

# Optimization of Biodiesel Production from *Jatropha* Seed Oil, Using Sulphated Zirconia as Catalyst

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## Abstract

The depletion of fossils fuels and increasing demand of conventional energy worldwide had been the main concern of scientist nowadays, in the process to find the sustainable alternative. The biodiesel appears to be promising alternative. The optimization of biodiesel production from *Jatropha* seed oil using sulphated zirconia as catalyst was investigated based on Box-behnken design. The optimum yield 97.91% was obtained at 1:8 oil to methanol ratio, 60°C reaction temperature, 2.15 hrs, and 2 w/w% catalyst loads. The response surface regression shows the variables constant, oil to methanol ratio, reaction temperature, reaction time, reaction temperature\*reaction temperature and methanol to oil\*catalyst load were significantly affect the biodiesel yield. The model adequately accounts for the empirical relationships between biodiesel and process variables.

**Keywords:** Biodiesel; Sulphated zirconia; *Jatropha* oil; Optimization; Transesterification

## Introduction

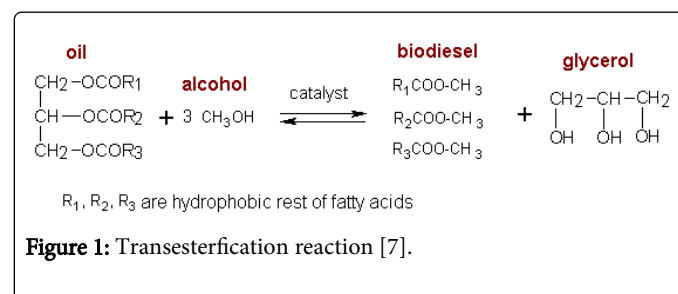
Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. The reaction requires a catalyst, which is usually a strong base, such as sodium or potassium hydroxide to produce new chemical compounds called methyl esters, this ester is also known as biodiesel [1]. Chemically, biodiesel is defined as mono alkyl esters of long chain fatty acids derived from renewable bio-lipids. It is typically produced through reaction of a vegetable oil or animal fat with methanol or ethanol in the presence of a catalyst to yield methyl or ethyl esters (biodiesel) and glycerol [2].

Generally, methanol is preferred for transesterification because it is less expensive than ethanol [3].

Biodiesel may be defined as a domestic and renewable fuel for diesel engines derived from vegetable biodiesel oil. Biodiesel is a clear amber-yellow liquid with a viscosity like petrol-diesel in a non-explosive form, it has a flash point of 423 K when compared to 337 K for petrol-diesel. Unlike petrol, biodiesel is biologically gradable and nontoxic, also reduces toxic significantly when burned in air as fuel. The production of biodiesel is more expensive compared to that of petrol-diesel, which is why there are less production and consumption of biodiesel [4].

The most common way to produce biodiesel is by transesterification of triglycerides of refined/edible types of oils using alcohol, in the presence of an acid or a basic catalyst [5]. In principle, although the transesterification is a reversible reaction, the back reaction does not occur or is negligible because the glycerol formed is not miscible with the biodiesel, leading to a two-phase system, similar yields of biodiesel can be obtained using either methanol (Figure 1). However, the reaction time is shorter in the methanolysis and is due to the physical and chemical properties of methanol which have short chain of alcohol and polar character. Instances are reported that the production of

biodiesel from castor oil was faster with methanol compared to ethanol [6].



## Materials and Methods

### Sampling

*Jatropha* seed was obtained from Sokoto Energy Research Centre, Usmanu Danfodiyo University Sokoto premises, Sokoto State, Nigeria.

### Sample preparation/Extraction of oil

The seed was sundried to remove moisture content and grinded to powdered form. The *Jatropha* oil extraction was carried out by Soxhlet extraction method, as stated by Akpan [8].

### Preparation of catalyst

The sulphated zirconia catalyst was prepared heterogeneously by a method called Ameliorated method as reported by Hara and Miyayama [9].

### Transesterification

The transesterification of *Jatropha* oil using sulphated zirconia was conducted under optimized condition. The optimization parameters of transesterification to be considered are oil to methanol ratio, reaction

temperature (°C), reaction time (hrs) and catalyst load (w/w%) which was observed at different level under the same agitation (600 rev/min).

Factors level	Units	Upper Level	Lower Level
Methanol to Oil ratio	-	8:01	6:01
Reaction temperature	°C	60	40
Reaction time	H	3	1.3
Catalyst load	w/w%	3	1

**Table 1:** Optimization parameters of the transesterification.

### Design of experiments

The experiment was designed using Box-Behnken design on Minitab 17 Statistical Software. The effect of four factors i.e., oil to methanol ratio, reaction time, reaction temperature and catalyst load (Table 1) at upper and lower level on yield were analyzed.

### Transesterification of the oil into biodiesel

The pretreated *Jatropha* oil (20 g) was placed in two necked round bottom flask, placed on hot plate magnetic stirrer heated to 50°C and

stirring at 600 rv/m. the methanol was mixed with 0.6 g (3 w/w%) catalyst load of sulphated zirconia in a beaker and heated to 40°C in water bath, then transferred into two necked round bottom flask containing oil. The reaction mixture under the same condition was allowed for 2.15 hrs. The mixture was then transferred into a separating funnel and allowed to separate overnight under gravity. Two distinct layers were observed, a dark bottom layer which is the glycerol and the light upper layer which is the biodiesel, in some cases when the layer did not separate distinctly enough, equal amount of distilled water and n-Hexane is added to aid the separation. After which the biodiesel was washed by adding 20% volume of warm distilled water and agitated gently for 5 minutes. The mixture could settle into a two layer from which the biodiesel was separated from the impurities, glycerol and water. The biodiesel was washed three times with distilled water to remove impurities and any remaining residual methanol [10]. The same procedure was applied for runs in the design. The biodiesel yield was calculated using equation 1.

$$\text{Biodiesel yield} = \frac{\text{Actual weight}}{\text{Theoretical weight}} \times 100 \quad (1)$$

### Results and Discussion

The results obtained from the optimized variables of biodiesel production from *Jatropha* seed oil is represented in the Table 2.

StdOrder	RunOrder	PtType	Blocks	Methanol to Oil ratio	Reaction Temperature	Reaction Time (hrs)	Catalyst Load	Yield (%)
43	1	2	1	7	60	3	2	85.56
25	2	0	1	7	50	2.15	2	81.76
45	3	2	1	8	50	1.3	2	90.05
47	4	2	1	8	50	3	2	90.44
54	5	0	1	7	50	2.15	2	81.7
53	6	0	1	7	50	2.15	2	88.22
24	7	2	1	7	60	2.15	3	95.55
48	8	2	1	7	40	2.15	1	72.77
50	9	2	1	7	40	2.15	3	73.73
6	10	2	1	7	50	3	1	84.12
14	11	2	1	7	60	1.3	2	80
12	12	2	1	8	50	2.15	3	69
27	13	0	1	7	50	2.15	2	88.31
9	14	2	1	6	50	2.15	1	90.23
32	15	2	1	7	50	1.3	1	72.11
52	16	0	1	7	50	2.15	2	87.9
4	17	2	1	8	60	2.15	2	90.16
42	18	2	1	7	40	3	2	79.62
2	19	2	1	8	40	2.15	2	75.77

1	20	2	1	6	40	2.15	2	66.33
38	21	2	1	6	50	2.15	3	82.24
46	22	2	1	6	50	3	2	84.84
23	23	2	1	7	40	2.15	3	73
37	24	2	1	8	50	2.15	1	91.34
26	25	0	1	7	50	2.15	2	87.9
35	26	2	1	7	50	3	3	85.9
8	27	2	1	7	50	3	3	86.03
28	28	2	1	6	40	2.15	2	67.1
51	29	2	1	7	60	2.15	3	95.5
31	30	2	1	8	60	2.15	2	97.91
49	31	2	1	7	60	2.15	1	94.34
15	32	2	1	7	40	3	2	78.9
21	33	2	1	7	40	2.15	1	72.79
3	34	2	1	6	60	2.15	2	82.37
10	35	2	1	8	50	2.15	1	96.1
18	36	2	1	8	50	1.3	2	90
11	37	2	1	6	50	2.15	3	82
7	38	2	1	7	50	1.3	3	77.9
5	39	2	1	7	50	1.3	1	80.23
30	40	2	1	6	60	2.15	2	81.58
33	41	2	1	7	50	3	1	84
41	42	2	1	7	60	1.3	2	80.22
17	43	2	1	6	50	1.3	2	72.77
13	44	2	1	7	40	1.3	2	62.76
16	45	2	1	7	60	3	2	85.51
19	46	2	1	6	50	3	2	84.88
29	47	2	1	8	40	2.15	2	76
36	48	2	1	6	50	2.15	1	83.25
20	49	2	1	8	50	3	2	90.5
22	50	2	1	7	60	2.15	1	93.99
40	51	2	1	7	40	1.3	2	59.89
44	52	2	1	6	50	1.3	2	81.99
34	53	2	1	7	50	1.3	3	83.76
39	54	2	1	8	50	2.15	3	70

**Table 2:** Box Behnken design with biodiesel yield obtained in each run.

### Optimization of transesterification reactions

The response surface regression was using to analyze the effect of the transesterification variables. The 'P' value was used to identify whether the variable or their interactions are statistically significant or not. The variable with p-value, greater than 0.05 is identified to be statistically insignificant and vice-versa. The correlation coefficient R<sup>2</sup> of the model is 71.13%, which indicates that the variable fits the model. The variables constant, oil to methanol ratio, reaction temperature,

reaction time, reaction temperature\*reaction temperature and oil to methanol ratio\*catalyst load were statistically significant on the biodiesel yield. The variables catalyst load, oil to methanol ratio\*oil to methanol ratio, oil to methanol ratio\*reaction time, oil to methanol ratio\*reaction temperature, reaction time\*catalyst load, and reaction temperature\*catalyst load have p-value greater than  $\alpha$ -value which shows that they are statistically insignificant on biodiesel yield (Table 3).

Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant	-	85.97	2.25	38.23	0.005	-
Methanol to Oil ratio	5.64	2.82	1.12	2.51	0.016	1
Reaction temperature	17	8.5	1.12	7.56	0.005	1
Reaction time (hrs)	7.39	3.69	1.12	3.28	0.002	1
Catalyst load	-3.39	-1.69	1.12	-1.51	0.14	1
Methanol to Oil ratio*Methanol to Oil ratio	-1.15	-0.58	1.69	-0.34	0.735	1.25
Reaction temperature*Reaction temperature	-9.34	-4.67	1.69	-2.77	0.009	1.25
Reaction time (hrs)*Reaction time (hrs)	-5.51	-2.76	1.69	-1.63	0.11	1.25
Catalyst load*Catalyst load	-0.77	-0.39	1.69	-0.23	0.82	1.25
Methanol to Oil ratio*Reaction temperature	1.44	0.72	1.95	0.37	0.713	1
Methanol to Oil ratio*Reaction time (hrs)	-3.52	-1.76	1.95	-0.9	0.372	1
Methanol to Oil ratio*Catalyst load	-9.8	-4.9	1.95	-2.52	0.016	1
Reaction temperature*Reaction time (hrs)	-6.26	-3.13	1.95	-1.61	0.116	1
Reaction temperature*Catalyst load	0.39	0.19	1.95	0.1	0.921	1
Reaction time (hrs)*Catalyst load	-1.38	-0.69	1.95	-0.35	0.725	1

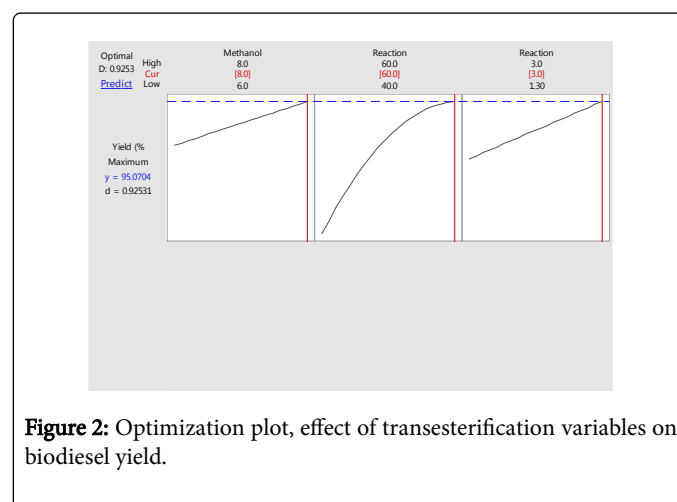
Coef=Regression Equation Coefficient, SE Coef=Standard Error Coefficients, T=t-Statistic and P-Value

**Table 3:** Factorial regression analysis of biodiesel yield (%) versus transesterification variables showing the estimate coefficient of the model.

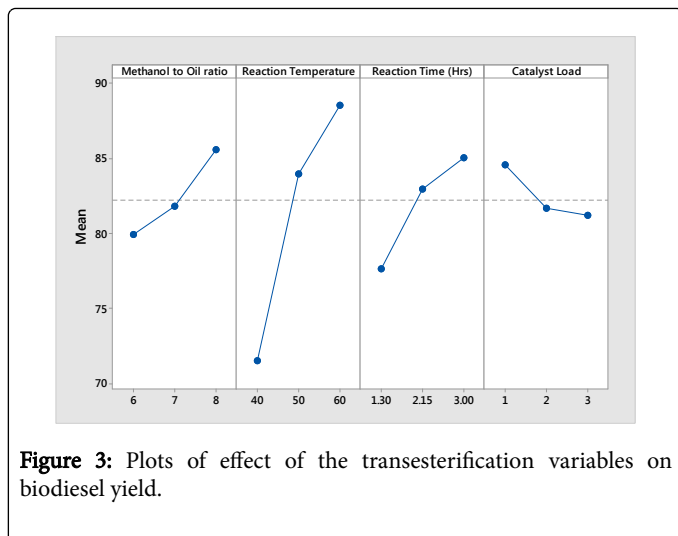
#### Regression Equation in Uncoded Units

Yield (%) = -85.8 + 2.82 Methanol to Oil ratio + 4.78 Reaction temperature + 4.34 Reaction time (hrs) - 0.0393 Reaction temperature\*Reaction temperature

The optimization plot as indicated in Figure 2, predicts the maximum yields (%) that can be determined as 98.95%, when target assigned at 97.91%. The condition of the transesterification variables to obtained the maximum yield as predicted by the statistical model (optimization plot) were (8:1) methanol to oil, 1 wt% catalyst load 60% temperature and 3 hrs reaction time with a prediction yield of 98.95% which is closely similar with experimental yield 97.91%, is clear that optimization of biodiesel production could be achieved through regression analysis using a known catalyst and other reaction variable.



**Figure 2:** Optimization plot, effect of transesterification variables on biodiesel yield.



**Figure 3:** Plots of effect of the transesterification variables on biodiesel yield.

The transesterification variables use for the Box-Bohnken design of the transesterification reaction of the optimization of biodiesel production from Jatropha seed oil are methanol ratio, reaction temperature, reaction time and catalyst load (Figure 3), their effect on the biodiesel yield are discuss as follows.

#### Effect of oil to methanol ratio on biodiesel yield

Figure 2 shows methanol to oil ratio increase from 6:1 to 8:1, the main biodiesel increases which may be due to the increase in the methanol, which was available to react with the oil to produce the biodiesel. The optimum yield was obtained at 8:1 methanol to oil ratio. Figure 3 which shows the interaction of oil to methanol ratio and reaction temperature on biodiesel yield, indicates that as the methanol to oil ratio increases from 6:1 to 8:1 with reaction temperature from 40 to 60°C, the yield of the biodiesel also increases toward optimum yield.

#### Effect of reaction temperature on biodiesel yield

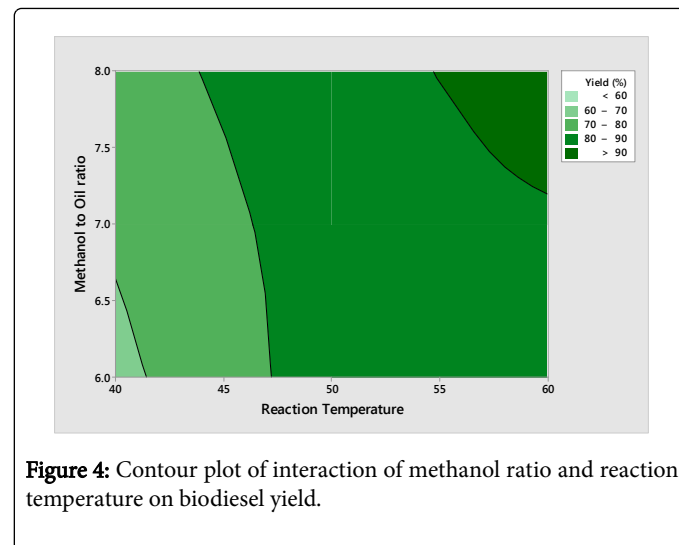
Figure 2 shows the effect of reaction temperature on biodiesel yield. As the temperature increases from 40 to 60°C, the biodiesel yield significantly increases. Initially, some thermal energy was needed for transesterification as the reaction was endothermic [11]. Since reaction mixture constitutes a three-phase system (methanol-oil-catalyst), the thermal energy was sufficiently needed to overcome the diffusion resistance between different phases. However, the high temperature is not preferred, as the temperature increase and reached the boiling point of methanol (64.70°C), the methanol immediately vaporize and form many bubbles, which inhibits the reaction on the two-phase interface and thus decreases the biodiesel yield [12].

#### Effect of reaction time on biodiesel

Figure 2 shows the effect of reaction time on biodiesel yield, as the reaction time increases from 1.3 to 3 hrs, the biodiesel yield rapidly increases until the reaction has reached equilibrium, beyond the optimum yield reaction time (2.15 hrs), the reaction reversibility of transesterification reaction [11].

Figure 4 shows interaction of catalyst load with the reaction time, as the reaction time increases from 1.0 to 1.5 hours with increase of catalyst load from 1 to 2.80 w/w%, the biodiesel yield remain

unchanged until above 2.8 w/w% catalyst load when the mean biodiesel yield increases (to the range of 80 to 90%), this may be due to availability of the catalyst to facilitate methoxy formation and lead to faster reaction which lead to formation of more methyl esters [10].

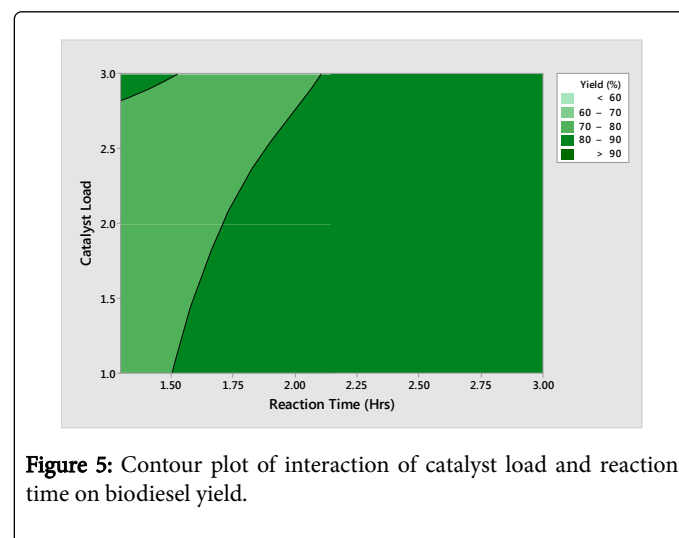


**Figure 4:** Contour plot of interaction of methanol ratio and reaction temperature on biodiesel yield.

As the catalyst load increases from 1.0 to 3.0 w/w% with increase in reaction time from 1.5 to 3 hours, the biodiesel yield significantly increases; this may be due to the increase in availability of acid side provided by S-ZrO<sub>2</sub> for transesterification reaction to speedily occur and enough time for the completion of the reaction [9].

#### Effect of catalyst load on biodiesel

Figure 2 indicates the decrease of the biodiesel yield with increase in the catalyst load. The optimum catalyst load was found to be 1 g with *Jatropha* biodiesel yield of 97.91%. The excess catalyst concentration increases the viscosity of reactant which also lower biodiesel yield as reported by Yang [13]. Figure 4 shows the effect of interaction of catalyst load with reaction time on biodiesel yield. It indicates that as the reaction time increases from 1.5 to 3 hrs at 1 w/w% catalyst load the biodiesel yield increases but as the catalyst load go beyond 1 w/w% the yield decreases and Figure 5 shows the Contour plot of interaction of catalyst load and reaction time on biodiesel yield.



**Figure 5:** Contour plot of interaction of catalyst load and reaction time on biodiesel yield.

## Conclusion

Optimization of the transesterification reaction of *Jatropha* seed oil to biodiesel using Box-behnken design was a success and able to produce the optimum yield of 97.91% at optimum transesterification variables were 60°C, 2.15 hrs, 1:8 and 2 w/w%. The model adequately accounts for the empirical relationship between biodiesel and process variables. The response surface regression shows the variables constant, oil to methanol ratio, reaction temperature, reaction time, interaction of reaction temperature\* reaction temperature and methanol to oil ratio\*catalyst load were statistically significant on the biodiesel yield.

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