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Extraction of castor oil from castor seed for optimization of biodiesel production

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Abstract. This research was carried out to optimize biodiesel production from castor oil using 2^4 full factorial central composite design (CCD). Transesterification method was used for the biodiesel production from castor using KOH & NaOH were used as catalysts. Physico-chemical properties including density, kinematic viscosity, acid value, saponification value, iodine value and pour point. The results were determined both on the castor oil and biodiesel produced. The predicted optimum conditions for the production of castor oil biodiesel are; reaction time of 60 minutes at the temperature of 60°C, catalyst concentration of 3.5 g and a methanol /oil molar ratio of 5:1. The biodiesel yield was 99.76% and the result of the measured properties of biodiesel was compared with the international standards of EN14214 and ASTM D6751. The weight composition of the fatty acid and methyl ester were both determined by the Gas Chromatography (GCMS)

1.   Introduction

Due to the development of communities of people there is an increment in growing energy demands [1]. The primary sources of energy across the globe are fossil fuels, although there are several problems with non-renewable fuels of which are depletion. Crude oil in its most basic form, for just over 150 years, has been found and exploited around the globe. There is no doubt that oil production is now blowing up all over the globe, as every oilfield has been mined and diminished we merely run out of resources [2]. Moreover, among the highest environmental threats faced by our planet is global warming, owing to the rise in atmospheric greenhouse gases (GHG) based on human activity since the beginning of the industrial period. In the quest for sustainable power sources including a non-toxic, biodegradable, agrarian source called Biofuels, these facts became united [3]. Biofuels can be gotten directly from power crops or indirectly obtained from agrarian, industrial, commercial, or domestic waste. Generally, renewable biofuels require contemporary carbon fixation, as in crops or microalgae by means of photosynthesis. While others are produced using or transforming biomass (referring to previously existing organisms, mostly plant or materials derived from plants) [4]. The three distinct methods of transforming biomass into energy-containing substances are chemical conversion, biochemical conversion and heat conversion [5]. Biofuels can be solid which may include charcoal, fuelwood and wood pellets; gaseous (biogas); or liquid including ethanol, biodiesel and pyrolysis oils. Biodiesel is an equivalent diesel fuel composed of alkyl monoesters of vegetable and animal lipids and as a fuel; it is biodegradable and non-toxic [6]. Due to its fuel properties and compatibility, biodiesel is gaining global consideration. For instance, it has preferred possibilities over petro diesel, inexhaustible, greater biodegradability than petroleum derivatives, non-toxic, great lubricity, and essentially Sulphur-free and aromatic [7]. Biodiesel can possibly decrease the level of pollutants and

likely cancer-causing agents. It is an environmentally amiable fuel, which can be utilized in any diesel engine devoid of the need to redesign the present technology [8]. It does not contribute to the development of atmospheric carbon dioxide levels and thus to the greenhouse influence. Despite greater NOx outflows, biodiesel burning emissions contained reduced CO, CO2, HC and smoke [9]**.** Feedstocks for biodiesel consist of animal fats, vegetable oils, palm oil, mustard, soy, rapeseed, mahua, jatropha, flax, sunflower, field pennycress, hemp, algae, and Pongamia pinnata. The major feedstock used for the manufacture of biodiesel is vegetable oils. Among them is castor oil that has two fascinating concepts as raw material for biodiesel; on the one side, it does not achieve parity with edible oils; on the other side, does not involve increased input [10].

2.   Materials and Method

2.1   *Materials*

Castor seed was gotten from a native market place called Sabo in Omu-Aran of Kwara State. Analytical Grade like methanol, potassium hydroxide, sulphuric acid and sodium hydroxide were purchased from Merck Chemicals, India and were used for this experimental study without further purification.

2.2   *Castor oil extraction*

The castor seeds contained foreign materials and grime isolated through physical removal and washing. The castor seeds after washing were openly subjected to the heat of the sun to dry for 5 days, to enable the removal of the endocarp. Furthermore, the seeds were dried in a furnace overnight at 120 $^{\circ}$C to decrease the moisture contained thereof. In order to realize a major yield, the shell was separated from the nibs (cotyledon) by means of a tray so as to fan the lid. Afterwards, the seeds were beaten to split open the cell walls to discharge castor fat using a mortar and pestle.60g of the sample was positioned into the thimble and 200 mL of hexane was tipped toward the cylindrical bottom container. Soxhlet apparatus was subjected to a temperature of 75˚C and permitted to run for 2 hours continuous extraction.

2.3   *Physiochemical properties of extracted Castor Oil*

The physiochemical properties of the castor oil produced were determined according to standard test methods. These properties include the following:

2.3.1   Determination of Density. 50 mL pyrometer container was meticulously cleaned using water, dried with petroleum ether and weighed. The bottle was filled with water and weigh. The bottle was dried, the sample poured into it, weighed and evaluated by:

$$\text{Specific gravity} = \frac{weight\ of\ oil\ sample}{weight\ of\ water} \tag{1}$$

2.3.2   Determination of Kinematic viscosity. A NDJ-1B rotational viscometer was used to measure dynamic viscosity. 100mL of sample was spindled and the viscosity was measured as:

$$\text{Kinematic viscosity} = \frac{Dynamic\ viscosity}{density} \tag{2}$$

2.3.3   Determination of Moisture content. The cleaned sample was weighed so as to get the initial weight and desiccated in a furnace at 80°C for 8 hours with the weight decided after every 2 hours. A consistent weight was gotten after repeating the process. The sample was removed from the furnace after every 2 hours, and then positioned in the desiccator for 30 minutes to become cold. After which, it was detached and weighed again. The moisture percentage within the seed was measured using:

$$\text{Moisture} = \frac{W_1 - W_2}{W_2}\ X\ 100 \tag{3}$$

Where W_1 is the initial weight of the sample prior to desiccation (g); W_2 is weight of the sample after desiccation (g).

2.3.4   Determination of Flash point. 50 mL of the castor oil sample was transferred into crucible while the heat of the oil sample is gradually raised. A thermometer was suspended into the sample to monitor the rise in temperature. The temperature at which the sample begins flashing and burning was not supported is called the flash point.

2.3.5   Determination of Fire point. A 50 mL of oil sample was transferred into crucible while the heat of the oil sample is gradually raised. A thermometer was suspended into the sample to monitor the rise in temperature. The temperature at which the sample begins flashing and ignition was supported is noted as fire point.

2.3.6   Determination of Pour point. IA 50mL oil sample was positioned within a cold water bath and permitted to stand until it loses its flow features. The point at which the sample appeared hazy, a thermometer was employed to measure the heat of the sample.

2.3.7   Determination of Saponification Value. A standard solution of HCl (0.5 M) was prepared and 40g of KOH was dissolved in one liter of distilled alcohol at 15.5˚C while the alkali was being dissolved. 5g of the oil was weighed and added to 50ml of alcoholic KOH permitting it to deplete with the same time frame. A blank was also prepared with the same measurements. Both were boiled for an hour in a reflux condenser, when cooled, 1ml of Phenolphthalein was combined and analyzed against 0.5M HCl while waiting for the pink pigment to vanish. The expression of Saponification value is given as

$$Saponification\ value = \frac{(B-S)\ X\ 0.5\ X 56.10}{weight\ of\ Sample(g)}\ \text{mg/g.} \tag{4}$$

2.3.8   Determination of Iodine Value. 1g of each of the oil samples was weighed into a clean dry conical bottle. 15ml of dichloromethane was combined to melt the oil. 25 mL of wiji's solution was then added and shaken vigorously but carefully to avoid splashing out. The mixture was then stoppered in the flask and kept in the dark for 30 minutes to complete the reaction. 10mL of 5% KI solution was then combined and the combination was immediately analyzed against 0.5M thiosulphate to pale yellow, 0.5 mL of 1% w/v starch was then added resulting in a blue-black color, titration was continued to the disappearance of the colour. The titre value was recorded and the process repeated to obtain at least two concordant titrations. A blank analysis was also undertaken. The value of the Iodine was given as:

$$\text{Iodine value} = 12.69 \times (VB - VT) \times M \div W \tag{5}$$

Where, M is molarity of thiosulphate, W is weight of oil sample, VB is Volume of the blank and VT is volume of the test sample.

2.3.9   Determination of Acid Value. 95 mL of absolute ethanol was diluted to 100 mL with distilled water. 1g of phenolphthalein was at that point dissolved in the 95ml of ethanol (i.e. 1% phenolphthalein in 95% ethanol). 5.06g of castor oil was melted in 50 ml of the detached solid in a 250ml pointed bottle. 4 drips of phenolphthalein were at that point combined. The mixture was analyzed against 0.1M KOH, after which it was thoroughly stirred pending until a pink colouration was obtained.

$$\text{Acid value mg/KOH/g} = \frac{Titre\ value \times 0.1M\ KOH \times 56.10}{Weight\ of\ sample} \tag{6}$$

2.3.10   Determination of Peroxide Value. 1g of each oil sample was melted in 30mLblend of glacial acetic acid and chloroform (3:2 v/v) after shaken carefully with 0.5mL of KI added. That mixture was stirred for a minute for the reaction to liberate iodine with the peroxide. The solution was then analyzed with standardized thiosulphate solution till yellow pigment was almost discharged. 1mL of 1% w/w starch was then combined and titration was continued till blue black pigment was discharged. The titration was carried

out again to obtain two concordance and a blank titration was performed (AOAC, 2001). The peroxide value was evaluated as:

$$\text{Peroxide value} = 1000 \times (VT - VB) \times M \div W \tag{7}$$

VT is volume of the test sample, VB is volume of the blank, M is molarity of thiosulphate used and W is weight of sample

2.3.11   Determination of Percentage Free Fatty Acid. This was calculated by multiplying acid value by 0.503

$$\% \text{ Free Fatty Acid (FFA)} = AV \times 0.503 \tag{8}$$

Where AV = Acid Value

2.4   Esterification and transesterification experiments. Esterification reaction took place by adding 1mL of undiluted sulphuric acid to a 100 mL of castor oil in a beaker, and it was preheated in a water bath at 60˚C. 1mL of the acid was added to 30 mL of methanol and then transferred to the beaker containing the castor oil. After which it was shaken on a magnetic stirrer for 1 hour. The resulting blend was moved into a detaching flask and permitted to calm by gravity. The transesterification reaction happened within 500 mL 3-neck circular glacial pack reactor equipped with reflux condenser. Through a regulated magnetic heat stirrer, castor oil was heated to the temperature wanted. In order to produce CH_3OK, KOH was combined with methanol with a precise weight. CH_3OK was mixed with castor oil immediately the oil attained the intended heat level. The level wherein the reactant mixture attains the intended heat level is described as the reaction starting point (t=0). Utilizing a thermocouple equipped with the digital magnetic heat shaker, heat was supervised and regulated. Once the recommended reaction duration has been reached, the blend was then calmed and moved to a detaching funnel, where at the base, glycerol was detached out of the biodiesel. For the effective separation for the mixture, settling separation time was 120 mins. Afterwards, glycerol was detached and biodiesel was progressed for catalyst detachment phase. Biodiesel was then on cleaned by means of a mild water to eliminate the unreacted dissolved KOH catalyst. Unreacted methanol from biodiesel was retrieved by applying basic distillation where biodiesel was heated to 90ºC for 45 min. The same experimental procedure was repeated using NaOH as catalyst and purified biodiesel weight was measured for yield which was evaluated as:

$$\text{Biodiesel Yield} = \frac{weight\ of\ bisdiesel\ obtained}{weight\ of\ castor\ oil\ used} \times 100 \tag{9}$$

2.5   Statistical analysis

Central composite design (CCD) an aspect of the response surface methodology (RSM) was chosen for the optimization and preparation of biodiesel from castor oil. The appropriate utilization of this design expert was responses, levels and factors selection. Biodiesel yield was chosen as responses. In Table 1, levels and range of the examined variables are catalogued. Factors were heat (A), time (B) catalyst concentration (C) and methanol/oil molar ratio (D).

Table 1. Independent variables of the experimental coded levels

		Coded levels		
Variables	Units	-1	0	+1
Temperature (A)	ºC	30	45	60
Time (B)	min	30	45	60
Catalyst weight (C)	wt%	0.5	2	3.5
Methanol/Oil ratio (D)	-	1:1	3:1	5:1

The statistical software package Design-Expert 11.0 from State-Ease, Inc., Minneapolis, USA, was implemented to pattern the 20 data encompassing the whole design of the four factors as presented in Table 1. In line with CCD matrix, 20 experiments were carried out and the response yield was corresponded to a quadratic model as predicted by the software. Additional illustrations were made with a likening of 3D response surface plots to display the interactions diagrammatically and to authenticate the model. The significance of the model statistics was verified using ANOVA (Analysis of Variance).

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x^2 \tag{10}$$

2.6   Characterization of Castor oil and Biodiesel produced

The physiochemical properties of the castor oil and biodiesel prepared were characterized by the kinematic viscosity, density, acid value, and pour points, flash point, iodine value, fatty acid value, Gas chromatography Spectroscopy analysis (GC-MS) and Fourier transform infrared spectroscopy (FT-IR).

3.   Results and Discussion

3.1   Physiochemical properties of Castor oil. The chemical and physical properties of castor oil as presented in Table 2 depicts that the properties of oil are within the class limit and the oil is mainly Methyl Ricinoleate acid with percentage composition of 73.97 wt%. Therefore according to the result obtained, castor oil extracted from castor seeds can be used for biodiesel preparation [11,12].

Table 2. Chemical and physical properties of castor oil

Property	Value	ASTM limits	Testing method
Density (15°C)	962 kg/m^3	957-968 kg/m^3	AOCS cc 10a-25
Refractive index (20 °C)	1.458	1.467-1.490	AOCS cc 7-25
Acid index	1.64 mgKOH/g	0.4-4.0	AOCS cd 3a-63
Iodine	85 gl^{-1}/100 g	82-88 gl^{-1}/100 g	AOCS cd 1-25
Saponification index	180 mg KOH/g	175-187 KOH/g	AOCS cd 3-25
Viscosity	6.8	6.3-8.8 st	AOCS Tq 1a-64
HHV	38.47mJ/kg		
Kinematic viscosity	22.26 ±0.12		
Flash point	163°C		
Fire point	203°C		
Pour point	1.9 – 2.0 °C		
Peroxide value	12.41		
Free Fatty Acids	7.871		
Molecular weight	926 kg/mol		
Ricionoleic acid	14.54 wt%		
Palmatic acid	2.84 wt%		
Stearic acid	0.46 wt%		
Phenol	0.58 wt%		
Tridecylic acid	2.28 wt%		
Methyl Ricinoleate acid	73.97 wt%		

3.2   Statistical analysis

The statistical approach selected for the optimization of biodiesel production was 2^4 full factorial central composite design. The implementation of this approach demands suitably choosing factors, responses, and levels. Biodiesel yield for both NaOH and KOH were chosen as response. Table 3 shows the levels and range of the examined variables. Factors included; temperature, catalyst concentration, time and

methanol/oil ratio. The higher temperature level of 60˚C was selected for slightly being below the boiling point of methanol. The level underneath was 30˚C also slightly higher than room temperature, which won't necessitate a cooling device thereby increasing the expense of the technique. Catalyst concentration levels were between 0.5 and 3.5 grams. Methanol/oil molar ratio levels were 1:5. The highest yields given by the experiments in both NaOH and KOH were at 60˚C for reaction temperature, 5:1 for methanol/oil ratio, and 3.5g for catalyst concentration.

Table 3. RSM matrix and experimental results for biodiesel production

Std	Temperature(A) (˚C)	Time(B) (min)	Catalyst(C) (g)	Methanol: Oil(D) Ratio	NaOH Yield (%)	KOH Yield (%)
1	30	30	0.5	1	66.22	69.22
2	60	30	0.5	1	69.34	72.45
3	30	60	0.5	1	72.67	75.21
4	60	60	0.5	1	77.88	79.87
5	30	30	3.5	1	79.56	81.24
6	60	30	3.5	1	82.34	84.89
7	30	60	3.5	1	86.56	85.97
8	60	60	3.5	1	88.2	89.67
9	30	30	0.5	5	91.45	93.97
10	60	30	0.5	5	92.11	93.89
11	30	60	0.5	5	91.6	93.44
12	60	60	0.5	5	93.56	95.45
13	30	30	3.5	5	94.77	96.22
14	60	30	3.5	5	95.12	96.88
15	30	60	3.5	5	96.23	95.78
16	60	60	3.5	5	97.34	99.76
17	45	45	2	3	93.45	96.56
18	45	45	2	3	93.76	95.87
19	45	45	2	3	93.45	94.85
20	45	45	2	3	94.1	96.21

3.3 Analysis of Variance (ANOVA)

The investigative matrix for the factorial design and outcomes for both responses are displayed in Table 4 and 5. The two investigations were undertaken at the middle point level for estimation of investigative errors. The major significance of the variables was quantified and a statistical analysis was applied using these investigative values. The ANOVA for NaOH yield was seen in Table 4. The Model F-value of 369.61 indicates the relevance of the model. Only a 0.01% probability exists above an F-value which could be as result of based noise. P-values below 0.0500 imply that model terms are significant. Based on this, A, B, C, D, AD, BD, CD are significant model terms. Values above 0.1000 shows the model terms are not relevant. The Lack of Fit F-value of 6.24 indicates there is an 8.13% probability that a Lack of Fit F-value with this enormity could happen on the basis of noise. The Predicted R^2 of 0.9795 is in a reasonable

agreement with the Adjusted R² of 0.9951; that is the difference is below 0.2. Table 5 shows the analysis of variance (ANOVA) for KOH yield for the selected response as well as the test of statistical significance. The Model F-value of 203.02 denotes the model is relevant [13,14]. The P-values are utilized as a device to determine the relevance of the corresponding coefficient. P-values below 0.0500 imply model terms are relevant. On this basis, A, B, C, D, AD, BD, CD are relevant model terms. The P-values above 0.05 indicates that the model terms are not significant.

Table 4. ANOVA for the biodiesel production using NaOH as catalyst

Sources of Variations	Degree of freedom	Sum of squares	Mean square	F-value	P-value
Model	10	1518.27	151.83	369.61	<0.0001
A-Temperature	1	17.70	17.70	43.10	0.0002
B-Time	1	68.60	68.60	167.00	<0.0001
C-Catalyst	1	266.42	266.42	648.59	<0.0001
D-Oil-Methanol ratio	1	1046.68	1046.68	2548.09	<0.0001
Interactions	-	-	-		-
AB	1	0.5663	0.5663	1.38	0.2741
AC	1	1.61	1.61	3.91	0.0834
AD	1	4.70	4.70	11.94	0.0096
BC	1	0.0002	0.0002	0.0004	0.9849
BD	1	31.84	31.84	77.51	<0.0001
CD	1	80.15	80.15	195.11	<0.0001
Residual error	8	3.29	0.4108		
Lack- of -fit	5	3.00	0.5996	6.24	0.0813
Pure error	3	0.2882	0.0961		
CorTotal	19	1714.03			

Standard Deviation = 0.6409, R² = 0.9978, Adjusted R² = 0.9951

Table 5. ANOVA for the biodiesel production using NaOH as catalyst

Sources of Variations	Degree of freedom	Sum of squares	Mean square	F-value	P-value
Model	10	1382.27	138.23	203.02	<0.0001
A-Temperature	1	29.73	29.73	43.66	0.0002
B-Time	1	43.53	43.53	63.93	<0.0001
C-Catalyst	1	202.42	202.42	297.30	<0.0001
D-Oil-Methanol ratio	1	1006.00	1006.00	1477.52	<0.0001
Interactions	-	-	-	-	-
AB	1	2.97	2.97	4.36	0.0703
AC	1	0.2943	0.2943	0.4323	0.5293
AD	1	4.70	4.70	6.90	0.0303
BC	1	0.3875	0.3875	0.5691	0.4722
BD	1	23.64	23.64	34.73	0.0004
CD	1	68.60	68.60	100.75	<0.0001
Residual error	8	5.45	0.6809		
Lack- of -fit	5	3.81	0.7630	1.40	0.4151
Pure error	3	1.63	0.5440		
Cor Total	19	1599.13			

Standard deviation = 0.8251, R² = 0.9978, Adjusted R² = 0.9912, Predicted R² = 0.9698

3.4   Three- dimensional curve

The relevance of all the coefficients were ascertained by F-values and P-values as depicted in Table 4-5. The larger the F-value and the lower the P-value, the higher the significance of the varied variables [15-17]. The results obtained observed that the variable having the most significant was methanol/oil ratio for both the KOH and NaOH. It is also illustrated that the F-values and P-values of interactions show that interactive effects are insignificant on biodiesel yield. The effects of catalyst concentration, temperature and methanol/oil ratio linearly are more relevant compared to the squared term of temperature and they also have a positive outcome on biodiesel yield [18-20]. The two-dimensional contour plots and three dimensional response surfaces are common for the diagrammatical illustrations of the regression equation. Figure 1– 6 shows the contour plots and response surface for the predicted values of the biodiesel yield as a function of oil/methanol ratio for both NaOH and KOH.
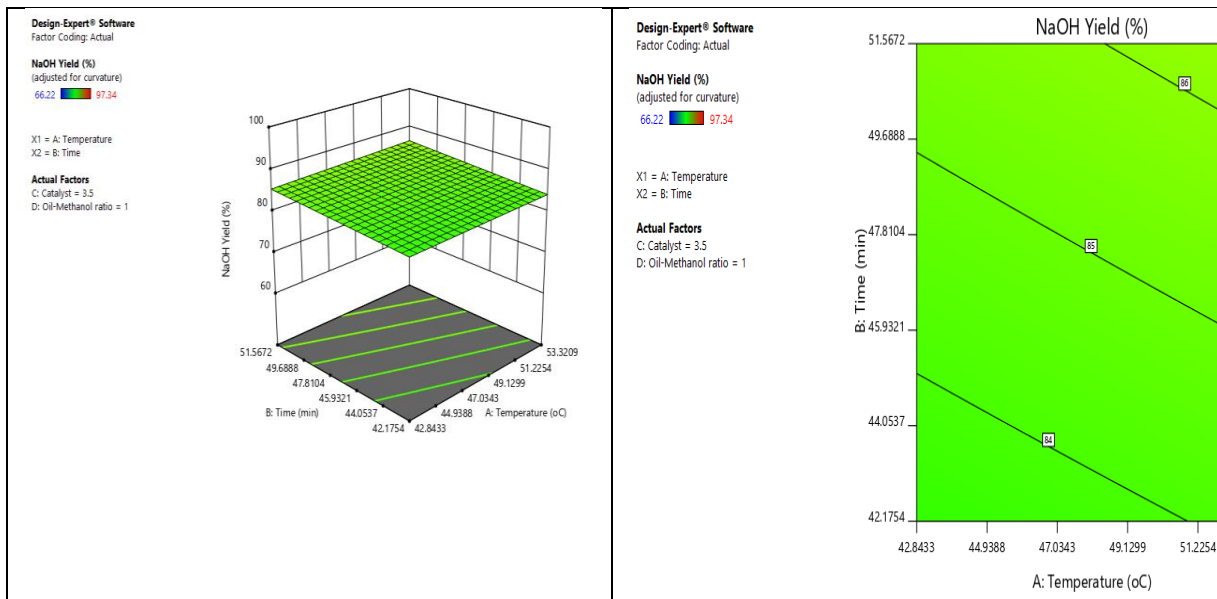
Figure 1. Three dimensional plots for effect of temperature and time on biodiesel yield using NaOH as catalyst.
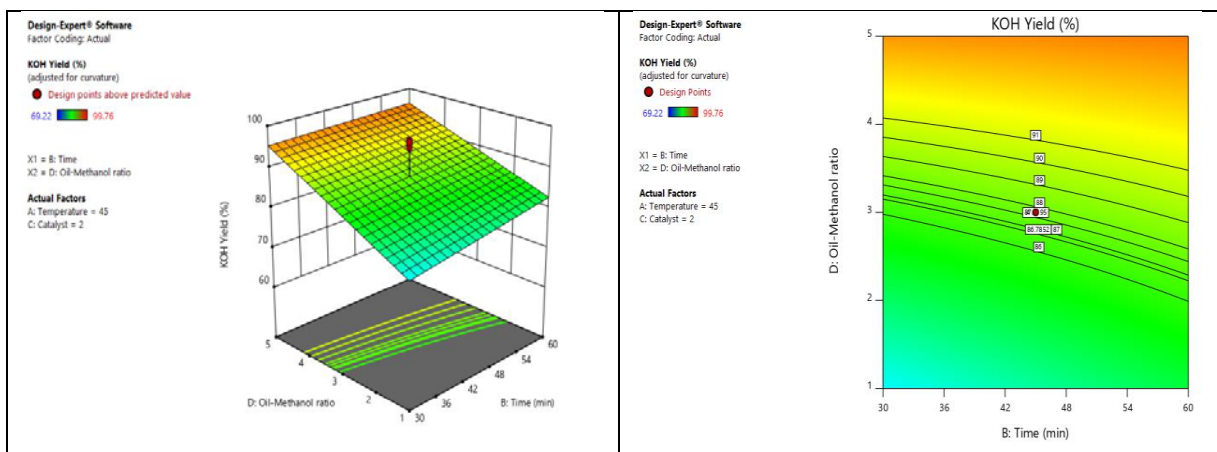

 Figure 2. Three dimensional plots for effect of Oil-Methanol ratio and time on biodiesel yield using KOH as catalyst.
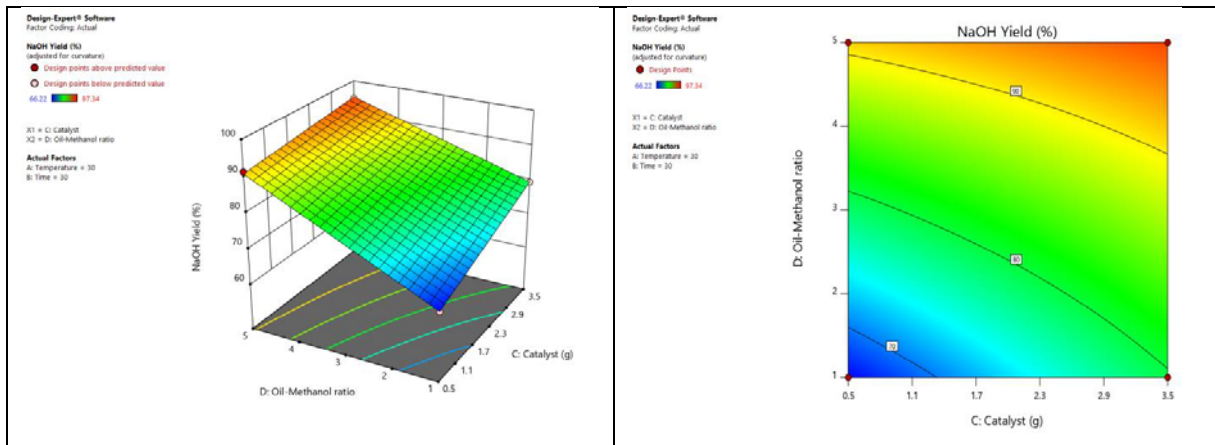
Figure 3. Three dimensional plots for effect of oil-methanol ratio and catalyst on biodiesel yield using NaOH as catalyst.
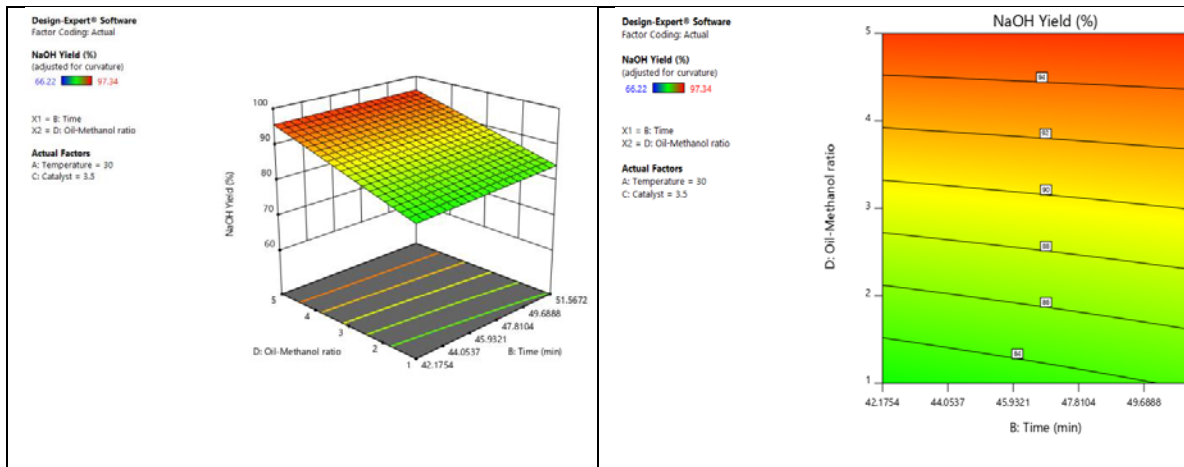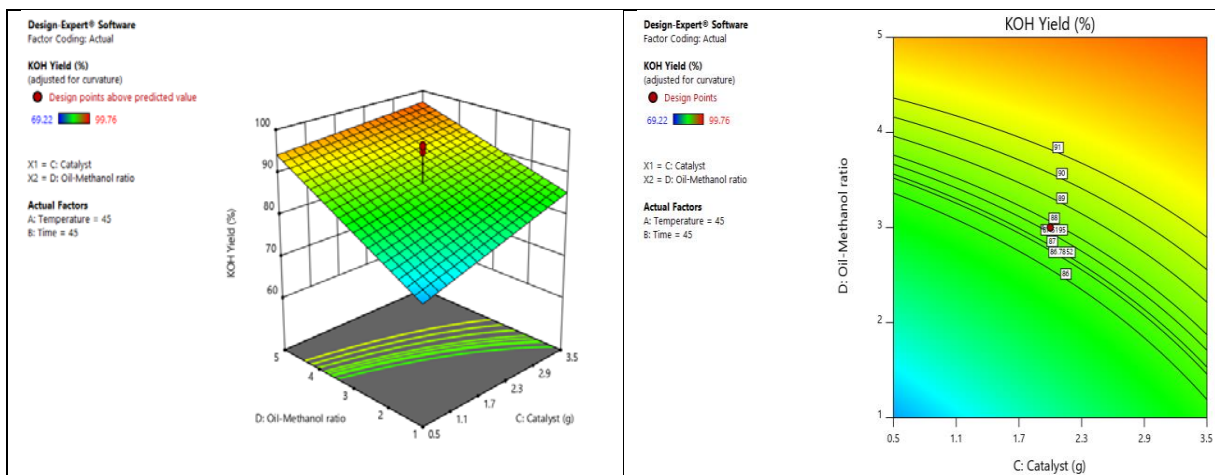

Figure 4. Three dimensional plots for effect of oil-methanol ratio and time on biodiesel yield using NaOH as catalyst.

Figure 5. Three dimensional plots for effect of oil-methanol ratio and catalyst on biodiesel yield using KOH as catalyst.
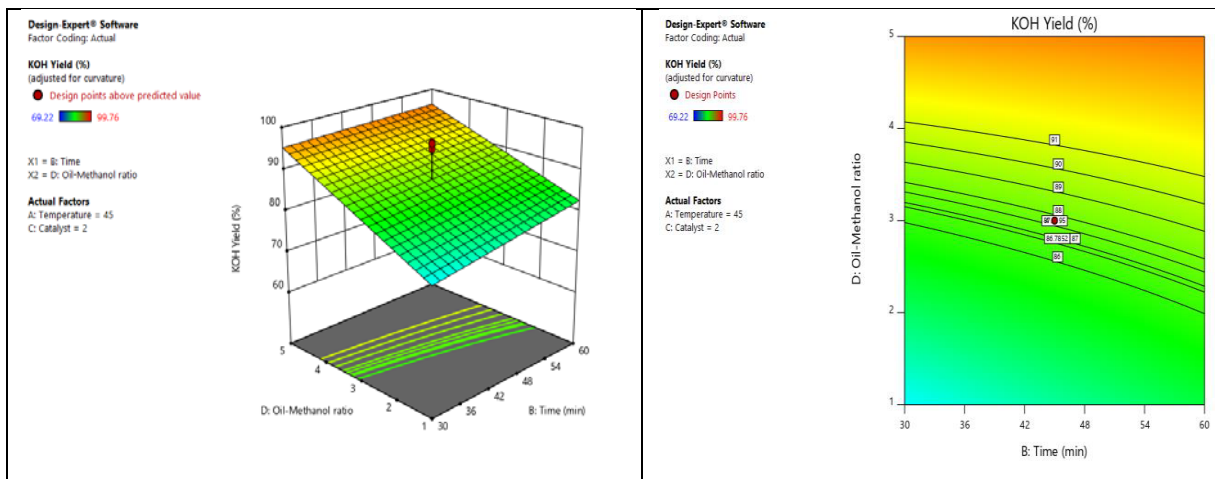
Figure 6. Three dimensional plots for effect of oil-methanol ratio and time on biodiesel yield using KOH as catalyst.

3.5 Catalyst effect

Based on the experimental design expert software, mid values were at 60˚C for reaction temperature, 5:1 for methanol/oil ratio, and 3.5g for catalyst concentration. Figure 7 illustrates the shows the effect of different catalyst on the castor oil biodiesel yield. The illustration indicates that KOH catalyst gave a superior biodiesel yield compared to the NaOH catalyst. It is indicated that after the transesterification reaction, both the lower and topmost layer phase contents created soaps when using NaOH catalyst. The formation of soap decreased when KOH catalysts was used [22, 23].
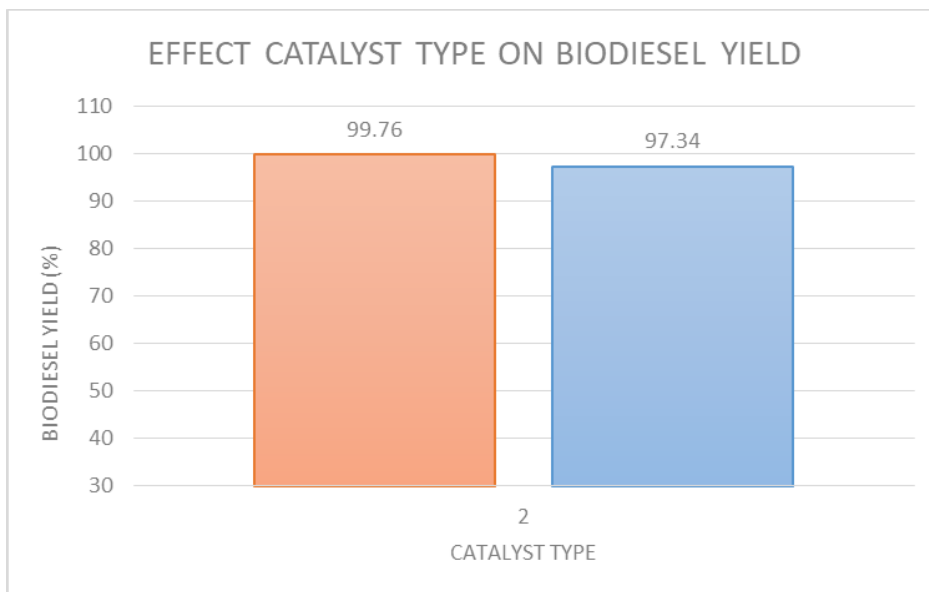

Figure 7. Effect of Catalyst Type on Biodiesel Yield

3.6 Fuel properties of Biodiesel

The produced biodiesel was compared with standards and the result was tabulated in Table 6. The result showed that it was in accordance with the European and American standard which makes it suitable to be used as an alternative fuel.

Table 6. Biodiesel fuel properties and standards

Property	NaOH results	KOH results	Standards	Test Method	Units
Density(25˚C)	821	857	860-900	EN14214	Kg/m³
Acid value	0.11	0.47	0.5max	ASTM D664	mg NaOH/kg
Pour point	4.9	6.3	-	-	-
Flash point	81	110	120 max	EN ISO3679	˚C
Kinematic viscosity	5.82	4.81	1.5-6.0	ASTM D6751	mm²/s
Iodine value	50	41.07	120 max	PR EN 1411	

4.0   Conclusions

Biodiesel production from Castor oil extracted from castor seed subjected to alkalis (NaOH and KOH) was effectively optimized by central composite design of RSM (response surface methodology).The experimental results from RSM revealed that the optimum condition for transesterification reaction for both catalyst used were 65°C reaction temperature, 3.5g KOH and NaOH catalyst concentration, 60min reaction time as well as 1:5 oil to methanol ratio to obtain 99.76% and 99.34% for KOH and NaOH respectively. ANOVA statistics showed that the models were very important with R^2 value of 0.9978 for both responses with a great connection to the predicted model. The FTIR result established that castor oil was absolutely transformed into biodiesel, FAME (Fatty acid methyl esters). The existence of palmitic acid, linoleic acid, tridecylic acid, stearic acid, ricinoleic acid and methyl ricinoleate were recognized as the prevailing esters in FAME by GC-MS analysis. The result of this research is beneficial in the optimization of parameters to manufacture biodiesel inexpensively from extracted castor oil. It may also be mixed with petroleum based fuel to enhance competence.

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