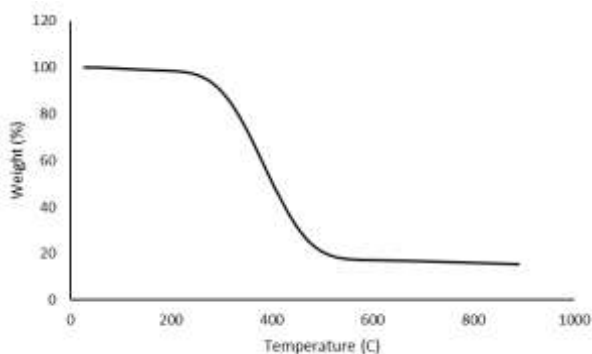


Figure 1: TGA curve for the Limestone sample

From the TGA plot in Figure 1 it was observed that calcium oxide catalyst would be obtained at temperatures exceeding 600 °C at which temperature all the moisture and volatile components in the limestone would have evolved leaving behind the calcium oxide catalyst (CaO). The limestone sample was calcined at a temperature of 850 °C to obtain the calcium oxide catalyst.

### Brunauer Emmet Teller (BET) analysis

Brunauer, Emmitt and Teller (BET) analysis was carried out at 850 °C in order to determine the surface area, pore size, and pore volume of the sample.

From Table 2 the BET analysis revealed that the calcined limestone has a higher surface area, pore volume, and pore size compared to the raw limestone. These properties show the suitability of the calcium for use as the catalyst for biodiesel production.

TABLE 2: BET ANALYSIS RESULT FOR THE LIMESTONE SAMPLES CALCINED AT 850 °C

<i>Sample</i>	<b>Surface area (m<sup>2</sup>/g)</b>	<b>Pore volume (cc/g)</b>	<b>Pore size (nm)</b>
<i>Raw Limestone</i>	11.320	0.005	1.794
<i>C-850</i>	25.540	0.138	1.798

### Fourier transform infrared spectra (FT-IR) analysis

Fourier transform infrared spectral (FT-IR) analysis was carried out in order to identify the functional groups present in the raw limestone and the catalyst. Figure 1 shows the characteristic absorption peak of raw limestone at 1394, 872 and 712  $\text{cm}^{-1}$ . The broad peak at 1394  $\text{cm}^{-1}$  shows the asymmetric vibration stretching of the C-O bond which indicates the presence of carbonate. The peaks at 872  $\text{cm}^{-1}$  and 712  $\text{cm}^{-1}$  show the planar bending of C-O and  $\text{CO}_3^{2-}$  (Junfeng *et al.*, 2009; Ravisankar *et al.*, 2010). Figure 2 shows the characteristic absorption peaks at 3641.6, 1394, 872.2, and 711.9  $\text{cm}^{-1}$  for limestone calcined at 850  $^{\circ}\text{C}$ . The peak at 3641.6  $\text{cm}^{-1}$  indicates asymmetric stretching of OH of  $\text{Ca}(\text{OH})_2$  as the CaO formed rapidly absorbs moisture. The 1394  $\text{cm}^{-1}$  indicates the asymmetrical and non-symmetrical C=O attached to the surface of the CaO. The peak at 872  $\text{cm}^{-1}$  indicate a planar bending of C-O of the carbonates as a result of the recarbonation of the CaO with  $\text{CO}_2$  evolved (Ravisankar *et al.*, 2010), The  $\text{Ca}(\text{OH})_2$  formed and recarbonation is observed because the calcination reaction is chemically reversible, quicklime is usually referred to as being highly unstable (Krukowski, S. T., 2004) the peak at 711  $\text{cm}^{-1}$  also indicate carbonate group (Mohadi *et al.*, 2018; Suprpto *et al.*, 2016).

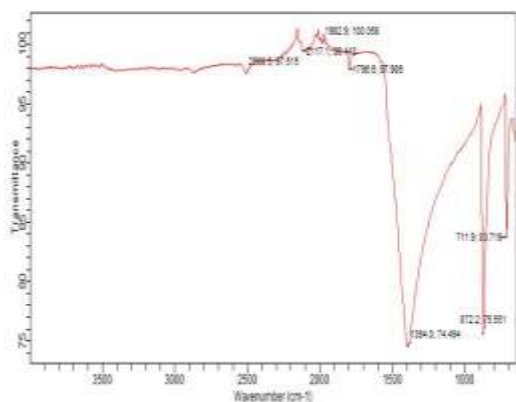


Figure 1: FTIR spectra for raw limestone.

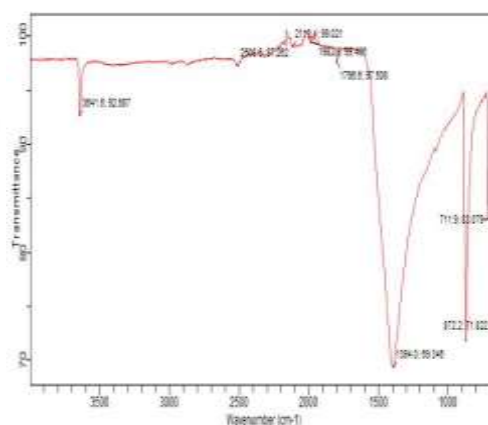


Figure 2: FTIR spectra for calcium oxide catalyst (CaO).

### Scanning electron microscopy (SEM) analysis

The morphological characteristics of the limestone sample and CaO produced from calcination at 850  $^{\circ}\text{C}$  was analysed using the Scanning Electron Microscopy (SEM). Figures 4 and 5 present the micrograph of the representative samples of limestone and calcium oxides respectively.



In figure 4, the absence of pores in limestone micrograph shows the presence of CO<sub>2</sub>, figure 5 shows the presence of pores in CaO micrograph which can be attributed to the release of CO<sub>2</sub> as a result of calcination of the limestone. The micrograph of CaO indicate grain growth and densification due to high temperature during calcination, the pore radii are therefore moved to larger pores with removal of smaller pores as a result of combination phenomenon which occurs during calcination (Bai *et al.*, 2009).

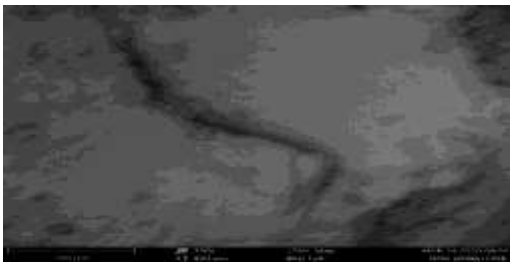


Figure 4: SEM micrograph of raw limestone

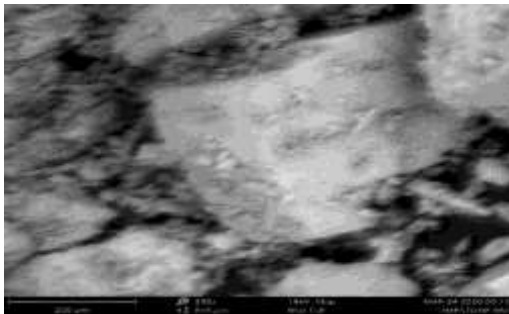


Figure 5: SEM micrograph of CaO

#### X-ray diffraction (XRD) spectrometry

The X-Ray diffractogram which shows the crystalline phase and diffraction pattern of CaO sample is presented in Figure 6.

The XRD pattern peaks 30.3° (d= 0.158nm), 37.5 ° (d= 0.196nm), 47.5° (d= 0.248nm), 64.3° (d= 0.336nm), and 66.7° (d= 0.348nm), show the presence of Cao and Ca(OH)<sub>2</sub> and aligns with the standard of CaO peaks at 2θ (Minaria and Risfidian, 2016).

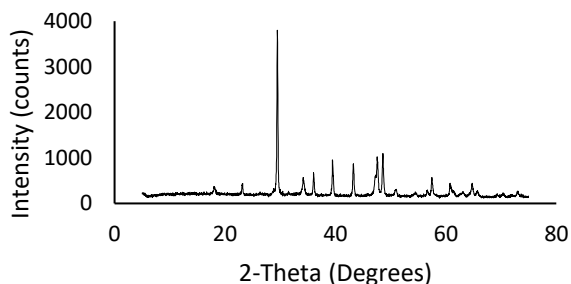


Figure 6: X-ray Diffraction (XRD) pattern of CaO

### X-ray Fluorescence (XRF) Spectrometry

X-rays fluorescent (XRF) analysis was conducted to determine the elemental compositions of the limestone and CaO samples. Table 3 shows the XRF elemental analysis of the limestone which reveals that the limestone sample mainly contains calcium oxide (55.04%), as a major component. Also present in varying proportions are oxides of silica, aluminium, magnesium, and iron, The loss on ignition (LOI) value of limestone from Obajana is 44.08%. According to Elueze *et al.*, (2015), the theoretical LOI value of pure calcium carbonate to weight of carbon dioxide is equal to 44%. Therefore, the nearness of the LOI value (44.08%) of Obajana limestone to the theoretical value indicates its purity. Table 4 indicates the XRF for CaO which shows that CaO is 92.7%, revealing that it is the major component of the limestone. Also present are varying percentages of silica, magnesium, and iron. (Nurhayati *et al.*, 2016)

TABLE 3: X-RAY FLOURESCENT (XRF) RESULT LIMESTONE SAMPLES

<i>Composition</i>	<i>Weight (%)</i>
<i>CaO</i>	55.04
<i>MgO</i>	0.42
<i>SiO<sub>2</sub></i>	0.35
<i>Fe<sub>2</sub>O<sub>3</sub></i>	0.03
<i>Al<sub>2</sub>O<sub>3</sub></i>	0.06
<i>L.O.I</i>	44.08
<i>Total</i>	99.98

TABLE 4: X-RAY FLOURESCENT (XRF) RESULT FOR CaO SAMPLE

<i>Composition</i>	<i>Weight (%)</i>
<i>CaO</i>	92.7
<i>MgO</i>	0.93
<i>SiO<sub>2</sub></i>	0.78
<i>Fe<sub>2</sub>O<sub>3</sub></i>	0.45
<i>L.O.I</i>	4.06
<i>Total</i>	98.92

### Feedstock Quality Characterization

The suitability of a feed stock for the production of biodiesel depends on its properties, such as its free fatty acid value (FFA), viscosity, and density amongst others. The results obtained in the characterization of the feed stock oil (orange peel) are presented in Table 5.

TABLE 5: CHARACTERIZATION OF ORANGE PEEL OIL

<i>S/N</i>	<i>PROPERTY</i>	<i>UNIT</i>	<i>PRESENT STUDY</i>
1.	Specific Gravity at 40 °C	-	0.8855
2.	pH Value	-	3.5
3.	Kinematic Viscosity	mm <sup>2</sup> /s	1.5
3.	Saponification Value	mgKOH/g	126.225
4.	Acid Value	mgKOH/g	12.716
5.	Ester value	wt. %	113.509
6.	Iodine Value	mgI/100g	25.76
7.	Peroxide Value	mmol peroxide/kg sample	22
8.	Flash Point	°C	235
9.	Pour point	°C	23
10.	Cloud point	°C	29
11.	Free Fatty Acid (FFA)	wt. %	6.396

### Fourier transform infrared spectra (FT-IR) analysis

Figure 7 shows the FT-IR spectra of the orange peel. The respective broad and sharp peaks at 3324.8 cm<sup>-1</sup> and 1017cm<sup>-1</sup> shows the presence of esters and carboxylic acid.

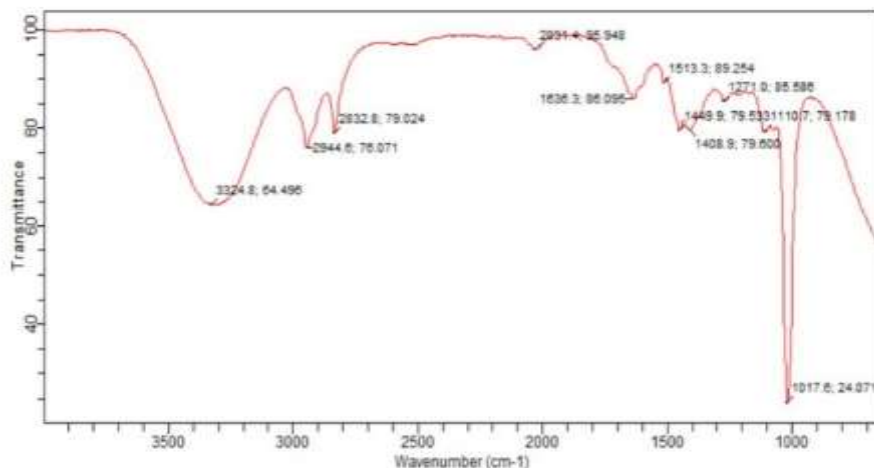


Figure 7: FT-IR of orange oil

### OPTIMIZATION OF BIODIESEL PRODUCTION FROM ORANGE PEEL

The optimization of solid catalyzed *in-situ* transesterification process of orange peel was conducted using the DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA) software. The parameters evaluated include Methanol to oil ratio, Catalyst Amount, Reaction time and Reaction temperature as shown in Table 6.

TABLE 6: DESIGN MATRIX FOR THE OPTIMIZATION OF BIODIESEL PRODUCTION FROM ORANGE PEEL

Run	Catalyst wt. (%)	M : O	Temp (°C)	Time (min)	Yield (%)
1	2.75	7.5	85	100	35.5
2	2.75	7.5	85	100	33.4
3	2.75	7.5	85	220	32.6
4	0.5	12	50	160	53.97
5	5	12	50	160	34.97
6	0.5	12	120	160	51.6
7	2.75	7.5	85	100	30.17
8	0.5	3	120	160	20.9
9	5	12	120	40	18.57

10	-1.75	7.5	85	100	24.9
11	2.75	7.5	85	100	38.3
12	2.75	-1.5	85	100	45.2
13	2.75	7.5	155	100	27.87
14	5	3	120	40	53.07
15	7.25	7.5	85	100	20.4
16	5	3	50	160	24.2
17	5	3	120	160	21.8
18	2.75	7.5	15	100	22.5
19	0.5	12	120	40	27.4
20	2.75	7.5	85	-20	19
21	0.5	3	50	160	33.27
22	0.5	3	50	40	41.1
23	5	12	50	40	33.27
24	2.75	7.5	85	100	18.7
25	0.5	12	50	40	23.47
26	5	3	50	40	14.3
27	5	12	120	160	19.96
28	0.5	3	120	40	38
29	2.75	16.5	85	100	70.1
30	2.75	7.5	85	100	19.96

TABLE 7: ANALYSIS OF VARIANCE OF THE *IN-SITU*  
TRANSESTERIFICATION OF ORANGE PEEL

Source	Sum of Squares	df	Mean Square	F Value	P value
Model	3454.67	14	246.76	2.52	0.0433
A-Catalyst wt.	257.22	1	257.22	2.63	0.126
B-M : O	183.54	1	183.54	1.87	0.1913
C-Tempt.	0.51	1	0.51	5.18E-03	0.9436
D-Time	62.37	1	62.37	0.64	0.4374
AB	55.39	1	55.39	0.57	0.4638
AC	26.45	1	26.45	0.27	0.611
AD	144.3	1	144.3	1.47	0.2437

<i>BC</i>	150.37	1	150.37	1.53	0.2345
<i>BD</i>	677.17	1	677.17	6.91	0.019
<i>CD</i>	203.42	1	203.42	2.08	0.1702
<i>A<sup>2</sup></i>	91.99	1	91.99	0.94	0.3479
<i>B<sup>2</sup></i>	1312.94	1	1312.94	13.4	0.0023
<i>C<sup>2</sup></i>	39.34	1	39.34	0.4	0.5359
<i>D<sup>2</sup></i>	29.89	1	29.89	0.31	0.5889
<i>Residual</i>	1469.74	15	97.98		
<i>Lack of Fit</i>	1133.15	10	113.31	1.68	0.2943
<i>Pure Error</i>	336.59	5	67.32		
<i>Cor Total</i>	4924.41	29			

TABLE 8: COEFFICIENTS IN TERMS OF CODED FACTORS

<i>Factor</i>	<b>Coeff Estimate</b>	<b>df</b>	<b>Std Error</b>	<b>95% CI Low</b>	<b>CI High</b>	<b>95% CI High</b>	<b>VIF</b>
<i>Intercept</i>	29.34	1	4.04	20.72	37.95		
<i>A-Catalyst wt.</i>	-3.27	1	2.02	-7.58	1.03	1	
<i>B-M: O</i>	2.77	1	2.02	-1.54	7.07	1	
<i>C-Tempt.</i>	0.15	1	2.02	-4.16E+00	4.45	1	
<i>D-Time</i>	1.61	1	2.02	-2.69	5.92	1	
<i>AB</i>	-1.86	1	2.47	-7.14	3.41	1	
<i>AC</i>	1.29	1	2.47	-3.99	6.56	1	
<i>AD</i>	-3	1	2.47	-8.28	2.27	1	
<i>BC</i>	-3.07	1	2.47	-8.34	2.21	1	
<i>BD</i>	6.51	1	2.47	1.23	11.78	1	
<i>CD</i>	-3.57	1	2.47	-8.84	1.71	1	
<i>A<sup>2</sup></i>	-1.83	1	1.89	-5.86	2.2	1.05	
<i>B<sup>2</sup></i>	6.92	1	1.89	2.89	10.95	1.05	
<i>C<sup>2</sup></i>	-1.2	1	1.89	-5.23	2.83	1.05	
<i>D<sup>2</sup></i>	-1.04	1	1.89	-5.07	2.98	1.05	

The analysis of the variance (ANOVA) for the response surface quadratic model is shown in Table 7. The Model F-value of 2.52 implies the model is significant. There is only a 4.33% chance that a "Model F-Value" this large

could occur due to noise. The model expression developed that relates the biodiesel yield and the four reaction parameters considered (A, B, C, D), was suitable because its p-value is less than 0.05. The significant factors from ANOVA analysis is the binary interaction of methanol to orange peel ratio with a p-value of 0.0023 which is less than 0.05. The other significant factor is the effect of the Methanol to Oil ratio and catalyst loading and the interaction effect of Methanol to Oil ratio and Reaction time with p-value of 0.019. The other factors of the model have no statistical significant effect. In this study, the value of the determination coefficient ( $R^2 = 0.7015$ ) indicates that the sample variation of 70.15% is attributed to independent variables and 29.85% of the total variations is not explained by the model.

The Biodiesel yield is governed by the equation

$$\text{Biodiesel Yield} = 29.34 - 3.27A + 2.77B + 0.15C + 1.61D - 1.86AB + 1.29AC - 3.00AD - 3.07BC + 6.51BD - 3.27CD - 1.83A^2 + 6.92B^2 - 1.20C^2 - 1.04D^2$$

The linear effect of A and B, the interaction effect of AD and BC and the quadratic effect of  $A^2$  and  $B^2$  are the general determining factors of *in-situ* transesterification of Orange Peel as they have the larger coefficients.

### The effect of interaction between process parameters

The Three-dimensional response surfaces are plotted on the basis of the generated model equation to investigate the interaction among the variables and to determine the optimum condition of each factor for maximum Biodiesel yield.

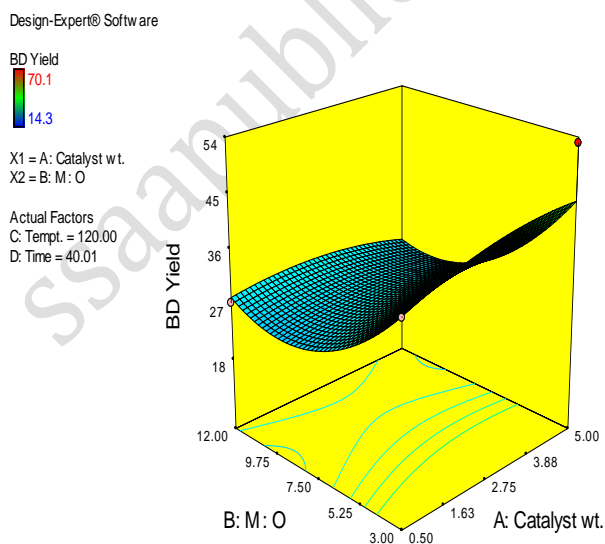


Figure 8a: Response Surface Plot of the Interaction Effect of Methanol to Orange Peel ratio and Catalyst loading on the Biodiesel yield.

Figure 8a represents the 3D plot of the interaction effect of methanol to orange peel ratio and catalyst loading on the biodiesel yield at reaction time of 40 minutes

and reaction temperature of 120 °C. It was observed on the plot increase in catalyst loading slightly increased the biodiesel yield which was later kept constant even with increase in catalyst loading. Thus is because at higher catalyst concentration the mixture become too viscous and causes mixing problem (Farooq *et al*, 2013). Also, higher catalyst loading results in catalyst accumulation on the wall of flask which has the tendency to lower the activity (Buasri *et al*, 2013).

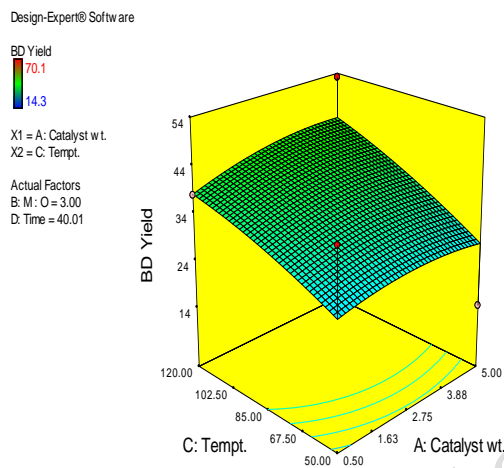


Figure 8b: Response Surface Plot of the Interaction Effect of Temperature and Catalyst loading on the Biodiesel yield

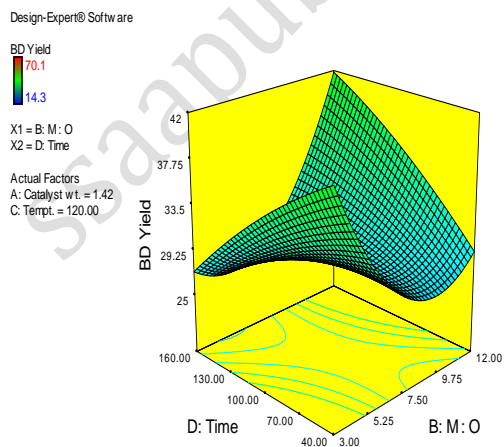




Figure 8c: Response Surface Plot of the Interaction Effect of Methanol to Orange Peel ratio and Reaction Time on the Biodiesel yield

Figure 8c represents the 3D plot of the interaction effect of methanol to orange peel ratio and reaction time on the biodiesel yield at a reaction temperature of 120 °C and a catalyst loading 1.42%. The plot shows decrease in biodiesel yield with decrease in methanol with a sharp increase in biodiesel yield as the methanol increases,

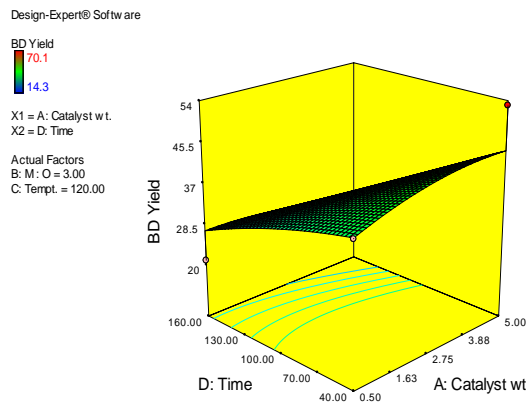


Figure 8d: Response Surface Plot of the Interaction Effect of Catalyst Loading and Reaction Time on the Biodiesel yield

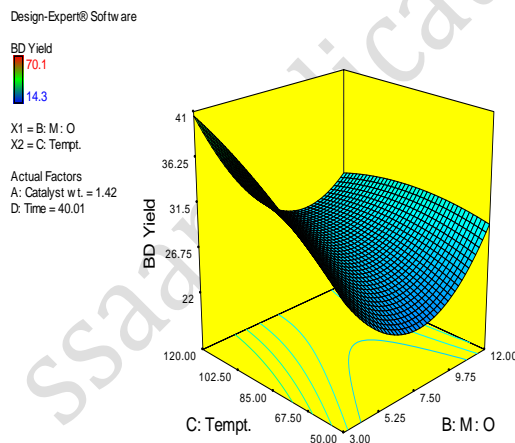


Figure 8e: Response Surface Plot of the Interaction Effect of Methanol to Orange Peel ratio and Reaction Temperature on the Biodiesel yield

Figure 8e represents the 3D plot of the interaction effect Methanol to Orange Peel ratio and Reaction Temperature on the Biodiesel yield at a

Reaction Time of 40 mins and a Catalyst loading of 1.42%. The plot shows biodiesel yield decrease steadily with the decrease of methanol to orange peel ratio and continued even with further increase above 7.5:1 ratio. It is assumed that the glycerol was mainly dissolved in excessive methanol and thus hinders the reaction of methanol to the reactant and catalyst subsequently interfering with the separation of glycerin (Buasri *et al.*, 2013). This results in dropping the conversion by shifting the equilibrium in the reverse direction (Lim *et al.*, 2009).

Figure 8f represents the 3D plot of the interaction effect of reaction temperature and reaction time on the Biodiesel yield at a methanol to orange peel ratio of 3:1 and a catalyst loading of 1.42%. The result shows that biodiesel yield is increasing with the increasing of reaction temperature. This is because high temperature results in increase in miscibility which results in higher reaction rate (Helwani *et al.*, 2009). Also, transesterification is an endothermic reaction which favors higher reaction temperature for production of biodiesel (Yu *et al.*, 2011).

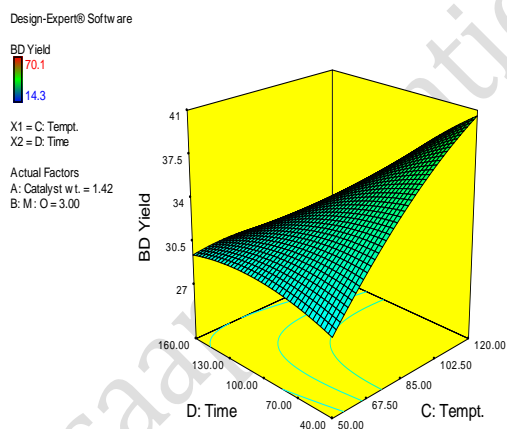


Figure 8f: Response Surface Plot of the Interaction Effect of Reaction Temperature and Reaction Time on the Biodiesel yield

Similarly, the RSM plots of the interaction effect of the various reaction parameters against Biodiesel yield as represented by Figure 8a-f resulted in different Biodiesel yield results at various operating conditions. However, the optimization solution obtained shows that a biodiesel yield

of 72.0% was obtained at a methanol to orange peel ratio of 16.5:1, a catalyst loading of 2.75%, a reaction temperature and time of 85 ° C and 100 minutes respectively.

### Biodiesel quality determination

The produced biodiesel is characterized and compared against established biodiesel standards such as the American Standards and Testing Materials. The ASTM D6751 serves as a guideline which provides information on the properties and quality of good Biodiesel.

**TABLE 9: CHARACTERIZATION OF BIODIESEL PRODUCED FROM ORANGE PEEL**

S/N	Property	Unit	Result Obtained	ASTM D6751
1.	Flash Point	°C	135	130 min
2.	Kinematic Viscosity at 40 ° C	mm <sup>2</sup> /s	5.4	1.9 – 6.0
3.	Cetane Index		99	47 min
4.	pH Value		6.1	-
5.	Color		Amber Yellow	-
6.	Pour Point	°C	16	18 ° C max
7.	Cloud point	°C	22	-
8.	Iodine Value	mgI/100g	70	120 max
9.	Ester Value	wt. %	94.46	96.5 min
10.	Acid value	mgKOH/g	1.12	0.8 max
11.	FFA	wt %	0.56	-

### *Kinematic Viscosity*

The Kinematic viscosity of a fluid is a measure of the resistance of that fluid to flow or shear. The kinematic viscosity describes the behavior of a fluid near a solid boundary and it is temperature dependent. The obtained kinematic viscosity of 0.8mm<sup>2</sup>/s which is low compared to the ASTM standard of 1.9 – 6.0 mm<sup>2</sup>/s. This can be attributed to the chain length, position, number and nature of double bonds present in the biodiesel from orange peel (Gerhard and Kevin, 2005).

### ***Cetane Index***

This is a measure of the fuel's ignition quality. The obtained value of 99 is significant since according to the ASTM standards a minimum value of 47 is required

### ***Acid Value***

The acid value serves as a measure of the breakdown of the triacylglycerol into free fatty acids in other words the acid value (AV) expresses in milligrams the quantity of potassium hydroxide required to neutralize the free acids present in 1 g of the substance. The acid value has gotten from the biodiesel is 1.12 which is above the required ASTM maximum, this is because rancidity of the orange peel increases the acid number (Wikipedia)

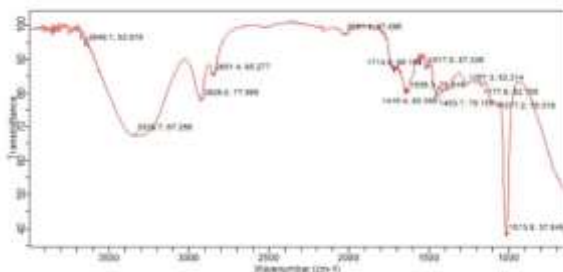
### ***Ester value***

This is simply the tendency of a sample to undergo esterification. A value of 94.46 was obtained. This value plays no role in Biodiesel use and the obtained value is close to ASTM standards which require a minimum of 96.5 min.

### ***Iodine Value***

The iodine value gives a measure of the average degree of unsaturation of a lipid. The higher this value the greater the C=C bonds. A value of 70 is conformity with ASTM standards which require that the iodine values do not exceed 120.

### **Fourier transform infrared spectra (FT-IR) analysis**



### Figure 9: FTIR of Biodiesel

Figure 9 shows the FT-IR spectrum of the biodiesel produced from orange peel. It can be observed that the C-H stretching absorption occurs at wavelength  $3339.7\text{ cm}^{-1}$ . While the  $2920\text{cm}^{-1}$  and  $1013.8\text{cm}^{-1}$  are associated with -C-H stretch and O-C stretch respectively.

### CONCLUSION

This research adopted the use of Response surface methodology to optimize the *in-situ* transesterification conditions which improved the yield of biodiesel from orange peel waste. It was determined that the use of *in-situ* transesterification and solid catalyst could produce up to 70% FAME. The highest FAME content was obtained reaction time of 100 mins, with 2.75 wt% of CaO catalyst, a temperature of  $85\text{ }^{\circ}\text{C}$ , and a methanol to orange peel ratio of 16.5:1. As a result, this concludes the purpose of the research that orange peel waste is viable to be used additionally for producing alternative fuel which is biodiesel. The *in-situ* transesterification shows an effective method in reducing cost and processing time of biodiesel production.

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