# OPTIMIZATION OF TRANSESTERIFICATION PARAMETERS FOR OPTIMAL BIODIESEL YIELD FROM CRUDE JATROPHA OIL USING A NEWLY SYNTHESIZED SEASHELL CATALYST

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## Abstract

Heterogeneous catalysts are promising catalysts for optimal biodiesel yield from transesterification of vegetable oils. In this work calcium oxide (CaO) heterogeneous catalyst was synthesized from *Polymedosa erosa* seashell. Calcination was carried out at 900°C for 2h and characterized using Fourier transform infrared spectroscopy. Catalytic efficiency of CaO was testified in transesterification of crude Jatropha oil (CJO). A response surface methodology (RSM) based on five-level-two-factor central composite design (CCD) was employed to optimize two critical transesterification parameters catalyst concentration to pretreated CJO (0.01-0.03 w/w %) and the reaction time (90 min - 150 min). A JB yield of 96.48% was estimated at 0.023 w/w% catalyst and 125.76 min reaction using response optimizer. The legitimacy of the predicted model was verified through the experiments. The validation experiments conformed a yield of JB 96.4%±0.01% as optimal at 0.023 w/w% catalyst to pretreated oil ratio and 126 min reaction time.

Keywords: Biodiesel, Jatropha, Transesterification, Heterogeneous catalyst, Seashell.

## 1. Introduction

In recent years, depletion of the world's petroleum reserves and impact of environmental pollution caused by extensive combustion of fossil fuels, have gained importance in search of a substantial alternative energy resources such as biodiesel [1,2]. Biodiesel is a green energy resource, comprises mono alkyl ester of long fatty acids derived from biologically produced oils or fats including vegetable oils, animal fats and microalgae oils [3]. Many researchers have reported that bio-

**Abbreviations**

| | |
|---|---|
| ANOVA | Analysis of variance |
| CCD | Central composite design |
| CJO | Crude Jatropha oil |
| FFA | Free fatty acid |
| FT-IR | Fourier Transform Infrared |
| JB | Jatropha biodiesel |
| JBY | Jatropha biodiesel yield |
| JCL | *Jatropha curcas* Linnaeus |
| MeOH | Methanol |
| PE | *Polymesoda erosa* |
| RSM | Response Surface Methodology |

diesel can be used alone or blended with petro diesel to produce biodiesel blend. The blends depict similar characteristics as petro diesels and emits lesser hazardous emissions compare to that of fossil fuels [4]. At present major challenges were developing a biofuel with international specifications, without affecting the food demand.

Jatropha was chosen as feedstock due to its adaptability in tropical and subtropical climates in marginal and non-agriculture areas. Apart from that, the *Jatropha curcas* Linnaeus (JCL) seed are found to be toxic to human and animals [5,6]. JCL comes from Euphorbiaceous family. It is a fast-growing tree which has a life span of about or more than 50 years and contains 27% to 40% of oil in the seeds [7,8]. Biodiesel production from vegetable oils or animal fats, triglycerides transesterification using methanol was the most prominent among all other methods like direct use or blending, pyrolysis, micro-emulsion and transesterification [9]. In transesterification, triglycerides in vegetable oil will react with alcohol to form a mixture of fatty acid alkyl esters. Chung and co-researchers [10] have reported,  transesterification based on the amount of free fatty acids (FFA), both acidic-catalysts and basic-catalysts can be used and concluded that homogeneous catalysts were not recommended for oils which contains 3% to 40% FFA. Marchetti et al. [11] and Gubitz et al. [12] reported that homogeneous catalyst and FFA will interact to produce soap and hence the amount of catalyst available for the transesterification would be reduced, and also it complicates the down streaming separation and biodiesel purification. The earlier works by many researchers manifests that heterogeneous origin catalysts were more promising catalyst in biodiesel production and there is a substantial need for their synthesis from alternative sources.

The *Polymesoda erosa (*PE) species has been widely reported from the Indo-Pacific region and it is known as a prominent fishery source in the many islands of tropical and sub-tropical regions and locally it is called as Lokan [13]. Response Surface Methodology (RSM) is an emerging statistical and optimization technique which facilitates the user to expedite inter-relationships among the independent input parameters in interactions and also their impact on the dependent [14]. The central composite design (CCD) based RSM method was utilized to testify the transesterification process parameters optimization so as to optimize the biodiesel yield with different combinations of the factors and levels [15-17].

The aim of this study is to synthesize a heterogeneous base catalyst, CaO from a new source, PE seashells, for biodiesel production from crude Jatropha oil (CJO). A comprehensive investigation was carried out on the two step transesterification process parameters. The key reaction parameters Catalyst concentration-to-pretreated oil (0.01-0.03 w/w %) and reaction time (90-150 min) were considered for optimal Jatropha biodiesel (JB) yield from pretreated CJO. A CCD based two factor-five level RSM model was adopted to analyze the impact of input parameters on the JB yield.

## 2. Material and Methods

The research and experiments were conducted in a laboratory scale setup developed at the Faculty of Engineering, Universiti Malaysia Sarawak. Material used for biodiesel production were CJO, Methanol (MeOH) >99% pure), $H_2SO_4$ 95-97% pure, Potassium Hydroxide, and CaO from PE.

### 2.1. Calcium oxide catalyst synthesis

The PE shells were collected from a local villager's stall. The edible portion attached to the shells and other impurities were removed, and rinsed thoroughly with tap water followed by double rising with distilled water. Further they were dried in hot air oven at 105ºC for 24h. The dried PE shells were ground in an agate mortar until it is in a powder form. The shell powder is calcinated in an open furnace at 900ºC for 2h. At 850ºC, the calcium carbonate of PE shell powder decomposed to calcium oxide and carbon dioxide.

### 2.2. Catalyst characterization

In order to investigate the chemical structure of newly synthesized CaO catalyst, powder samples of CaO were tested using a Fourier Transform Infrared (FT-IR) Spectrophotometer (Model 100 series, Perkin Elmer) over a range of 4000 to 280 cm$^{-1}$ region.

### 2.3. Biodiesel production

Biodiesel production from CJO using newly synthesized CaO catalyst was carried out by using a standard laboratory procedure. Firstly acid pretreatment of CJO was carried out by designing an experimental protocol as reported by Deng et al. [18]. The FFA was estimated in terms of KOH in mg entail to neutralize one gram of fatty acid methyl ester. The process was repeated for three times to achieve accuracy in experimental results and finally the value of FFA was measured as 29.5%. Since, the FFA was greater than 4%, acid pretreatment is required and hence, biodiesel conversion was carried out using two-step transesterification [19,20] 25 ml CJO was heated over 100ºC to remove the water content in it. A mixture of sulphuric acid and methanol were prepared and added to the catalyst mixture then heated over 50ºC to 60ºC by using magnetic stirrer for 1 h, and allowed to settle down for one more hour. Methanol-water fraction was separated from the mixture and the remaining oil was washed using distilled water. The

pretreated oil was heated up to 100ºC with a magnetic stirrer to remove the excess water content present. Different proportion of acid catalyst over 1% to 6% to oil ratio by volume, was tested among 1% of sulphuric acid had shown the best result of which the FFA of the CJO sample was reduced to 1%.

Pretreated CJO as obtained from the optimum conditions in acid pretreatment which has less FFA value was selected to proceed with transesterification with CaO catalyst. A mixture of CaO catalyst concentration (0.01-0.03 w/w %) and 5 M solution of methanol was prepared. The contents were allowed to react at 60ºC with a variable reaction time of 90 min to 150 min., together with rigorous agitation using a magnetic stirrer. The mixture was shaken for 2h using an orbital Shaker at room temperature at a speed of 250 rpm. Further it was allowed to settle for 24h. The glycerol stocked at bottom layer was separated from the methanol-water fraction which was at the upper layer. The remaining biodiesel was washed by using distilled water and allowed to settle for 30 min to remove water from the lower layer by using a separation funnel. The filtered biodiesel was heated to 100ºC with a magnetic stirrer, to remove the water content and to get a pure biodiesel.

## 2.4. Design of experiments for maximum biodiesel yield

A two-factor five-level CCD based RSM was employed for design of experiments. In this study, the experimental model was made using two independent variables Catalyst-to-pretreated oil ratio and reaction time to investigate their effects on the dependent factor, JB yield, during second step of transesterification. The coded and uncoded (actual) levels of the independent variables were presented in Table 1. Two replications were carried out for all design points (factorial and axial) except the center points (0, 0) and the experiments were carried out in randomized order. Table 1 lists the range and levels of the two independent factors studied. The value of α (distance of the axial point from center point) for this CCD is fixed at 1.414.

The experimental data obtained was analyzed by the response surface regression procedure using a second-order polynomial Eq. (1) where Y is the response (percentage of JB yield); $x_i$ and $x_j$ are the uncoded independent factors and $\beta_0$, $\beta_i$, $\beta_{ii}$ and $\beta_{ij}$ are intercept, linear, quadratic and interaction constant coefficients respectively. Minitab16® Software was employed for response surface regression analysis of the model equation as well as evaluation of the analysis of variance (ANOVA). Confirmatory experiments were also performed to validate the equation.

$$Y = \beta_0 + \sum_{i=1}^{2} \beta_i x_i + \sum_{i=1}^{2} \beta_{ii} x_i^2 + \sum \sum_{i<j=1}^{2} \beta_{ij} x_i x_j \tag{1}$$

**Table 1. Levels of the factors chosen for the study.**

| Variable | Level | | | | |
|---|---|---|---|---|---|
| | -1.414 | -1 | 0 | 1 | 1.414 |
| C | 0.01 | 0.015 | 0.02 | 0.025 | 0.03 |
| T | 90 | 105 | 120 | 135 | 150 |

(C) Catalyst to pre-treated oil ratio; (T) Reaction time

## 3. Results and Discussion

### 3.1. CaO catalyst characterization analysis

FTIR spectrum of CaO nano-catalyst as synthesized from PE Shells was presented in Fig. 1. The most prominent peak of CaO was appeared at the region of 3645 cm$^{-1}$ and 1445cm$^{-1}$ due to the asymmetric vibration -OH and carbonyl group (C=O). The absorption band due to -OH group indicated that a small amount of moisture interacted with CaO during sampling [21]. The characteristic peaks as observed in the region of 1445cm$^{-1}$ correspond to the asymmetric stretching vibrations of carbonyl group (C=O). This result confirmed the formation of CaO [22].
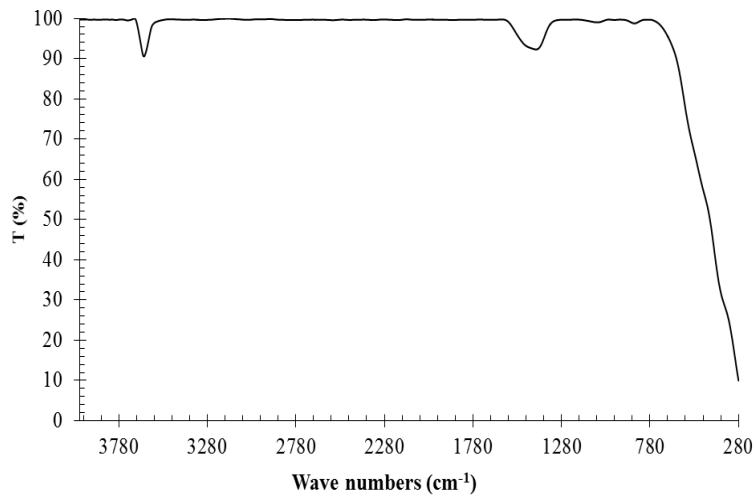


**Fig. 1. FTIR spectrum of CaO catalyst as synthesized from PE shells.**

### 3.2. Regression model

Experimental as well as predicted values of JB yield (JBY), obtained as response at the design points were shown in Table 2. A total of 13 experimental runs were conducted in randomized order to avoid the effect of uncontrolled factors. Table 2 shows, the range and levels of the two independent variables as well as complete experimental matrix of CCD.

Among $2^n$ factorial designs (n is the number of factors, each at two-levels) 4 runs correspond axial points with combination of the variables at either its lowest (-1.414) level or highest (1.414) level together with the other variables at zero. 5 runs were carried out at the center point to determine the experimental error and the reproducibility of the data.

Multiple regression coefficients of the model are indicated in Table 3, it shows the linear and quadratic terms of C, T are significant model terms. Using the coefficients determined the predicted model for percentage conversion is given in Eq. (2). The negative sign in front of a term indicates combative effect, while

positive sign coadjuvancy effect. Based on Eq. (2), Catalyst-to-pretreated oil ratio 'C' and reaction time 'T' shows positive effect on the yield of JB, however the interaction between these two variables 'CT' shows negative effect on the yield of JB. R-squared value for the developed correlation was found to be 0. 8214, implying that 82.14% of the total variation in the yield of JB is attributed to the experimental variables studied.

$$JB\ yield = +95.924 + 2.895C + 1.655T - 5.019C^2 - 3.434T^2 + 1.09CT \quad (2)$$

The regression model equation was found to provide a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the variables to the yield of JB. The adequacy of the model was also checked with ANOVA as shown in Table 4. Based on 99% confidence level, the model was tested to be significant as the computed. Effect of C and T on percentage JB yield is shown in contour plot of Fig. 2, were as the Fig. 3 shows the surface plot of percent JB yield.

**Table 2. Central composite design matrix for JB yield prediction.**

| Std. Order | Run Order | Point type | Variables: actual (coded) | | JBY% (Exp.) | JBY% (Pred.) |
|---|---|---|---|---|---|---|
| | | | C (w/w %) | T (min) | | |
| 5 | 1 | Axial | 0.010 (-1.414) | 120 (0) | 89.33 | 88.01 |
| 8 | 2 | Axial | 0.020 (0) | 150 (1.414) | 94.37 | 94.15 |
| 6 | 3 | Axial | 0.030 (1.414) | 120 (0) | 93.97 | 93.80 |
| 7 | 4 | Axial | 0.020 (0) | 90 (-1.414) | 92.1 | 90.84 |
| 9 | 5 | Center | 0.020 (0) | 120 (0) | 96.35 | 95.92 |
| 13 | 6 | Center | 0.020 (0) | 120 (0) | 96.53 | 95.92 |
| 2 | 7 | Fact | 0.025 (1) | 105 (-1) | 93.27 | 94.70 |
| 3 | 8 | Fact | 0.015 (-1) | 135 (1) | 91.92 | 93.46 |
| 4 | 9 | Fact | 0.025 (1) | 135 (1) | 95.42 | 95.81 |
| 1 | 10 | Fact | 0.015 (-1) | 105 (-1) | 88.68 | 91.26 |
| 12 | 11 | Center | 0.020 (0) | 120 (0) | 96.61 | 95.92 |
| 10 | 12 | Center | 0.020 (0) | 120 (0) | 96.43 | 95.92 |
| 11 | 13 | Center | 0.020 (0) | 120 (0) | 96.68 | 95.92 |

**Table 3. Regression coefficients of predicted quadratic polynomial model.**

| Term | Coefficient | SE Coef. | T value | P value |
|---|---|---|---|---|
| Constant ($\beta_0$) | 95.924 | 0.6381 | 150.321 | 0.000 |
| C ($\beta_1$) | 2.895 | 0.8873 | 3.263 | 0.014 |
| T ($\beta_2$) | 1.655 | 0.8873 | 1.865 | 0.104 |
| $C^2$ ($\beta_1^2$) | -5.019 | 1.2842 | -3.908 | 0.006 |
| $T^2$ ($\beta_2^2$) | -3.434 | 1.2842 | -2.674 | 0.032 |
| $C \times T$ ($\beta_{12}$) | -1.09 | 3.0736 | -0.355 | 0.733 |
| **S = 1.53682** | Press = 124.442 | | | |
| **R-Sq = 82.14%** | R-Sq(pred) = 0.00% | | R-Sq(adj) = 69.38% | |

**Table 4. Analysis of variance for optimal JB yield %.**

| Source | DF | Seq SS | Adj SS | Adj. MS | F | P |
|---|---|---|---|---|---|---|
| **Regression** | 5 | 76.016 | 76.016 | 15.203 | 6.44 | 0.015 |
| **Linear** | 2 | 33.360 | 33.360 | 16.680 | 7.06 | 0.021 |
| **C** | 1 | 25.143 | 25.143 | 25.143 | 10.65 | 0.014 |
| **T** | 1 | 8.217 | 8.217 | 8.217 | 3.48 | 0.104 |
| **Square** | 2 | 42.359 | 42.359 | 21.179 | 8.97 | 0.012 |
| **$C^2$** | 1 | 25.472 | 36.073 | 36.073 | 15.27 | 0.006 |
| **$T^2$** | 1 | 16.887 | 16.887 | 16.887 | 7.15 | 0.032 |
| **Interaction** | 1 | 0.297 | 0.297 | 0.297 | 0.13 | 0.733 |
| **$C \times T$** | 1 | 0.297 | 0.297 | 0.297 | 0.13 | 0.733 |
| **Residual Error** | 7 | 16.533 | 16.533 | 2.362 | | |
| **Lack-of-Fit** | 3 | 16.462 | 16.462 | 5.487 | 310.02 | 0 |
| **Pure Error** | 4 | 0.071 | 0.071 | 0.018 | | |
| **Total** | 12 | 92.549 | | | | |

Response optimizer was utilized to optimize critical parameters for optimal JB yield. According to Fig. 4 the optimal values were found to be 0.023 w/w% 'C' and 125.76 min 'T' and an optimal JB yield of 96.48% was estimated. To ensure the validity and accuracy of the estimated response, a series of transesterification experiments were performed at the optimal parametric levels 0.023 w/w% 'C' and 126 min 'T' and 96.4%±0.01% JB yield was reported consistently.
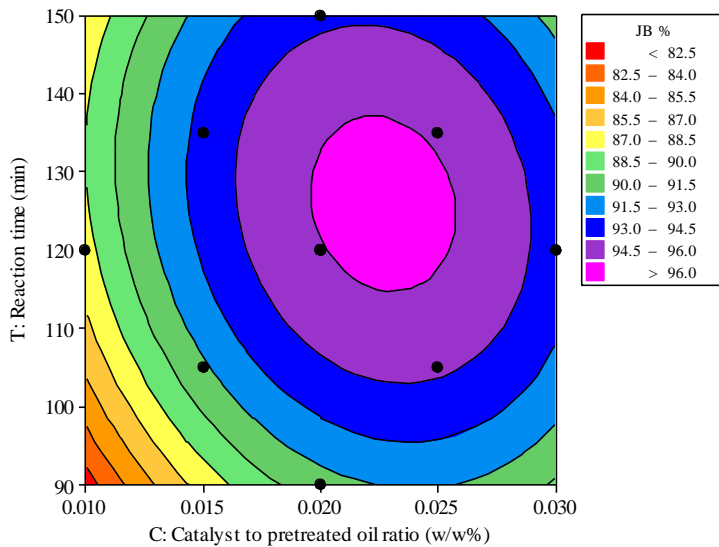


**Fig. 2. Contour plots of catalyst to pretreated oil ratio and reaction time effect on JB yield %.**
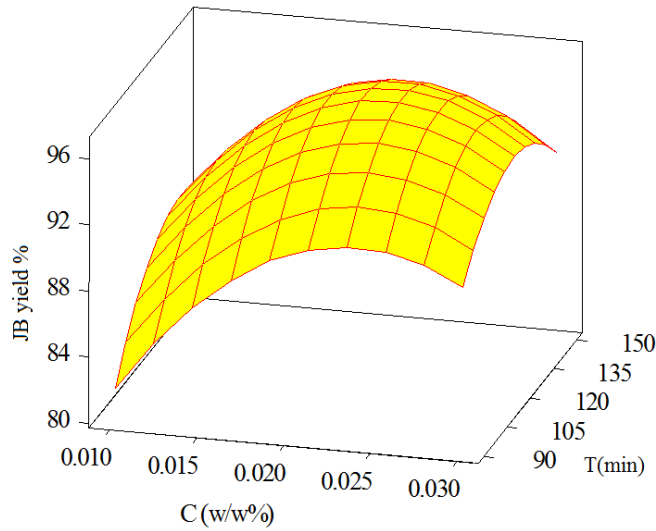
**Fig. 3. Surface plot of catalyst to pretreated oil ratio and reaction time effect on JB yield %.**
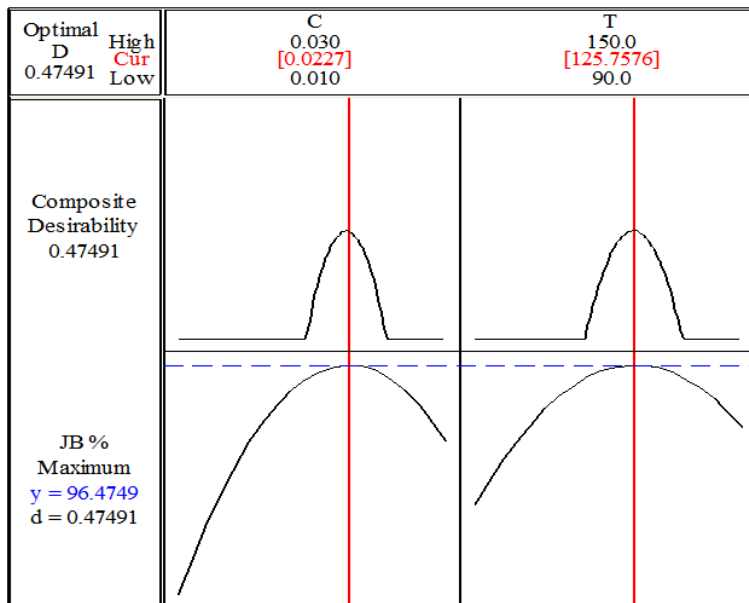


**Fig. 4. Optimization of JB yield % using response optimizer.**

## 4. Conclusions

From the present study, it can be concluded that a potential CaO catalyst was successfully synthesized from a new species, PE seashell. FTIR spectrographic

test conforms the CaO presence in the synthesized catalyst. CaO catalytic efficiency was investigated in production of JB from CJO using two step transesterification. A two-factor five-level CCD based RSM was utilized to optimize the critical two parameters so as to optimize JB yield. The study has shown an optimum yield of JB 96.4%±0.01% at 0.023 w/w% catalyst to pretreated oil ratio and 126 min reaction time.

## Acknowledgements

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