EFFECT OF TEMPERATURE AND PERCENTAGE OF INITIAL CATALYST ON THE *IN-SITU* PRODUCTION OF BIO-DIESEL FROM CASTOR OIL BEAN SEED USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

The use of vegetable oil and animal fats for biodiesel production has recently become a great concern because of the competition with food materials. As the demand for vegetable oil increase tremendously in recent years it has become impossible to justify the use of these oils for fuel production. *In-situ* trans-esterification process uses the oil (triglycerides) in the oil seed directly without the need for initial extraction as compared with the conventional trans-esterification. Castor oil bean seed contains between 35 and 55% oil and does not compete with food grade oil because of the seed's toxicity. This study evaluated the effect of temperature and percentage of initial catalyst on yield of castor ethyl ester. Raw castor oil bean seed kernel at moisture content of 4.68 % (db) was subjected to *in-situ* trans-esterification in a batch processor with ethanol as the solvent and sodium hydroxide as the catalyst. Central composite design (CCD) of the Response surface methodology was applied to evaluate the main and interactive effects of initial catalyst amount (0.5 – 1.5%) and reaction temperature (40 – 70°C), on yield of castor ethyl-ester, at reaction time of 120 minutes and alcohol-seed weight ratio of 1:1. A quadratic non-linear polynomial model was obtained to describe the effect of the factors on yield. The model was significant ($P < 0.05$) with a non- significant Lack-of-Fit value ($P < 0.05$) and R^2 value of 0.944. Second order response surfaces and contour plots obtained from the model revealed that initial catalyst amount was the more effective factors on yield while reaction temperature had less effect. The Temperature–percentage of initial catalyst interaction was small and negative, due to the combined effects of formation of by-products (soaps) and saponification. The biodiesel produced from ground castor oil bean seed during this study met the requirements of ASTM standard D6751-02 but specific gravity was higher than the ASTM standard confirming that biodiesel produced from castor bean seed using the *in-situ* technique can be used as replacement fuel for fossil diesel.

Keyword: *In-situ*, Trans-esterification, Biodiesel, Castor bean seed, Response surface, Modeling.

INTRODUCTION

Biodiesel is derived from vegetable oils and hence is renewable. It is chemically a mono-alkyl ester of long chain fatty acids derived from renewable biological sources such as vegetable oils and animal fats (Khan, 2002; Srivastava and Prasad, 2000). The potential

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production capacity, sustainable feed stock and cost of production have been identified as the main hurdles to commercialization of biodiesel (Ma and Hanna, 1999; Meher *et al.,* 2006; Van Gerpen *et al.,* 2007). The use of vegetable oil and animal fats for biodiesel production has recently become a great concern because of the competition with food materials. As the demand for vegetable oil increase tremendously in recent years it has become impossible to justify the use of these oils for fuel production. Nigeria and other developing countries do not have sufficient edible oil to fulfill the requirement of the food sector hence are imported with attendant high cost. The leeway for sustainable biodiesel feedstock would be a choice of seed oil preferably those that do not compete with food, underutilized and inedible oil seed that can be grown in the large arable land available in these developing countries. Castor oil bean seed is one of such non-edible vegetable seed oil and viable feedstock for biodiesel production in Nigeria. Castor oil bean seed contains between 35 and 55% oil and does not compete with food grade oil because of the seed's toxicity (Weiss, 1983). The seed contains ricin and ricine which are poisonous to both human and animal; however, the oil extracted from the seed is not poisonous. Castor oil dissolves easily in alcohol, ether, glacia, acetic acid, chloroform and benzene (Ogunniyi, 2006 and Ogunleye *et al.,* 2008.) and the density, viscosity and reactivity of castor oil are higher than triglycerides found in other vegetable oils (Heidbreder *et al.,* 1999). The high solubility of the oil in alcohol makes it most favourable for biodiesel production (Asadaukas and Erhan, 1999).

Trans-esterification is the most commonly used methods of biodiesel production, which is the reaction of an alcohol with oil (triglyceride) in the presence of a catalyst to produce biodiesel (ester) and glycerol as a by-product. *In-situ* trans-esterification process uses the oil (triglycerides) in the oil seed directly without the need for initial extraction as compared with the conventional trans-esterification where the oil is usually first extracted and refined, leading to high cost of procuring the biodiesel feedstock and increased production cost of biodiesel. The cost of oil has been reported to contribute to over 70% of the total cost of biodiesel when refined oil was used (Holmberg and Peeples, 1994; Bender, 1999; Haas *et al.,* 2006). *In-situ* trans-esterification process would have removed the expression, purification and degumming processes of the raw oil thereby reducing the production cost and providing a favourable comparison worth available fossil diesel (Haas and Scot, 2007).

Researchers' such as Zeng *et al.* (2009); Harrington and D'Arcy-Evans (1985); Obibuzor *et al.*(2002); Haas *et al.* (2004, 2007); Silver-Marinkovic and Tomasevic (1988); Khalil and Leite (2006); Ozgul and Turkay (2003) have all reported that biodiesel produced using *in-situ* method compared favorably with biodiesel obtained with the conventional process. The ratio of seed to alcohol, amount of catalyst, reaction temperature, time and moisture content of seed has been reported to affect the *in-situ* process.

The Energy Commission of Nigeria (ECN, 2005) reported that Nigeria's fossil-led economy is under severe pressure. Today, large hydropower plants are increasingly threatened by a shrinking River Niger, shaking the security of electricity supplies. Alamu *et al.* (2007) reported that Nigeria currently imports about 80% of its petroleum requirements. There is little documented work on

the production of biodiesel from castor bean seed using *in-situ* trans-esterification as affected by process factors, therefore, the objective of the study was to evaluate the effect of temperature and percentage of initial catalyst on yield of castor ethyl ester using central composite experimental design and establish a model to describe the effect of experimental variables.

MATERIALS AND METHODS

Castor bean seeds used for the study were procured from the experimental field of the Forestry and Wildlife Department of the University of Agriculture, Abeokuta and Odeda Farm Settlement of Ogun State, Nigeria. Initial moisture contents of the seed samples were determined (6.5% db) and were further reduced (4.68% db) by sun drying. The dried seeds were hand threshed, passed through a Tyler sieve set to remove impurities, chaffs and other foreign matter. The seed were ground in a blending machine to reduce its size and consequently increase its surface area. The ground seeds were divided into specified weights, sealed in double polythene bags and stored in the refrigerator prior to use.

The *in-situ* reactor was a 1.25 litre wet and dry mill multi speed Osterizer blender (Pulsematic, model Cycleblend 10, Pulsematic UK) with a 500W electric heating element (240V, Semyem Electronics, Japan) incorporated. The blender had a clear glass with stainless steel cutting blades. The temperature was monitored and controlled with a temperature controller (Kazuki, model KZ 200DT, Kazuki China) of 2oC accuracy connected together with a T-type thermocouple and a mercury in glass thermometer.

The ethanol used had a boiling point of 78oC therefore reaction temperatures of between 40 and 70oC were selected. Reaction temperature for trans-esterification must be below the boiling point of alcohol used (Van Gerpen *et al,* 2004). The catalyst amount was usually between 0.1 and 1.5% by weight oil (Van Gerpen *et al.,* 2007), therefore catalyst amount was taken as between 0.5 and 1.5% by weight of oil. Chitra *et al.* (2005) reported that reaction times ranges from 30min to 2h, therefore a reaction time of 120 min was selected. The catalyst, sodium hydroxide was of analytical grade manufactured by Aldrich Chemical Co. Ltd, England.

Laboratory production of castor biodiesel (Castor ethyl-ester)

✦ 400 g of ground castor bean seed was charged from the top into the reactor with the same amount of alcohol (400 g) at ambient conditions (29 – 32oC).

✦ Both seed and alcohol were mixed for 20 minutes to obtain a homogeneous suspension.

✦ The catalyst with quantities of 0.5, 1.0 and 1.5% by weight of seed was then added to the homogeneous mixture while still stirring.

✦ The temperature of the homogenous suspension in the reactor was raised from ambient conditions (29 – 32oC) to the desired level (40, 55, 70oC) and kept constant with a calibrated thermostat attached to the heating system.

✦ At the end of the reaction time (120min), the reaction was stopped by adding ethanoic acid (1:1) to neutralize the catalyst (Ma *et al.,* 1998). The hot mixture was decanted and filtered into the solid and liquid phases.

✦ The solid phase was removed from the filter and dried to remove excess alcohol. The decanted liquid was allowed to settle into the heavy phase (glycerol) and the light phase (ethyl-ester) in a sealed glass jar.

✦ The ethyl-ester was transferred into a

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plastic bottle for washing to remove contaminants such as ethanol, glycerol or catalysts. Washing was done for a minimum of four times or when water below the ethyl-ester became clear.

✦ The washed biodiesel was weighed and weight recorded to determine the yield.

✦ The above procedure was performed in triplicates for all levels of experimental variables for all levels of experimental variables according to experimental design.

Experimental design

The Central Composite Design (CCD) of the Response Surface Methodology (RSM) was used for the study. The CCD is an experimental design useful for building a second order model for responses without the need to use a complete three-level factorial experiment. It allows seeing interactions among experimental variables within the range studied, leading to better knowledge of the process and therefore reducing research time and costs (Box and Hunter, 1978). Reaction temperature and percentage of initial catalyst were taken as the independent variable with the yield as the dependent variable or the response. The experimental coded and actual levels are presented in Table 1 while the CCD design matrix in coded values as obtained from Design Expert 7.1 software (Stat-Ease, 2007) is shown in Table 2.

The Yield is the ratio of the weight of washed castor ethyl ester to that of the expressible weight of oil in castor bean seed, Eq. (1), was the dependent variable and referred to as the response.

$$Y = \frac{W_{ester}}{W_{oil}}$$

(1)

Where Y is the yield, W_{ester} (g) is the weight of washed ester (g) and W_{oil} (g) is the weight of expressible oil in seed.

Table 1: Central Composite Experimental Design Variables in Coded and Actual Values

Actual Process Variables	Experimental Coded Variables	Experimental Coded Levels		
		-1	0	+1
Reaction Temperature (oC)	X_1	40	55	70
Percentage Initial Catalyst (%)	X_2	0.50	0.1	1.5

Statistical analysis

Multiple regression procedures following a second order polynomial equation, Eq. (2), was used on data obtained from the *in-situ* experimental runs using Design Expert 7.1 software (Stat-Ease, 2007)

$$Y = \beta_0 + \sum_{i=1}^{2} \beta_i x_i^1 + \sum_{i=1}^{2} \beta_{ii} x_i^2 + \sum \sum_{i<j=1}^{2} \beta_{ij} x_i x_j$$

(2)

Where Y is the response, x_i and x_j are the un-coded independent variables and b_0, b_i, b_{ii} and b_{ij} are intercepts, linear, quadratic and interaction coefficients respectively.

The Analysis of variance (ANOVA) and the lack-of-fit statistics were used to determine whether the constructed model was adequate to describe the observed data. The lack-of-fit test is performed by comparing the variability of the current model residuals to the variability between observations at replicates settings of the process factors. The coefficient of determination (R-squared) statistic is a measure of the percentage of the variability of the parameter that is explained by the model, the higher the R-squared value the better the model.

der polynomial equation, Eq. (2). The coefficients of Eq. (2) were determined by multiple regression analysis procedure of Design Expert 7.16 software. The regression included all experimental variables and interactions regardless of their significant levels. The ANOVA revealed a highly significant model (p-value < 0.05) with an F-value of 23.60 at 95% confidence level and a coefficient of determination (R^2) of 0.944 as shown in Table 3. The lack-of-fit as determined by the ANOVA (p-value <0.05) is not significant, indicating that the response model represented well the actual relationships of experimental factors within the ranges of experimental study. The model obtained from the analysis is presented in Eq. (3).

RESULTS AND DISCUSSION

The experimental results presented in Table 2 was analyzed and fitted to the second or-

$$Y = 13.231 + 1.028 X_1 + 71.243 X_2 - 0.040 X_1 X_2 - 0.007 X_1^2 - 28.461 X_2^2$$

(3)

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where X_1 is the reaction temperature (oC) , X_2 is the initial percentage catalyst (%) and Y is the yield of biodiesel (%).

Influence of reaction temperature on yield of castor ethyl ester

The singular effect of temperature with percentage of initial catalyst can be captured in the two dimensional graph presented in Fig. 1. It revealed that as a single factor, reaction temperature (X_1) had a slightly positive effect on the yield as temperature increased though the effect appears negligible on the yield at temperatures above 62.5oC at all levels of percentage initial catalyst used in the study. This observed effect of temperature may be due to the fact that castor-oil is highly soluble in alcohol at temperatures as low as 25oC, thus it is expected that temperature might not have significantly affected the ethanolysis reaction as a single factor. Several researchers (Ma and Hanna, 1999; Freedman et al., 1984; Pinto et al., 2005; Van Gerpen et al., 2007) have reported that increase in temperature influence trans-esterification in a positive manner, however, the temperature must not exceed the boiling point of the reacting alcohol to prevent the volatilization of the alcohol during trans-esterification. However, in this study temperature only had a slightly positive effect on the yield of castor ethyl-ester at all levels (-1, 0, +1) of percentage initial catalyst used in the study.

Table 2: The Central composite design employed for reaction temperature and percentage of initial catalyst variables, experimental data, response model predicted data and residuals

Temperature (X_1) (oC)	Catalyst Amount (X_2) (%)	Experimental Yield (%)*	Predicted Yield (%)	Residuals
40	0.5	70.27±0.20	70.10	0.17
40	1.0	84.40±0.42	83.58	0.82
40	1.5	81.84±0.31	82.83	-0.99
+55	0.5	74.71±0.24	74.55	0.16
+55	1.0	89.19±0.32	87.74	1.45
+55	1.0	86.27±0.62	87.74	-1.47
+55	1.0	85.32±0.53	87.74	-2.42
+55	1.0	88.98±0.51	87.74	1.24
+55	1.0	86.29±0.30	87.74	-1.45
55	1.5	89.18±0.41	86.69	2.49
70	0.5	75.31±0.22	75.64	-0.33
70	1.0	90.35±0.23	88.53	1.82
70	1.5	85.69±0.33	87.18	-1.49

+ centre points

* mean of three replicates

Table 3: Analysis of variance (ANOVA) for full response surface quadratic model

Source of Variation	Sum of Squares	Mean Square	F-Value	p-value (Prob > F)	Remark
Model	460.38	92.08	23.60	0.0003	significant
X_1- Temperature	36.70	36.70	9.41	0.0181	
X_2-Catalyst Amount	221.07	221.07	56.66	0.0001	
X_1X_2	0.35	0.35	0.091	0.7720	
X_1^2	7.84	7.84	2.01	0.1992	
X_2^2	139.82	139.82	35.84	0.0005	
Residual	27.31	3.90			
Lack of Fit	14.96	4.99	1.61	0.3198	not significant
R^2				0.944	
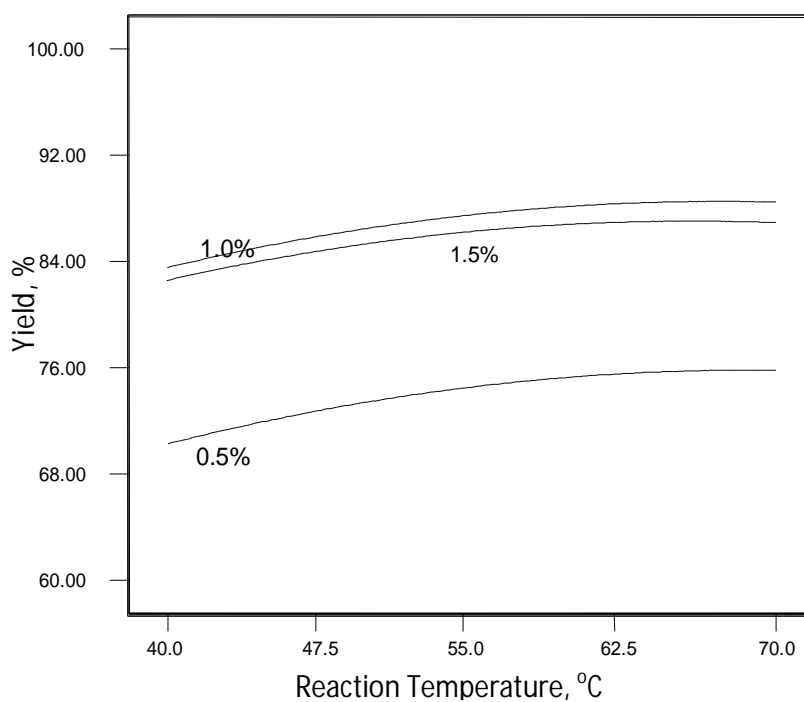
Figure 1: Effect of reaction temperature on yield of biodiesel at 0.5, 1.0 and 1.5 percentage initial catalyst

Influence of percentage of initial catalyst on yield of castor ethyl-ester

The amount of catalyst significantly affected the castor ethyl-ester yield, with increased ester yield resulting from increased percentage of initial catalyst from 0.5 to between 1.0 and 1.25% for all levels of temperature as shown in Fig. 2. However, at higher levels of percentage of initial catalyst (from 1.25 to 1.5%) the yield decreased, indicating that a curvature existed and that optimum value for percentage of initial catalyst would be between 1.00 and 1.25%. The influence of catalyst could be attributed to the fact that percentage of initial catalyst determines the rate of reaction (production of ethyl-ester), thus as the percentage of initial catalyst was increased, side reactions favored by increased percentage of initial catalyst occurred. Such side reactions are the formation of by products such as soaps and the neutralization of the free fatty acid (FFA) of the oil. The average free fatty acid of the castor oil which is regarded as half of the acid value was between 5.25 and 5.36 mg KOH/g. The soaps that are formed are dissolved into the glycerol during phase separation because of the polarity of the soap; the dissolved soap increases the solubility of ethyl-ester in the glycerol resulting in additional losses of ethyl-ester. The soap formation also consumes catalyst consequently reducing the amount of catalyst available for the ethyl-ester production. This might also have resulted in decreased yield of castor ethyl-ester. These observations are in consonance with reports of Ramadhas *et al.* (2005); Meher *et al.* (2006); Freedman *et al.* (1984); Dorado *et al.* (2002); Zeng *et al.* (2009). Fig. 2 also revealed that there was a slight effect of temperature on yield after 55°C, this might be that an optimum temperature after which significant increase in yield might not be achieved.
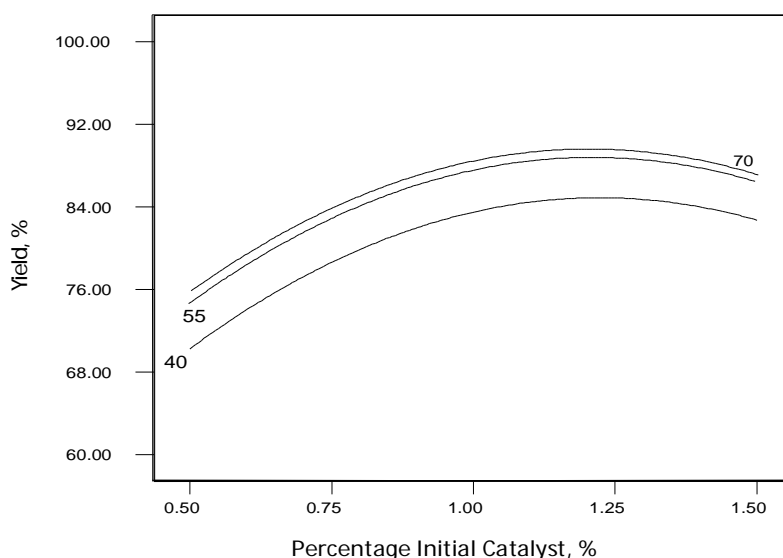

Figure 2: Effect of percentage of initial catalyst on yield of biodiesel at reaction temperatures of 40, 55 and 70°C

Interactions of experimental variables (influence of interaction)

The response surface methodology allows researchers to understand interactions between experimental variables and thus better understand process lines. The interactive plot of reaction temperature and percentage of initial catalyst on yield is shown in Fig. 3 as obtained from Eq. (3). The non -linear model gives the binary influences of all the factors used in the design, the interaction of reaction temperature and percentage of initial catalyst (T-C) is significant and had a negative influence on the process, this might be due to the formation of by-products (soaps) which reduced the yield of biodiesel produced.
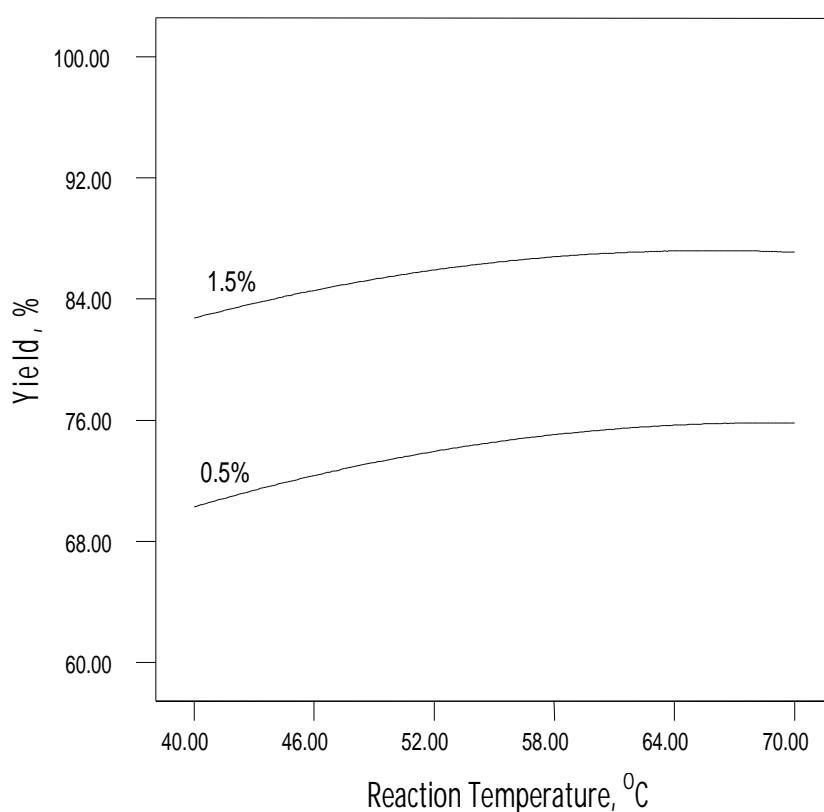

Figure 3: Interactive effect of reaction temperature and percentage of initial catalyst on yield of biodiesel

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Analysis of response (yield of castor ethyl-ester)

The ester yield generally increased with increased percentages of initial catalyst and reaction temperature, but progressively decreases at higher levels of these factors as depicted in response plot of Fig. 4. This observation may be explained by the formation of by-products, possibly due to triglycerides saponification processes, side reactions which are favoured at high percentage of initial catalyst concentrations and temperatures. This side reaction produced sodium soaps and thus, decreased the ester yield. Since the acid value of castor oil was 1.69 mg KOH/g, another possible side reaction, the neutralization of free fatty acids, also produces sodium soaps and may be considered partly responsible for the decrease in the reaction (ester) yield. Owing to their polarity, the soaps dissolved into the glycerol phase during the separation stage after the reaction. In addition, the dissolved soaps increased the ethyl ester solubility in the glycerol and this involved an additional loss of yield. Both soaps formation and triglycerides saponification are undesirable side reaction because they partially consume the catalyst, decrease the biodiesel yield and make the separation and purification steps more difficult. The surface plot and contours of ester yield versus temperature and percentage of initial catalyst obtained from Eq. (3) are plotted as shown in Fig. 4. The response surface plot shows that the maximum ester yield is achieved at the centre levels for both reaction temperature and percentage of initial catalyst.

Fuel characteristics

Fuel qualities such as specific gravity, pour point, heating value, flash point and the viscosity of produced biodiesel are shown in Table 3. These parameters were compared with the ASTM standard D6751-02 (ASTM, 2004) for biodiesel and the European Standards, EN 14214. The specific gravity obtained was higher than the specification of the ASTM and EU standard; this might be due to the presence of some impurities that may still be residing in the biodiesel (Sharma, *et al.,* 2008).
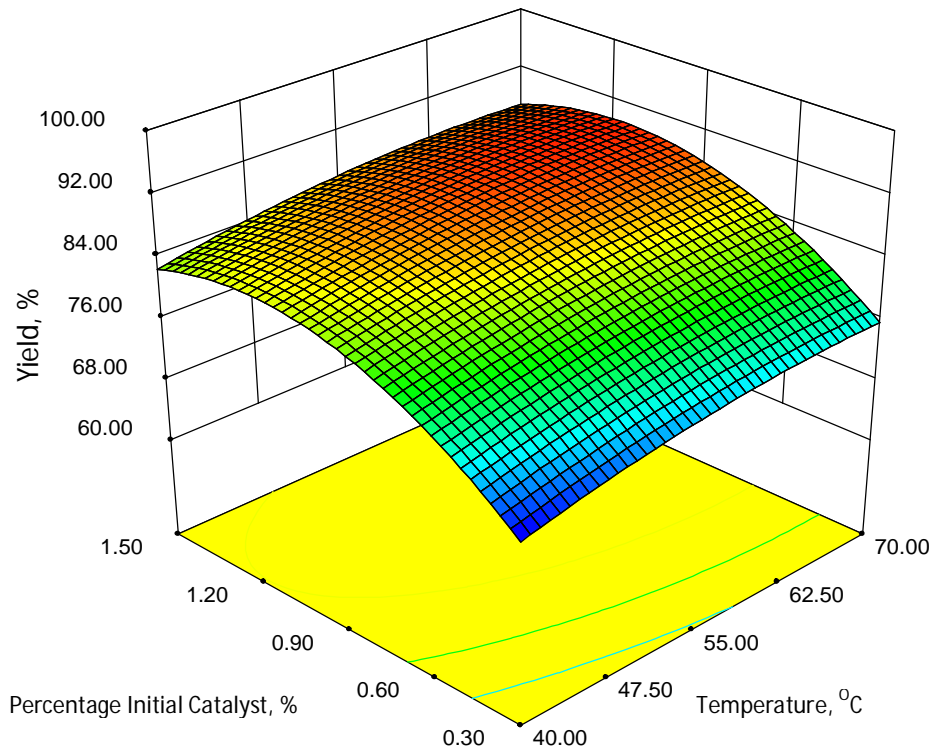
Figure 4: Response surface plot showing the effect of temperature and catalyst amount on yield of biodiesel

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Table 3: Fuel properties of experimental castor bio-diesel in comparison with ASTM ,EU standards, fossil diesel and esters from some oil seeds

Property	Unit	Castor [a] Ethyl-ester (Biodiesel)	ASTM[e] Standard D6751-02	EU [e] Standard EN 14214	Soy [b] Ethyl Ester (biodiesel)	Palm Oil[c] Ethyl-ester	Jathropha [d] Bio diesel	Fossil Diesel[e] Fuel
Specific Gravity @ 15°C	g/cm³	0.932	0.880	0.86–0.90	0.881	0.883	0.880	0.850
Viscosity @ 40°C	mm²/s	5.75	1.9 -6.0	3.5 – 5.0		4.839	4.84	2.0 – 3.0
Flash Point	°C	177	>130	>120	160	167	192	74
Heating Value	MJ/kg	40.5	-	-	40.0	40.56	37.2	42.9
Acid Value	mg KOH/g	0.34	<0.8	<0.50	-	-	0.24	-

a, Present study; b, Cvengros et al.(2006);); c, Alamu et al. (2007); d , Raheman and Phadatare (2004); e, Canakci and Van Gerpen (2003)

CONCLUSION

A statistical design of experiments has been applied to study the effect of reaction temperature and percentage of initial catalyst on the production of biodiesel from castor oil bean seed using the *in-situ* method. A reaction time of 120 min and alcohol seed weight ratio of 1:1 was used in the study. The yield of biodiesel, taken as the response revealed that, within the experimental range considered, the more important factor is the percentage of initial catalyst; this factor had a positive influence on the yield of biodiesel produced. The reaction temperature only had a slightly positive influence in the yield obtained. The temperature – percentage of initial catalyst interaction (T-C) was small and negative, due to the combined effects of formation of by-products (soaps) and saponification. A non-linear polynomial model was obtained to describe the effect of the factors on yield. The model was significant ($P < 0.05$) with a non-significant Lack-of-Fit value ($P < 0.05$) and R^2 value of 0.944. This model can be used to determine the optimum operating conditions for the industrial process using a minimal number of experiments with the consequent economical benefit. Fuel properties of the biodiesel produced was also found to meet the ASTM standard (D6751-02) for biodiesel.

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