

Biodiesel Production from Castor Seeds by Reactive Extraction conventionally and via Ultra-Sound Using Response Surface Methodology

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Abstract:

The goal of this study is to reduce the production cost of biodiesel, so we used non edible oil (castor seeds oil) which has a unique structure; suitable for biodiesel production and has lower cost compared to other biodiesel from other vegetable oils. Reactive extraction via ultrasonic-assisted process was used offering the potential for shorter reaction times, cheaper reagents and less insignificant physical conditions, leading to less expensive and smaller chemical plants. A factorial design of experiments and a central composite design have been used to evaluate the influence of operating conditions on the process. The response was the yield while the studied variables were the initial catalyst concentration and the methanol to oil molar ratio at room temperature. In case of ordinary reactive extraction, the experimental results are adequately described by a first order model where the methanol to oil molar has the most effective influence on the reaction yield. In case of ultrasonic reactive extraction, the catalyst concentration has the most significant effect on the yield of biodiesel and the experimental results are adequately described by a second order model.

1. Introduction:

Biodiesel is an alternative diesel fuel produced from biological sources such as vegetable oils, animal fats or microbial oils (algae, bacteria and fungi) [1]. Biodiesel has various advantages, it is complement or substitute to petroleum based fuel, it is a renewable fuel, it has a favorable energy balance, it is nontoxic, eco-friendly and useful in CO₂ recycling over short periods [2-3]. In the last few years, there has been a major concern about the use of edible oils such as soybean, rapeseed, canola, sunflower, palm, coconut and even corn oil [4-5] for transportation purposes. Therefore, a possible solution to this issue is to produce biodiesel from non-edible oils such as *Jatropha curcas* L. seeds [6], beeftallow [7], waste cooking oil [8] and *Cerberadollar*(sea mango)[9] which are not suitable for human consumption because of the presence of some toxic components in the oils. Furthermore, non-edible oil crops can be grown in waste lands that are not suitable for food crops and the cost of cultivation is much lower because these crops can still sustain reasonably high yield without intensive care [10-12].

Castor oil, *Ricinus communis* L., (castor bean, castor, castor oilplant, ricin, higuerrilla, mamona, mamoeira, palmachristi) is a member of the tropical spurge family (Euphorbiaceae) and can nowadays be found naturalized and cultivated in all temperate countries of the world. Just like other vegetable oils, castor oil is a triglyceride of various fatty acids and about 10% glycerin. The fatty acids consist of approximately 80–90% ricinoleic acid, 3–6% linoleic acid, 2–4% oleic acid and 1–5% saturated fatty acids. The high content of ricinoleic acid is the reason for the versatile value of castor oil in technology [13, 14]. Compared with other vegetable oils, castor oil has a very high proportion of simply unsaturated fatty acids (18:1). A comparatively high proportion of those acids can be found only in the oil of the high oleic (HO) sunflower, appearing, however, as oleic acid. In castor oil it is ricinoleic acid, the only unsaturated fatty acid occurring in natural

vegetable oils with a hydroxyl function of the carbon atom 12. The extraordinarily high viscosity of castor oil is attributed to the presence of this hydroxyl group [15]. Castor oil biodiesel has lower cost compared to the one obtained from other vegetable oils due to its solubility in alcohol and thus the transesterification reaction can occur under the ambient temperature. Moreover, it does not contain sulfur, it has greater cetane number, which indicates a better quality of ignition, and it has more oxygen, making its combustion more complete. [16]

Conventional method for production of biodiesel involves the steps like extraction of oil; refining and transesterification, apart from that, in-situ transesterification or reactive extraction is an alternative processing method involves the simultaneous extraction and transesterification of oil from seeds, the alcohol acts as an extraction solvent and an esterification reagent [17,18]. This route could eliminate the cost of the product and time of oil extraction [19]. Harrington and D'Arcy-Events [20] observed ester production with yields up to 20% greater in the in situ than in the transesterification of pre-extracted oil in case of sun flower seeds.

Several authors have reported the in situ-alkaline- catalyst transesterification of cotton seed oil [21], sunflower seed [17], castor seed [22], rape seed [23], *Jatropha curcas* [24], *Pongamia pinnata* oil [25], and rice bran [26]. Some work has been carried out on the in situ-acid- catalyst transesterification of sunflower seed [27], rice bran [28] and *Jatropha* seed [29, 30]

Although there have been different studies reported on production of biodiesel from castor oil [31, 32], however reactive extraction of castor seed is rarely studied [33] and reactive extraction via ultrasonic irradiation is not studied.

Ultrasound (US) is simply a sound pitch above human hearing ability i.e. usually above 20 kHz. It is a mechanical energy and has plenty of applications in our daily life [34]. Ultrasonic radiation causes cavitations of bubbles near the phase boundary between the alcohol and oil phases. As a result, fine micro bubbles are formed. The asymmetric collapse of the cavitations bubbles disrupts the phase boundary. Impinging of the liquids creates micro jets leading to intensive mixing of the system near the phase boundary. The cavitations may also lead to a localized increase in temperature at the phase boundary, enhancing the transesterification reaction. Neither agitation nor heating are required to produce alkyl esters by ultrasound application because of the formation of micro jets and localized temperature increase [35, 36]

Georgogianniet al. [37, 38] carried out the transesterification from waste oils in the presence of alkaline catalysts and that from soybean frying oils in the presence of other heterogeneous catalysts, respectively, using low-frequency ultra-sonication (24 kHz) and mechanical stirring (600 rpm). Their results showed that many advantages of the ultrasonic irradiation, such as high yields of methyl esters, time saving procedure and so on compared over the mechanical stirring method. These results agree with several researchers [39-42]. Many efforts have been dedicated to investigate the influence of the type of alcohol that is used for biodiesel production under ultrasonic irradiation [43-45].

Response surface methodology (RSM) is an effective statistical technique dealing with the development and non-parametric simulative models. This model approximates the functional relationships between input variables and the output (response) of the process using experimental data [46]. It is a powerful tool that involves the following general advantages; more information per experiment than unplanned approaches, a reduction in the number and cost of experiments, it makes possible the calculation of the interactions among experimental variables within the range studied, leading to a better knowledge of the process and it facilitates the determination of the operating conditions necessary for the scale-up of the process [47].

In this sense, the methodology has been used extensively to develop and optimize different ester synthesis processes, biodiesel production and many references can be found in the background literature [33, 47-49].

The objective of this study was to study the conventional reactive extraction and the reactive extraction via ultrasound waves for the biodiesel production from castor oil seeds. It also focuses on the optimization of catalyst amount and methanol: oil molar ratio to produce the highest yield of biodiesel using response surface methodology.

2. Experimental Work:

2.1 Reagents and materials:

All the chemicals used in experiments were of analytical grade. Chemicals were used without further purification. Cultivated castor seeds were procured from Agriculture Research Division, National Research Centre.

2.2 Procedures:

2.2.1 Oil extraction:

In order to evaluate the different properties of oil, the seeds were decorticated to separate kernel and husk. The oil was extracted from the grinded seeds in Soxhlet apparatus once by using hexane and another time by using methanol as solvent. The solvent was collected using rotary evaporator and the residual oil was dried and weighed. The fatty acid profile of the oil was determined using gas chromatography.

2.2.2 Reactive extraction of castor seeds:

- **Conventional in-situ transesterification:**

100 g of dried crushed castor seeds in screw capped bottles were covered with methanol and homogenate for 5 min at 800 rpm, and then the rest of the calculated amount of methanol in which the KOH had been previously dissolved is added. The screw capped bottles were stirred in a shaker 150 rpm (AHAAM Model 3060, ORBITAL SHAKER) for 3 hr. at room temperature. The mixture was then filtered and the filtrate was evaporated using Rota vapor to separate methanol. The residual was transferred to a separating funnel, and allowed to separate gravitationally. The upper biodiesel layer was dried at 80°C.

- **In-situ transesterification via ultra-sonic waves:**

In the same way that above, the castor seeds in screw capped bottles were covered with methanol and homogenate for 5 min at 800 rpm, and then the rest of the calculated amount of methanol in which the KOH had been previously dissolved is added. The screw capped bottles were immersed in an ultrasonic bath (Model WUC-D10H, 60Hz, 230 volts, 665 W, 3 AMPS). Wave intensity was fixed at 40W; reaction time was 30 min at room temperature. Finally, the reaction mixture was filtered, separated as described above and dried at 80°C.

2.3. Experimental design:

The effects of process variables (catalyst concentration and methanol: castor oil molar ratio) on biodiesel conversion (Y) were verified using experimental design. The experiments were carried out and optimized following the Factorial Design and Response Surface Methodology. The factorial design was performed to study the effect of the variables on the process and the interaction between them, while the response surface methodology was applied to optimize the process. The software Statistic (6.0.8 Portable) was used to analyze the results.

The experimental design applied to this study was a full 2^2 factorial design (two factors each at two levels). Selection of factors was based on the operating conditions that have a significant

influence of biodiesel process, according to previous work (33,50). The factors chosen were catalyst concentration and methanol: castor oil molar ratio.

3. Results and discussion:

3.1. Characterization of castor oil:

The oil contained in the seed is about 30%. The extraction with methanol gives the maximum oil yield as compared to hexane in the same conditions. This is due to the presence of ricinoleic acid in castor oil which is soluble in alcohols. This result agrees with Swaroopa and Vaibhav[51]. They studied the effect of different solvents on extraction of oil from castor seeds and found that nature of solvent (polar or non polar) and extraction time had influence on the oil yield. They also state that ethyl acetate and methanol showed higher castor oil yields compared to hexane. The fatty acid composition of the oil is presented in Table (1)

3.2. Conventional Reactive extraction:

The linear state was considered in a first step. Table (2) shows the experiments corresponding to the 2^2 factorial designs and 2 experiments were carried out at the centre point, coded 0, to evaluate the experimental error. It also shows the results of biodiesel yield. A statistical analysis was carried out on the experimental results, and the two main effects and interaction effect were estimated in the form of analysis of variance (ANOVA) for the chosen response. The P-values are used as a tool to check the significance of the corresponding coefficient. The smaller the P-values are, the bigger the significance of the corresponding coefficient [52]. Values of "Prob > F" less than 0.0500 indicate model terms are significant. The P-value of the model, found by ANOVA, was 0.0123 which indicates that the model is suitable. In addition, the coefficient determination ($R^2=0.9999$) and adjusted coefficient of determination (Adj. $R^2=0.9996$) indicated that, the accuracy and general availability of the model were adequate. Also the low value of the coefficient of variation ($CV=0.68$) indicates that results of the fit model are reliable. In this case C, MR, C*MR are significant model terms [33], but the molar ratio is more significant [50] followed by the catalyst concentration then the interaction between them.

Final equation in terms of (actual factors):

$$\text{Yield} = 57.98 + 6.76 * C + 18.76 * MR + 2.56 * C * MR \quad \text{eq. [1]}$$

Figure (1) illustrates Response surface plot and contour plot of biodiesel yield as function of catalyst concentration and methanol: oil molar ratio, at room temperature using shaker. As shown from figure as the catalyst concentration and molar ratio increase the yield increases. The plot of experimental values versus predicted is shown in figure (2), and shows that the values of the response predicted from empirical equation are in agreement with the observed values over the selected range of the operating values.

3.3 Reactive extraction via ultra-sonic waves:

The linear stage was first considered. Table (3) shows the experiments corresponding to the 2^2 factorial design (Experiments 1-4) and four experiments in the centre point to evaluate the experimental error (Experiments 5-8) and the last column shows the % yield of biodiesel. Experiments were done at random.

A statistical analysis was carried out on these experimental values, and the final equation of experimental data was

$$\text{Yield} = 71.32 + 15.02 * C - 0.85 * MR + 2.81 * C * MR \quad \text{eq. [2]}$$

To evaluate the analysis of variance (ANOVA) and check the adequacy of the empirical model, statistical analysis of the model was performed. The results of ANOVA for fitting 2F1 model are summarized in table (4).

According to table (4) the model was very significant because the values of “Prob>F” less than 0.0500, in this case C, C*MR are significant model terms while MR is not significant. A statistical analysis of experimental values also suggests that there is a significant curvature effect for the yield response. Therefore, the 2F1 model obtained from the first statistical analysis does not adequately describe the experimental results considered here.

Therefore, the first order polynomial expression obtained from the first statistical analysis does not adequately describe the experimental field considered here. It is therefore necessary to consider a more complex design to fit the data to a second order model.

As curvature effect was detected, four additional runs called star points and coded $\pm\alpha$ were added to the 2^2 factorial designs, as shown in table (3). The distance of the star points from the center point is given by $\alpha=2^{n/4}$ (for two factors, $\alpha=1.414$).

A statistical analysis was carried out on these experimental values, and the final equation of experimental data was

$$\text{yield} = +78.08 + 16.32 * C - 0.23 * MR - 5.38 * C^2 - 5.6 * MR^2 + 2.81 * C * MR \quad \text{eq. [3]}$$

The results of ANOVA for fitting the second order response surface model by a mean square method are summarized in table(5). According to table(5) values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case C, C^2 , MR^2 , C*MR are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The "Lack of Fit F-value" of 4.21 implies the Lack of Fit is not significant relative to the pure error. There is a 13.45% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good .

The "Pred R-Squared" of 0.8857 is in reasonable agreement with the "Adj R-Squared" of 0.9814. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 30.888 indicates an adequate signal. This model can be used to navigate the design space.

The second order model can be plotted as response surface graph and counter graph representing the response (yield) as a function of catalyst concentration and molar ratio at room temperature Figure (3). As shown from equation (3) and figure (3) for the experimental range the catalyst concentration is the most important factor in the biodiesel process. This agree with Avramovic et al. [54,55] studied three parameters of reaction variables under ultra-sonication .Levels of methanol-to- sunflower oil molar ratio, KOH catalyst loading and the temperature of reaction were subsequently optimized. The most significant factor on the production process was found to be the loading of the catalysts. They explained that the increase in catalyst loading resulted in an increase in the formation of methoxide (the complex formed from the reaction between catalyst and methanol). This yielded an enhancement in the FAME formation and an increment in the positive catalyst affect on the rate constant of the forward reaction. A yield of nearly 90% was achieved in just 60 min.

Figure (4) shows that the values of the response predicted from the empirical model are in agreement with the observed values over the selected range of the operating variables with a reasonable high value of coefficient of determination ($R^2 = 0.9907$).

3.4. Effect of mixing intensity:

Two wave intensities were investigated, 40W,100W at different methanol oil molar ratio (330:1,220:1,and 120:1)at one hour and catalyst concentration 2%. The data obtained are plotted in figure (5). As shown from figure the % yield increased as the intensity increased. It reached 60.6,87.47 at 330:1 molar ratio respectively at 40,100 W. The result is in agreement with Hingu et al [53], they investigated the ultrasonic rated power dissipation and found that under a power of 200 W, the conversion reached about 89% in less than 40 min. It was mainly attributed to the effect of ultrasound mixing. However, the conversion suffered a decrease when the power was increased to 250 W. That could be associated with the cushioning effect which, in turn, decreased the cavitation activity due to the reduction of the transferred power into the system.

4. Conclusion:

In this study biodiesel was produced by conventional reactive extraction and reactive extraction via ultrasound waves of castor seed, with base catalyst, implementing response surface methodology method to optimize the reaction conditions. Effect of catalyst concentration and methanol: oil molar ratio on the biodiesel yield was investigated. In case of conventional reactive extraction, the most important one is the methanol: oil molar ratio followed by catalyst concentration then the interaction between them. A first-order approach fits the data for the biodiesel yield. In case of reactive extraction via ultrasound waves, a first-order approach did not adequately fit the data and quadratic model was required. Second-order model was developed to predict the biodiesel yield, and the catalyst concentration has the most significant effect on the yield of biodiesel. Analysis of the observed values versus the predicted ones demonstrated the efficiency of the model obtained. The effective of mass transfer in the ultra sonic field enhanced the higher rate of transesterification reaction compared to shaker (stirring condition). Reduction in the reaction time from 3hr (84% yields) to 1/2hr (88.26% yields) could help to improve the economics of biodiesel production.

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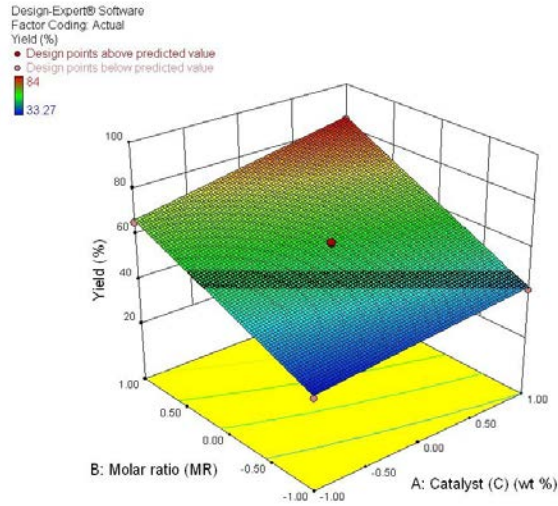


Figure (1-a): Combined effect of molar ratio and catalyst loading on the biodiesel yield during reactive extraction of castor seed at room temperature and 150 rpm. (3D response)

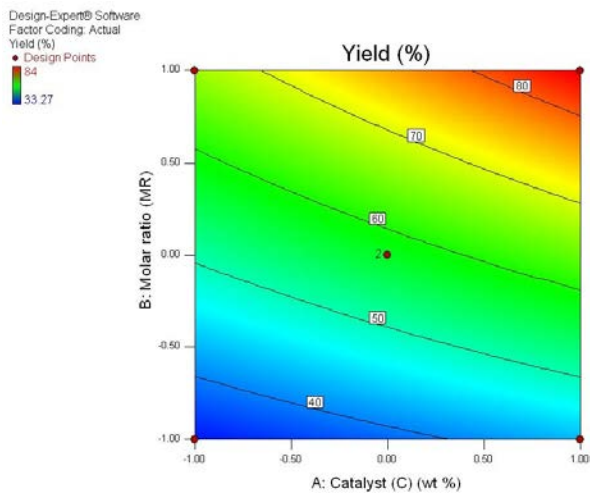


Figure (1-b): Combined effect of molar ratio and catalyst loading on the biodiesel yield during reactive extraction of castor seed at room temperature and 150 rpm. (2D response contour)

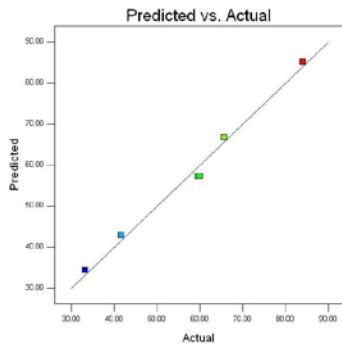


Figure (2): Graphical comparison between actual and predicted biodiesel yield during reactive extraction of castor seed

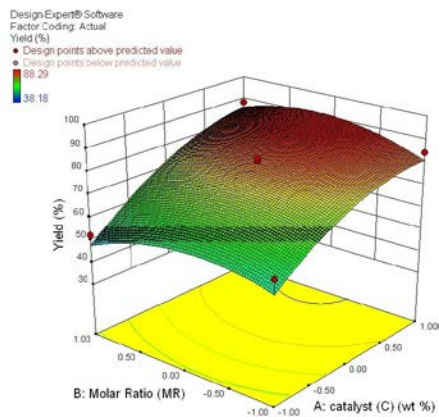


Figure (3-a): Combined effect of molar ratio and catalyst loading on the biodiesel yield during reactive extraction via ultrasonication of castor seed at room temperature (3D response)

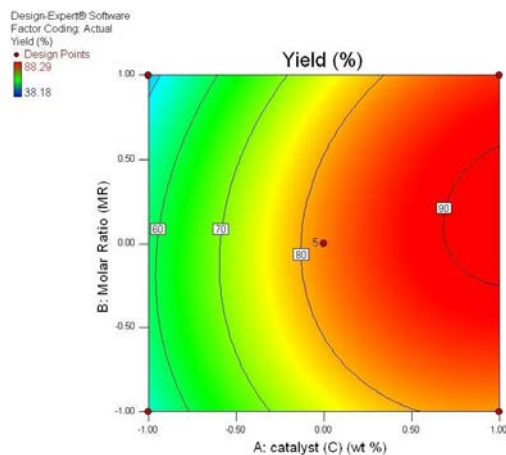


Figure (3-b): Combined effect of molar ratio and catalyst loading on the biodiesel yield during reactive extraction via ultrasonication of castor seed at room temperature, (2D response contour)

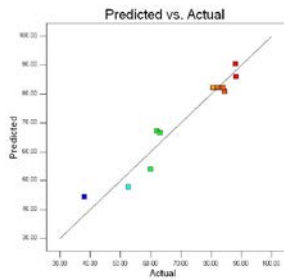


Figure (4): Graphical comparison between actual and predicted biodiesel yield during reactive extraction of castor seed via ultrasonification

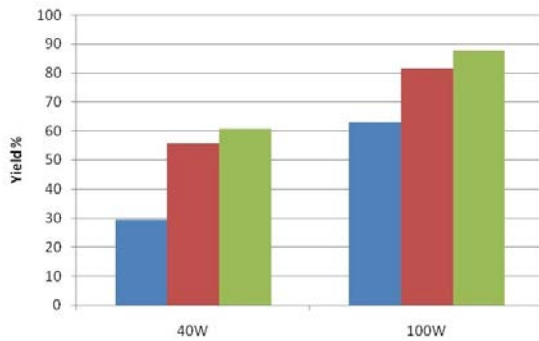


Figure (5): Effect of mixing intensity at different molar ratios (120:1,220:1,330:1)

Table (1) Gas chromatographic analysis of castor oil fatty acid [56]

Fatty acid	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Ricinoleic (18.1OH)
Wt%	1.45	1.7	8.24	8.50	0.97	79.14
Mw (g/mol)	256	284	282	280	278	298

$$Mw_{tri} = 919.58$$

Table (2) Experimental design matrix and results

Experiment Type	Run	C(% wt)	MR	X _C	X _{MR}	Y (%)
Linear stage	1	1	100:1	-1	-1	33.27
	2	1	300:1	-1	1	65.67
	3	3	100:1	1	-1	41.67
	4	3	300:1	1	1	84
Center points	5	2	200:1	0	0	59.45
	6	2	200:1	0	0	60

Table (3) Experimental design matrix and results

Stages	Run number	C (wt %)	MR	X _C	X _{MR}	% Yield
Linear stage	1	3	330:1	1	1	88.29
	2	1	120:1	-1	-1	59.95
	3	3	120:1	1	-1	84.37
	4	1	330:1	-1	1	52.65
Center points	5	2	220:1	0	0	82.84
	6	2	220:1	0	0	81.75
	7	2	220:1	0	0	80.66
	8	2	220:1	0	0	83.93
Star points(non linear)	9	2	375:1	0	1.41	63.22
	10	2	79:1	0	-1.41	62.13
	11	0.6	220:1	-1.41	0	38.18
	12	3.4	220:1	1.41	0	88.04

Table (4) Analysis of variance (ANOVA) for response surface

Source	Prob.>F	Remark
Model	0.0008	significant
(catalyst concentration)	0.0002	
(methanol: oil molar ratio)	0.3159	
(interaction)	0.0283	
Curvature	0.0016	significant
R ²	0.9937	
Adj. R ²	0.9874	

Table (5): Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of squares	Degree of freedom	Mean squares	F value	Prob.>F	Remark
Model	2404.36	5	480.87	106.27	<0.0001	significant
C	2131.15	1	2131.15	470.96	<0.0001	
MR	0.42	1	0.42	0.093	0.7722	
C ²	154.44	1	154.44	34.13	0.0021	
MR ²	167.18	1	167.18	36.94	0.0017	
C*MR	31.47	1	31.47	6.96	0.0461	
Residual	22.63	5	4.53			
Lack of Fit	16.68	2	8.34	4.21	0.1345	Not significant
Pure Error	5.94	3	1.98			
Cor. total	2943.14	11				
R ² =0.9907 Adj R ² =0.9814 Predicted R ² =0.8857						