Synthesis and Optimization of Biodiesel from Castor Seed Oil

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Abstract— **Among the various alternatives for fossil fuel, biodiesel is emerging as a promising choice for compression ignition engine due to its renewable nature and superior emission characteristics. This research work focused on the Synthesis and optimization of castor seed oil fatty acid methyl ester (CSOFAME). Solvent extraction was employed for extraction of oil from castor seed. The oil was characterized based on American Society for Testing and Materials (ASTM) method. The fatty acid profile of castor seed oil (CSO) was analyzed using gas chromatography mass spectroscopy (GC MS) while the functional groups of the triglyceride were determined using Fourier transform infrared spectroscopy. The effects of process parameters on the yield of CSOFAME was investigated using one factor at a time method .The oil was pretreated to reduce the free fatty acid beolw 1% and then trasersterified using methanol in the presence of sodium hydroxide catalyst. The fuel properties of the CSOFAME produced were determined based on ASTM standards. Optimization of castor seed oil biodiesel was carried out using response surface methodology. The physiochemical properties of the oil density, free fatty acid, saponification value, iodine value, flash point, pour point, moisture content gave the values of, 766kg/m3, 3.04%, 180.5mgKOH/g, 78.2gI2/100g, 2630C, 0.50C, 0.5%, respectively. The fatty acid profile of CSO consist of saturated fatty acids; stearic acid 0.98%, palmitic acid 1.8% and unsaturated fatty acids; oleic acid 6.i%, linolenic acid 0.91% and recinoleic acid 80.41%. The process parameters of methanol to oil molar ratio, catalyst concentration, reaction temperature reaction time and agitation speed immensely affected the biodiesel yield as their increase resulted in the increase of biodiesel yield until an optimum value was attained when the yield started decreasing. The fuel properties of the COFAME which is within the ASTM standards were determined as acid value 0.460mgKOH/g, density 866Kg/m3, flash point 1560C, cetane number 60.9, calorific value 40.02MJ/Kg, pour point 30C, iodine value 35.20gI2/100g. The use of quadratic regression model from design expert version 12.0 for response surface methodology (RSM) showed optimal biodiesel yield of 91.9% at the optimum reaction conditions of methanol to oil molar ratio 7:1, catalyst concentration 0.9%wt. reaction temperature 600C, and reaction time 65 minutes.**

Index Terms— **ASTM method, Castor seed oil. transesterification, optimization.**

I. INTRODUCTION

The major sources of world energy, petroleum, coal and natural gas known as fossil fuel are neither renewable, biodegradable nor environmentally friendly. These shortfalls have made it imperative for a search for fuels to fill the gap. Various fuel options to replace diesel have been investigated and biodiesel has been universally found to possess the

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required qualities to be a substitute for diesel [1]). A mono-alkyle ester of long chain fatty acid, biodiesel is known to have characteristics similar to that of diesel with additional advantages of nigh lubricity, high cetane number biodegradable and being environmentally friendly [2, 3]. Burning of fossil fuel results in environmental pollution such as emission of green house gasses , including sulphur oxides (SOx), nitrogen oxides (NOx) and methane [4].Biodiesel is produced by the reaction oil or fat with an alcohol usually in the presence of catalyst which could ba a base, acid or an enzyme. If an alcohol typically monohydric alcohol like methanol contacts a fatty acid, it will bond to form biodiesel [5]. Various processes have been adduced for production of biodiesel, including, micro-emulsion with alcohol, catalytic cracking, pyrolysis and transesterification [6, 7, 8, 9]. Among these processes, transesterification has proved to be the most useful means of converting oil or fat into environmentally safe biodiesel [10, 11].

Although, biodiesel is gaining popularity, more than 95% of the renewable resources used for its production are edible oils [12], which will in a long term have serious implications on food availability and the cost of biodiesel as it may be more expensive than petro-diesel. Worldwide, biodiesel production is mainly from edible oils such as soybean, sunflower and canola oils etc. Utilization of edible oils as feedstock for biodiesel production poses a lot of concerns as this practice competes with food supply leading to high cost of edible vegetable oil, and consequently results in relative increase in biodiesel production cost. Therefore, concerted research efforts are geared towards identifying and evaluating non-edible seed oils as suitable feedstocks. There are vast numbers of non-edible oil plants in nature; these include neem (A. indica), jatropha tree (J. curcas), karanja (P.pinnata), tobacco seed (N. tabacum L.), rice bran, mahua (M. indica), rubber plant (H. brasiliensis), castor, linseed, and microalgae [6]. Jatrophacurcas oil plants have been widely studied with respect to biodiesel production from non-edible oils [13,14,8,15] but the use of most of other non-edible oil plants such as neem, castor etc have not been as intensely studied as Jatrophacurcas. This research work is therefore geared towards the use of none-edible oil, castor seed oil for synthesis and optimization of biodiesel.

Castor (Ricinuscommunis L.) is cultivated in approximately all parts of the world as a result of the economic relevance of its oil. It is an important non-edible oilseed crop and is grown especially in arid and semiarid region [16].The castor plant bears flower and belong to the spurge family Euphorbiaceae [17]. The comparative advantage of castor is that it posses less maturity period compared toJatropha and Pongamia, and there is considerably greater experience and awareness among

farmers about its cultivation [18]. It is a fast-growing, suckering perennial shrub which can reach the size of a small tree (about 12 metres / 36 feet). Castor oil properties indicate a very low pour and cloud points which make this biofuel a good alternative in winter conditions [18]. It is a non-drying oil that neither becomes stiff with cold nor unduly thin with heat hence is used as a lubricant for jet and racing car engines. It is the sole supply of 18-carbon hydroxylatedfatty acid with one covalent bond in every of thecarboxilic acid chain andrecinoleic acid constituting about 89% of the fatty acid composition [18]. The fatty acid composition of castor seed oil consist of high percentage of monounsaturated fatty acid and low percentages of polyunsaturated fatty acid and a regulated amount of saturated fatty acids makes the oil fatty acid balanced and suitable for biodiesel production. Optimization of castor seed oil was carried out using response surface methodology of central composite design (CCD), in order to determine the optimum reaction conditions for biodiesel production. The five processing factors, methanol to oil molar ratio, catalyst concentration reaction temperature, reaction time, and agitation speed are the independent variables while percentage biodiesel yield is the dependent variable or response. Design expert software version 12.0 was used for the design of experiment and optimization of the reaction conditions.

II. MATERIALS AND METHODS

A. Materials

Castor seeds, reagents, glass wares, equipments including gas chromatography mass spectrometer (GC-MS), Fourier transform infrared spectroscopy (FTIR), viscometer, magnetic hot plate, soxhlet extractor. Design expert software version 12.0 etc.

B. Sample preparation

The used castor seed was bought from Ogbete main market in Enugu, Enugu State. The seeds were cleaned by removing the dirts and accompanying foreign bodies through hand picking. The clean beans ware then de-shelled and oven-dried for 7 hours at 600C to obtain dry seeds. The inner seed cover was then removed by winnowing. Then the clean dry seeds were grind using meanical grinder.

C. Extraction of oil from castor seed

Solvent extraction was used to extract the oil from the castor seeds. The oil content of the seed was evaluated using soxhlet extractor. For the oil used in the work, 5kg of the dried, ground castor seed was measured into a plastic container containing 3 liters of n-hexane. The mixed content of the container was vigorously shaken after covering the container. The container was made air-tight to prevent evaporation of hexane and then kept to macerate for a day. Then the dissolved oil in hexane was decanted and the slurry filtered. The filtrate was then distilled to recover the hexan at 650C [19]. The percentage oil content of castor seed was calculated thus,

% oil yield = wight of oil extracted ÷ wt of the seed sample x 100   (2.1)

D. Characterization of castor seed oil

The physiochemical properties of the oil extracted from castor seed was characterized based on American Society for Testing Materials, ASTM 6751 (1973) method. Analytical equipments, GC- MS (QP2010 plus Shimadzu, Japan) and FTIR (M530 Bulk scientific FTIR) were used to determine the fatty acid profile and the functional groups of the oil respectively.

E. Effect of process parameters on biodiesel yield

The effects of process parameter on biodiesel yield from CSO were investigated based on one factor at a time method involving keeping a factor constant at a time and varying the others in turn. The five factors investigate are, molar ratio of methanol to oil, catalyst concentration, reaction time, reaction temperature and agitation speed.

F. Production of biodiesel by transesterification

Pretreatment of the Oils Extracted.

A pre-treatment procedure was followed to reduce the excess free fatty acid of the oil below1%. The oil samplewas first heated on a heating mantle at 110˚C for 10 minutes for any available moisture to be driven off. The sample was cooled to 60°C in a water bath, and then weighed into 500ml three necked round bottomed flask. Then methanol of 60%w/w of oil mixed with concentrated sulphuric acid of 7% w/w of oil was added. A reflux condenser was fitted into the middle arm of the flask and water circulated at the outer jacket of the condenser. A thermometer was inserted into the sample in the flask from one of the side arms. The whole setup was placed on a magnetic heating mantle and heated at 600C for 120 minutes at an agitation speed of 450rpm. The mixture was then transferred into 500ml separating funnel where it later separated into three layers comprising water at the bottom, pre-treated oil in the middle and methanol at the upper layer. The various components were carefully tapped off, water fist, followed by the oil and finally methanol. Hot distilled water was poured into the oil in a seperating flask, shaken and allowed to stand when it separated into water and oil layers below and above the flask respectively. The water was tapped off from the separating funnel and the pre-treated oilwas poured into beakers and dried carefully in an oven regulated at a temperature of 1050C until the residual water evaporated completely. After this process, the pre-treated oil was made ready for transesterification [16].

Production of biodiesel by transesterification

The oil was transesterified using methanol and sodium hydroxide catalyst. A 500ml three-necked round bottomed flask fitted with a condenser on the middle arm, a thermometer and sample outlet on the side arms respectively served as the reactor. The heating system consists of an electromagnetic hot plate which heats the reactor and rotates the metal knob in the reactor through an electromagnetic field. Specified quantity of the oil sample was introduced into the flask and the flask content heated to the temperature established for the reaction. Then methanol and the catalyst mixture (NaOH) was added in the amount established for the reaction, and the stirrer switched on at a specified speed, taking this moment as zero time of the reaction. The reaction mixture was vigorously stirred and refluxed for the required reaction time. At the end of methanolysis, the transesterfied

product was made to stand for a day in a separating funnels where it separates into the upper biodiesel layer and the lower glycerol layer. The lower glycerol layer was tapped off first followed by the upper biodiesel layer.

Biodiesel purification by wet washing

After transesterification, the upper ester layer may contain traces of methanol and glycerol. The remaining un-reacted methanol has safety risk and might corrode engine components, and glycerin within the biodiesel will lessen the fuel lubricity and cause injector coking and other deposits[20]. Such trace of methanol is soluble in water and is therefore removed by wet washing. The methyl ester or biodiesel layer was gently washed with hot distilled water in the ratio of 3:1 water to methyl ester. The methyl ester was gently washed to prevent its loss due to formation of emulsion that results in complete phase separation [21]. The washed biodiesel was dried by heating at 1050C on a laboratory hot plate until all residual water molecules evaporated. This conforms with the findings of [22]. The percentage biodiesel yield is given by the expression,

% biodiesel yield = Volume of biodiesel produced÷ volume of oil used x 100   (2.2)

G. Determination of the fuel properties of castor seed oil biodiesel.

The properties of the biodiesel fuel were characterized based on ASTM standards. The properties characterized for include density, viscosity, iodine value, saponification value, cetane number acid value , free fatty acid , calorific value and flssh point.

H. Optimization of biodiesel production

Design of experiment for transesterification of castor oil catalyzed by NaOH

Design Expert software (version 12) was used in this study to design the experiment and to optimize the reaction conditions. The experimental design employed in this work was a two-level-five factor fractional factorial design, including 32 experiments. Reaction temperature, catalyst concentration, methanol to oil molar ratio, reaction time and agitation speed are the independent factors for the optimization study. The response chosen was the methyl ester yields obtained from transesterification of castor oil.25 (2n) factor fractional factoriaexperimentsl, 10(2n) star points and 6 center points were carried out in order to predict a good estimation of errors and experiments were performed in a randomized order. The actual and coded levels of each factor are shown in Table 2. 1. Alpha is defined as a distance from the center point which can be either inside or outside the range, with the maximum value of 2n/4, where n is the number of factors [23]. The empirical equation is represented as shown in equation 2.1.

$$Y = \beta_0 + \sum_{i=1}^{5} [\beta_i X_i] + \sum_{i=1}^{5}\sum_{j=i+1}^{5}[\beta_{ij} X_i X_j] + \sum_{i=1}^{5}[\beta_{ii}[X^2]_i] \qquad (2.1)$$

Where Y is the predicted yield of FAME (%),$[X]_i$ and X_j represent the transesterification process variables, β_0 is the offset term, β_i is the coefficient of linear (single) effect,$[\beta]_{ij}$ is the coefficient of interaction effect and β_{ii} is the coefficient of quadratic effect. Selection of levels for each factor was based on the values obtained from experiments performed to study the effects of process variables on the yield of biodiesel from castor oil transesterification. The lower level of temperature was 500C since below that the reaction rate is relatively slow and the upper level of temperature was 700C. The levels of methanol to oil molar ratio were selected between 2:1 and 10:1 and the catalyst concentration was limited between 0.25 wt% and 1.25wt%(based on the initial weight of the oil) with agitation speed range of 150 rpm to 350 rpm. The range and levels of the independent variables and the experimental design matrix for the transesterification were presented in Figure 2.1 and 2.2 respectively.

Table 2.1: Experimental range and levels of independent process variables for biodiesel production.

Independent Variables	Units	Range and Level				
		$-\alpha$	-1	0	1	$+\alpha$
Molar Ratio(X_1)	Mol/mol	2:1	4:1	6:1	8:1	10:1
Catalyst Concentration (X_2)	Wt %	0.25	0.50	0.75	1.00	1.25
Temperature (X_3)	°C	50	55	60	65	70
Reaction time (X_4)	Min.	30	45	60	75	90
Agitation speed (X_5)	Rpm	150	200	250	300	350

III. RESULTS AND DISCUSSION

A. Castor seed oil yield

The percentage of oil extracted from the **castor seed using equation 2.1 is 45%. The** observed yield of castor was found competitive with the yields of some edible oil such as soybeans, 50% and cotton seed, 47% [24]. The relatively high oil content of castor seed will encourage less dependence on edible oils as feedstock for biodiesel production, thereby promoting food security and food

availability.

B. **Physiochemical properties of CSO**

The summary of the characteristics of CSO are as shown in table 3.1. From the table, it could be seen that the fatty acid and therefore free fatty acid of castor seed oil are relatively high. In any case the free fatty acid of 3.04 is higher than the 1% maximum value recognized to give high yield of biodiesel by alkali catalyzed transesterification. The oil therefore need be esterified using acid catalyst before transesterification. Oil of free fatty acid in excess of 1% has the tendency for soap formation, inhibition of glycerol separation from biodiesel and therefore retardation of biodiesel production [13]. The kinematic viscosity and the density of the oil are higher than that of the biodiesel produced from it and much higher than that of diesel. High density and viscosity makes atomization of the oil in internal combustion engine difficult and has been associated with increase in engine deposits, hence they cannot be used directly as bio-fuel [25]. The determined density of the oil $966kg/m^3$ is I agreement wirh the literature findings of [22, 26] but at variance with [27, 28].

Table 2.2 Experimental design Matrix for the transesterification studies of neem, castor and used soya oil FAME's

Run order	Methanol/Oil molar ratio X_1		Catalyst conc. (wt %) X_2		Temperature (^{o}C) X_3		Time (Mints) X_4		Agitation Speed (Rpm) X_5		Biodiesel Yield (%)
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real	
1	-1	4	-1	0.5	-1	55	-1	45	+1	300	
2	+1	8	-1	0.5	-1	55	-1	45	-1	200	
3	-1	4	+1	1	-1	55	-1	45	-1	200	
4	+1	8	+1	1	-1	55	-1	45	+1	300	
5	-1	4	-1	0.5	+1	65	-1	45	-1	200	
6	+1	8	-1	0.5	+1	65	-1	45	+1	300	
7	-1	4	+1	1	+1	65	-1	45	+1	300	
8	+1	8	+1	1	+1	65	-1	45	-1	200	
9	-1	4	-1	0.5	-1	55	+1	75	-1	200	
10	+1	8	-1	0.5	-1	55	+1	75	+1	300	
11	-1	4	+1	1	-1	55	+1	75	+1	300	
12	+1	8	+1	1	-1	55	+1	75	-1	200	
13	-1	4	-1	0.5	+1	65	+1	75	+1	300	
14	+1	8	-1	0.5	+1	65	+1	75	-1	200	
15	-1	4	+1	1	+1	65	+1	75	-1	200	
16	+1	8	+1	1	+1	65	+1	75	+1	300	
17	-2	2	0	0.75	0	60	0	60	0	250	
18	+2m	10	0	0.75	0	60	0	60	0	250	
19	0	6	-2	0.25	0	60	0	60	0	250	
20	0	6	+2	1.25	0	60	0	60	0	250	
21	0	6	0	0.75	-2	50	0	60	0	250	
22	0	6	0	0.75	+2	70	0	60	0	250	
23	0	6	0	0.75	0	60	-2	30	0	250	
24	0	6	0	0.75	0	60	+2	90	0	250	
25	0	6	0	0.75	0	60	0	60	-2	150	
26	0	6	0	0.75	0	60	0	60	+2	350	
27	0	6	0	0.75	0	60	0	60	0	250	
28	0	6	0	0.75	0	60	0	60	0	250	
29	0	6	0	0.75	0	60	0	60	0	250	
30	0	6	0	0.75	0	60	0	60	0	250	
31	0	6	0	0.75	0	60	0	60	0	250	
32	0	6	0	0.75	0	60	0	60	0	250	

Iodine value, a measure of degree of un-saturation of the oil was obtained as 78.2 which is below $100gI_2/100g$ oil, indicative of the oil being nondrying and therefore suitable for biodiesel production. High iodine value of oil corresponds to high degree of unsaturation of the fatty acid in the triglyceride. If heated,such an oilis prone to thermal oxidation and polymerization of the triglyceride causing formation of deposits. The calorific value of castor oil like that of any oil is relatively lower than that of diesel. The determined calorific value of the oil 35.20MJ/kg is in conformity with literature values [26, 28]. The cloud and pour point of 5^0C and 0.5^0C respectively determined for the seed oil re relatively but not to the extemt of being suitable for

operation and handling during cold weather especialy in cold climates. Peroxide value, an index of rancidity obtained as 10.5meq/kg was high and indicative of poor resistance of the oil to peroxidation during storage and handling. The saponification value determined as 184.5 is in agreement with literature findings of [22, 29,30].. The flash point of 230^0C is in agreement with literature values [28, 30]. The high flash point shows that the oil is not prone to fire hazard as the ignition temperature is high.

C. **The Fatty Acid Profile of Castor Oil (GC –MS)**

The fatty acid profile of castor oil was carried out using gas chromatography mass spectrometry (GC-MS). The summary of fatty acid composition of castor oil is shown in Table 3.2. Castor oil interestingly comprises of 2.98% of saturated acids

(stearic acid and palmitic acid) and 87.42% unsaturated acids (oleic, linolenic acid and ricinoleicacid). The dominant monounsaturated fatty acid of the oil is recinoleic acid, which accounted for 80.48% of the total fatty acid content, hence, the oil belongs to oleic acid category [29]. The oleic acid content of castor oil is comparatively higher than 7-40% reported for coconut oil, palm oil and cottonseed oil (Ampaitepin*et al.,* 2006; Rashid *et al*., 2009). This shows that castor oil is highly unsaturated triglycerides. Nevertheless, the fatty acid components of the castor oil were found to be consistent with the fatty acids present in typical oils used for the synthesis of FAME.

D. Fourier Transform Infrared (FT-IR) Spectra Analysis of Castor oil

The FTIR spectrum of castor oil was also carried out as shown in Figure 3.1. This was done to determine the different functional groups present in the feedstock. From the result, noticeable peaks were recorded. The region 723.1 cm^{-1}(679.61 cm^{-1} – 886.65 cm^{-1}) indicate the presence of =C-H (alkenes) functional groups. They possess bending type of vibrations appearing at low energy and frequency region in the spectrum and they are all double bonded. They are attributed to olefinic (alkenes) functional groups and are

unsaturated. They will be part of fatty acid methyl esters with unsaturated bond in the biodiesel, such as methyl oleate and methyl linoleate (Saifuddin*et al*., 2014; Jimoh*et al*., 2012). The characteristics peaks found in the region 900 – 998 cm^{-1}as found in the feedstock indicate stretching vibrations of olefinic (alkenes) functional groups. The characteristics peaks found in the region 1096.15 – 1232cm^{-1} indicate stretching vibrations of C-O and C-O-C. They can also indicate the bending vibration of O-CH_3 in the spectrum (John *et al*., 2000; Isah*et al.,* 2015). The band region of 1376 cm^{-1} can be ascribed to the bending vibration of C-H methyl groups , while the band at 1401-1744 cm^{-1} is ascribed to C=C bending vibrations (Shuit*et al*.,2010). The peaks at 2899cm^{-1} and 2922cm^{-1}indicate symmetric and asymmetric stretching vibrations of C-H alkane groups respectively. They could be methyl (CH_3) or methylene groups and they require high energy to cause stretching vibrations within their bond when compared to the ordinary C-H bending vibrations of alkene groups detected at low energy and frequency region (Saifuddin*et al.,* 2014; Jimoh*et al.,* 2012). The peak at 3011cm^{-1} is attributed to the stretching vibration of =C-H alkene groups. They are detected above wavenumber 3000 cm^{-1} in the spectrum compared to corresponding alkane C-H stretching groups detected below 3000 cm^{-1}.

Table 3.1: Physiochemical properties of castor seed oil

Properties	Unit	CSO
Density	Kg/m^3	966
Specific graviyty		0.966
Moisture content	%	0.5
Refractive index		1.4670
Saponification value	mgKOH/g	I84.5
Iodine value	g/100g	78.2
Peroxide value	Meq/Kg	10.5
Acid value	mgKOH/Kg	6.08
Free fatty acid	%	3.04
Flash point	^{0}C	230
Cloud point	^{0}C	5.0
Pour point	^{0}C	0.5
Calorific value	MJ/Kg	35.2

Table 3.2: Summary offatty acid composition of castor oil.

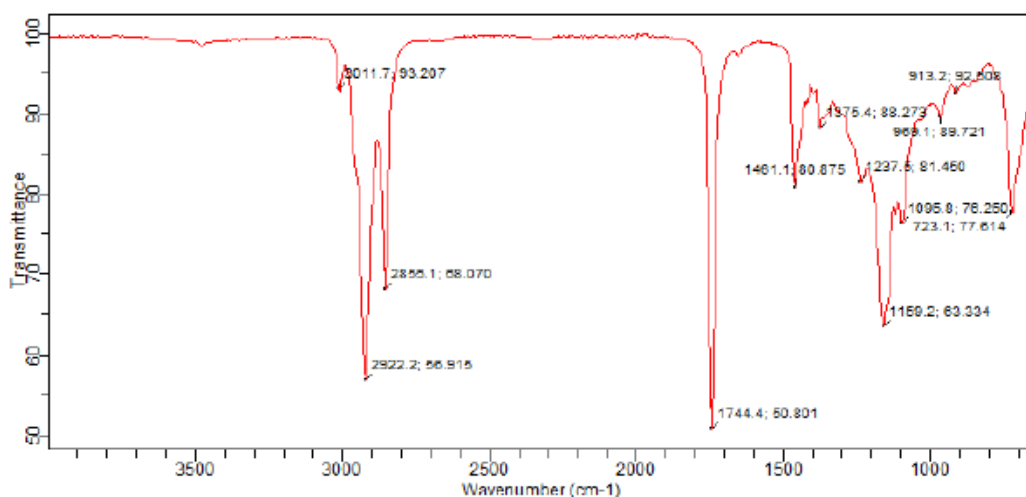| Fatty Acid	Structure	Composition (%)	Molecular Weight (g/mol)
Linolenic acid	C18:3	0.91	278.43
Oleic acid	C18:1	6.1	282.465
Stearic acid	C18:0	0.98	284.48
Palmitic acid	C16:0	1.8	256.4
Ricinoleicacid	C18:1	80.41	298.461

Figure 3.1: FT-IR spectra for castor oil.

E. Effects of Process Parameter on Biodiesel Yield

Effect of methanol/oil molar ratio on biodiesel produced.

The alcohol to oil molar ratio is one of the most vital factors that can affect the yield of esters. The stoichiometry of the transesterification reaction requires 3:1 molar ratio of methanol to oil to yield 3 moles of ester and 1 mole of glycerol, but most researchers have found that excess alcohol was required to drive the reaction close to completion. In this work, the effect of methanol to oil molar ratio of 2:1 to 12:1 was investigated, when other process parameters were fixed (catalyst concentration, reaction temperature reaction timet and agitation speed). The yield of methyl esters at the different molar ratio of methanol to oil is shown in Figure 3.2. The results indicated that methanol to oil molar ratio has significant impact on FAME yield. The maximum ester yield was obtained at a methanol to oil molar ratio of 8:1 for castor oil. The yield reduced when the methanol to oil molar ratio was higher than 8:1. This trend can be explained by the fact that while the increase in methanol to oil molar ratio favourstransesterification reaction. Very high ratio of methanol to oil molar ratio decreases the catalytic activity of the catalyst, resulting in the reduction of biodiesel produced. This is in agreement with the findings of Zhang et al.,

(2003) and Freedman et al., (2003). Again, methanol with one polar hydroxyl group can act as emulsifier on the ester resulting to difficulty in separation of ester from the water layer (Leung and Guo 2006).

Effect of catalyst concentration on iodiesel produced.

Catalysts provide alternative reaction pathways for breaking of bonds in chemical reaction. The activation energy for this new pathway is often less than the activation energy of the normal pathway. Sodium hydroxide was used as a base catalyst for the transesterification reaction in this work. The effect of NaOH concentrations expressed as weight percentage of the oil on the production yield is presented in Figure 3.3. The yield of methyl ester increased with increase in catalyst weight up to 1.0%wt for castor oil, and then began to decrease. Initially the amount of catalyst helped to accelerate the reaction by increasing the reaction

rate. The higher yield of ester with increase in catalyst weight is due to the higher reaction rate due to high catalyst concentration. Increasing the catalyst weight beyond 1.0%wt for castor oil led to the decrease in ester yield. This observation could be explained by the fact that initially increase in catalyst concentration helped to accelerate the rate of reaction . However, exceeding the optimal concentration of the catalyst hinders the effective dispersion and mixing of the reactants, thereby resulting in the formation of soap and retardationof ester yield. This is in conformity with the findings of [31]. However, on exceeding the optimal catalyst concentration of 1wt%, the excess catalyst react with the triglyceride to form soap which increases the viscosity of the reaction mixture, hinders effective dispersion and mixing of the reactants and also separation of glycerol from biodiesel which gives rise to reduction of biodiesel production. This is in agreement with the findings of {31, 32].

Effect of temperature on biodiesel yield.

The reaction rate can be accelerated at higher reaction temperatures. For the study of the effect of temperature on the yield of castor oil biodiesel, the reaction temperature was varied thus; 500C, 55 0C, 600C, 650C, 700C and 750C while the other parameters (catalyst concentration, methanol to oil molar ratio, reaction time and agitation speed) were kept constant. As shown in Figure 3.4, FAME yield first increased with increase in temperature to an optimal value of 650Cand then decreased with the increased in the reaction temperature beyond 650C for castor oil. This may be explained thus. At a temperature below the boiling point of methanol ester formation was favored, but about the boiling point of methanol, the backward reaction was favored coupled with much amount of methanol lost by evaporation, thus reducing the bodieselyield.This trend conforms with the findings of [8].

Effect of reaction time on biodiesel yield.

In this work, the effect of reaction duration (15, 30, 45, 60, 75 and 90 minutes) on the yield of biodieselfrom castor oil was investigated. It was found that reaction time of 60

minutes was needed for a maximum yield of FAME for castor oil investigated and beyond this the yield decreased as shown in Figure 3.5. The decrease in the yield after 60 minutes may be due to reversible reaction of transesterification resulting in loss of esters [33]. Also longer reaction time most times allows the fatty acids present to react with alkali resulting to soap formation. The presence of soap retards the formation of ester [8, 16].
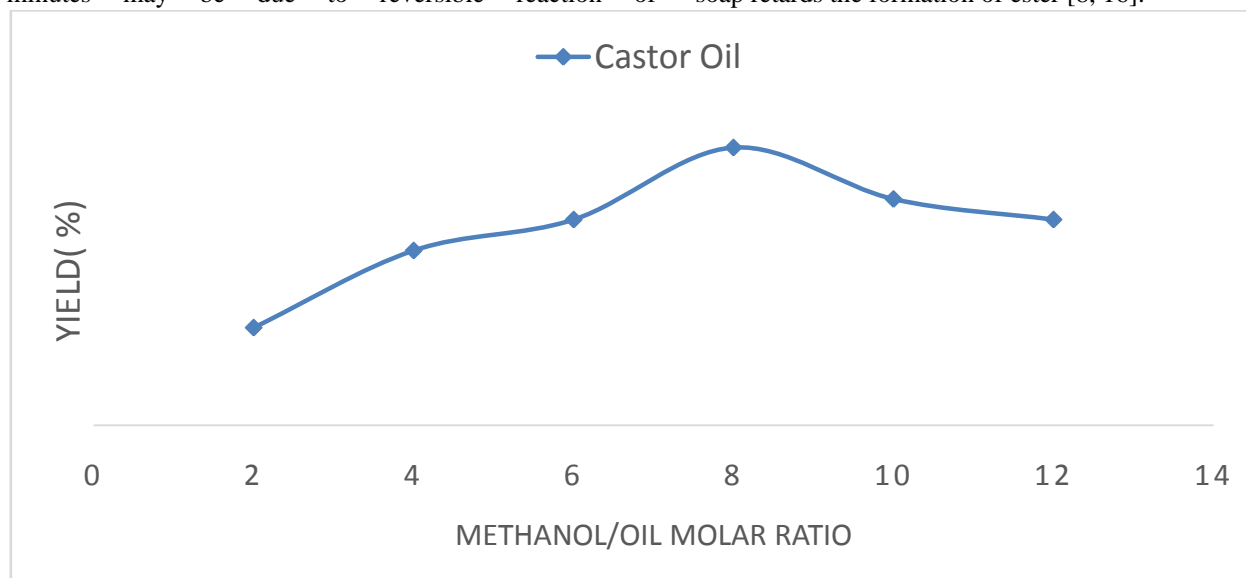

Figure 3.2: Effect of methanol/ oil molar ratio on biodiesel Yield.

Effect of agitation speed on biodiesel yield.

Transesterification was conducted in this study at different agitation speed, 150, 200, 250, 300, 350 and 400 revolutions per minutes (rpm). Mixing is particularly very important for transesterification process as it ensures homogeneity within the reaction mixture. The biodiesel yield at different rate of mixing is shown in Figure 3.6. At the lowest stirring speed of 150rpm it was observed that the reaction of methanolysis was practically incomplete as it only exhibited a yield which was difficult to separate. The yield was observed to decrease as the stirring rate went above 250rpm for castor oil. The backward reaction may have been favored when mixing intensity was accelerated beyond the above condition, thereby retarding the formation of biodiesel. These results are in conformity with observations made by [16],who studied the effect of agitation speed on the transesterification of non-edible oil and concluded that higher agitation promoted the homogenization of the reactants and thus led to higher yields.
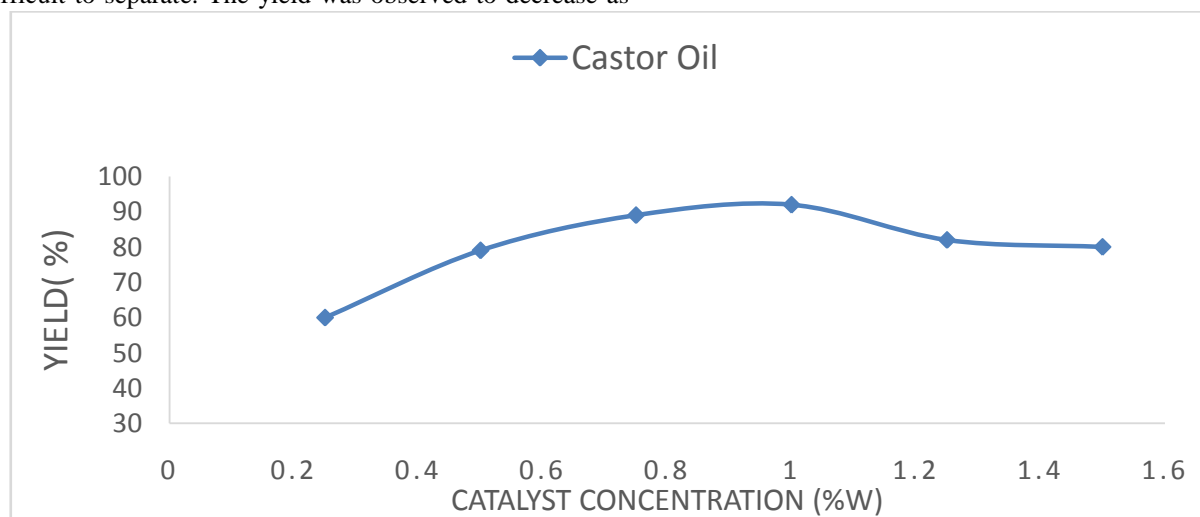

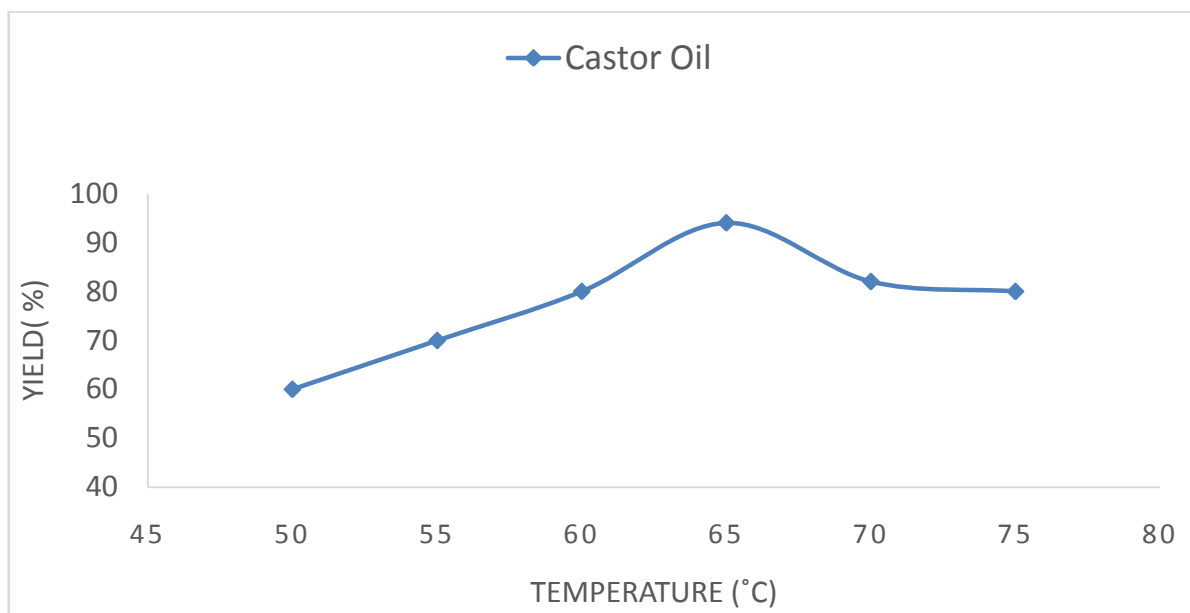Figure 3.3: Effect of catalyst concentration on biodiesel yield

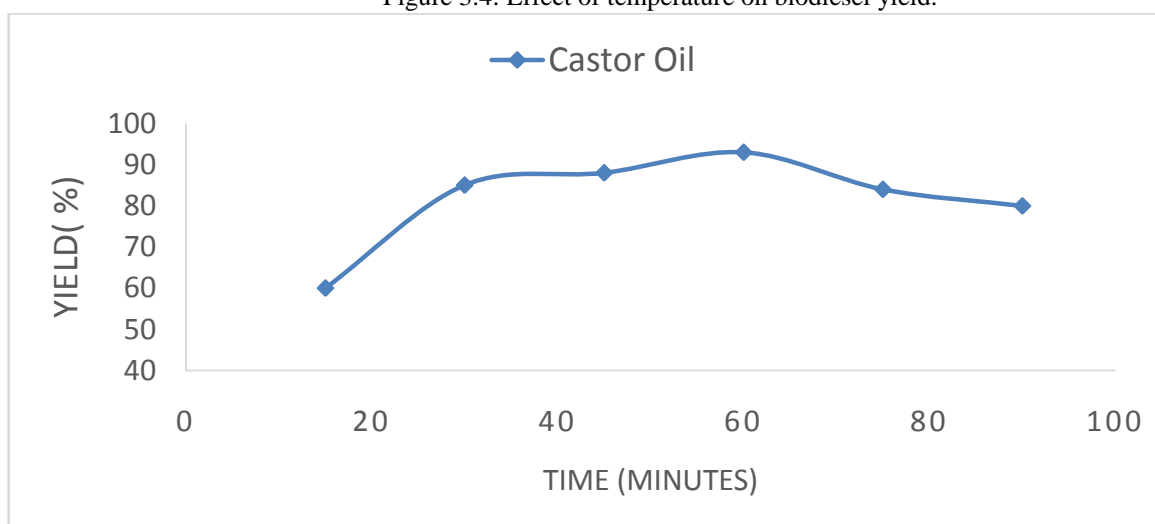Figure 3.4: Effect of temperature on biodiesel yield.

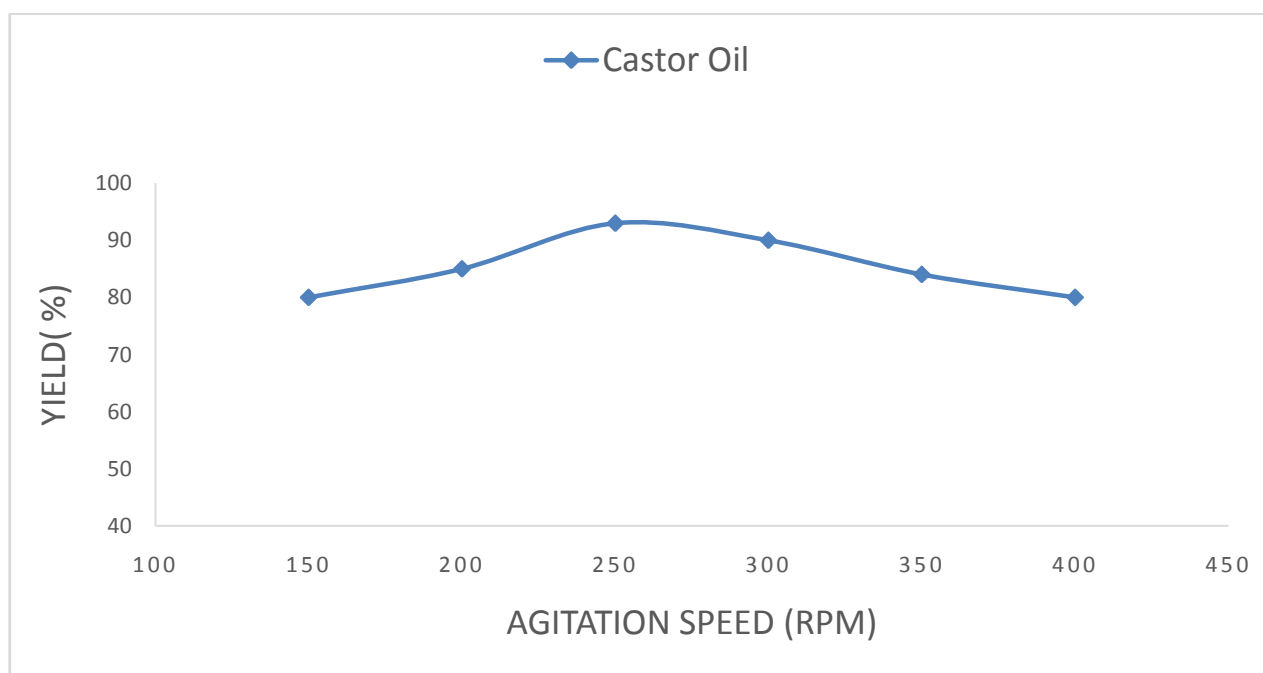Figure 3.5: Effect of reaction time on biodiesel yield

Figure 3.6: Effect of agitation speed on biodiesel yield.

F.   Fuel Properties of the FAME Produced.

Table 4.5 gives the summary of the fuel properties of the COFAME studied in the course of this
research work.

Biodiesel generally has a higher density than petro-diesel. This has a significant impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically. The densities were evaluated to be, 866 kg/m3 for ester of castor oil which is within the ASTM limits for biodiesel. The biodiesel has lower density compared to the density of castor oil of value 966 kg/m3.
The value of kinematic viscosity obtained for the biodiesel

produced from castor oil is 4.78mm2/s as shown in Table 4.5, and it could be observed that they are within the standard range of ASTM limit. The increase in viscosity results in poor atomization, incomplete combustion which leads to coking of injector tips and engine power loss. Low-viscosity fuel produces a very subtle spray which cannot properly get into the combustion cylinder, thus forming a fuel rich zone which lead to the formation of soot (Endahet al., 2012; Ezekwe and Ajiwe, 2014). From the result it could be inferred that FAME from castor oil have a good injection and atomization performance. Furthermore it will offer superior lubrication and protection for the moving parts of enginethan the diesel.

Table3.3: Fuel properties of COFAME, ASTM and EN standards.

Properties	CASTOR FAME	ASTM D6751	EN 14214
1.Biodiesel yield (%)	91.0	-	-
2.Density (Kgm3)	866	880	860-900
3.Moisture content (%)	0.03	0.05max.	0.05max.
4. Refractive index	1.4600	1.4580	1.4540
5.Acid value (mgKOH/g)	0.460	0.50	0.50
6,Free fatty acid (%)	0.230	0.25	0.25
7.Iodine value(gI2/100g oil)	35.20	42-46	120max.
8.Saponification value(mgKOH/g)	174.36	170-240	170-240
9.Kinematic viscosity (cst)	4.78	1.9-6.0	3.5-5.0
10.Flash point (0C)	156	130	120
11.Cloud point (0C)	7	3 to12	-1 to 10
12.pour point (0C)	3	-15 to 16	-10 to 8
13.Calorific value (MJ/kg)	40.02	42.46	35
14.Cetane number	60.90	47	51

The flash point is a determinant for flammability classification of materials. The typical flash point of pure methyl ester is ≥1300C, the value classifying the substance as "non-flammable". However, during production and purification of biodiesel, not all the methanol may be removed, making the fuel flammable and dangerous to handle and store if the flash point falls below 1300C. The flash points for the ester is1560C for castor oil biodiesel. This value falls within the ASTM standard as shown in Table 3.3, indicative of its safety in handling and storage.

Cetane number serves as a measure of ignition quality. This is the most pronounced change from vegetable oil to the transesterified product. Fuels with low cetane number show an increase in emission due to incomplete combustion. The lower limit for cetane number by ASTM and EN standards are 47 and 51 respectively. The values obtained for the castor oil biodiesel is 60.90. Thus the obtained results which are within the acceptable ASTM limits indicates that the produced biodiesel possess good ignition response.

The cloud point which is the lowest temperatureof first appearance of wax-like material on cooling the biodiesel was determined as 70C for castor oil biodiesel. The pour point which is the lowest temperature at which the fuel will still pour was determined as 30C for castor oil biodiesel.. The cloud and pour points might give rise to cold flow problems in cold season. This problem however could be overcome by

the addition of suitable cloud and pour point depressants or by blending with diesel oil [34].

G.   Optimization of CSOFAME production

Statistical Analysis of Transesterification Using Central Composite Design (CCD)
To optimize transesterificationof castor oil, central composite design (CCD), a response surface methodology (RSM) was used to determine the optimum values of the process variables. The fractional factorial design was used to obtain a quadratic model, consisting of factorial trials to estimate quadratic effects. To examine the combined effect of the five different factors; catalyst concentration, methanol to oil molar ratio, reaction temperature, reaction time and agitation speed, on biodiesel yield and derive a model, a two-level- five –factor (2^(5-1) + 2*5 + 6) central composite response design = 32 experiments were performed. The factors levels are shown in Table 3.1. The matrix for the five variables was varied at two levels (-1 and +1). The lower level of variable was designated as "-1" and higher level as "+1". Theexperiments were performed in random order to avoid systematic error. Equations (3.1) and (3.2) represent the mathematical model relating the transesterification reaction castor oil with the independent process variables obtained with the Design Expert 11. The design of the experimental matrix of transesterification of castor oil with the experimental values of the biodiesel yield are presented in

Table 3.4. The response was expressed as % yield, calculated as {(V_b)/Vo} x 100 where Vo is the initial volume of oil and Vbis the volume of biodiesel produced.

Transesterification of castor oil.

The design plan as shown in Table 3.4 of appendix was used to optimize the yield of FAME production from castor oil.

The coded and un-coded values of the test variables were used to optimize the variables. The experimental values of percentage yield are presented in Table 3.4.. The empirical relationship between yield (Y) and five variables in coded values obtained by using the statistical package design-expert 12 for determining the levels

Table 3.4: Experimental Design Matrix for the Factorial Design of FAME Produced from   Castor seed oil

Run order	Methanol/Oil molar ratio X_1		Catalyst conc. (wt %) X_2		Temperature (^{o}C) X_3		Time (Mints) X_4		Agitation Speed (Rpm) X_5		FAME Yield (from castor oil) (%)
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real	
1	-1	4	-1	0.5	-1	55	-1	45	+1	300	56
2	+1	8	-1	0.5	-1	55	-1	45	-1	200	67
3	-1	4	+1	1	-1	55	-1	45	-1	200	61
4	+1	8	+1	1	-1	55	-1	45	+1	300	76
5	-1	4	-1	0.5	+1	65	-1	45	-1	200	64
6	+1	8	-1	0.5	+1	65	-1	45	+1	300	73
7	-1	4	+1	1	+1	65	-1	45	+1	300	70
8	+1	8	+1	1	+1	65	-1	45	-1	200	76
9	-1	4	-1	0.5	-1	55	+1	75	-1	200	71
10	+1	8	-1	0.5	-1	55	+1	75	+1	300	75
11	-1	4	+1	1	-1	55	+1	75	+1	300	67
12	+1	8	+1	1	-1	55	+1	75	-1	200	77
13	-1	4	-1	0.5	+1	65	+1	75	+1	300	72
14	+1	8	-1	0.5	+1	65	+1	75	-1	200	70
15	-1	4	+1	1	+1	65	+1	75	-1	200	72
16	+1	8	+1	1	+1	65	+1	75	+1	300	94
17	-2	2	0	0.75	0	60	0	60	0	250	30
18	+2m	10	0	0.75	0	60	0	60	0	250	45
19	0	6	-2	0.25	0	60	0	60	0	250	80
20	0	6	+2	1.25	0	60	0	60	0	250	91
21	0	6	0	0.75	-2	50	0	60	0	250	80
22	0	6	0	0.75	+2	70	0	60	0	250	90
23	0	6	0	0.75	0	60	-2	30	0	250	79
24	0	6	0	0.75	0	60	+2	90	0	250	93
25	0	6	0	0.75	0	60	0	60	-2	150	83
26	0	6	0	0.75	0	60	0	60	+2	350	89
27	0	6	0	0.75	0	60	0	60	0	250	92
28	0	6	0	0.75	0	60	0	60	0	250	92
29	0	6	0	0.75	0	60	0	60	0	250	92
30	0	6	0	0.75	0	60	0	60	0	250	92
31	0	6	0	0.75	0	60	0	60	0	250	92
32	0	6	0	0.75	0	60	0	60	0	250	92

Table 3.5: Significance of regression coefficients of the yield of FAME produced from Castor oil using the dsign-expert version 1

Source	Mean Square	Degree of freedom	Sum of square	F-value	P-value (Prob>F)
Model	347.82	20	6956.39	559.90	< 0.0001
A	459.38	1	459.38	739.48	< 0.0001
B	187.04	1	187.04	301.09	< 0.0001
C	155.04	1	155.04	249.58	< 0.0001
D	287.04	1	287.04	462.07	< 0.0001
E	57.04	1	57.04	91.82	< 0.0001
AB	60.06	1	60.06	96.69	< 0.0001
AC	1.56	1	1.56	2.52	0.1411
AD	3.06	1	3.06	4.93	0.0483
AE	60.06	1	60.06	96.69	< 0.0001
BC	27.56	1	27.56	44.37	< 0.0001
BD	0.0625	1	0.0625	0.1006	0.7570
BE	18.06	1	18.06	29.08	0.0002
CD	1.56	1	1.56	2.52	0.1411
CE	52.56	1	52.56	84.61	< 0.0001
DE	7.56	1	7.56	12.17	0.0051
A^2	5545.83	1	5545.83	8927.44	< 0.0001
B^2	89.83	1	89.83	144.61	< 0.0001
C^2	103.13	1	103.13	166.01	< 0.0001
D^2	77.46	1	77.46	124.69	< 0.0001
E^2	77.46	1	77.46	124.69	< 0.0001

$R^2 = 0.99$ Predicted $R^2 = 0.980$ Adjusted $R^2 = 0.974$

of factors which give optimum percentage yield is given by equation 3.1. A quadratic regression equation that fitted the data is:

$$Y_{FAME(CASTOR)} = 92.12 + 4.38A + 2.79B + 2.54C + 3.46D + 1.54E + 1.94AB - 0.3125AC - 0.4370AD + 1.94AE + 1.31BC - 0.0625BD + 1.06BE - 0.3125CD + 1.81CE + 0.6875DE -$$
$$13.75A^2 - 1.75B^2 - 1.88C^2 - 1.630D^2 - 1.63E^2 \qquad (3.1)$$

Where $Y_{FAME (Castor)}$ is the response of the variables (percentage yield of FAME) and A-E are the coded values of the independent variables. The above equation represents the quantitative effect of the factors (A, B, C, D, and E) upon the response (Y). Equation 3.1 suggested that the yield of FAME has linear and quadratic effects on the five variables studied. Coefficients with one factor represent the single effect of that particular factor while the coefficients with more than one factor represent the interaction between those factors. Positive sign in front of the terms indicates synergistic effect while negative sign indicates antagonistic effect of the factors. The adequacy of the above proposed model was tested using the Design Expert sequential model sum of squares and the model test statistics. From the statistical analysis, the regression coefficient (R2 = 0.99) is reasonable , and the predicted R2 of 0.980 is in a reasonable agreement with the adjusted R2 of 0.974. This test result is shown in Table 3.5

Analysis of variance (ANOVA) for yield of FAME from castor oil

The ANOVA results for the model terms are given in Table 3.5. ANOVA was applied to estimate the significance of the model at 5% significance level. From the p-values presented in the table it could be stated that all the linear terms A, B, C, D and E ,the interaction terms AB, AD, AE, BC,BE, CE, DE and the quadratic terms A^2, B^2, C^2, D^2 and E^2 are significant model terms. Based on this, the insignificant terms of the model AC and CD were removed and theadjusted model obtained for biodiesel produced from castor oil as a function of the more significant variables, is given in equation. (3.2).

$$Y_{FAME(Castor)} = 92.12 + 4.38A + 2.79B + 2.54C + 3.46D + 1.54E + 1.94AB - 0.4370AD + 1.94AE + 1.31BC + 1.06BE + 1.81CE + 0.6875DE -$$
$$13.75A^2 - 1.75B^2 - 1.88C^2 - 1.630D^2 - 1.63E^2$$
(3.2)

Also, the adjusted model obtained for FAME produced from castor oil as a function of the more significant variables in real format, is shown in Eq. (3.3).

$$Y_{FAME(Castor)} = 92.12 + 4.38 methanol\ oil\ ratio + 2.79 catalyst\ conc + 2.54 temperature + 3.46 time + 1.54 agitation\ speed +$$
$$1.94 methanol\ oil\ ratio\ x\ catalyst\ conc - 0.4370 methanol\ oil\ ratio\ x\ time + 1.94 methanol\ oil\ ratio\ x\ agitation\ speed + 1.31 catalyst\ conc\ x\ temperature +$$

1.06$catalyst\ conc\ x\ agitation\ speed$ +
1.81$temperature\ x\ agitation\ speed$ +
0.6875 $time\ \ x\ agitation\ speed$ −
13.75$methanol\ oil\ ratio$ ^{2} −1.75$catalyst\ conc$ ^{2}
−1.88$temperature$ ^{2} – 1.630$time$ ^{2}
– 1.63$agitation\ speed^2$ (3.3)

From Table 3.4, it was clearly shown that among the five variables studied, methanol to oil molar ratio (A) has the highest effect on the yield of FAME from castor oil as it has the largest F-test value (739) for single effect followed by the reaction time (D). Agitation speed (E) showed the most insignificant single effect as it has the lowest F-test values.

Predicted and experimental or actual Values for yield of

FAME from castor oil.

Analysis was also carried out on the experimental data in Table 3.4 to check the correlation between the experimental and predicted biodiesel yield from castor oil, the actual and predicted plot is shown in Figures 3.7. It could be seen that the data points on the plot were linearly distributed, indicating a good relationship between the experimental and predicted values of the response, and the underlying assumptions of the above analysis were appropriate. The result also suggests that the selected quadratic model was proper and adequate in predicting the response variables for the experimental data.
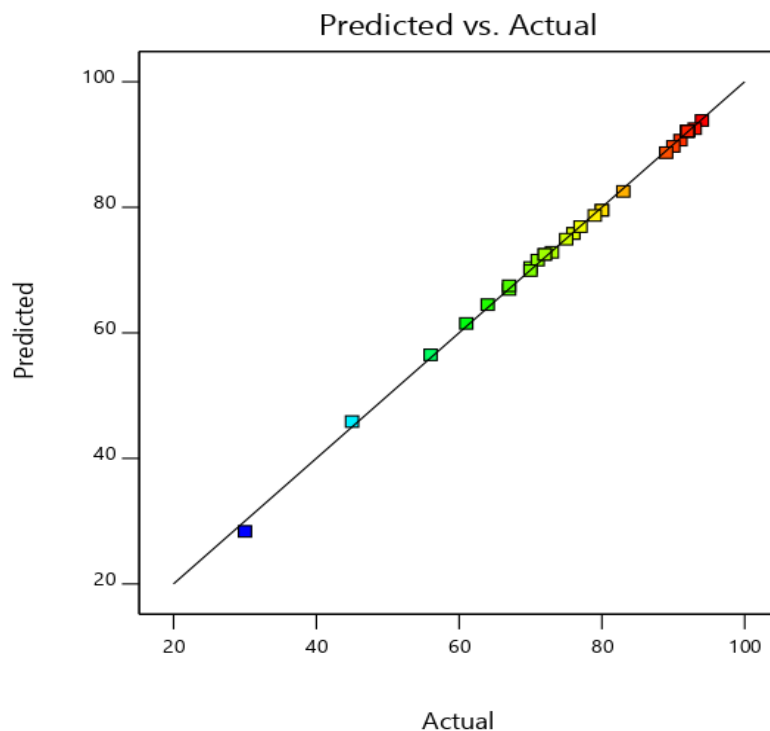

Figure 3.7: Plot of predicted values against the experimental values of FAME yield from castor oil.

Optimization of process parameters of FAME from castor oil

The optimization of process variables in this study was carried out using design expert version11. The optimum conditions suggested by the result analysis for maximum FAME yield of 90% within the ranges studied were: methanol to oil molar ratio 7:1, catalyst concentration 0.9%wt, reaction temperature of 65^{0}C, reaction time of 60 minutes and agitation speed 250rpm. Actual experiment

based on the optimum conditions produced 91.9% yield of FAME with small percent errors of 2.1%. This percentage errors of actual values compared to the predicted values indicated that the regression model developed in this study was accurate in representing the overall data and reliable in predicting the yield at any given conditions within the range studied for FAME produced from castor oil. The validation of results for the FAME yeild isas shown in table 3.6.

Table 3.6: Validation of result for yield of FAME from castor oil.

Methanol/ Oil molar ratio	Catalyst concentration (wt %)	Temperature (^{0}C)	Time (minutes)	Agitation speed (rpm)	Experimen- tal FAME yield (%)	Predicted FAME yield (%)
7:1	0.9	65	60	250	91.9	90

Three dimensional response surface plots for FAME yield from castor oil.

The 3D response surface plots of the different interaction effects were generated to estimate the effect of the combinations of the independent variables on the FAME yield. Figure 3.8 show that the amount of methyl ester yield increases with methanol/oil molar ratio and catalyst

concentration. However, at higher catalyst concentrations a reduction in the yield was observed. This may be due to the fact that high catalyst concentration has negetive effect on the yield of FAME from castor oil. High catalyst concentrations also encourages formation of soap which hinders and reduces ester formation.

Figures 3.9 shows the interaction effect between methanol to oil molar ratio and agitation speed on yield of FAME from castor oil. The figure shows that the FAME yield increases with methanol/oil molar ratio and agitation speed as a result of good homogenity, good reaction rete and enough alcohol. However, at higher methanol to oil molar and agitation speed, a reduction in the yield was observed . This may be due to poor contact between the reacting system, and the fact that the quadratic terms of the two factors are more significant with a negative effect on yield from castor oil.

Figures 3.10 shows the interaction effect between reaction temperature and catalyst concentration on FAME yield from castor oil. The figure indicated that the yield of FAME increases   with   reaction   temperature   and   catalyst concentration. This may be as a result of the fact that more rapid reaction rate could be obtained at high temperatures and high concentration of the catalyst which improved the yield. However, at higher catalyst concentration and reaction temperature above the boiling point of the alcohol , a decrease in the yield was observed due to evaporation of methanol at higher temperature and the fact that the quadratic terms of the two factors are more significant with a negative effect for yield of FAME fromcastor oil.
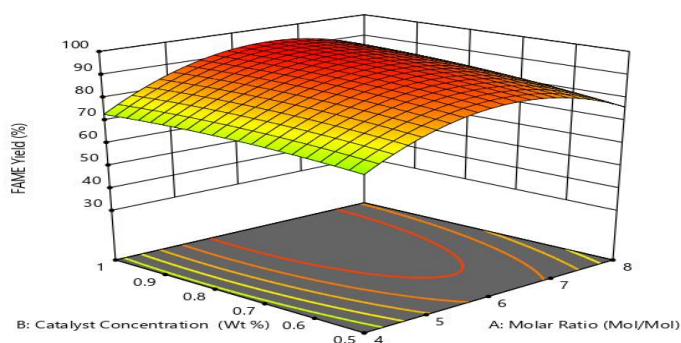

Figure 3.8: 3D response surface plot showing the effect of methanol/oil molar ratio and catalyst concentration on the yield of FAME from castor oil.
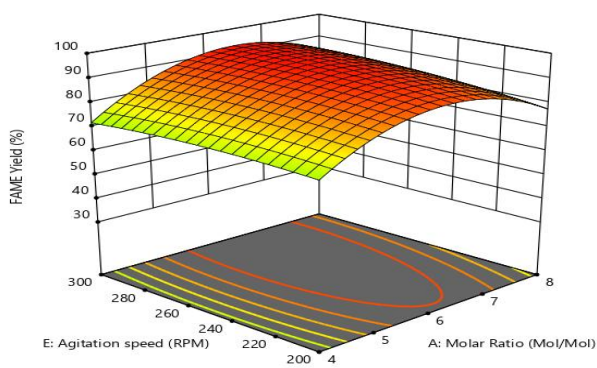

Figure 3.9:3D response surface plot showing the effect of methanol/oil molar ratio and agitation speed on the yield of FAME from castor oil.
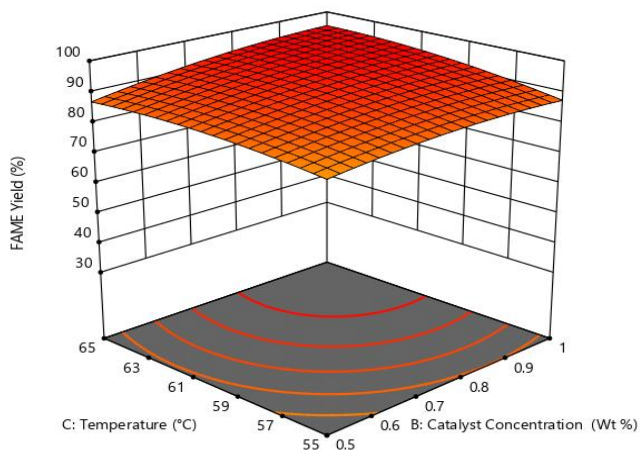

Figure 3.10 3D response surface plot showing the effect of temperature and catalyst concentration   on the yield of FAME from castor oil.

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