Optimization of Biodiesel Production from Castor Seed Oil Using NaOH Catalyst

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Abstract: *This research work optimized the production of biodiesel from castor seed oil using NaOH catalyst. The castor seed oil was mix with methanol and NaoH catalyst to undergo a tranesterification reaction. The characterization of the castor seed oil was done using American Society forTesting Materials (ASTDM). The transesterification reaction was repeated with varying catalyst weight, oil to methanol ration, reaction time and reaction temperature. The biodiesel produced was characterized and compared with fossil Diesel fuel. High-Performance Liquid Chromatography (HPLC) was used to analyze the various biodiesel samples produced to identify the level of conversion to methyl ester and also identify the component mixture of the fatty acid methyl esters (FAMEs). Central Composite Design (CCD) was used to optimize the reaction process. Optimal value of the reaction shows a high conversion of 94.68%. The effects of process variables were also studied with regard to conversion. This research work has shown that catalyst play a major role in biodiesel production both in conversion and in quality.*

1. Introduction

Research has been conducted and is still ongoing for alternative renewable energy sources such as solar energy, wind and hydro energy and most importantly on biofuels [8]. Among the biofuels, biodiesel seems to be at the forefront because of its environmental credentials such as renewability, biodegradability and clean combustion behavior essentially free of sulphur and aromatics. [5]

However, it is widely accepted that bio fuels are neither a panacea, nor without their disadvantages and risks. Major drawback is that converting edible vegetable oils like sunflower, soybean, peanut, palm oil to fuel will almost certainly compromise food security (especially within the global market context).The vegetable-oil derivative 'biodiesel' offers several advantages as an alternative fuel for diesel engines. These include improved fuel performance and lubricity, a higher octane rating than petro-diesel, a higher flashpoint that makes it safe to handle [5][13][4]. It is a local renewable source of energy and highly biodegradable [9].

Biodiesel is one of the easiest alternatives to fuel, the main feedstock for biodiesel fuel are; Virgin oil feedstock, Vegetable oil, Animal fats, Algae. Castor seed oil as a vegetable oil has widely being considered as a feed stock due to its high oil yield and as a none- edible oil. Under normal conditions, the reaction of biodiesel feed stock to produce biodiesel reaction will proceed either exceedingly slowly or not at all, so heat, as well as catalysts (acid and/or base) are used to speed the reaction. It is important to note that the acid or base are not consumed by the transesterification reaction, thus they are not reactants, but catalysts. Catalysts are thus known to be a major determining factor in biodiesel product and viability of its use as an alternative to fossil fuel diesel.

A comparative and a process optimization study of the transesterification catalytic processes which is an important goal in improving the quality and reducing production costs in biodiesel production processes needs to be investigated [10]

Consequently, since biodiesel can be produced from varied feed stocks resulting in biodiesel with different properties, it has become necessary to have a standard that will serve as a point of reference for biodiesel that is produced from all feed stocks in terms of material and operating parameters to guarantee engine performance without difficulty. The biodiesel produced is not classified as diesel fuel substitute unless they meet the requirements established by standards. Thus the need for comparison of some standard parameters.[2]

2. Materials and Methods

Sample Collection and Preparation
The castor seeds used for this work was obtained in Kapil – Lankan District in Pankshin LGA of Plateau State Nigeria. They were prepared for oil extraction by Cleaning, Drying, Winnowing and Grinding.

Castor oil extraction and pre-treatment
Kemtech America synthware Soxhlet Extractor 40MM ID was used to extract oil from the castor seed grinded paste.
The extracted crude castor seed oil was pretreated with strong NaOH (0.5N) to neutralize the crude oil removing the high FFA in the crude oil sample.

Physiochemical and Fatty Acid Profile Analysis of Castor Seed Oil Feed Stock
The physiochemical properties of the pre treated castor seed oil was determined following standard methods, while the Fatty acid profile was determined using Gas chromatography; Shimadzu Gas Chromatograph-Mass Spectrometer (GCMS-QP 2010 Plus) With a flame ionization detector (FID).

Biodiesel Production and Washing
200ml of castor seed oil and 40 ml of methanol (i.e 20% by volume of oil) were utilized in the batch production. 200 ml of castor seed oil was pre-heated to a steady temperature of 60°C using a magnetic heater/stirrer. With the aid of the measuring cylinder 40 ml of methanol was measured and poured into the beaker. 0.5g of NaOH was measured and

added to the methanol. The content of the beaker was stirred vigorously using the second magnetic stirrer until the NaOH was completely mixed in the methanol. The mixture formed is called sodium Methoxide. The Methoxide was poured into the conical flask containing the preheated oil. The content of the conical flask was stirred with the magnetic stirrer at a steady speed and temperature of 55°C. Then heating and stirring was stopped after 2.5 hours and the product was poured into a separating funnel mounted on a clamp stand. The mixture was allowed to settle down for about 20 hours. The separating funnel was opened at the bottom allowing the glycerin at the bottom to be run off after which the biodiesel was collected in a beaker after which it was poured into a container for storage. The experimental procedure was repeated at different varying temperatures, reaction time, catalyst weight and molar ratio of methanol.

After separation from the glycerin layer, the FAME layer was purified by washing with warm distilled water until the warm water leaving the funnel remained clear as it was before being introduced into the funnel and the oven dried at 120°C.

The biodiesel produced was analyzed using HPLC equipment (Agilent 120 series MWD) to determine the composition by percentage of FAME in each sample and subsequent characterized using standard methods.

3. Results and Discussion

Result of Physiochemical Analysis of castor seed oil feed stock
The physical and chemical characterization was accomplished following American Standard of Testing Materials ASTM, (1984) and the International Organization for Standardization (ISO).The physiochemical characteristic are shown in Table 1while the Acid profile are shown in Table 2. It follows a similar study by Marter 1981[7], that identified castor seed oil as pale straw colour oil with high %FFA which was reduced as a result of the pre treatment of the oil.

The fatty acid profile (table 2) revealed that Ricinoleic acid was higher in percentage composition as against other acid with 89.5% composition in the oil sample after pre-treatment. This agrees with an investigation by Shrirame et al 2011[11], which puts Ricinoleic acid as the major fatty acid content in castor seed oil.

Table 1: Physiochemical characteristic of pre treated castor seed oil

Characteristics	Test
Appearance @ 25°C	Pass
Odour	Pass
Free Fatty Acid %	0.985
Specific Gravity @ 25°C	0.961
Saponification value	180.08
Iodine value	86
Calorific value	40.76
Acid value	1.97
viscosity@ 40°C (St/dpas)	9.5

Table 2: Fatty Acid Profile of castor seed oil sample feed stock

Faty Acid Name	Actual %
Ricinoleic Acid	89.5
Oleic Acid	5
Linolenic acid	3.5
&- linolenic Acid	0.5
Stearic Acid	0.4
Palmitic Acid	0.5
Dihydroxystearic Acid	0.3
Others (unknown)	0.3

Results of Characterization of Biodiesel Sample
The characterization of the biodiesel sample was done following American Standard of Testing Materials ASTM, (1984) and the International Organization for Standardization (ISO), taking the sample with the highest FAME conversion table 3. The properties of the biodiesel sample as compared with fossil fuel are in line with prior investigation by Anton et al 2008.[1]

Table 3: Result of Physiochemical Analysis of different biodiesels samples compared to petro-diesel

Characteristics	Units	Biodiesel	Fossil Diesel Fuel	Reference (ASTM D6751)
FAME	%	93		
Density	Kg/m³	892	848	860-900
Viscosity	mm²/s	3.8	2.37	3.5-5.0
Flash Point	°C	132	70	120-130
Calorific Value	MJ/kg	41.9		42
Cetane Number		49.4	41	51min
Water content	mg/kg	360	26.2	500max
Acid value	mgkoHg	0.25	0.002	0.05max
Iodine Value	gI₂/100g	88		120max

Modeling and Optimization
Central Composite Design (CCD) of Response surface methodology (RSM) was used to successfully optimize the biodiesel production process and conditions for the catalyst CCD at fractional factor level (½ or small) was used.
The design matrixes together with the experimental response values are presented in Tables 4 below

Table 4: Experimental data for the conversion of biodiesel obtained from the central composite experimental design (CCD)

Std	Factor 1 A:Temperature	Factor 2 B:molar ratio	Factor 3 C:Catalyst weight	Factor 4 D:Reaction time	Response 1 conversion
	Deg K		%	Minutes	%
1	343.1	12.2	5	30	57.12
2	343.1	12.2	1	30	44.12
3	343.1	3.8	5	80	70.47
4	322.9	12.2	1	80	67.13
5	343.1	3.8	1	80	69.12
6	322.9	3.8	5	30	92.56
7	322.9	12.2	5	80	92.87
8	322.9	3.8	1	30	83.22
9	318.7	8	3	55	60.63
10	347.3	8	3	55	91.57
11	333	2.1	3	55	79.28
12	333	13.9	3	55	93.24
13	333	8	0.17	55	57

14	333	8	5.83	55	74.86
15	333	8	3	19.7	81.74
16	333	8	3	90.3	93.77
17	333	8	3	55	90.63
18	333	8	3	55	84.12
19	333	8	3	55	91.54
20	333	8	3	55	82.17
21	333	8	3	55	83.25

Analysis of Variance (ANOVA)

The ANOVA results as presented in Tables 5 with an F-value of 22.54 it show that the lack of fit P-value was greater than 0.05. The CV value obtained was 3.88%, a CV value less than 10% shows that the model is reproducible [3]

Table 5: Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value	Prob> F
Model	4078.73	14	291.34	22.54	0.0005	significant
A-Temperature	478.59	1	478.59	37.03	0.0009	
B-molar ratio	97.44	1	97.44	7.54	0.0335	
C-Catalyst weight	464.91	1	464.91	35.97	0.001	
D-Reaction time	72.36	1	72.36	5.6	0.0558	
AB	5.47	1	5.47	0.42	0.5395	
AC	53.72	1	53.72	4.16	0.0876	
BC	98.35	1	98.35	7.61	0.0329	
CD	2.82	1	2.82	0.22	0.6569	
A^2	221.1	1	221.1	17.11	0.0061	
B^2	0.04	1	0.04	3.07E-03	0.9576	
C^2	897.51	1	897.51	69.44	0.0002	
D^2	5.84	1	5.84	0.45	0.5265	
Residual	77.55	6	12.92			
Lack of Fit	0.24	2	0.12	6.22E-03	0.9938	Not significant
Pure Error	77.31	4	19.33			
Cor Total	4156.28	20				

Std. Dev.	3.03	R-Squared	0.9779
Mean	78.11	Adj R-Squared	0.9558
C.V. %	3.88	Pred R-Squared	0.9416
PRESS	242.88	Adeq Precision	23.234
-2 Log Likelihood	90.59	BIC	124.08
		AICc	141.92

Final Equation in Terms of Coded Factors:

The final equation in terms of coded factors for the reaction is represented in equation below. P-values less than 0.05 indicate that the model term is significant[12]. Thus the significant model terms are A, B, C, D, AB, AC, BC, CD, A^2, C^2

Conversion = 86.637 + 10.938A + 4.935B + 6.224C + 3.298D - 2.591AC + 11.701AD + 3.506BC + 22.807BD – 4.9144A^2 - 10.00104C^2

Normal Probability Plot of the Models

The normal probability plot identify and substantiate departures from normality [6]. Figure 1 shows that the data were closely distributed on the straight line of the plots for the models.
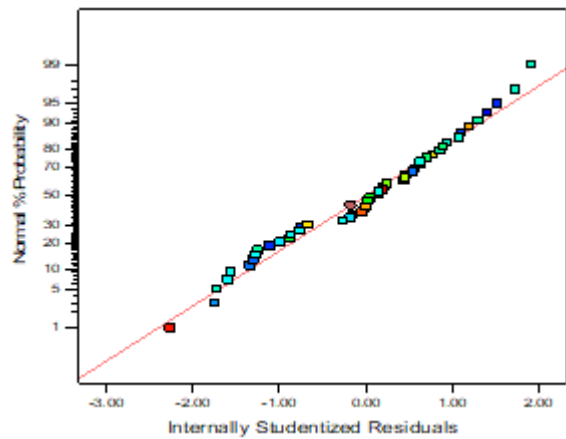

Figure 1: Normal plot of residuals for NaOH catalyzed reaction

Predicted and Actual Plots

The predicted vs actual plot shows how the model predicts over the range of data:
 The Plot exhibits random scatter about the 450 line showing a good prediction. The plots equally confirm that the selected model was adequate in predicting the response variables in the experimental values (Figure 2)
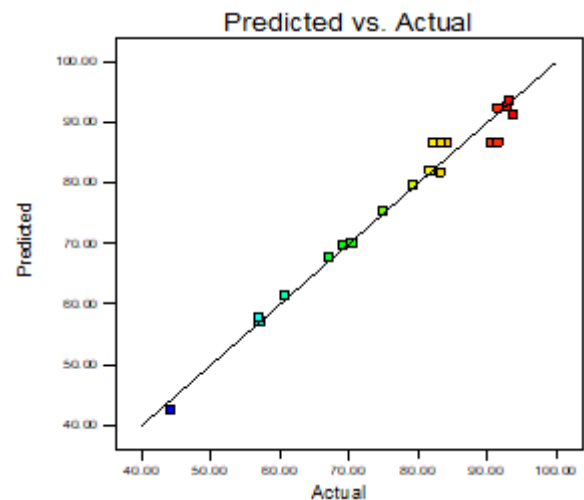

Figure 2: Predicted Vs Actual plot for NaOH catalyzed reaction

Three Dimensional (3-D) Response Surface Plots

 Figures 3 presents the 3-D response surface plots. The interactive effect given in Figure 3a between temperature and molar ratio reveals that percentage conversion is favored by a slight increase in both temperature and molar ratio. Also, the interaction between catalyst weight and temperature (Fig 3b) indicates that a gradual increase in both catalyst weight and reaction temperature gives a good conversion. Similarly interaction between catalyst weight and molar ratio (Fig 3c) shows that high percentage conversion is favored by a high catalyst weight and a higher molar ratio, a further increase in both variables leads to excess conversion above the model predicted value. (Fig 3d) shows the interaction between reaction time and catalyst weight and a high conversion is a function of high reaction time.
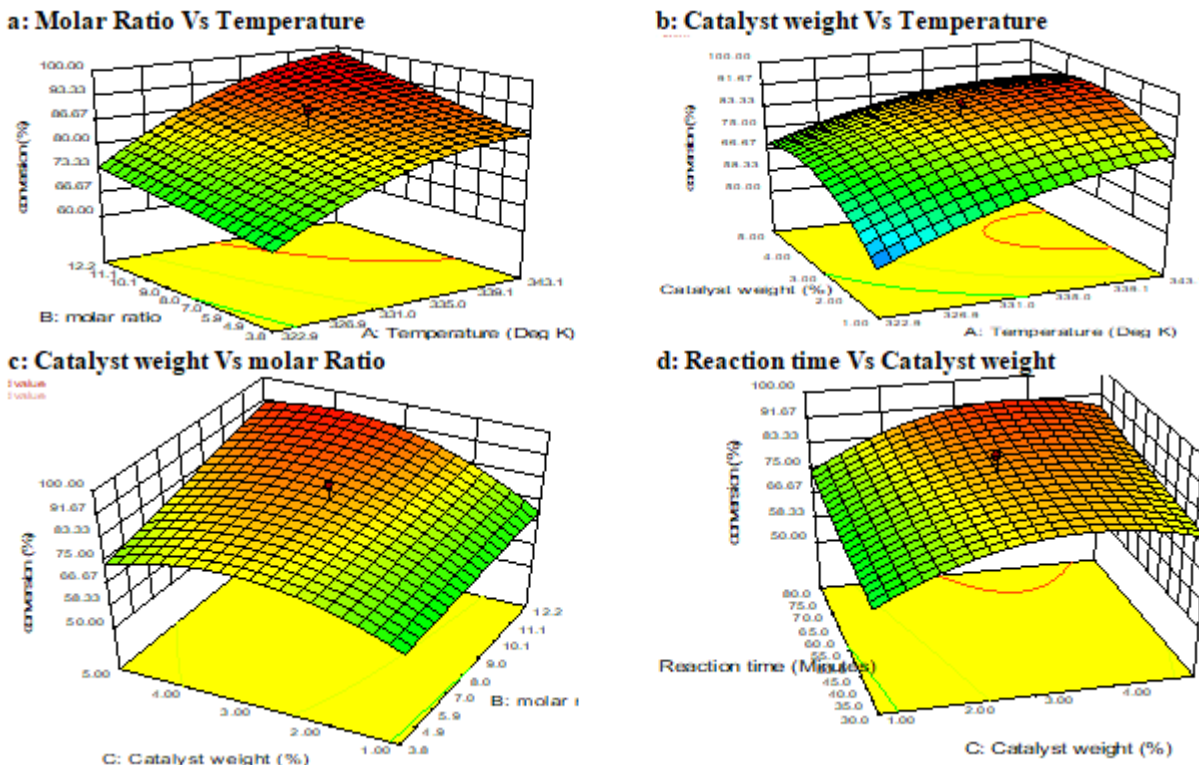
Figure 3: 3D plot for NaOH catalyzed reaction

Effects of Process Variables on Biodiesel Conversion

Figure 4 shows how each of the process variables affect the conversion. Figure 4a shows high decline in conversion after the optimum temperature of 333.15k, this could be as a result of the fact that high temperature does not favour alkaline catalyst conversion. Figure 4b shows the response to change in molar ratio which shows no significant changes after the initial slight increase in conversion percentage. Figure 4c illustrates the effect of catalyst weight on conversion; this shows a steady increase in conversion as the catalyst weight increases and a gradual decline in conversion as the percentage catalyst weight increases after the optimal level. Finally figure 4d shows the effect of reaction time on conversion. It can be seen that the reaction tend to maintain a steady rate as time increases after the initial sharp increase within the first 30mins.
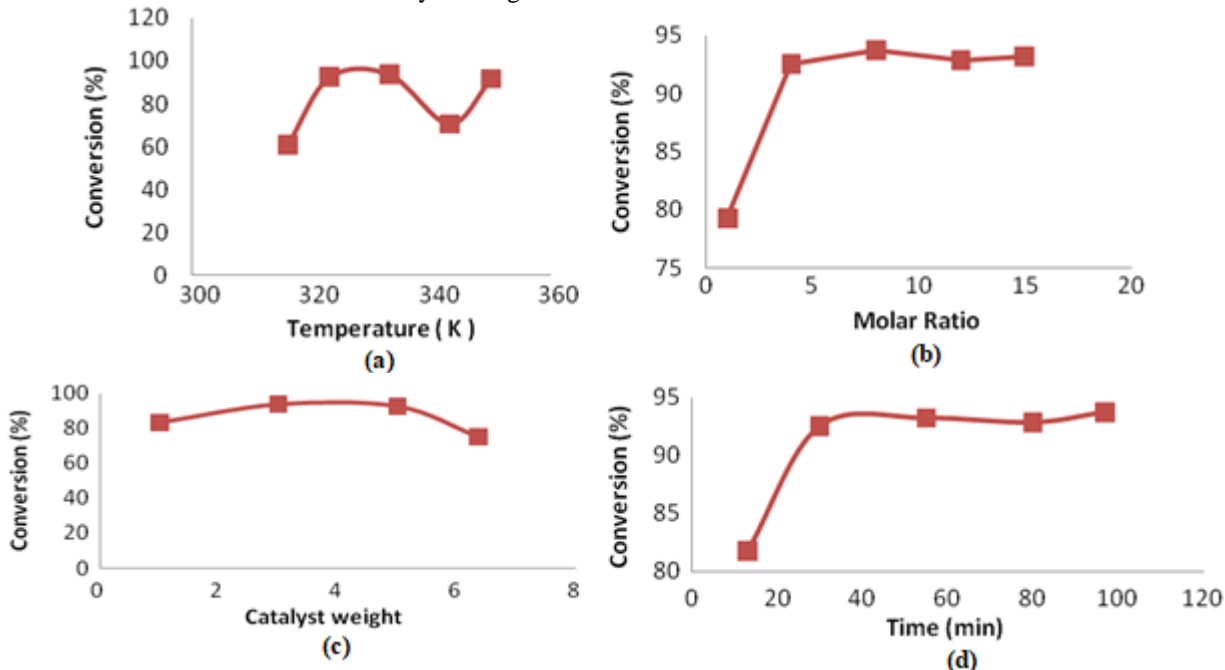

Figure 4: Effects of process variables on Biodiesel Conversion

Model Validation

The determination of the optimum levels of the transesterification reaction processes factors for maximizing the production of biodiesel is one of the primary objectives of this optimization study. A combination of the experimental and predicted optimum values for the

processes is presented in Table 6. The experimental values obtained were closely related to the predicted results obtained at the optimum conditions. This confirms the significance of the models developed.

Table 6: Predicted and Experimental validated results of the reaction process

Variables	Reaction Temp. (K)	Molar Ratio	Catalyst Conc. (wt%)	Reaction Time (min)	Conversion (%)
Predicted	324.45	3.95	4.69	30.26	94.68
Validatede	324.5	4:1	4.7	30.3	95.48

4. Conclusion

The production of biodiesel from castor seed oil using NaOH catalyst was successfully optimized. Also it was ascertained that reaction parameters; such as the quantity of catalyst, amount of methanol, reaction temperature and the reaction time affected the production and yield of methyl esters significantly with catalyst weight playing a major role. Response surface methodology (RSM) was also successfully applied for the transesterification of methanol using Central Composite Design (CCD). This showed a conversion of 93.931% at optimum conditions.

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