International Journal of Progressive Sciences and Technologies (IJPSAT)
ISSN: 2509-0119.

http://ijpsat.ijsht-journals.org
Vol. 22 No. 1 August 2020, pp. 97-104

The Effect of H_2PO_4 Catalyst on Biodiesel Production from Castor Seed Oil

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Abstract – This research work studied the effect of H_2PO_4 catalyst on biodiesel production from castor seed oil. The Castor seed oil was mix with methanol and H_2PO_4 catalysts to undergo a tranesterification reaction. The characterization of the castor seed oil was done using American Society Testing Methods (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). Kinetics study revealed by the experimental data from the transeterification reactions, showed best conformity to a pseudo second-order kinetic model. Central Composite Design (CCD) was used to optimize the reaction process. Optimal value of the reaction shows a conversion of 62.60%. H_2PO_4 catalyst was found to be an effective transesterification catalyst.

Keywords – High-Performance Liquid Chromatography, Transesterification, Fatty acid methyl esters, Central Composite Design, Miscella.

I. INTRODUCTION

The resent dwindling in petroleum reserves and instability in crude price has led to a considerable debate among world leaders about the future of petroleum based fuels and the need for alternative energy sources.

Alternative renewable energy sources such as solar energy, wind and hydro energy and most importantly on biofuels have being investigated [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. This is Majorly the fact that converting edible vegetable oils like sunflower, soybean, peanut, palm oil to fuel will certainly compromise food availability.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].

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. 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.

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]

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II. Materials And Methods

2.1 Sample Collection and Preparation

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

2.2 Castor oil extraction

The castor oil was extracted using Kemtech America synthware Soxhlet Extractor 40MM ID with 300ml of normal Hexane as solvent for every 10g of crushed castor seed paste. At the end of the extraction process, the resulting mixture (miscella) containing the oil was heated to recover solvent from the oil and the oil pre treated with NaOH.

2.3 Fatty Acid Profile and Physiochemical analysis of Castor Oil Feed Stock

The Fatty acid profile was determined using Gas chromatography; Shimadzu Gas Chromatograph-Mass Spectrometer (GCMS-QP 2010 Plus) With a flame ionization detector (FID) while the physiochemical properties of the pre treated castor seed oil was determined following standard methods.

2.4 Transesterification Process using H_2PO_4 Catalyst

A mixture of castor oil and methanol (20% by volume of oil) were utilized in the batch production process. The 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 methanol was measured and poured into the beaker. 0.5g of H_2PO_4 was measured and added to the methanol. The content of the beaker was stirred vigorously using the second magnetic stirrer until the H_2PO_4 was completely mixed in the methanol. The mixture formed is called a 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 and the FAME produced purified with warm distilled water and dried.

The biodiesel produced was also 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.

III. Results And Discussion

3.1 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 put 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

FATTY 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

3.2 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]

Table3. Result of Physiochemical Analysis of the biodiesel sample compared to petro-diesel

CHARACTERISTICS	UNITS	BIODIESEL	FOSSIL DIESEL FUEL	REFERENCE (ASTM D6751)
FAME	%	62.4		
Density	Kg/m^3	867	848	860-900
Viscosity	mm^2/s	4.1	2.37	3.5-5.0
Flash Point	^oC	140	70	120-130
Calorific Value	MJ/kg	- 8		42
Cetane Number		41.89	41	51min
Water content	mg/kg	48	26.2	500max
Acid value	mgkoHg	370	0.002	0.05max
Iodine Value	$gI_2/100g$	0.42		120max

3.3 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)

	Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	A:Temperature	B:molar ratio	C:Catalyst weight	D:Reaction time	conversion
	Deg K		%	Minutes	%
1	343	12	5	30	45.24
2	343	12	1	30	41.53
3	343	4	5	80	48.06
4	323	12	1	80	47.64
5	343	4	1	80	46.73
6	323	4	5	30	55.87
7	323	12	5	80	54.2
8	323	4	1	30	49.99
9	316	8	3	55	46.19
10	350	8	3	55	48.2
11	333	1	3	55	49.13

12	333	15	3	55	49.13
13	333	8	0.35	55	44.58
14	333	8	6.36	55	48.46
15	333	8	3	13	49.57
16	333	8	3	97	62.46
17	333	8	3	55	52
18	333	8	3	55	51.98
19	333	8	3	55	52.23
20	333	8	3	55	49.88
21	333	8	3	55	51.58

3.4 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]

ANOVA for Response Surface Reduced Quadratic model						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**Df**	**Square**	**Value**	**Prob> F**	
Model	381.76	12	31.81	48.38	< 0.0001	significant
A-Temperature	42.02	1	2.02	73.07	0.0011	significant
B-molar ratio	47.86	1	47.86	75.54	< 0.0001	significant
C-Catalyst weight	56.45	1	56.45	85.85	< 0.0001	significant
D-Reaction time	83.08	1	83.08	126.35	< 0.0001	significant
AB	36.84	1	36.84	56.03	< 0.0001	significant
AC	6.84	1	6.84	10.41	0.0121	significant
AD	7.86	1	7.86	11.95	0.0086	significant
BD	49.96	1	49.96	75.99	< 0.0001	significant
A^2	33.18	1	33.18	50.47	0.0001	significant
B^2	9.6	1	9.6	14.6	0.0051	significant
C^2	59.23	1	59.23	90.08	< 0.0001	significant
D^2	39.45	1	39.45	60	< 0.0001	significant
Residual	5.26	8	0.66			
Lack of Fit	1.62	4	0.41	0.45	0.7734	not significant
Pure Error	3.64	4	0.91			
Cor Total	387.02	20				

Std. Dev.	0.81	R-Squared	0.9864
Mean	49.75	Adj R-Squared	0.966
C.V. %	1.63	Pred R-Squared	0.9292

PRESS	27.42	Adeq Precision	32.033
-2 Log Likelihood	30.52	BIC	70.1
		AICc	108.52

3.5 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, AD, BD, A^2, B^2, C^2, D^2

$$Conversio = 51.50 + 0.60(A) + 0.39(B) + 2.16(C) + 3.83(D) + 3.51(AB) - 0.94(AC) + 1.52(AD) + 4.01(BD) - 1.50(A^2) - 0.81(B^2) - 2.31(C^2) + 1.62(D^2)$$

3.6 Normal Probability Plot of the Model

The normal probability plot identifies and substantiates departures from normality [6]. Figure 1 show definite pattern like an 'S-shaped' curve. This suggests adequate models within the range of experimental data studied and normality of assumption.

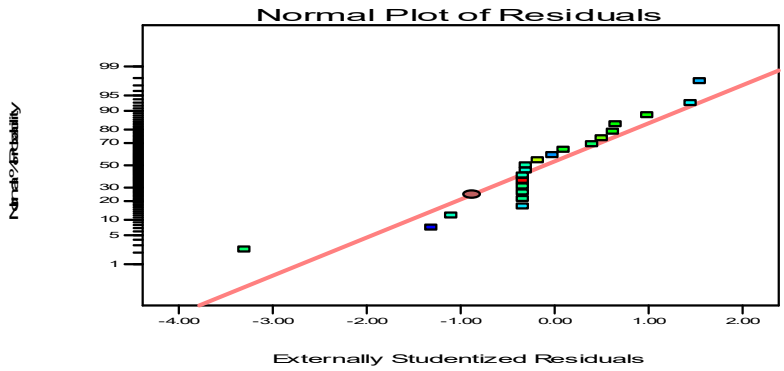

Figure 1 : Normal plot of residuals for the catalyzed reaction

3.7 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)

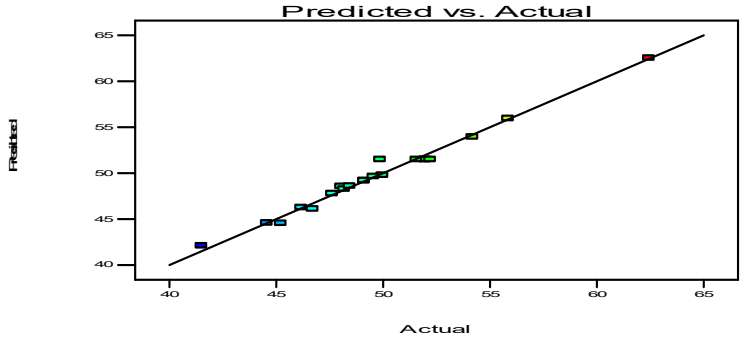

Figure 2: Predicted Vs Actual plot for the catalyzed reaction

3.8 Three Dimensional (3-D) Response Surface Plots

The 3-D response surface plots is presented in Figure 3 below. The interactive effect given in Figure 3a between catalyst weight and reaction time reveals that percentage conversion is favored by a slight increase in both reaction time and catalyst weight. 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. Fig 3d shows the interaction between reaction time and temperature and a high conversion is a function of high reaction time.

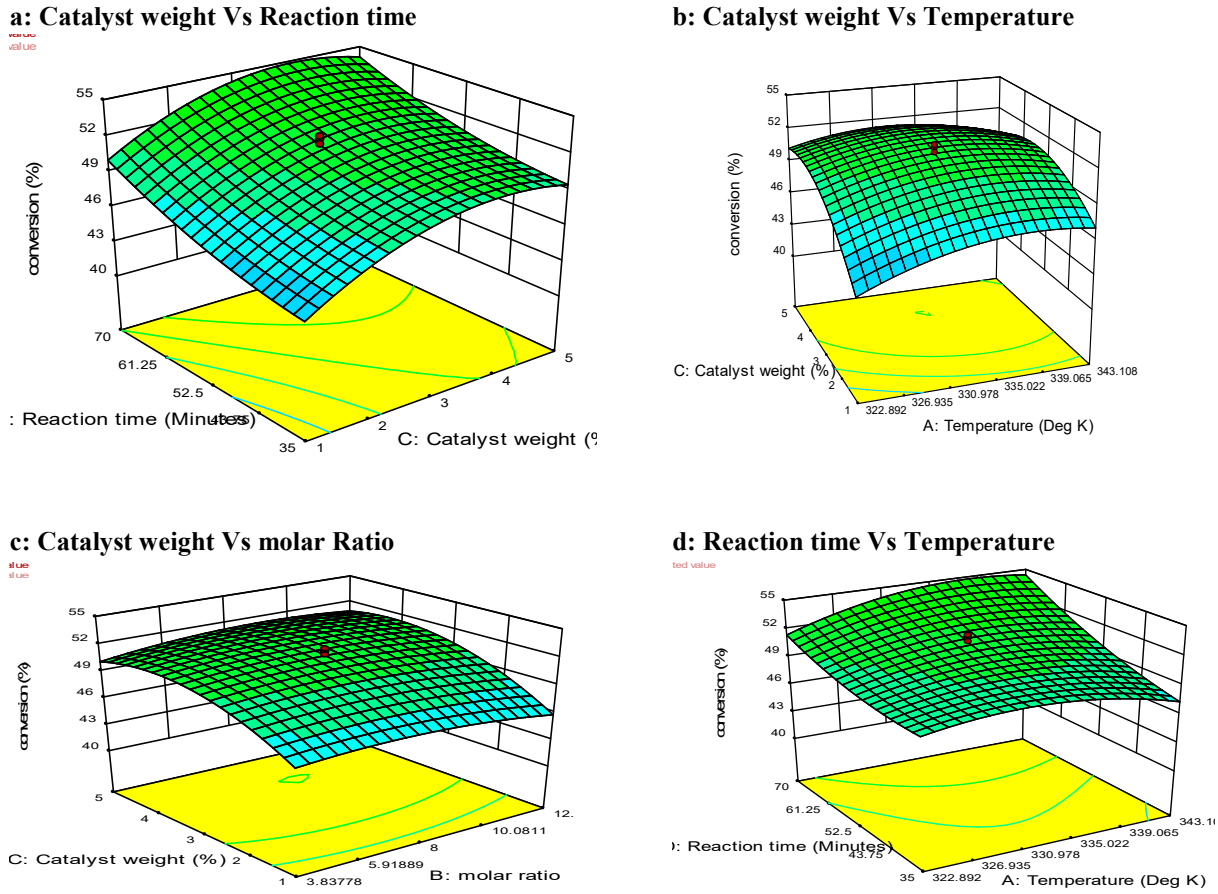

Figure 3: 3D plot for the catalyzed reaction

3.9 Effects of Process Variables on Biodiesel Conversion

Figure 4 shows how each of the process variables affect the conversion. Figure 4a shows gradual decline in conversion after the optimum temperature of 333.15k, this could be as a result of the fact that low temperature does not favour acid catalyst conversion. Figure 4b shows the response to change in molar ratio which shows no slight 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 gradual increase within the first 30mins.

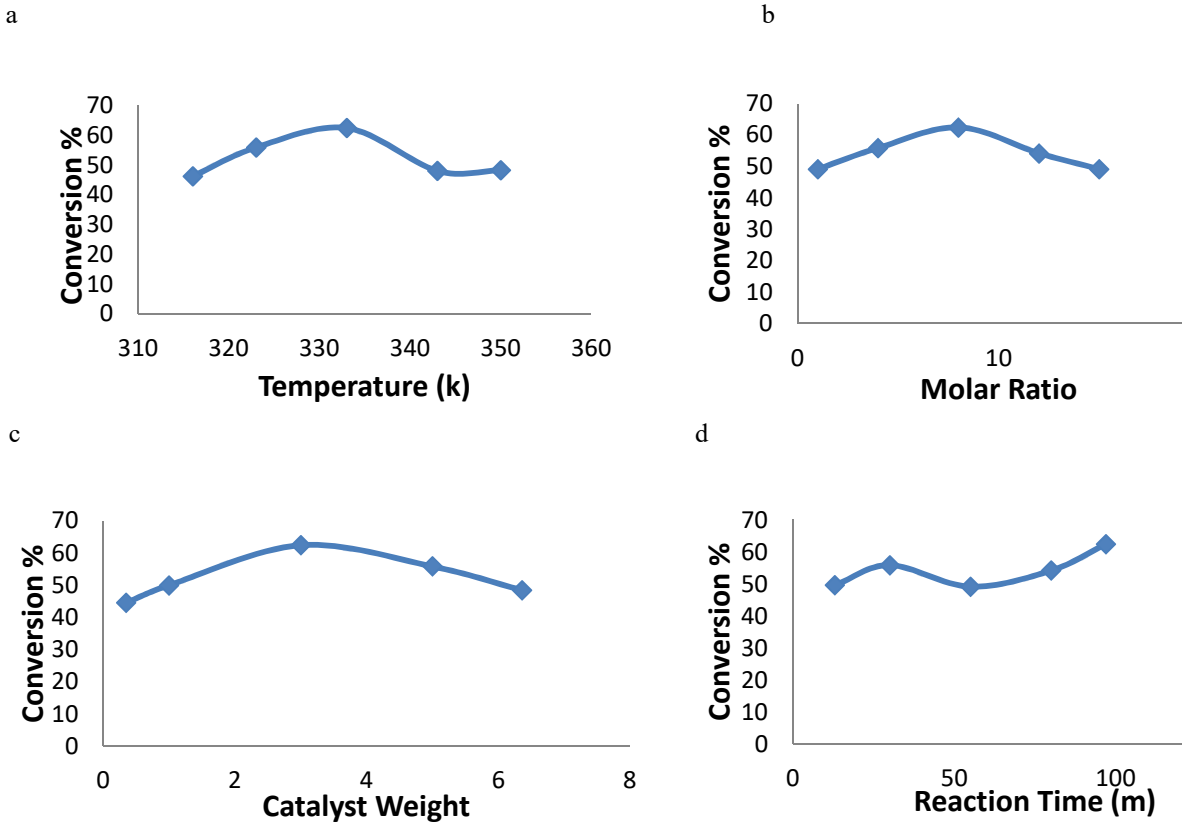

Figure 4: Effects of process variables on the biodiesel conversion

3.10 Model Validation

The determination of the effect of the catalyst type on the transesterification reaction processes for the selection of catalyst in production of biodiesel is one of the primary objectives of this 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	337.99	11.96	3.80	79.81	62.60
VALIDATEDE	338.0	12:10	3.80	79.80	63.30

IV. Conclusion

The production of biodiesel from castor seed oil using H_2PO_4 catalyst was successfully and gave a favourable outcome in terms of conversion.

Also, 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 62.60% at optimum conditions which shows the acceptability of H_2PO_4 as a catalyst for biodiesel production

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