Optimization of Biodiesel Production from Jojoba Oil Using Red Sea Coralline limestone as a heterogeneous Catalyst

Taiseer Hassan M., Ahmed A. A. Youssif, Isameldeen Ibrahim H. A.

Abstract— **Jojoba oil (Simmondsia chinensis Link Schneider) has potential as an alternative, nonfood feedstock for Biodiesel production. Jojoba seed which obtained from Erkaweit – Sudan was used in biodiesel (JME) production using Coralline limestone rocks as a heterogeneous catalyst. Coralline limestone rocks is a abundant and environme-ntally friendly in the Red Sea area, the main characteristic of this rock is the high content of calcium carbonate (CaCO3), which was transformed into CaO by calcinations. The transesterification reaction variables; methanol / oil molar ratio, catalyst weight% and reaction time were fully optimized using response surface methodology (RSM) based on a central composite design (CCD). The catalyst was characterized by X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and HPGe gamma spectrometry. Jojoba seeds were investigated for agronomical parameters, the analysis of jojoba seed gives, 45.187g weight of 50 seeds, the seeds measurements were 16.256 mm length, 10.551 breadth and 9.721mm thickness, the proximate composition of the seed were 46.711 oil content, 3.486 Moisture, 1.71 Ash, 15.45 Protein and 32.633 Carbohydrates (by diff.). Jojoba oil was also tested for its physiochemical properties including acid value, peroxide value, FFA, flash point, pour point, refractive index, density, viscosity @ 40 ˚C, saponification and iodine values. Proximate analysis of extracted oil gives (0.936 mgKOH/g, 2.469 mEq/kg, 0.47%, 150 ˚C, +9 ˚C, 1.464, 0.864 g/ml, 22.507 Cst, 95.011 mgKOH/g and 84.20 I2/100g) respectively. The important fuel properties of Jojoba oil methyl ester (JME) were evaluated including kinematic viscosity @ 40 ˚C (6.783 Cst), acid value (034 mgKOH/g), Flash point (154 ˚C), density (865 kg/m3) and cetane number (53.33 min.). The fatty acids profile fatty jojoba oil and jojoba methyl ester were established by GC analysis. According to this study, the maximum yield of JME was 81.93% at 12/1 methanol/oil molar ratio 5% catalyst weight and 3 hours reaction time.**

Index Terms— **Jojoba seeds, Biodiesel, JME, coralline limestone rock, CaO catalyst.**

I. INTRODUCTION

The world is currently challenged with global warming, depletion of non-renewable fossil fuel and environmental pollution [1], due to rapid population and industrialization growth globally [2]. Increase in demand for energy and more consciousness about the environment have led to search for an alternative fuel which can supplement or replace fossil fuel

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[3]. Biodiesel is an excellent alternative fuel for replace fossil fuel that could produce from renewable sources and it is biodegradable [4], free of sulfur [5], nontoxic [3], environmental friendly and inexpensive [4]. It can be also used either pure or to blend with petroleum diesel in the unmodified diesel engine, and it reduces exhaust pollutants [6].

The availability and sustainability of biodiesel resources will be the limiting factor in the widespread use of biodiesel [7]. The most common way to produce biodiesel is the transesterification of vegetable oils or animal fats with short chain alcohol such as methanol or ethanol to yield the fatty acid alkyl esters (biodiesel) and glycerol [8].

Jojoba *(Simmondsia chinensis* {Link.}Schneider) is a shrub which grows wild in the semi-arid region of the Sonora desert in northern Mexico and the south-western USA [9]. Jojoba is now cultivated in United States, Israel, Mexico, Peru, Australia, India, Egypt, Thailand, South West Africa, Costa Rica, Argentina, Chile and other countries [10].

Sudan was one of the pioneer countries to introduce jojoba in 1974 through a combined work between the U.N Developmental Program and the University of California– Riverside. Many areas of different climates and soil types such as Arkaweit, Eddamer, Sagelneiam, Bara, Dungla, Elhudeiba and ELrwakib have been selected as experimental sites. The results were very successful and the plant growth exceeded its growth in native areas and proved to be well adapted to Sudan climate [11].

Jojoba seeds contain from 40 to 60% of oil which is chemically classified as liquid wax because unlike most vegetable seed oils that are composed of triglycerides, jojoba oil consists of esters [12]. The main uses of Jojoba oil-wax are in the cosmetics and pharmaceutical industry, but new uses could arise related to the search of new energetic crops [13].

At chemical level, the jojoba wax consists of extremely long (C36 - C46) straight chain entirely of mono-ethynelic linear fatty acids & monounsaturated linear fatty alcohol having high molecular weight. Each constituent molecule has 2 double bonds and 1 an ester group in it. Prevailing fatty alcohols and fatty acids are C-20 and C-22 in length [14]. The Jojoba oil-wax has a low chemical reactivity and a very high normal boiling point (398 °C) that gives this product very important physico-chemical properties and uses.

There are basically two types of catalyst that are used in the production of biodiesel namely homogenous and heterogeneous. The term of homogeneous means the catalysts are in the same phase with its reactants, whereas heterogeneous means that the catalysts are in a different phase from its reactant. Further homogenous catalyst can be categorized into homogenous bases and acids [15].

Optimization of Biodiesel Production from Jojoba Oil Using Red Sea Coralline limestone as a heterogeneous Catalyst

Currently, heterogeneous catalysts have been developed for use in a transesterifiation reaction for biodiesel production due to the problems of homogeneous catalysts in terms of water treatment and the nonreusability of the catalyst. Although heterogeneous catalysts have many advantages, their disadvantages are also many such as a high oil-to-alcohol molar ratio, high temperature, and a long reaction time [16]. Calcium oxide is one of the most promising heterogeneous base catalysts and it has many advantages such as mild reaction conditions, low cost, high reusability and easy availability [17]. CaO has attracted many interests as a heterogeneous catalyst because it can be synthesized from cheap sources like calcium carbonate, calcium acetate and calcium nitrate [18].

Coralline limestone (CLR) is a biological sedimentary rocks, composed primarily of calcium carbonate, the exactly mineral composition depend on its origin and the surrounding environment.

The objective of this study is optimisation of biodiesel production from jojoba wax ester using calcined Reds Sea coralline limestone rock as a heterogeneous catalyst.

II. MATERIALS AND METHODS

A. Materials

Jojoba seeds from Erkaweit, Red Sea hills area, 2016 season. Coralline limestone rocks sample obtained from the Dama Dama coast, which produced from the digging and deepening operations in the sea port of Port Sudan.

Chemicals, like n-hexane (Loba Chemie), petroleum ether 40-60 °C (Wagtech), methanol and hydrochloric acid 37% (Charlo Erba), sodium hydroxide 97-100.5%, potassium iodide and potassium hydroxide (Scharlau). All chemical reagents were used as purchased with no further purification.

B. Methods

1. Catalyst preparations

Highly active CaO catalyst was prepared by the calcinations - hydration - dehydration treatment [3]. Coralline limestone rocks were washed with distilled water and then dried in hot air oven at 105 °C for 24 h. The dried CLR were crushed to small pieces and calcined in a muffle furnace at 900 C for 2.5 hours to transform the calcium carbonate into CaO particle. Then the CaO derived from the CLR was refluxed in water at 60 C for 6 hours, filtered and dried in hot air oven at 120 C overnight. The solid product was dehydrated by performing calcination at 600 C for 3 h to change the hydroxide form to oxide form.

2. Catalyst Characterization

The elemental chemical compositions of the material were analyzed by X-ray fluorescence spectroscopy (XRF - Oxford). The microstructure of the calcined CLR was observed by Tescan Vega3 XMU scanning electron microscope. Due to the origin of the coralline limestone rock, the radioactivity of the catalyst was studied by HPGe Gamma Spectrometry.

3. Seed morphology, oil extraction and parameters
All seeds were dried in hot air oven at 60 °C till constant weight achieved. Five samples were drawn from each seed lot and 50 random undamaged seeds (total 250 seeds) were measured for their weight, length, breadth and thickness [19].

Jojoba seeds were ground in porcelain mortar and placed in a Soxhlet extractor for refluxing with n-hexane [20]. After 8 hours, the solvent was removed from the extract by heating and evaporating at 80 °C.

The proximate composition of seeds and main physiochemical properties of extracted jojoba oil were evaluated according to the methods described in Pearson´s composition and analysis of food [21].

4. Transesterification reaction
Reactions were carried out in a 250 ml two-necked round bottom flask. The reactor was initially filled with the desired amount of oil, and then placed in the constant-temperature equipped with reflux condenser, stopper and heated to a predetermined temperature. While CaO and methanol were mixed and stirred at room temperature (30 °C) for 30 minutes. Then the mixture was added to oil in the reactor and stirred at rate of 750 rpm for the desired time. At the end of the reaction, the product of each part was filtrated into separator funnel to remove the catalyst and allowed to separate overnight. The lower layer was then evaporated under vacuum in order to get rid of the of the excess methanol. After that the product was washed to eliminate the remaining base catalyst and evaporated the water at 120 °C for 24 hours [22].

5. Physicochemical properties of the biodiesel
The obtained biodiesel have been characterized by some physical measurements: Kinematic viscosity at 40˚C ASTM D 445, density EN ISO 3675 and EN ISO 12185, flash point, ASTM D 93 and cetane number ASTM D613 and acid value ASTM D664

6. Fourier transform infrared (FTIR) spectroscopy
FTIR analysis of the catalyst, jojoba oil and produced biodiesel (JME) samples, were carried out using a Shimadzu ir prestige 21 spectrometer. A total of 32 scans were taken from 400-4000 cm-1 with a resolution of 4 cm^{-1} for each sample.

7. Gas Chromatography (GC)
The analysis of FAMEs was performed on a Shimadzu GC-2010 gas chromatograph equipped with flame ionization detector (FID), inertcap FFAP fused silica capillary column (30M, 0.25mm, 0.25μM) and split sample inlet system. The gases flow rates were kept as follows: nitrogen as carrier gas 0.5 ml/min, makeup gas nitrogen 30 ml/min, hydrogen 40 ml/min and air 400 ml/min for the detector, sample volume of 1 μl was used as injection volume and the split ratio was 1:5, temperature setting were as follows; injector 260 C° detector 270 C°, and the oven temperature was programmed as follow; intial temp. Was 140 C° at which it was held for 3 min and increased at 5 C°/min until 160 C° and held for 5 min and increased at 5C°/min until 240 C° and finally which was held for 12 min., a total of 40 min. Was necessary to assay the FAMEs. The peak areas were normalised & integrated with SHIMADZU GCsolution chromatography data system version 2.3.
FAMEs were prepaired according to method described by wang et al 2015 [23]. 40 μl was placed into 10 ml centrifuge tubes to which 0.7 ml of potassium hydroxide (10 M) solution and 5.3 ml of methanol were added. The reaction was performed at 55 °C for 1.5 h with mixing for 5 s every 20 min.

After cooling to room temperature, 3 ml of n-hexane was added and mixed for 5 min. Subsequently, the tubes were centrifuged for 5 min. And the extracts were removed for GC. FAMEs were identified by comparing the retention times of the unknown components with a known FAMEs standard mixture which was injected under the same instrument condition and quantified by comparing their peak areas of the FAMEs standard mixture.

8. Experimental design

Statistical experimental design forms an essential part of any laboratory work as it limits the number of time consuming experiments and also ensures that most suitable data can be obtained from minimum experimental work [24]. The experimental design selected for this study is Central Composite Design (CCD) and the response measured which is the dependent variable is the yield of biodiesel.

In order to optimize the process variables for biodiesel production from jojoba oil transesterification, examine the combined effect of the three different independent variables; methanol to oil ratio, reaction time, catalyst weight on yield and derive a model, five levels, four factors central composite factorial design (CCD) which includes 14 factorial points plus 6 central points leading to a total of 20 experiments (Table 1) were adopted in this study. Variables investigated were chosen by considering the preliminary tests on effect of individual variables on biodiesel yield and operating limits of the biodiesel production process conditions [25].

The obtained experimental data was analyzed using a second-order polynomial (see (1)) to find the relationship between the independent variables and the % FAME conversion [16]

$$Y_i = \beta_0 + \sum_{i=1}^{k} \beta_i\, X_i + \sum_{i=1}^{k} \beta_{ii}\, X_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k} \beta_i\, X_i\, X_j \qquad (1)$$

Where Y is the response factor (fatty acid methyl ester contents), X_i = the Ith term of independent factor, β_o = intercept, β_i = linear model coefficient, β_{ii} = quadratic coefficient for the factor i, and β_{ij} = linear model coefficient for the interaction between factors i and j.

Table 1. Independent variables and their levels for central composite design of the jojoba oil transesterification.

Variables	Units	Symbols	Range and levels				
			-Alpha	Low	0	High	+Alpha
Methanol/JWE	Molar ratio	A(X1)	11.0518	12	15	18	18.9482
Catalyst Weight	%	B(X2)	4.20981	5	7.5	10	10.7902
Reaction Time	Hours	C(X3)	2.68393	3	4	5	5.31607

III. RESULTS AND DISCUSSION

A. Characterisation of jojoba seed and oil

The proximate composition of jojoba seeds obtained from Arkaweit was shown in Table 2. Jojob seed contains; 3.486 moisture, 46.711 lipids, 15.45 protein, 1.71 ash and 32.633 carbohydrates (by difference). The agronomical parameters of the seeds were; 45.187g Weight of 50 seeds, 16.256 mm, 10.551 mm and 9.721 for the seeds Length, Breadth and Thickness respectively.

The Physiochemical properties are the most important criteria to check the quality of oils. The physiochemical properties were evaluated and the result obtained is shown in the Table 3. Agarwal et al 2015 [19] reported that the biochemical characteristics of jojoba oil, which were obtained from jojoba seeds having different origin were quite variable and mainly dependent on their geographical origin.

B. Characterisation of Catalyst

The chemical compositions of the catalyst were characterized by XRF technique. The major mineralogical component is CaO. Calcined CLR had concentration of 97.793% CaO, 1.194% SrO, 0.638% K_2O, 0.201% BaO and 0.109% Fe_2O_3.

The morphology of the obtained CaO was probed by SEM as shown in Fig. 1. The particles were rough and crack with high porosity. Because, the heat burning effected to organic compounds [4], and results in increasing surface area of catalyst pores and whitened catalyst colour [26].

Table 2. Physicochemical and agronomical parameters of jojoba seeds

Parameter	Unit	Result
Weight of 50 seeds	g	45.187
Seed Length	mm	16.256
Seed Breadth	mm	10.551
Seed Thickness	mm	9.721
Oil contents	%	46.711
Moisture	%	3.486
Ash	%	1.71
Protein	%	15.45
Carbohydrates (by diff.)	%	32.633

Table 3. Physiochemical parameters of jojoba oil

Parameter	Test method	Unit	Result
Refractive index at 25 °C	Pearson`s		1.464
Density at 15 °C	ASTM D 4052	g/ml	0.864
Viscosity at 40 °C	ASTM D 7042	Cst	22.507
Viscosity at 100 °C	ASTM D 7042	Cst	6.1637
Viscosity Index	ASTM D 7042	-	247.9
Flash point	ASTM D 92	Deg C	150
Pour point	ASTM D 5950	Deg C	+ 9
Acid value	Pearson`s	mgKOH/g	0.936
FFA	Pearson`s	%	0.47
Peroxide value	Pearson`s	mEq/kg	2.469
Saponification Value	Pearson`s	mgKOH/g	95.011
Iodine Value	Pearson`s	$I_2/100g$	84.20
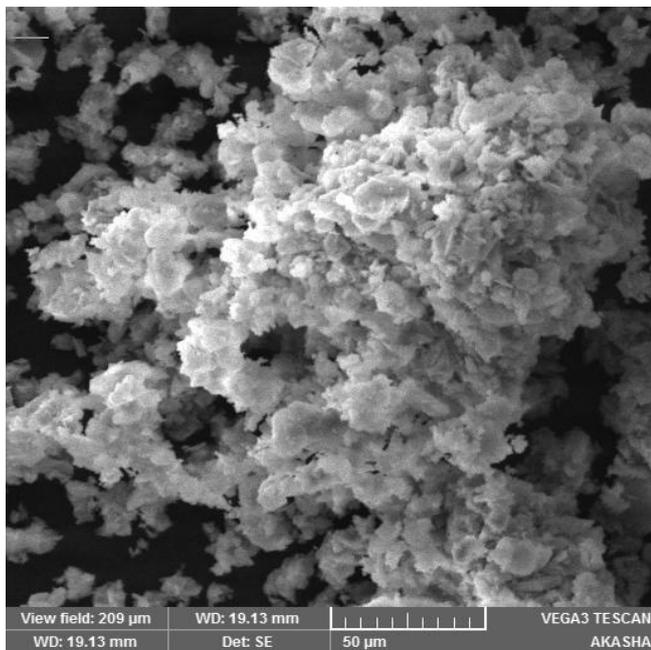
Figure 1. SEM analysis of CaO catalyst
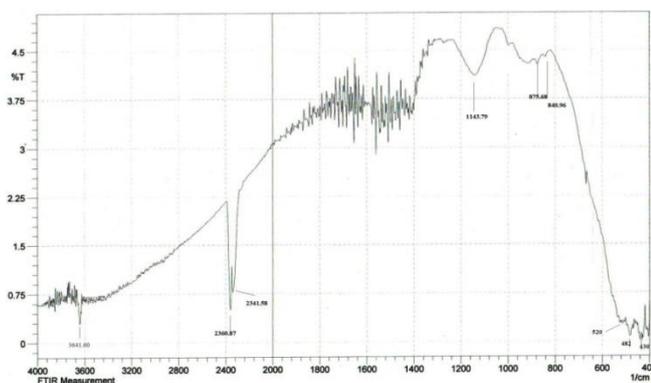
Figure 2. IR spectrum of calcium oxide from decomposition of coralline limestone rocks.

The FTIR spectra of CaO catalyst derived from calcined CLR shown in Fig. 2. The broad band at ~1621 cm^{-1} and sharp band at 3641 cm^{-1} areassociated with OH stretching vibration mode of water physisorbed on the surface of the CaO [27], calcium oxide can absorb water vapor from the air easily [26]. The weak band at 875.68 cm^{-1}shows the presence of Ca – O bond [28],[29].

Gamma spectrometry analysis of the coralline limestone rock was performed with a computer-based gamma spectrometry system for qualitative and quantitative determination of gamma-emitting radionuclides.

The results displayed in table 4 and Fig. 3 shows that the obtained activity of ^{238}U concentration activity is 65 (Bq/kg) and ^{226}Ra concentration activity is 56.6 (Bq/kg), this values fall within the range of corresponding values published for other locations in the world [30].

C. Physicochemical properties of Jojoba biodiesel (JME)
The physiochemical properties of jojoba methyl ester were measured under corresponding ASTM standards. Some of important fuel properties of the jojoba biodiesel are presented in Table 5. The density at 15 °C was found to be 865 kg/m^3 which is in the acceptable limits of standards. The kinematic viscosity was found 6.783 mm^2/s which is slightly higher than the ASTM standards, due to high fatty acid composition [31],

[32]. The flash point, acid value and cetane number of JME were 154 ℃, 0.34 mgKOH/g and 53.33 min. respectively.

Table 4. Radioactivity of coralline limestone rock

Nuclides/ Lines	Area [impulse]	Activity, Bq/kg	Relative uncertinity, %	MDA, Bq
U-238	311	65	14	26.97
Ra-226	5190	56.6	1.9	0.5
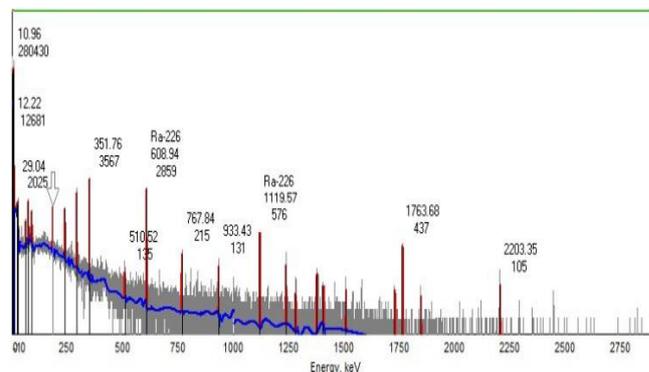
Figure 3. Gamma spectrum of coralline lime stone rock.

Table 5. Physicochemical properties of JME.

Parameter	Test Method	Unit	JME	ASTM D6751-07b
Kinematic Viscosity at 40°C	ASTM D 445	Cst	6.783	1.9 – 6.0
Flash Point	ASTM D 93	Deg C	154	130 min
Density	EN ISO 3675 EN ISO 12185	kg/m^3	865	860 - 900
Cetane number	ASTM D 613	min.	53.33	47 min

Table 6. Fatty acid profile of jojoba oil and jojoba methyl ester (JME).

Ester profile	Jojoba oil	JME
Lauric acid (C12:0)	1.05	0.98
Palmitic acid (C16:0)	0.40	
Oleic acid (C18:1)	6.17	9.26
Eicosenoic acid (C20:1)	69.83	53.68
Behenic acidC22:0	7.23	
Erucic acid (C22:1)	13.71	15.41
Nervonic acid C24:1	1.61	2.5

Gas chromatography (GC)
The results, based on GC analyses, of the jojoba seed oil and jojoba methyl ester indicated that the oil contains fatty acids of carbon atoms from C 12 to C 24 (saturated and unsaturated). The main fatty acids constituents (average) of Jojoba seed oil (Table 6) are ecosenoic acid (69.83), erucic acid (13.71), behenic acid (7.23), oleic acid (6.17), Nervonic acid C24:1 (1.61) and Lauric acid (1.05) The fatty acids profile of JME biodiesel (Table 6), showed that methyl-cis-11-eicosenoate, C 20:1 is the major constituent followed by methyl-cis-13-docosenoate, C 22:1), C18:1 and 24:1 respectively. whereas C12.0 was present at

low concentration amounted. These results were slightly different from the neighbouring countries [33], [34]. Beside, some studies have shown that the content and composition of jojoba oil is strongly related to the genetic variability of the plant [12].

FT-IR Spectroscopy

The FT-IR spectrum of jojoba oil (figure 4) indicate that it contains the following peaks; 3462.22, 3005.10, 2925.60, 2854.65, 2682.98, 1739.79, 1654.92, 1456.18, 1170.79, 1043.49 and 721.38 cm-1 [35]. The stretching and bending absorption peaks at 3005.10 and 721.38 cm-1 which correspond to olefinic (-CH) group [36]. The spectra also show other stretching absorption bands at 1654.92, 1739.79 and 1170.79 cm-1 which correspond to (C=C) bond, C=O and C–O of ester group respectively. The bands of CH3 and CH2 groups appear at 2925.60 and 2854.65 cm-1 [36].
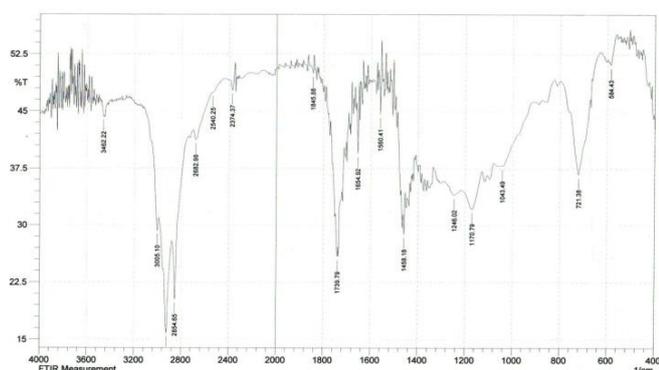
Figure 4. FT-IR spectrum of jojoba oil
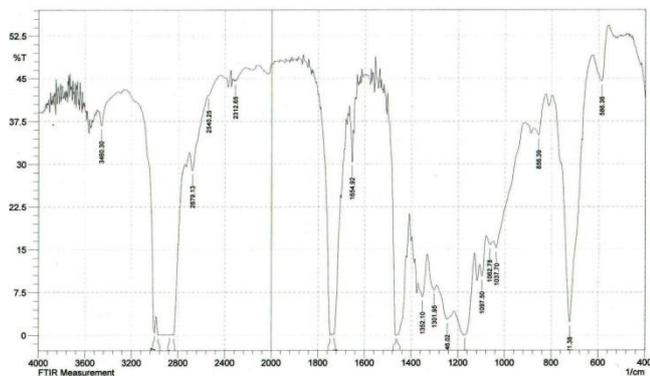
Figure 5. FT-IR spectrum of jojoba methyl ester (JME)

The FT-IR spectrum of jojoba methyl ester (figure 5) indicate that it contains the following peaks; 3460.30, 3008.95, 2931.80, 2862.38, 1749.44, 1728.22, 1654,92, 1469.76, 1352.10, 1301.95, 1246.02, 1170.79 and 721.38 cm-1 [35]. JME seem to be in a purer state due to absence of this wide broad band at 33460.30 cm-1 [37], carbonyl stretching at 1749.44 cm-1 and C-O-C asymmetric stretching at 1170.79 [20]. The band at 1352.10 corresponds to the –CH2 and –CH3 flexion vibration [38]. The olefinic chain vibration were; 3008.95 cm-1 vinylic C-H stretching, 2931.80 cm-1 aliphatic C-H stretching and 1469.76 cm-1 C-H in-plane bending [20], and the band at 1654.92 cm-1 due to the double bond [37]. Which is not conjugate with the carbonyl group [20].

D. Optimization of Reaction Conditions

RSM was employed to evaluate the relations between the response (% JME conversion) and the three reaction variables. The coded and uncoded independent variables for reaction experiment parameter were designed as shown in Table 7. 20 experiments were performed in a randomized order. The response obtained from the regression analysis was correlated with the three independent variables using second-order polynomial equation.

The JME% conversion obtained at the design points of different reaction conditions is shown in Table 7. The observed values varied between 70.45% at 15/1 methanol/oil molar ratio 10.7902% catalyst weight and 4 hours reaction time, and 81.93% at 12/1 methanol/oil molar ratio 5% catalyst weight and 3 hours reaction time.

The Design-Expert software was used to determine and evaluate the coefficients of the full regression model equation and their statistical significance. The quadratic regression model used to predict the % JME conversion is shown in eq. 2. [16]

$$1/(JME) = +0.014 + 3.335E\text{-}004A + 1.967E\text{-}004B + 8.726E\text{-}005 - 2.328E\text{-}004\ AB - 9.621E\text{-}005AC - 7.335E\text{-}006BC - 3.946E\text{-}004\ A^2 + 2.871E\text{-}005\ B^2 - 3.209E\text{-}004\ C^2 \qquad (2)$$

Where is the response variable of % JME conversion and *A*, *B*, and *C* are the actual values of the predicted methanol/oil molar ratio, catalyst concentration and reaction time respectively.

Table 7: Experimental Results for the Central Composite Design

\	Run	Original Factors and Levels			Coded Factors and Levels			Yield
		A	B	C	X1	X2	X3	Y (%)
11	1	15	4.2098	4	0	-1.32	0	72.87
18	2	15	7.5	4	0	0	0	71.91
19	3	15	7.5	4	0	0	0	71.93
1	4	12	5	3	-1	-1	-1	81.93
10	5	18.948	7.5	4	1.316	0	0	73.18
7	6	12	10	5	-1	1	1	74.21
4	7	18	10	3	1	1	-1	74.14
3	8	12	10	3	-1	1	-1	75.89
14	9	15	7.5	5.3161	0	0	1.316	74.49
6	10	18	5	5	1	-1	1	73.77
2	11	18	5	3	1	-1	-1	73.46
20	12	15	7.5	4	0	0	0	71.9
15	13	15	7.5	4	0	0	0	72.03
13	14	15	7.5	2.6839	0	0	-1.32	75.29
17	15	15	7.5	4	0	0	0	71.71
9	16	11.052	7.5	4	-1.32	0	0	78.21
8	17	18	10	5	1	1	1	73.71
5	18	12	5	5	-1	-1	1	78.75
16	19	15	7.5	4	0	0	0	71.89
12	20	15	10.79	4	0	1.316	0	70.45

Analysis of Variance for the Response Surface Model

The results of analysis of variance (ANOVA) for the response surface model are shown in Table 3. The result shows that The Model F-value of 223.06 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of (Prob > F) less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, A^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The (Lack of Fit F-value) of 10.19 implies the Lack of Fit is significant.

Table.8: ANOVA for Response Surface Quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	4.55E-06	9	5.05E-07	223.06	< 0.0001	significant
A-Methanol/JWE	1.28E-06	1	1.28E-06	563.29	< 0.0001	
B-Catalyst wt.	4.44E-07	1	4.44E-07	195.9	< 0.0001	
C-Time	8.73E-08	1	8.73E-08	38.56	0.0001	
AB	4.33E-07	1	4.33E-07	191.45	< 0.0001	
AC	7.41E-08	1	7.41E-08	32.71	0.0002	
BC	4.30E-10	1	4.30E-10	0.19	0.6721	
A^2	1.09E-06	1	1.09E-06	479.3	< 0.0001	
B^2	5.74E-09	1	5.74E-09	2.54	0.1423	
C^2	7.17E-07	1	7.17E-07	316.84	< 0.0001	
Residual	2.26E-08	10	2.26E-09			
Lack of Fit	2.06E-08	5	4.12E-09	10.19	0.0118	significant
Pure Error	2.02E-09	5	4.05E-10			
Cor Total	4.57E-06	19				

There is only a 1.18% chance that a (Lack of Fit F-value) this large could occur due to noise. Significant lack of fit is bad -- we want the model to fit

Coefficient of Regression Analysis

Table 9 contains the result of the coefficient of regression analysis. The Coefficient of determination (R-Squared = 0.9950) shows that the fit of the model is good. The closer the value to unity, the better the empirical model fits the actual data. It implies that 99.50% of the total variability in the response is explained by the model.

The (Pred R-Squared) of 0.9435 is in reasonable agreement with the (Adj R-Squared) of 0.9906, That is to say the difference is less than 0.2. Which shows high accuracy of the model in predicting the yield of the biodiesel for given factor combination settings [39].

Adeq. Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. This ratio of 57.933 indicates an adequate signal. This model can be used to navigate the design space.

Table 9 Coefficient of Regression Analysis

Std. Dev.	4.758E-005	R-Squared	0.9950
Mean	0.014	Adj R-Squared	0.9906
C.V. %	0.35	Pred R-Squared	0.9435
PRESS	2.579E-007	Adeq Precision	57.933
-2 Log Likelihood	-355.23	BIC	-325.27
		AICc	-310.78
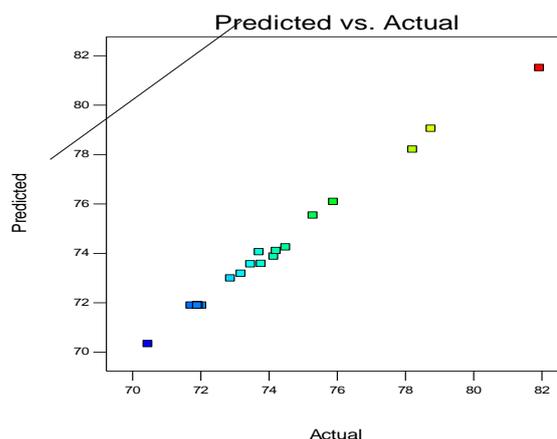
Figure 6. Parity chart for the model employed. Plot of predicted vs. actual value.

Figure 6 represents the actual results obtained from the experiments versus the predicted data by empirical model. The values of the adjusted determination coefficient (R^2 adj) and the determination coeffient (R^2) were 0.9906 and 0.9435, respectively. The high value of both coefficients justifies an excellent correlation between the independent variables and supports a high significance of the model. Meanwhile, the coefficient of variation was 0.35%. The relatively low value of the coefficient of variation reveals better reliability for this fitted model [16].

Interaction of variables

The effects of the process variables on the JME conversion were studied by plotting three-dimensional surface curves against any two independent variables while keeping the third variable at their central (0) level [16]. The 3D curves of the response from the effect of independent variables are shown in Figures 7(a)–7(c).

Figure 7(a) illustrates the effect of methanol/oil molar ratio and catalyst weight on % JME conversion at 4 hours reaction time. The result reveals that the % JME conversion decreases with increasing catalyst concentration and methanol/oil molar ratio. For the amount of catalyst, there is a significant negative effect on the transesterifiation of jojba oil to JME, due poor mixing of the reaction mixture hence aggregation and dilution of catalysts [1].

Figure 7(b) illustrates the effect of methanol/oil molar ratio and reaction time on % JME conversion at 7.5 catalyst weight. The % JME conversion increases with increasing reaction time and decrease with increasing methanol/oil molar ratio.
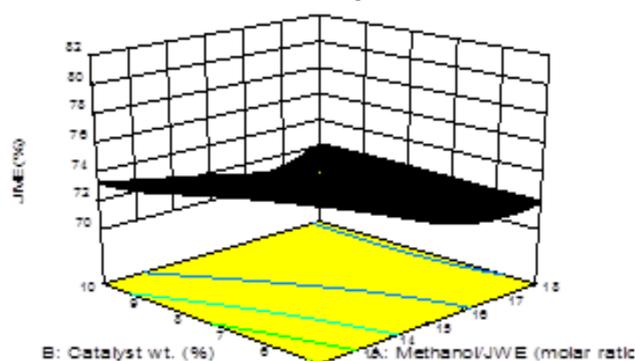
Figure 7(a). The effect of catalyst weight and methanol/oil molar ratio on % JME conversion at 4 hours reaction time
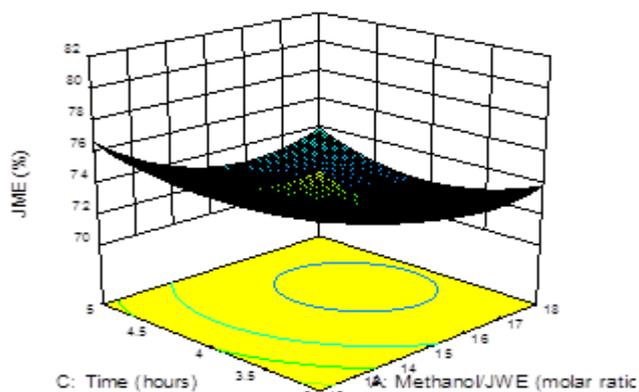
Figure 7(b). Effect of methanol/oil molar ratio and reaction time on % JME conversion at 7.5 catalyst weight

Figure 7(c) illustrates the effect of catalyst weight and reaction time on % JME conversion at 15:1 methanol/oil molar ratio. The % JME conversion increases when catalyst weight decrease and reaction time increase.

Then, there is a slight decrease when the reaction period is too long due to the influence of the reversible reaction in transesterification [16]. Too long reaction time resulted in the appearance of a white gel in the product, which increased the viscosity of the product and affected the purification process [40].
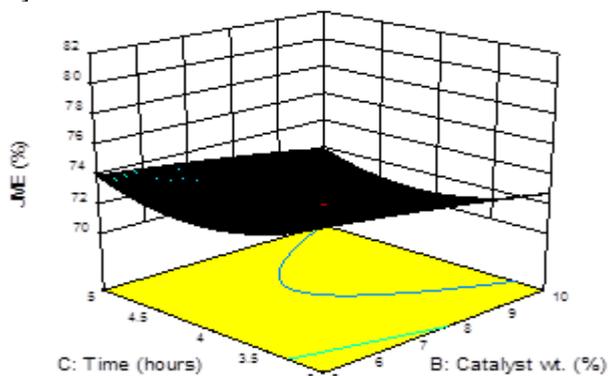
Figure 7(c). Effect of catalyst weight and reaction time on % JME conversion at 15:1 methanol/oil molar ratio.

IV. CONCLUSION

RSM was applied to the transesterifiation reaction between jojoba oil and methanol using a CaO as a heterogeneous catalyst. Experimental conditions such as methanol/oil molar ratio, catalyst weight and reaction time, were evaluated and optimal conditions for achieving the higher yields were evaluated The calcined corallined limestone rocks (catalyst) was characterized by The SEM, FTIR and HPGe gamma spectrometry. The catalyst showed excellent performance in biodiesel production.
The feedstock and produced biodiesel were characterized by FTIR and GC techniques. The physical, chemical and fuel properties of biodiesel were conformed to EN/ASTM standards.

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