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Utilization of Agro-waste and Non-conventional *Eruca sativa* Seed Oil for Getting Optimized Process to Acquire Better Yield of Biodiesel by Using Response Surface Methodology (RSM)

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ABSTRACT

The Response Surface Methodology (RSM) based on Central Composite Rotatable Design (CCRD), was used to evaluate four trans-esterification reaction parameters i.e. reaction temperature, catalyst concentration, reaction time and methanol-to-oil molar ratio in order to obtain high and better yield. A 2^4 full factorial CCRD was applied, using four different variables at five levels; each parameter leads to 30 experiments to yield *Eruca sativa* oil-methyl esters (EOMEs). The molar ratio of methanol to oil and catalyst concentration were the most significant ($P < 0.5$) factors affecting the yield of EOMEs. A linear relationship was recorded between observed and predicted values ($R^2 = 0.97$). Using multiple regression analysis, a quadratic polynomial equation was recognized for methyl ester yield (MEY). The quadratic terms of molar ratio and catalyst concentration showed a significant impact on yield. The interaction terms of molar ratio and catalyst concentration with reaction time revealed positive influence on MEY ($P < 0.05$). The optimal reaction conditions for transesterification of oils were catalyst concentration of 0.8%, reaction temperature 65 °C, CH_3OH to oil ratio of 6:1 and reaction time 120 min leading to production of 95.88% *Eruca* oil MEY. The RSM was found to be a suitable technique for optimizing transesterification process, and manufactured fuel properties were within the ranges of EN 14214 and ASTM D6751 standards.

Keywords: *Eruca sativa* oil, methanolysis, optimization of transesterification variables, fuel properties, response surface methodology tool

1. INTRODUCTION

Globally energy need has been a dread key for the 21st Century. Continuously developing human population, increase in global temperature, quick consumption of fossil fuels and climate change are the fundamental issues behind this dread. Remnant fuels are non-renewable assets of energy and reduction of these universally sources are compulsory. The world organizations forecast that the consumption of energy especially in transport sector will be twice as compared to present consumption [1, 2]. Moreover, utilization of fossil fuel is producing various problems i.e. acid rain, water pollution, worldwide increase of temperature, desertification and thus numerous extreme biological inconveniences [3]. The outlook of energy resources are being imagined in light of various factors. However, to choose the energy assets there is need to satisfy the expanding stress of country. Renewable resources of energy include energy from biomass (biogas, bioethanol, biodiesel, bio-methanol and so on.), wind, solar energy, tidal, geothermal and hydropower. Due to the rise in demand for energy and deterioration of the eco-environment, developing clean and renewable sources of alternative energy attracts more attentions [4]. As a result an alternative fuel is prepared from biological sources for example animal fat and vegetable oil. This alternative diesel fuel is termed as biodiesel, which is easily available, cost-effective, technically viable and environmentally tolerable [5].

It is stated that biodiesel is the mono-alkyl ester of fatty acid which are derivatives of animal fats, algae, edible and inedible vegetable oils [6]. In the transesterification reaction, vegetable oils react with alcohol (methanol or ethanol) in the vicinity of catalyst, producing fatty acid methyl esters (FAME) along with glycerol [7].

Biodiesel demonstrates various advantages including decreases in net emission of carbon-dioxide in the environment by 78 % compared to petroleum diesel fuel and decrease in smoke being dirt free [8]. Biodiesel is renewable, promptly accessible, harmless, convenient, non-combustible, eco-friendly, biodegradable, maintainable, and without any aromatic and sulfur substances, which make it perfect fuel for vigorously polluted urban areas [9]. The cetane number of biodiesel is around 60-65 % depending upon the vegetable oil, which is greater than conventional diesel i.e. 53 % which decreases the ignition delay [10]. As a matter of fact, the worldwide production of advanced biofuels is less than 1 billion gallon per year at present [11].

Consequently, every state has capability to synthesize biodiesel as fuel. Although, minor adjustment is required for higher blending levels [12]. Lubricity of biodiesel has a great significance because it expands the age, effectiveness and durability of engine [13]. Biodiesel diminishes the ecological impact of a waste item and can be made out of utilized cooking oils and greases. Biodiesel consist of 10-11 % of oxygen which proved it to be a specialized fuel with high burning qualities [14].

Transesterification is a commonly employed method for biodiesel production. The purpose of this method is to reduce the viscosity of oil or fat using acid or base catalyst in the presence of methanol or ethanol [15]. The transesterification creates some ecological impacts, for example, waste transfer and need of water for washing of biodiesel, creation of soap and so on [16]. More than 95 % of biodiesel is produced by using edible oils which may promote monetary issues. By producing biodiesel from non-edible oils can promote the business sector [17]. Biodiesel has less oxidative stability as compared to diesel fuel resulting in the corrosion of fuel injector, tank and pipe [18].

The worldwide distributed Taramira (*Eruca sativa*) is an annual oil seed crop has a place with the family *Cruciferae*. It is particularly suitable for arid and semi-arid districts. The seeds of taramira consist of 30-35 % oil and 20-25 % protein. The cake (contents left after the removal of the oil from seeds) is used as food for animals [19]. It possesses health promoting agents owing to the presence of flavonoids, glucosinolates, calcium, sodium, potassium, magnesium, dietary fiber, iron and vitamins A, B, C and E. Medicinally and therapeutically, this plant acts as anti-ulcer and anti-bacterial agent [20], also involved in hepatoprotective actions. Moreover it is used for the treatment of fungal infection, respiratory and urinary tract infection and hair loss. In industry, oil of taramira is used for soap formation, paper formation, as an ointment, in massaging and also in cooking [21, 22].

The objective of the present study was to explore the utility of *Eruca sativa* oil-methyl esters (EOMEs) as a potential source for biodiesel. Although considerable work has been reported but after deeply going through the literature, it is obvious that there is still much need to develop RSM-based comprehensive protocol for transesterification process, using *Eruca sativa* oil-methyl esters, with the main purposes of increasing high biodiesel quality and yield. ASTM and European biodiesel standards were used as a reference.

2. MATERIALS AND METHOD

2.1 Sample Collection

Seeds of *Eruca sativa* were collected from the local market of Mianwali, province Punjab, Pakistan.

2.2 Pretreatment of *Eruca sativa* Seed and Oil Extraction

Seeds were initially made clean of any impurity and afterward dehydrated in an oven at 100 °C overnight and then converted in to fine powder in electrical grinder and packed in plastic bags.

Oil extraction

In a soxhlet apparatus 100 g of powdered seeds were taken and activated on a heating mantle for extraction of oil. Extraction of fatty acids was completed via solvent n-hexane for 8-10 hours. Afterward solvent is separated from extracted oil in rotary evaporator under vacuum at 50 °C.

2.3 Preliminary Test for *Eruca sativa* Oil

The tests performed by using methods given in AOCS (American Oil Chemist's Society) for physicochemical properties of *Eruca* oil including specific gravity, refractive index, free fatty acid analysis, acid value, iodine value, peroxide value, and saponification number. Experimental design of transesterification reaction using response surface methodology (RSM): Impact of different reaction parameters such as catalyst concentration percent (A), reaction temperature °C (B), reaction time min (C), and molar ratio of methanol to oil (D) on biodiesel yield were examined by Central Composite Response Surface Design (CCRD). Variables adjusted for the reaction were A (0.8 % - 1.50 %), B (40 °C -65 °C), C (40 min-120 min$_)$, and D (6:1-8:1). A CCRD design with 2^4 full factorial was applied by means of four various variables at five levels each lead to 30 experiments.

2.4 Experimental Procedure for Transesterification Reaction

2.4.1 Optimization of reaction variables

Different reaction variables such as catalyst concentration, reaction temperature, reaction time and methanol to oil molar ratio were optimized to obtain highest yield and excellent quality biodiesel by using central composite response surface design (CCRD). A quadratic polynomial (second order) was used to predict the response as a function of independent variables and their interactions and a second-order polynomial equation was used as shown below in the equation:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ij} X_i^2 + \sum_{i_i>j}^{k} \sum_{j}^{k} b_{ij} X_i X_j$$

2.4.2 Pretreatment of *Eruca sativa* Oil

FFAs value of crude *Eruca sativa* oil was 2.1 % which was minimized up to 0.6 % by pretreated the oil with sulfuric acid before methanolysis. Acidic-catalyzed esterification performed to convert the FFAs into esters by reacting unrefined oil with methyl alcohol by using acidic catalyst such as H_2SO_4. FFAs value of oil regularly determined after each interval of 20-35 minutes; further processing stopped as soon as the FFAs value decreased up to 0.6 %.

Production, separation and purification of biodiesel

The transesterification reaction and purification of biodiesel was done by following the procedure reported by Mehmood *et al.*, [23].

2.5 FT-IR Monitoring of *Eruca sativa* Methyl Esters

Feasibility of *Eruca sativa* biodiesel was checked by performing FT-IR analysis (IR Prestige-21, SHIMADZU, Tokyo Japan spectrophotometer) and gets the various spectral lines of different functional groups.

2.6 Gas Chromatography (GC)

Presence of significant fatty acids in biodiesel sample was confirmed through GC analysis.

2.7 Fuel Properties of *Eruca sativa* Biodiesel

Eruca sativa biodiesel fuel properties were examined with the assistance of Pakistan state oil (Karachi). Triplicate estimations of Cetane number, Flash point, Kinematic viscosity, Acid value, Density, Pour point, Cloud point, Cold filter plugging point, Oxidative stability, Sulphur contents, Sediments, Water, Free glycerin and Carbon residues and every test were made.

2.8 Statistical Analysis

Statistical evaluation was made through Minitab Software 17 by using surface plots, contour plots, normal plots and diagnostic checks.

3. RESULTS AND DISCUSSION

The physicochemical analysis of *Eruca* oil includes the investigation of the following properties. All the approximations were taken more than three times and all data was recorded as ± SD of mean as shown in Table 1.

Table 1. Physicochemical characteristics of *Eruca sativa* seeds oil.

Sr. No.	Parameters	Results
1	Yield of oil (%)	36.60 ± 0.386
2	Refractive index	1.468 ± 0.003
3	Density (g/cm^3)	0.964 ± 0.157
4	Specific gravity	0.901 ± 0.036
5	Iodine number	107.8 ± 0.570
6	Peroxide value	4.000 ± 0.152
7	Free fatty acid value (%)	0.624 ± 01.15
8	Acid value (mg KOH/g)	1.248 ± 01.20
9	Saponification number (mg KOH/g)	178.8 ± 2.828

Here, '±' shows standard mean of deviation.

3.1 Optimization Process By Using CCRD For Manufacturing Of Biodiesel From *Eruca sativa* Oil

Optimization of process factors was fulfilled with the aid of CCRD. A five-level, four-factorial CCRD was utilized with the total 30 runs. Experimental design of four independent parameters at five levels, methanol/oil molar ratio, temperature, catalyst concentration and time of reaction is given in Table 2.

Table 2. Conditions of experimental work for CCRD.

Run	Catalyst Concentration (%)	Reaction Temperature (°C)	Reaction Time (Minutes)	Methanol/Oil Molar Ratio	Biodiesel Yield (%)	% Yield Predicted	Residual Values
1	1.5	65	120	8	95.50	92.39	0.80
2	0.8	40	120	6	85.19	78.11	0.18
3	1.15	65	80	7	88.21	85.64	-0.14
4	1.15	52.5	80	7	79.18	89.54	-0.24
5	1.5	65	120	6	77.36	86.11	-0.41
6	1.15	40	80	7	83.88	88.34	-0.24
7	0.8	40	40	6	83.62	82.14	-1.24
8	1.5	40	120	8	95.68	80.98	1.92
9	1.15	52.5	120	7	83.32	89.54	0.15
10	1.15	52.5	80	6	75.84	77.48	0.82
11	1.5	40	120	6	73.87	77.78	-0.88
12	1.15	52.5	80	7	88.96	88.81	0.48
13	1.15	52.5	80	7	74.84	91.18	0.92
14	0.8	65	40	8	77.93	87.49	0.03
15	1.5	40	40	6	91.76	77.51	-0.01
16	1.5	52.5	80	7	89.81	81.04	0.45
17	0.8	65	120	6	80.45	89.54	-0.84
18	0.8	65	40	6	85.95	77.23	-0.43
19	0.8	65	120	8	95.88	89.54	-0.04
20	1.5	65	40	8	92.86	93.13	-1.23
21	1.15	52.5	80	7	89.54	87.00	0.39
22	1.5	40	40	8	78.46	95.27	-2.57
23	0.8	40	40	8	76.85	90.15	-0.25
24	1.15	52.5	40	7	86.88	90.59	0.01
25	0.8	40	120	8	86.31	94.44	-0.64
26	0.8	52.5	80	7	87.86	76.35	-0.95
27	1.15	52.5	80	7	74.88	94.80	0.59
28	1.5	65	40	6	86.91	87.79	0.71
29	1.15	52.5	80	8	89.22	93.17	2.32
30	1.15	52.5	80	7	84.25	94.80	0.39

Second-order polynomial model for all experiments is shown in equation:

Y = 92.46 + 0.80 A + 2.49 B - 1.75 C + 0.02 D - 0.71 A*A - 2.71 B*B - 1.02 C*C - 0.93 D*D- 0.36 A*B - 0.47 A*C + 0.07 A*D + 1.77 B*C - 2.67 B*D - 2.76 C*D

Here,

Y = Biodiesel yield (dependent or response variable)

A, B, C, D = independent variables (correspondingly catalyst concentration, reaction temperature, reaction time and methanol/oil molar ratio)

Table 3 indicates the detail of fitted quadratic model for ANOVA (analysis of variance) by least square method. For fitted quadratic model lack of fit should be insignificant. According to model source of variation fitted quadratic model is significant because it has high F-value i.e. 38.54 among the smallest *p*-value of less than 0.0001 while it is insignificant due to 17.51 F-value for lack of fit.

Table 3. ANOVA (analysis of variance).

Sources of variation	Degrees of freedom	Sum of squares	Mean squares	F- value	*p*- value
Models	15	173.80	71.58	38.54	< 0.0001
Residuals	14	26.00	1.85		
Pure error	4	0.58	0.14		
Lack of fit	10	25.42	2.54	17.51	0.007
Total	29	1099.81			

In this study values of coefficient of variable that is 1.36 %, adjusted R^2 = 94 %, R^2 = 97 %, shows the consistency and accuracy of the results.

p-values lower than 0.05 are suggested for this model. F-values and *p*-values of different variables used in these research experiments for response variable that is yield of biodiesel is shown in Table 4. In this research model the less *p*-value of catalyst concentration and molar ratio are significant. A, D, BC, CD, D^2, B^2 are significant expressions for this suggested model.

Table 4. Variables estimation by least square fit and *p*-values for its significance.

Source	Estimated Co-efficient	Sum of squares	F-values	*p*-values
Intercept	85.89			
A-Catalyst Conc.	1.01	38.507	1.58	0.000
B-Temperature	2.01	9.127	0.38	0.245
C-Time	1.01	104.167	4.28	0.087
D-Molar ratio	0.82	16.007	0.66	0.000
AB	1.23	1.103	0.05	0.125
AC	-1.89	57.003	2.34	0.058
AD	0.23	223.502	9.19	0.90
BC	0.52	4.410	0.18	0.000
BD	-1.77	50.410	2.07	0.008
CD	1.23	148.840	6.12	0.001
A^2	0.94	49.527	2.04	0.000
B^2	-0.04	0.053	0.09	0.001
C^2	-0.194	1.030	0.04	0.069
D^2	0.581	9.267	0.38	0.000

Standard % probability of the residuals is checked through normal plot is shown in Figure 1.In Figure 2 linear plot depicted the normality of actual results and predicted results. According to this design huge number of values fall in the range 87-95 % while very less amount of values found in the range of 76-79 %.

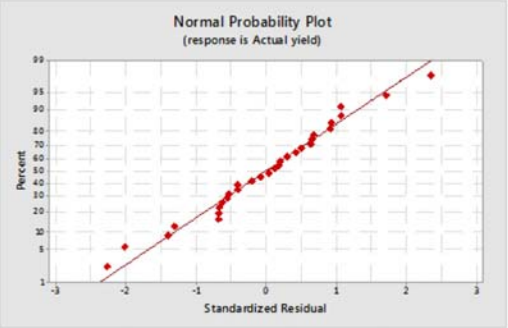


Figure 1. Plot for normal vs residuals values.

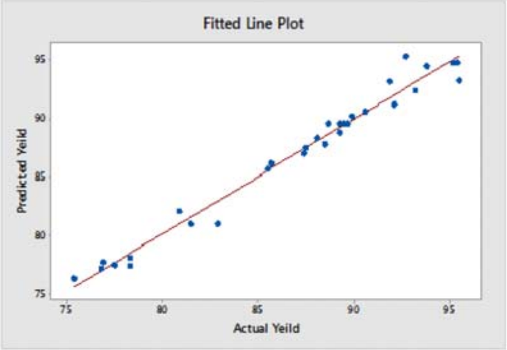
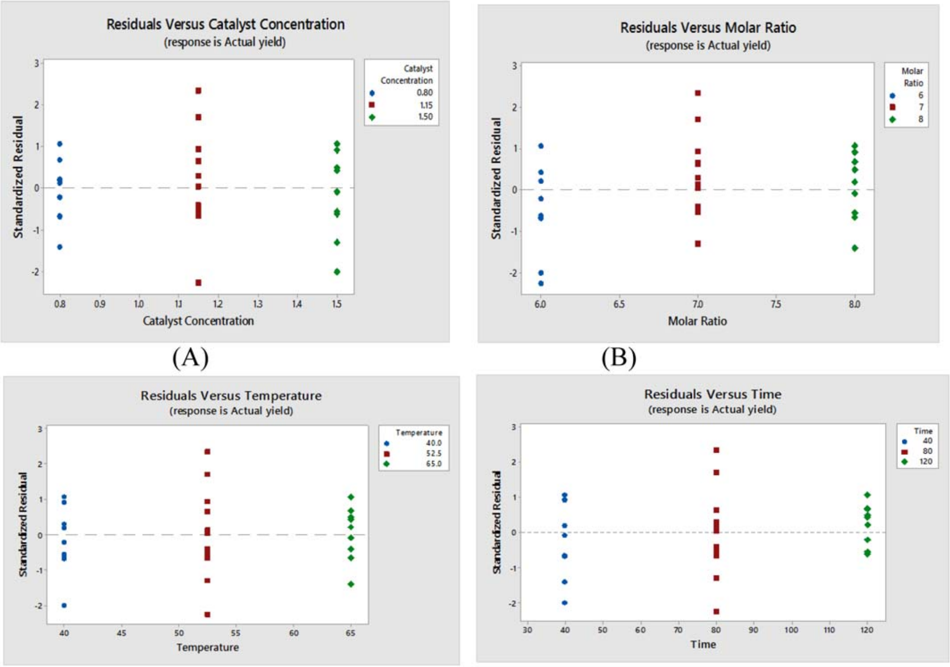


Figure 2. Plot for predicted versus actual values.

To analyze the effect of individual components on the residuals, plots of residuals versus different variables are revealed in Figure 3 (A-D). According to Figure 3 (A) maximum numbers of residuals are present at the catalyst concentration of 1.15 % while according to the plot maximum yield is obtained at 0.8 % where % yield is high. Figure 3 (B) assigns that a greater number of residuals are present at the molar ratio of 7:1 while maximum yield is obtained at 6:1. Figure 3 (C) shows the relationship of temperature with standardized residuals. It is appeared that maximum number of residual are present at 65 °C whereas plot indicates the maximum yield at 65 °C. Overall yield is highest. Figure 3 (D) depicted that according to plot maximum results are obtain at the time of 120 minutes and % yield is also higher at this time.

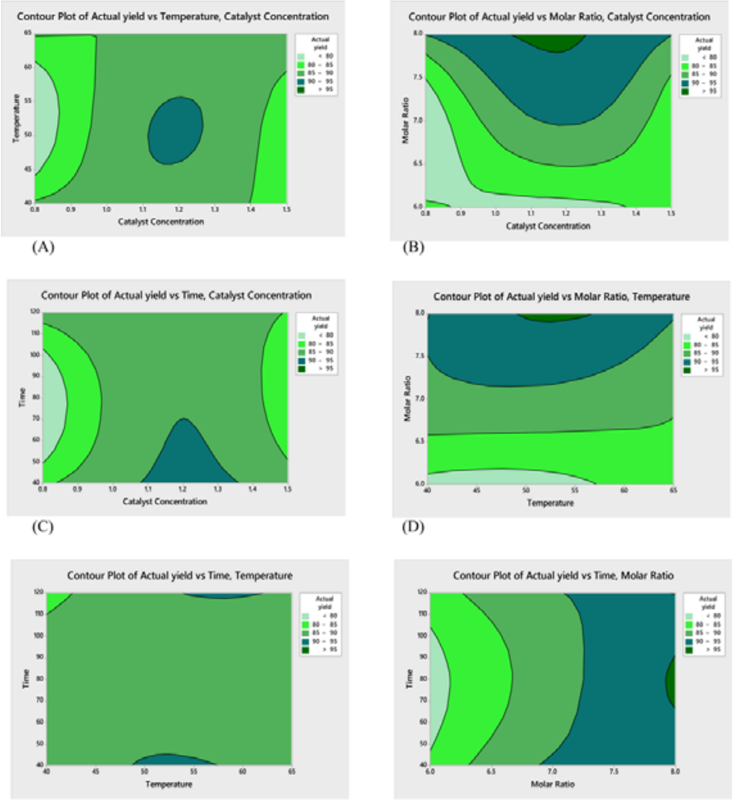
Regression equation can be analyzed by 3-D surface and contour plots, which demonstrate the connection of two parameters on biodiesel manufacturing yield. Contour plots and 3-D surface plots are shown in figure 4 and figure 5 respectively. Relationship of catalyst concentration and temperature are demonstrated in Figure 4 (A), which describes that highest yield i.e. 90-95 % of biodiesel is found at the catalyst concentration of 1.12-1.15 % with the temperature range of 46 °C to 56 °C but there is insignificant relationship between these variables. Catalyst concentration and molar ratio have direct relationship and it is clearly shown in Figure 4 (B) that with the increase of molar ratio and catalyst concentration, yield is increased. Relationship of time and catalyst concentration is shown in Figure 4 (C). It is seen in graph that maximum yield is obtained at 70 min with a catalyst concentration of 1.06 to 1.35 %. Figure 4 (D & F) demonstrates a direct relationship with the increase of yield. While Figure 4 (E) assigns that time and temperature shows a insignificant relationship. Like contour plots, 3-D surface plots have same collaboration as appeared in Figure 5 (A-F). These plots show significance of relationship between catalyst concentration, temperature, time and molar ratio. Finally it is concluded that catalyst concentration and molar ratio have more influence on the variables as well as on yield of biodiesel.



(A) (B)

(C) (D)

Figure 3. Plots for residuals versus variables.

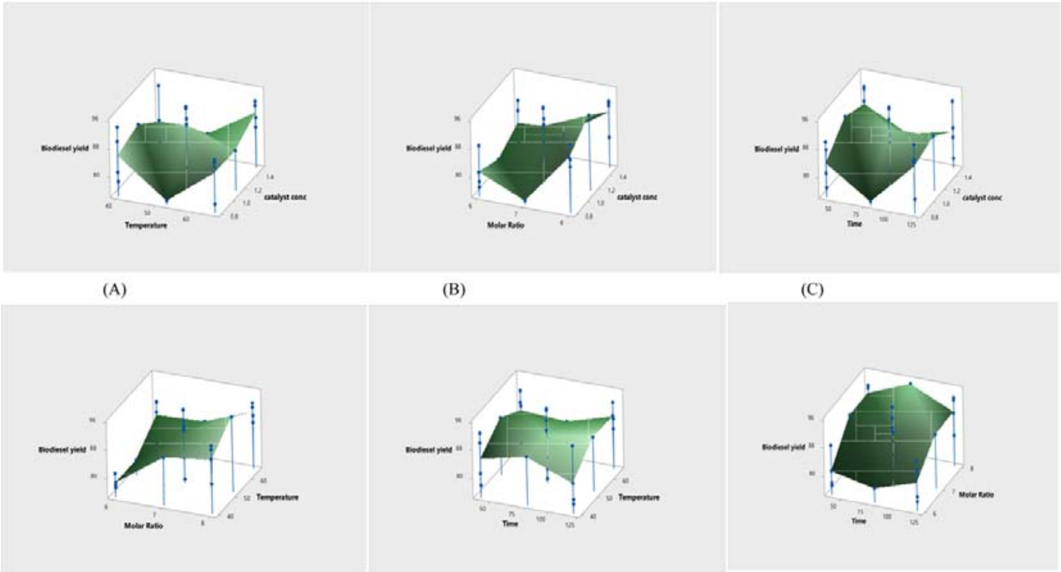


(A) (B)

(C) (D)

(E) (F)

Figure 4. Contour plots for production biodiesel from *Eruca sativa* oil.



(A) (B) (C)

(D) (E) (F)

Figure 5. Surface plots for the production of biodiesel from *Eruca sativa* oil.

3.2. Functional Group Identification of *Eruca sativa* Biodiesel Through FT-IR Spectroscopy

Sample of *Eruca sativa* biodiesel was analyzed through FT-IR spectroscopy which confirms the presence of ester group like -C=O and location of different groups. *Eruca sativa* methyl esters spectrums of FT-IR are depicted in figure (6) i.e. -C=O stretching peaks at 1741.72 cm^{-1}, -CH^3 asymmetric bending at 1446.6 cm^{-1}, C-O stretching at 1184.29 cm^{-1} and trifurcated peak for CH^3 and CH^2 asymmetric stretching at 2858.51 cm^{-1} -2989.66 cm^{-1}. These results are consensus to the previous research [24].

3.3 Analysis of Oil by Gas Chromatography

Sample of *Eruca sativa* oil was analyzed by GC-17A SHIMADU, which confirms the presence of different fatty acid in sample given in Table (5). Fatty acids present in waste cooking oil [25], karanja oil [26] and mustard oil [27] are also discussed in Table 5.

Table 5. Fatty acid profile of *Eruca sativa* biodiesel.

Fatty acids	Results	Waste cooking oil	Karanja oil	Mustard oil
Erucic acid (C22:1)	38.6	-	-	30.5
Linolenic acid (C18:3)	6.4	2.04	2.6	10.0
Linoleic acid (C18:2)	15.2	12.39	16.0	15.5
Oleic acid (C18:1)	25.0	79.75	51.5	23.5
Stearic acid (C18:0)	13.3	2.09	7.5	2.50
Palmitic acid (C16:0)	1.7	3.34	11.6	2.0

3.4 Fuel Properties of *Eruca sativa* Methyl Ester

Fuel properties of optimized *Eruca sativa* biodiesel shown in Table 6 are quite comparable to the American standard ASTM D6751. Cetane number was found to be 52.01 ± 2.340 min which is compatible to the ASTM D6751 cetane number of > 47 [28]. According to results of *Eruca sativa* methyl esters 5.67 ± 0.382 cSt value of kinematic viscosity was obtained which meets to the standard value of ASTM D6751 standard. *Eruca sativa* FAMEs indicate the value of flash point 92 ± 0.021 min which is lower than mahua biodiesel [29].

Pour point °C, cloud point °C and CFPP °C for *Eruca sativa* biodiesel are -3.21 ± 0.427, 1.83 ± 0.019 and 17.92 ± 1.203 respectively. For *Eruca sativa* biodiesel the acid value to be obtained is 0.45 mg (KOH/g) and density at 15 °C is 0.8412. The result of lubricity test for *Eruca sativa* biodiesel is 1.59 ± 0.704, which lie in the limits of ASTM standard. Oxidative stability of *Eruca sativa* biodiesel is 7 ± 1.239.

As well as the other significant properties of *Eruca sativa* biodiesel are also found to be practically inside of the universal norm of ASTM D6751 i.e. free glycerin of 0.021 %, sulphur of 0.102 %, carbon residues of 0.03 %, sediments of 0.07 %, water of 0.04 % and Copper Strip Corrosion at 50 °C of 1.2.

Table 6. Comparison of *Eruca sativa* biodiesel fuel properties to the literature [19, 30].

Properties of biodiesel Fuel	According tothis research work	According to *Mumtaz et. Al*	According to *Chakrabarti et. al*
Cetane Number	52.01 ± 2.340	59.08	48
Oxidative Stability (h)	7 ± 1.239		6
Kinematic Viscosity (cSt, 40 °C)	5.67 ± 0.382	5.71	5.9
Lubricity (HFRR, µm)	1.59 ± 0.704	-	-
Cloud Point (°C)	1.83 ± 0.019	1.5	-
Pour Point (°C)	-3.21 ± 0.427	-2.97	-
Flash Point °C (PMCC)	92 ± 0.021	197.3	52
Cold Filter plugging Point (°C)	17.92 ± 1.203	-	-
Copper Strip Corrosion (50 °C)	1.2 ± 0.90	-	1 (100°C)
Sulphur % wt	0.102 ± 0.009		0.02
Density @ 15 °C (g/cm3)	0.8412 ± 0.008	0.871	-
Water % Vol	0.04 ± 0.001	-	0.05
Sediments % wt	0.07 ± 0.002	-	0.05
Acid Value (mg KOH/g)	0.45 ± 0.032	-	0.40
Free Glycerin (%)	0.021 ± 0.002	-	-
Carbon residues (%)	0.03 ± 0.001	-	0.04 %

4. CONCLUSIONS

Optimum conditions for trans-esterification reaction were found to be with catalyst concentration of 0.8 % (w/w), molar ratio 6:1, reaction temperature 65 °C, and reaction time 120 min. *Eruca* Biodiesel exhibited the maximum yield of 95.88 % under these conditions. The fuel properties of *Eruca* biodiesel were found to be within the range of ASTM D6751 and European standards 14214 showing that *Eruca sativa* oil can be used as a potential source for biodiesel production that can be combusted in compression-ignition engines, in this way substituting the common petro-diesel. The outcomes of our study might lead to explore such under-utilized seed oils for production of superior quality of renewable, ecofriendly and sustainable biodiesel as substitute to petro-diesel.

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