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BIODIESEL PRODUCTION FROM WASTE COOKING OIL AND ISOPROPANOL FLUID BY USING TRANSESTERIFICATION TECHNOLOGY AND OPTIMIZING THE PROCESS BY USING RESPONSE SURFACE METHOD (RSM)

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ABSTRACT

Biodiesel represents an important future source of renewable energy, and it consists of waste cooking oil. Waste cooking oil is fatty acid that needs transesterification to produce a methyl or ethyl ester. This research is a study of biodiesel production from two sources, isopropanol and waste cooking oil by using a process of transesterification. The temperature during the experiment was between 300 and 350 °C, the co-solvent(hexane) was between 0 and 8 ml, and the ratio of oil to isopropanol molar ratio was between 4 and 12. According to the findings of optimization studies. The supercritical isopropanol reaction can produce an ideal yield of 91.625% under optimal conditions (the molar ratio of isopropanol to oil is 8.413, the temperature is 326.762 °C, and the solvent is 4.984 ml). The technique was optimized by looking at the biodiesel yields from waste cooking oil and isopropanol under various circumstances. The parameters of the process for the transesterification reaction were optimized using response surface methodology (RSM). The models were effective in explaining the response of the variations regard the three investigated factors. The fuels quality of the produced biodiesel was compared to those required by ASTM for biodiesel.

KEYWORDS: *Isopropanol, Transesterification, Supercritical, Biodiesel, Waste cooking oil.*

1 . INTRODUCTION

Given the significant apprehensions created by the phenomenon of climate change, a substantial cohort of specialists within the industry are presently engaged in the exploration of potential advancements in renewable energy sources. Due to its inherent characteristics that contribute to the mitigation of greenhouse gas emissions. Biodiesel fuel is often regarded as a promising biofuel option for mitigating reliance on conventional diesel fuel. The potential for biodiesel fuel to replace conventional diesel fuel is the reason behind this. When comparing biodiesel to petroleum-derived diesel fuel, biodiesel presents some notable benefits. The aforementioned benefits encompass a notable degree of biodegradability and a minimal level of toxicity. The presence of a reduced amount of sulfur and aromatic compounds [1] contributes to a decrease in the release of particulate matter, total hydrocarbons, and carbon monoxide (CO) emissions [2]. Furthermore, it exhibits similarities to commercial diesel fuel in relation to both the cetane number and the quantity of soot generated [3, 4]. The predominant method employed for the production of biodiesel in contemporary times is alkali-catalyzed transesterification. Unfortunately, over the course of recent years, numerous issues have been uncovered with this particular strategy. One of the foremost obstacles encountered in this context pertains to the imperative task of effectively isolating the catalyst and the saponified product from the free fatty acids subsequent to the reaction. The user's text is already academic and does not need to be rewritten. One of the issues that arises is the following. The purification procedures employed for free fatty acids may potentially result in increased production duration and the emergence of supplementary complexities. The application of supercritical technology is widely regarded as a highly promising alternative approach for the production of biodiesel. This technique presents numerous advantages, including the flexibility to

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utilize a diverse range of feedstocks, a higher reaction rate, and a simplified separation process. The aforementioned method is characterized by its lack of effluent production and its independence from the need for a catalyst. Numerous investigations undertaken thus far have primarily centered on the behavioral aspects [6, 7], kinetics [6, 7], and energy analyses [6, 7] pertaining to the production of biodiesel through the utilization of supercritical methanol and ethanol (SCM and SCE). Furthermore, substantial research has been conducted on advanced methodologies for the synthesis of glycerol-free biodiesel. Some of these methodologies involve the application of supercritical methyl acetate, dimethyl carbonate, and tert-butyl methyl ether [8]. In a novel methodology for biodiesel manufacturing, the reactor's internal pressure was kept equivalent to the ambient air pressure, while the solvent's temperature was elevated above its critical point.

This approach derived advantages from the utilization of non-catalytic superheated methanol technology. Given the observation that alcohols with lower carbon content, such as methanol and ethanol, possess corrosive properties, hygroscopic tendencies, and exhibit relatively low energy content [9], it is advisable to utilize alcohols with higher carbon content, such as propanol, as a preferable alternative. In a commercial environment, propanol can be produced from glucose by both fermentative and petrochemical processes. The utilization of metabolically engineered Escherichia coli and the incorporation of the keto-acid route are essential prerequisites for the successful execution of this manufacturing procedure. Besides D-glucose, many additional chemicals, including L-rhamnose, glycerol, and D-glucose, can now be employed in the process of synthesizing propanol. Propanol exhibits a superior carbon output compared to ethanol within the context of the fermentation process. Propane can be generated from glucose without the emission of carbon dioxide (CO2), but the biosynthetic pathway for ethanol involves stages that result in the release of CO2. Therefore, the potential use of propanol as a solvent in the biodiesel synthesis process shows excellent prospects for future applications. In comparison to the investigations conducted on the synthesis of biodiesel in media containing methanol and ethanol, there has been a limited amount of research conducted on the utilization of supercritical propanol (SCP) as a medium. The primary objective of this study was to investigate the production of biodiesel by the utilization of alcohols, such as propanol, in a batch reactor operating under supercritical conditions. The upper limit of the temperature that the reaction can attain was 300 degrees Celsius. The objective of this work is to investigate the optimal circumstances for maximizing biodiesel production. This investigation focuses on three key parameters, namely temperature, oil to isopropanol molar ratio, and the usage of a co-solvent [2].

2 METHOD AND MATERIAL

2.1Material

High purity chemicals were employed in this study without further treatment or purification. the oil collected from various restaurants in Diwaniyah. A supplier of propanol (99%) was used (TEDIA.COMPANY.INC. USA). Well purchased n-hexane (99%) co-solvent from srichem, (new Mumbai. India).

2.2Experiment

A high-pressure batch reactor with thick walls was used to conduct the reactions. To maintain a steady temperature while the gadget is in use a container with a capacity of 100ml is used. Science Avenue, High-tech District, Zhengzhou, China (as shown in fig. of the experimental setup graph in Figure 1, a control circuit connected to the device to control the temperature, stirrer speed, and time).

To demonstrate the experiment's process According to the calculations specified in the research, the liquid sample (alcohol, oil, and co-solvent) was put in the reactor. To get the reactor to the proper temperature, a heater was used. Since the pressure had to be above the critical pressure in order to establish the reaction time, it was computed using a pressure gauge. The resultant combination of biodiesel and glycerin was removed when the reaction had stopped. The separator used the difference in density to separate the glycerin from the diesel fuel. Diesel fuel was eventually acquired.

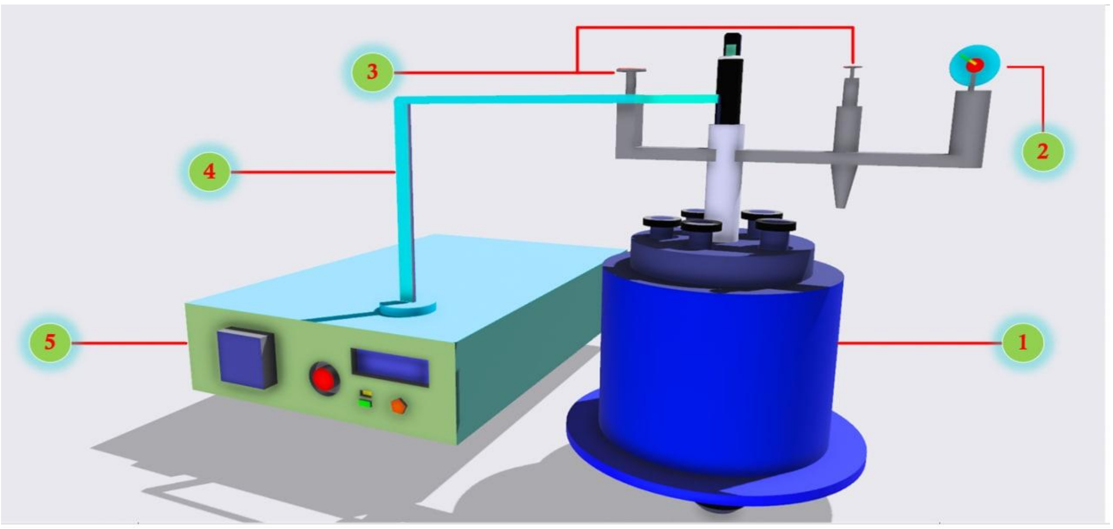

Fig.(1):- Schematic of Experimental Setup where 1. Electrical Heater, 2. Presser Gauge, 3. Safety valve, 4. Thermocouple, 5. controller

2.3 Analytical methods

The liquid product components are examined using a GC-MS (Agilent 6890N series GC with a 5973 N Inert MS detector and 7683 Injector). The GC-MS approach entails a number of steps, including sample preparation, internal standard selection and the generation and analysis of experimental data using GC-MS software's analytical method. Each stage of technique development is evaluated by experimental design, testing, and evaluation. To establish a data analysis procedure in the GC-MS software and interpret experimental results, for instance, changes in sample concentration, selection, and internal standard concentration are created in the sample preparation stage alone. The evaluation of each stage of technique development using an experimental design.

3 .EXPERIMENTAL DESIGN

Response surface approach uses mathematical and statistical tools to determine a regression model equation that connects an objective function with its independent variables (RSM). This study examined how process factors affected yield using a 3-level 3-factor Box-Behnken design (BBD). Yield was a reaction to temperature, co-solvent, and isopropanol-to-oil ratio. Process factors were coded using low, middle, and high levels. Table 2 displays the experiment array suggested by BBD for the current work and obtained by Design expert-11 program. Table 1 shows the process parameters with their specified levels.

Table (1):- Process factors and their impact on biodiesel yield

Name	Code	Low (-1)	Middle (0)	High (+1)
Isopropanol to oil	A	4	8	12
Temperature	B	300	325	350
Co-solvent	C	0	4	8

Table (2):- Box- Behnken experimental design

Run	Isopropanol to oil - A	Temperature. B	Co-solvent C
1	8	300	0
2	8	325	4
3	8	350	8
4	4	300	4
5	8	325	4
6	12	325	0
7	12	350	4
8	4	325	0
9	8	350	0
10	4	350	4
11	8	300	8
12	4	325	8
13	12	325	8
14	12	300	4
15	8	325	4

The correlation between the answer and their independent variables was investigated in this study by employing the second-order model listed below, which was solved for using the least-squares approach [10]:

$$Y = a_0 + \sum a_0 x_i + \sum a_{ii} x_i 2 + \sum a_{ij} x_i x_j \qquad (1)$$

Where Y stands for the output (Yield), i and j for the pattern index numbers, a_0 for the intercept term, and x_1, x_2,..., x_k for the process variables in coded form. The letters a_i, a_{ii}, and a_{ij} stand for the first order (linear) main effect, the second-order main effect, and the interaction effect, respectively. After completing the analysis of variance, the model's appropriateness was verified by estimating the regression coefficient (R^2).

4 .RESULTS AND DISCUSSION

4.1Results of Experimental Design

15 runs were carried out in accordance with BBD design to look into the ideal circumstances for biodiesel production. The experimental findings involving actual Yield and predicted Yield are shown in Table 3.

Table (3):- Experimental results of Box–Behnken design for production biodiesel

Run	isopropanol to oil - A	temperature B	Co-solvent C	Actual Value	Predicted Value
1	8	300	0	65	65.25
2	8	325	4	92	91
3	8	350	8	77	76.75
4	4	300	4	70	70.5
5	8	325	4	91	91
6	12	325	0	72	72.25
7	12	350	4	75	75.5
8	4	325	0	73	73.25
9	8	350	0	67	67.25
10	4	350	4	76	76.5
11	8	300	8	72	71.75
12	4	325	8	79	78.75
13	12	325	8	83	82.75
14	12	300	4	75	74.5
15	8	325	4	90	91

Findings indicated that biodiesel production efficiency was in the region of (65- 92). The results of the ANOVA can be used to determine the precise impact of various parameters.

The production biodiesel results were examined using design Expert-11 software, and the following quadratic model of the production biodiesel in terms of real units of process parameters was developed.:

$$Yield = 9 + 0.875A + 1.62B + 4.25C - 1.5AB + 1.25AC + 0.75BC - 5.25A^2 - 11.75B^2 - 9.00\,C^2 \quad (2)$$

The three-way interactions of the model's parameters are denoted as AB, AC, and BC. The summation of the squared values of variable A and variable B provides a reliable measure for assessing the magnitude of alterations made to the parameters of the model, denoted as variable C. The estimation of Yield values was conducted using Equation 2, and the outcomes are presented in Table 3. The effectiveness of BBD was evaluated by the utilization of analysis of variance (ANOVA). The utilization of Fisher's F-test and the P-test provide a valuable analytical framework for evaluating the significance of the model and its parameters. Higher F-values and lower p-values indicate greater statistical significance of the coefficient terms. The analysis of variance results for the response surface model are presented in Table 4. In this table, the degrees of freedom for the model and parameters are represented by the abbreviation DF. Additionally, the statistical terms for the sum and adjusted mean are denoted as Seq. SS and Adj. MS, respectively. The regression model exhibited a high level of significance, as evidenced by a p-value of 0.0001 and an F-value of 245.8. The comparison between the projected and experimental values, as depicted in Figure 2, demonstrates a favorable agreement with the existing operating data. This is evident from the line with a unit slope. The model's multiple correlation coefficient, which was determined to be 0.9977, suggests that the regression is statistically significant, since only a small proportion (0.0032) of the total variables are not accounted for by the model. In the present model, the multiple correlation coefficients exhibit a strong alignment as the discrepancy between the adjusted multiple correlation coefficient (adj. R^2) and the projected multiple correlation coefficient (pred. R^2) is below 0.1.

Table (4):- Study of variance for biodiesel production

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	995.48	9	110.61	245.8	< 0.0001
A-isopropanol to oil	6.12	1	6.12	13.61	0.0142
B-temperature	21.12	1	21.12	46.94	0.001
C-Co-solvent	144.5	1	144.5	321.11	< 0.0001
AB	9	1	9	20	0.0066
AC	6.25	1	6.25	13.89	0.0136
BC	2.25	1	2.25	5	0.0756
A^2	101.77	1	101.77	226.15	< 0.0001
B^2	509.77	1	509.77	1132.82	< 0.0001
C^2	299.08	1	299.08	664.62	< 0.0001
Residual	2.25	5	0.45		
Lack of Fit	0.25	3	0.0833	0.0833	0.963
Pure Error	2	2	1		
Cor Total	997.73	14			
	R^2	Adjusted R^2	Predicted R^2	Std. Dev.	PRESS
	0.9977	0.9937	0.9915	0.6708	8.5

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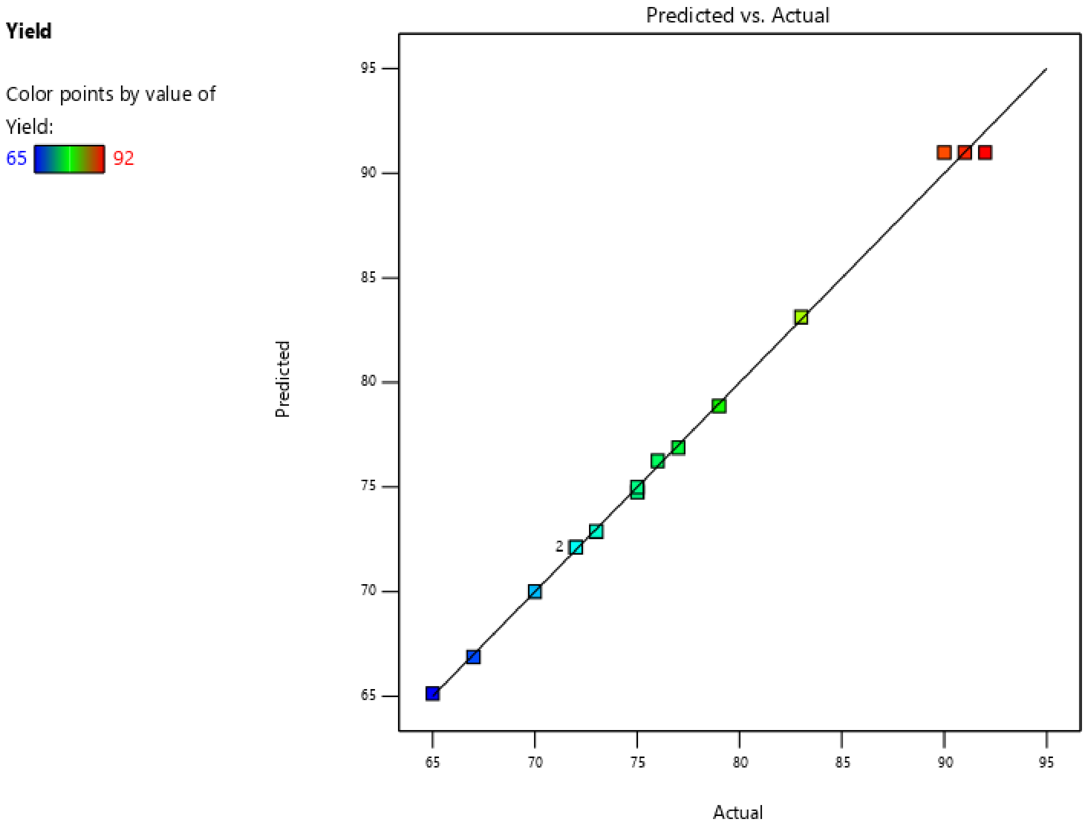
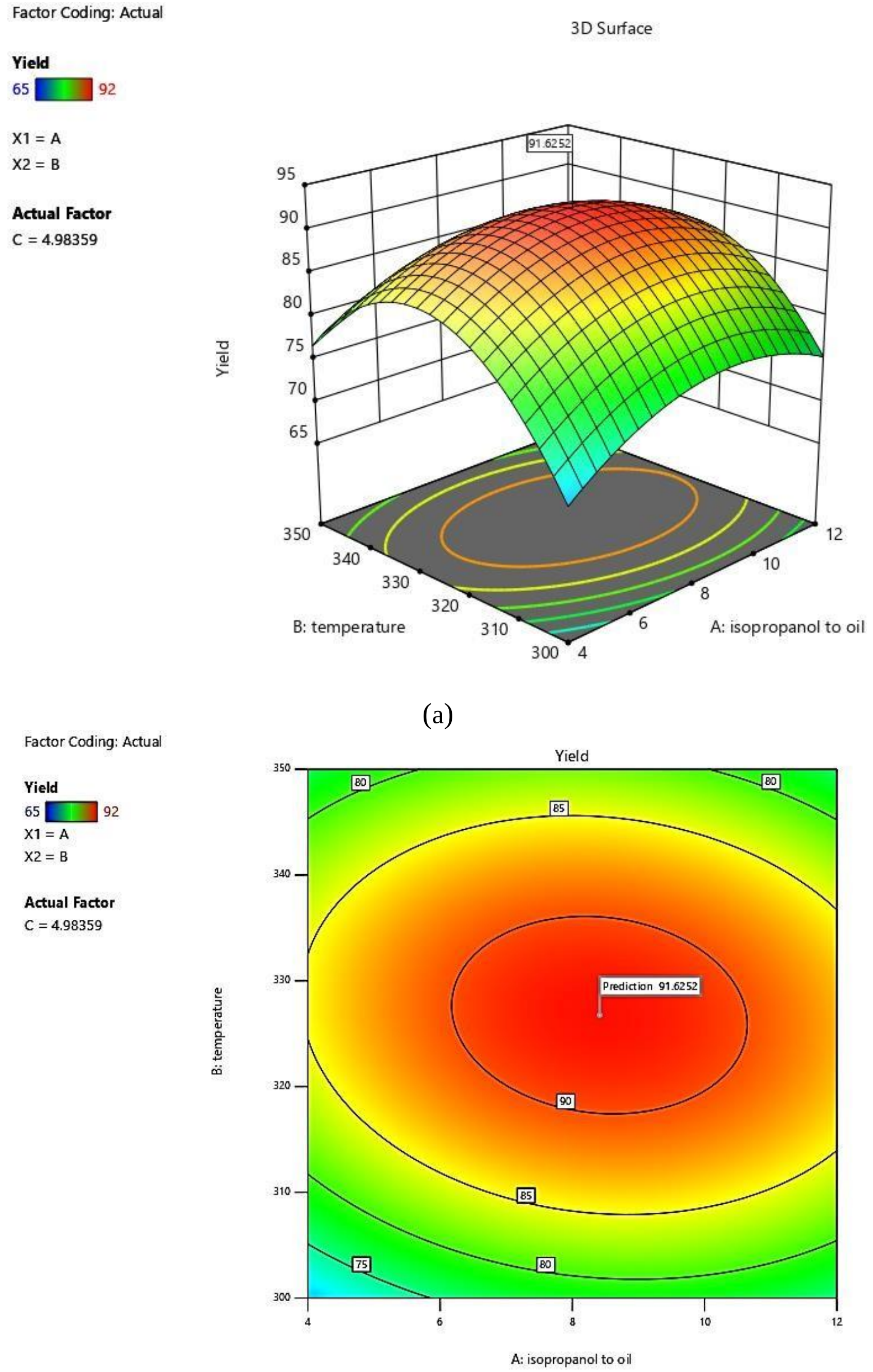


Fig.(2):-Yield biodiesel experimental data versus expected data

The interactive effects of the chosen factors and their impact on the response can be shown graphically using RSM. Figures 3a, b illustrate how the Yield for different ratios of isopropanol to oil (4–12) at constant co-solvent changes with temperature (4.98359). Figure 3-b depicts the corresponding contour plot, while Figure 3a illustrates the response surface plot. The control plot's form reveals the type and degree of the interaction. It was noted from the surface plot that, at isopropanol to oil (4), an increase in Yield occurs as the temperature increases from 300-350. At any temperature, Yield increases linearly with increasing of isopropanol to oil 4 to 12.

Based on the stoichiometry of the transesterification reaction, it is necessary to employ a ratio of three moles of alcohol to one mole of triglyceride in order to yield three moles of biodiesel and one mole of glycerol. In order to promote a higher yield of biodiesel, an increased amount of isopropanol was necessary to shift the reaction towards greater production. The potential cause for the enhanced efficiency of biodiesel could be attributed to heightened interaction between the alcohol and oil constituents. Furthermore, the augmentation of isopropanol as a reactant has the potential to enhance the rate of the reaction [11] .

The related contour figure shows that the Yield value of 92% is within a narrow range where the isopropanol to oil ratio was (6.2–10.3) and the temperature was in the range of (317-335).



(a)

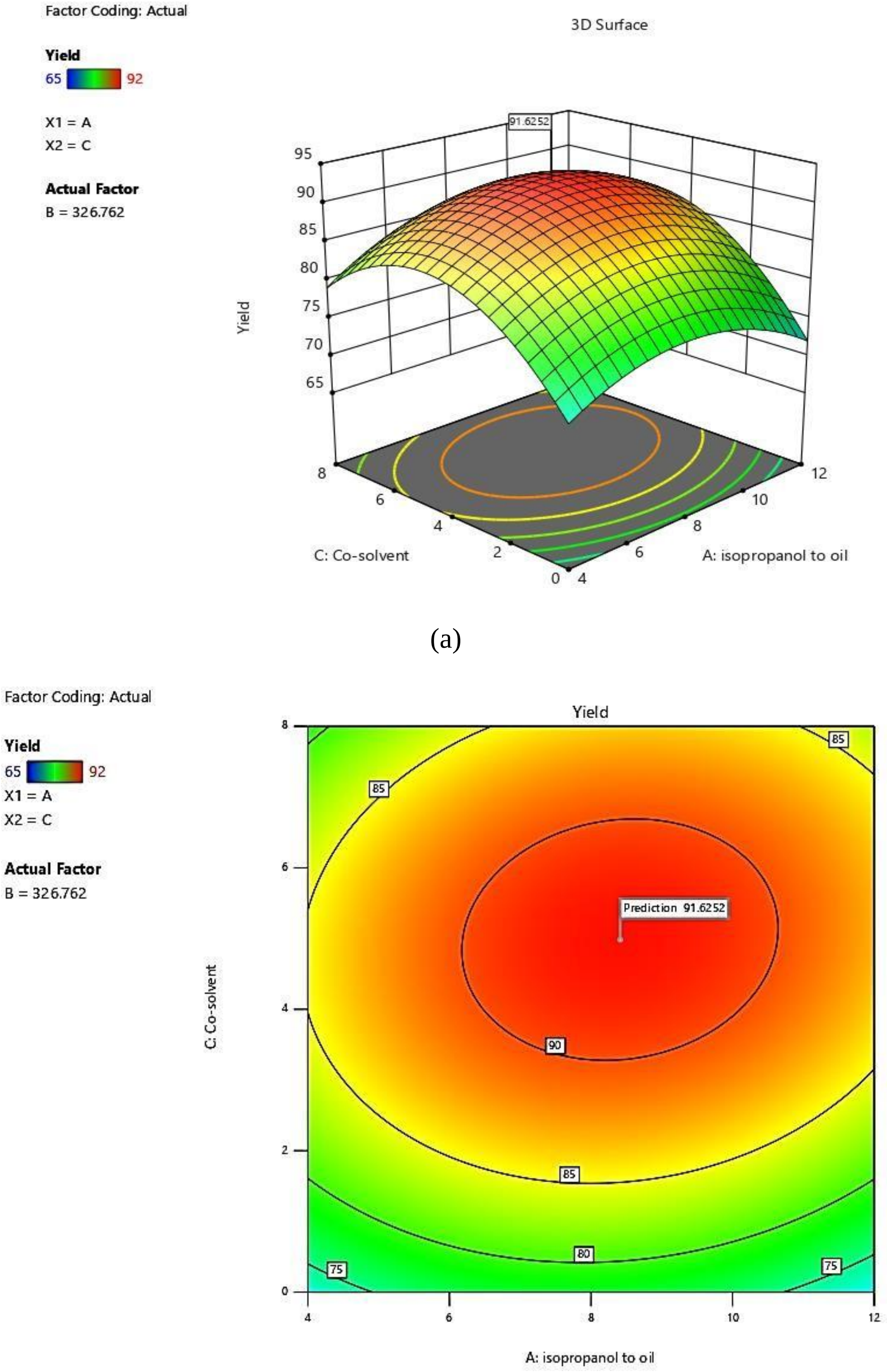
(b)

Fig.(3):-Response surface plots (a) and contour plots (b) showing how temperature and the ratio of isopropanol to oil affect yield.

The influence of the co-solvent on the Yield for different ratios of isopropanol to oil (4-12) at constant temperature is shown in Figures 4a, b (326.762). The response surface plot is shown in Figure 4a, and the matching contour plot is shown in Figure 4b. The size and type of the interaction are shown by the control plot's shape. It was noted from the surface plot that, at isopropanol to oil (4), an increase in Yield occurs as the co-solvent increases from 0-8. At any co-solvent, Yield increases linearly with increasing of isopropanol to oil 4 to 12.

In this study, as it is clear from equation (2), the presence of additional n-hexane as a co-solvent had a negative impact on the efficiency of biodiesel production. This result contrasts with the results of some articles but is very interesting and meaningful[12]; it can be hypothesized that the presence of Hexane as a Co-solvent cannot be beneficial in all situations. Abedini et al.

The related contour map shows that the Yield value of 92% is within a narrow range where the isopropanol to oil ratio was (6.2–10.2) and the co-solvent ranged from (3.7-6.3).



(a)

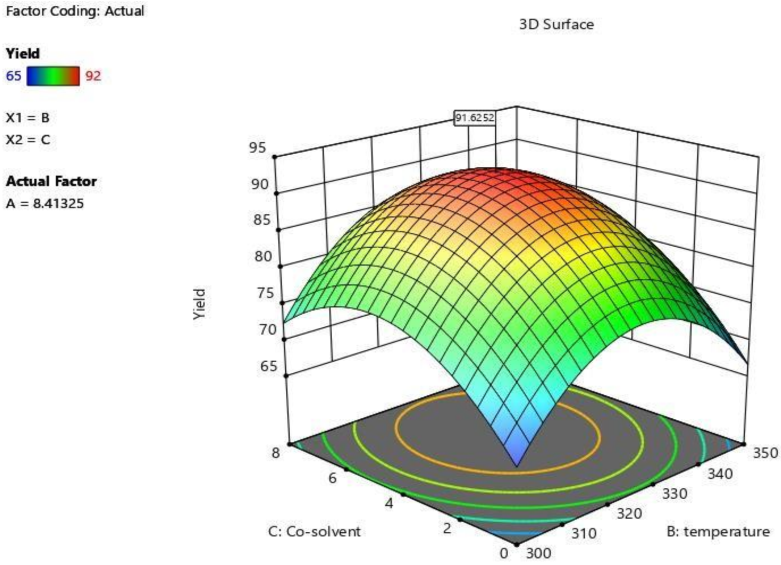
(b)

Fig.(4):-Impact of co-solvent and isopropanol to oil on the Yield as represented by the response surface plot (a) and contour plot (b).

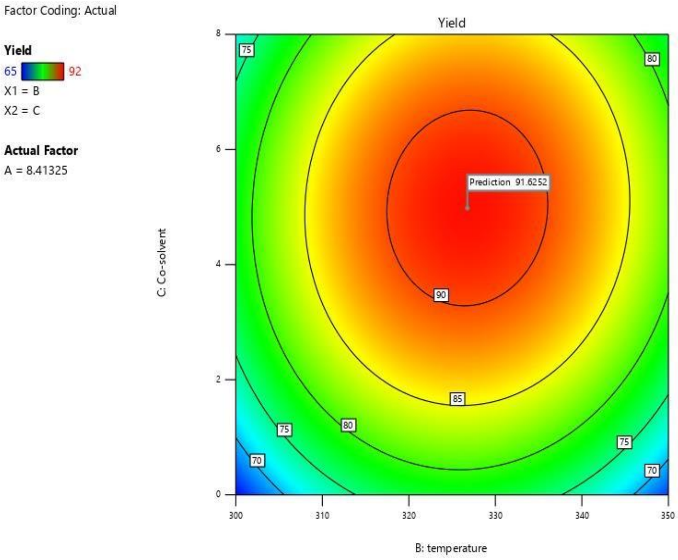
Figures 5a, and Figure 5b demonstrate how the co-solvent on the Yield for various values of temperature (300-350) at constant isopropanol to oil 8.41325. Figure 5a represents the response surface plot while Figure 5b shows the associated contour plot. The shape of control plot indicates the nature and extent of the interaction. From the surface plot, it was observed that, at temperature (300), an increase in Yield occurs as the co-solvent increases from (0-8). At any co-solvent, Yield increases linearly with increasing of temperature 315 to 330 ℃

The impact of temperature on the production of biodiesel has been extensively studied. It has been observed that an increase in temperature promotes the endothermic reaction, leading to a higher yield of biodiesel at equilibrium. Moreover, the elevation in temperature has been observed to have a direct correlation with the rate of reaction, hence leading to a subsequent enhancement in the degree of conversion. Additionally, it contributes to the uniformity of the oil and alcohol mixture.[13].

The associated contour diagram verifies that the value of the Yield 92% lies in a small area in which the temperature ranged between (315-330) and co-solvent in the range of (2.7-6.4).



(a)



(b)

Fig.(5):-The effect of temperature and co-solvent on yield is depicted by a response surface plot (a) and a contour plot (b).

4.2The Optimization and Confirmation Test

Many criteria should be recognized during system optimization in order to maximize the desirability function (DF) and achieve the intended target [14]. Target functions that are being evaluated include maximize, objective, minimize, within the range, and none. When DF=1.0, the Yield objective was referred to as the "maximum." The co-solvent at range of the process parameters investigated in the present work were (0-8), temperature at range of (300-350), and isopropanol to oil at range of (4-12). yield of 65was taken as lower limit value of the production biodiesel, while 92 was designated as the upper maximum value. Under these boundaries and settings, optimization was carried out and the results are shown in Table 5.

Table (5):- Optimum of process parameters for maximum Yield.

Response	Goal	Lower	Target	Upper
Yield	maximum	65	Maximum	92
parameters	A: isopropanol to oil	B: temperature	C: Co-solvent	Yield
Optimum parameters	8.413	326.762	4.984	91.625

5 .CONCLUSION

In this study, supercritical transesterification processes involving oil were analyzed with response surface methodology (RSM), and the influence of alcohol on those reactions was investigated in great detail. A rate of mixing of 600 revolutions per minute (rpm) and a reaction time of fifty minutes (min) were also implemented. According to the data, it was possible to convert a significant amount of oil into biodiesel at a temperature of 326.762 degrees Celsius, a molar ratio of 8.413, and a co-solvent of 4.984, I, with a maximum biodiesel production of 91.625 %. This model has a p-value that is more than 0.0001 and an R2 value that is equal to 0.9977. The response surface method was utilized in order to study the transesterification process that occurs during the production of biodiesel from sunflower oil (RSM). The fact that the models and the results of the experiments agreed well demonstrates that the methodology in question is beneficial to the process of optimization.

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