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Optimization and modeling of biodiesel production from oleic acid in plug flow reactor

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Abstract − In recent years, biodiesel has been preferable to fossil fuels because of its renewability, biodegradability, and producibility from various wastes. In this study, the esterification reaction between oleic acid and methanol was carried out in the presence of sulfuric acid, which is a homogeneous acid catalyst, to produce biodiesel. Experiments were carried out in a plug flow reactor (PFR) and a batch reactor. The experimental conditions with the highest conversion obtained in the PFR were determined and applied to the batch reactor and results were compared. The effects of temperature (45, 55, 65 in Celsius), catalyst concentration (2%, 4%, 6% by weight), and methanol/oleic acid mole ratio (3, 6, 9) on oleic acid conversion were examined in the PFR. Retention times at different flow rates were calculated to determine the reaction time in the PFR and reactions were carried out between 2 and 6 minutes. In the reactions carried out in the PFR, the highest conversion value was obtained as 97.33% under conditions where the catalyst concentration was 6% by weight, the temperature value was 55°C and the alcohol/acid mole ratio was 6:1. These conditions were applied to the batch reactor and the conversion value was found to be 50%. When the experimental results were examined, it was seen that the effect of temperature and alcohol/acid ratio on the conversion was greater than the effect of the catalyst concentration on the conversion. The modeling of oleic acid/methanol esterification, i.e., biodiesel production, at specific boundary values was found to follow a cubic dependence in the general dependence equation via Response Surface Methodology.

Keywords: *Plug flow reactor, biodiesel, oleic acid, batch reactor, response surface methodology (RSM)*

1. Introduction

Biodiesel is a renewable and environmentally friendly fuel composed of methyl or ethyl esters derived from the transesterification of triglycerides or the esterification of free fatty acids (FFA). Today, research into the use of vegetable and animal oils as raw materials for its production is still ongoing [1]. Biodiesel is produced from the triglycerides present in vegetable oils through the transesterification process, resulting in long-chain alkyl esters [2]. Rapid population growth and increasing industrial developments have proportionally increased the energy demand. Fossil fuels such as oil, coal, and natural gas have been utilized to meet this growing energy demand. However, with time, issues such as the depletion of oil reserves and greenhouse gas emissions, which contribute to environmental pollution, have emerged using fossil fuels. This has led to the search for alternative energy sources, and subsequently, biodiesel production from waste oils has commenced. Compared to fossil fuels, biodiesel has a significantly lower emission of CO_2 and CO into the atmosphere.

Biodiesel offers numerous advantages compared to petroleum-based diesel: it contains approximately 10-11% oxygen, and its combustion results in 78% less CO_2 emission compared to petroleum-based diesel [2-8]. When considering production costs, energy content, and environmental impact, biodiesel demonstrates advantages in all three aspects, as illustrated in Tables 1 and 2.

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Table 1. Biodiesel production plants [9]

Facility	Annual capacity (ton/year)	Location	Start
Hellenic Biopetroleum Industrial and Commercial S.A	40,000	Kilkis	2005
VERT OIL S.A.	25,000	Thessaloniki	2006
Pettas Industrial and Commercial S.A.	60,000	Patra	2006
Agroinvest S.A.	200,000	Fthiotida	2006
Elinoil S.A.	80,000	Volos	2006
Biodiesel LTD	20,000	Thessaloniki	2005
Total	**425,000**		

Table 2. Properties of fossil fuels and biodiesel [9]

Fuel	Energy content (MJ/I)	Energy content ratio
Bioethanol (BE)	21.2	1.472 (BE/FG)
Fossil gasoline (FG)	31.2	0.679 (FG/BE)
Biodiesel	32.8	1.088 (BD/FD)
Fossil diesel (FD)	35.7	0.919 (FD/BD)

Besides these advantages, biodiesel is renewable, non-toxic, non-flammable, transportable, easily obtainable, biodegradable, environmentally friendly, and free from sulfur and aromatic compounds [10]. Additionally, it is considered safer for human health due to its lower toxicity. It also surpasses petroleum-based diesel fuels in terms of flash point, cetane number, and sulfur content [11]. The production of biodiesel requires less time, as it does not involve processes such as drilling, transportation, and refining compared to petroleum-based diesel fuels.

Biodiesel is produced through the esterification or transesterification reactions of animal or vegetable oils in the presence of alcohol and a catalyst. Non-renewable raw materials generally contain higher amounts of fatty acids compared to edible raw materials, and the production of biodiesel from these materials involves a two-step process: esterification of fatty acids followed by transesterification. If oils are used in the reaction, glycerol is produced as a by-product; if fatty acids are used, water is released. For the convenience of the processes and the easy disposal of by-products, the production of fatty acid methyl esters or ethyl esters is more advantageous [4]. In biodiesel production, the esterification method is commonly chosen via the transesterification method. The esterification process produces water, which is easily separable from biodiesel, whereas in the transesterification method, glycerol is produced along with biodiesel, and the separation of this glycerol is more challenging. Thermal processes, membrane processes, adsorption, absorption, and cryogenic techniques are employed to separate glycerol from biodiesel. After a significant quantity of glycerol has been extracted, chemical reactions can be utilized to produce fuel additives and chemicals with polymer fuel value [12].

Various raw materials are used in biodiesel production. These include vegetable oils (both edible and non-edible), waste cooking oils, animal fats, and algal oils [13]. Among these options, the most economical and sustainable method is the production of biodiesel from waste oils. This process not only facilitates the recovery of waste oils but also contributes to the generation of a valuable product. The most important chemical characteristic of vegetable oils is the composition of fatty acids. Oils are categorized into saturated and unsaturated types: saturated fatty acids have all carbon atoms fully bonded to hydrogen atoms through their valence orbitals. The most common saturated acids found in vegetable oils are palmitic (16:0) and stearic (18:0) acids. Unsaturated fatty acids, on the other hand, have not all carbon atoms bonded to hydrogen atoms. They are classified into monounsaturated and polyunsaturated fatty acids. Some commonly used unsaturated fatty acids include lauric (12:0), myristic (14:0), palmitoleic (16:1), stearic (18:0), oleic (18:1), linoleic (18:2), and linolenic (18:3) acids [14]. Biodiesel can be categorized into three types based on its raw materials: first-generation, second-generation, and third-generation sources.

One of the critical parameters in biodiesel production is the selection of the reactor. There are several types of reactors available for biodiesel production through the transesterification of oils. These reactors are categorized based on their operating conditions into batch reactors, membrane reactors, continuous stirred-tank reactors, ultrasonic reactors, and piston-flow/ tubular reactors [15]. Plug flow reactors have recently begun to be used in biodiesel production [16]. Due to several advantages, these reactors have gained preference in recent years. These advantages can be summarized as follows:

i. The product is obtained in a shorter time in these reactors, partly due to the absence of accumulation and the continuous flow in piston-flow reactors [17].

ii. Compared to traditional batch reactors, piston-flow reactors achieve high-efficiency biodiesel production at lower reaction temperatures and lower alcohol/acid ratios [18].

There is a considerable amount of literature on biodiesel production using plug flow reactors. In a study published in 2010, biodiesel production was carried out using rapeseed oil in a plug flow reactor (PFR). The reaction was conducted at a temperature of 65 °C; methanol was used with a 6:1 molar ratio of alcohol to acid, and a 1.2% (w/w) KOH catalyst was employed in that paper. It was observed that the reaction achieved the highest conversion rate of 91.7% at the 19th minute [14]. In another study published in 2016, biodiesel production was performed using rubber seed oil in a plug flow reactor at a temperature of 140 °C. Methanol was used with a 5:1 molar ratio of alcohol to acid, and a 1.5% (v/v) H_2SO_4 catalyst was applied in that paper. The methyl ester conversion rate was observed to be 98.2% at the 20th minute [19]. In a study conducted by Gumus and colleagues, the transesterification of sunflower oil with methanol was carried out in a piston-flow tubular reactor. The effect of varying the alcohol/oil ratio from 3:1 to 6:1 and 9:1, as well as adjusting the temperature (25-60 °C), on reaction efficiency was investigated. In a reaction performed at 60 °C with a reaction volume of 487.7 liters, the highest reaction conversion achieved was 90%. The study identified high feed rate and high temperature as significant parameters affecting conversion [20]. Sawangkeaw et al. conducted an optimization study using supercritical methanol to refine palm kernel oil in a piston-flow tubular reactor. The study was conducted at a reaction temperature of 325 °C and a pressure of 18 MPa, with an alcohol/acid ratio of 42:1. The biodiesel conversion was calculated to be 94% [21].

Besides these studies, in 2021, Nigiz [22] conducted the esterification reaction of lauric acid and methanol in an inert and catalytic pervaporation membrane reactor (PVMR). Phosphotungstic acid (PTA), a heteropolyacid, was used as the catalyst. When a methanol/lauric acid molar ratio of 6, catalyst concentration of 2% (w/w), and temperature of 65 °C were set, the conversions were 98.9% in the inert membrane reactor and 97.5% in the catalytic membrane reactor. These processes were also carried out in a batch reactor, achieving a conversion rate of 80.7%.

Flow reactors produce high-quality products consistently with a steady feed. Due to their continuous operation, they can be used in serial production processes. This capability leads to lower production costs because they can be used in series. Consequently, they are generally employed when rapid, high-quality production is desired [23].

Plug flow reactors consist of a cylindrical structure and operate with a stable design. In a cylindrical reactor, the reactants flow downwards through pipes along the length of the reactor in a turbulent flow at a uniform rate, leading to continuous consumption [17,24]. In tubular reactors that operate with a stable design, the concentration of the consumed reactants and the resulting products varies along the flow direction. Due to these characteristics, the piston-flow/tubular reactor is considered an idealized reactor and is classified as a one-dimensional flow reactor [23]. The parameters of a piston-flow reactor include the time constant, concentration, volumetric flow rate, and volume. Among these parameters, the time constant is the most critical. The time constant, when kept constant, does not alter the conversion amount whether the piston-flow reactor operates in series or parallel [24]. Equations can be established for the piston-flow tubular reactor based on these parameters.

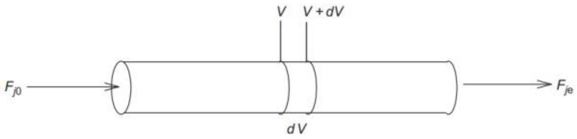


Figure 1. Plug flow Reactor control volume

Since the total mass amount cannot be determined in chemical reactions, a mass balance is established by taking differential volumes as shown in Figure 1.

$$F_{j_0} - F_{j_e} + \int_0^V r_j dV = \frac{dN_j}{dt} \tag{1.1}$$

When the obtained design equations are organized, the design equation for a piston-flow reactor is determined by establishing the molar balance [17]

$$\frac{dF_j}{dV} = r_j \tag{1.2}$$

To determine the reaction time in piston-flow/tubular reactors, the time constant, also known as the residence time, is calculated. The time constant is computed by dividing the reactor volume by the flow rate [17].

$$\tau = \frac{V}{V_0} \tag{1.3}$$

A continuous process is generally more suitable than a batch process for biodiesel production using supercritical methanol (SCM), as it operates under high temperature and pressure to maximize the yield of fatty acid methyl esters (FAME) in an industrial context. This continuous approach facilitates efficient heat recovery from the heated product via a heat exchanger and eliminates the need for heating and cooling phases. However, energy consumption becomes nearly equivalent when these systems are integrated, particularly when supplementary techniques, such as the use of co-solvents or catalysts to mitigate reaction conditions, are employed [25]

In industrial production, piston-flow reactors are preferably operated at maximum capacity to enhance production efficiency. Maintaining maximum capacity also helps minimize the unit cost. PFR reactors are used extensively in various industrial applications because they provide higher conversion rates per unit volume compared to other flow reactors.

The operation of a piston-flow/tubular reactor in steady-state conditions facilitates the creation of temperature profiles due to its lower reactor volume compared to continuous stirred-tank reactors (CSTRs) and the ability to apply heat transfer effectively within desired sections of the reactor [24]. The continuous contact of the reactant mixture flowing through the reactor's tubes ensures a homogeneous mixture, enhancing the mass transfer area and achieving high conversion rates. In this study, the esterification reaction between methanol and oleic acid was experimentally optimized in a PFR reactor. The reaction was also performed in a batch reactor to compare the performance of the two reactors.

2. Materials and Methods

2.1. Experimental Set-up

In the experiments, biodiesel production was carried out in a plug-flow reactor, as illustrated in Figure 2. The experimental setup consists of a tubular reactor, a control panel, a collection vessel, a heater, and chemical tanks located behind the reactor. The reactor, which is the most critical component of the system, is encased in a 20-meter-long plastic tube and is placed inside a water-filled tank. The electric heater is used to heat the water bath, while the mixer motor ensures uniform temperature distribution throughout. The control panel includes a heater temperature indicator, a product outlet temperature indicator, and pump controls. Flow meters were used to adjust the flow rates of oleic acid and methanol throughout the reaction time. The esterification reaction was conducted with sulfuric acid, a homogeneous acid catalyst, to produce biodiesel.

Figure 2. Experimental set-up of PFR

2.2. Determination of Reaction Time

The residence time for the reaction in the PFR reactor had to be determined. This was calculated using (1.3) provided in the theoretical fundamentals section. Initially, the reactor volume was determined, and then the reaction times were calculated based on the flow rate of methanol. Accordingly, the reaction times ranged between 2 and 6 minutes.

2.3. Experimental optimization of Biodiesel Production from Oleic Acid and Methanol in Plug Flow Reactor

Response surface methodology (RSM) is a statistical approach used for developing and enhancing the quality characteristics of products or processes. This technique effectively analyzes, models, and determines the optimal parameter levels associated with a given process and its quality attributes. RSM employs experimental designs that enable the reliable and sufficient measurement of the response variable using a limited number of observable values. This allows for the creation of a mathematical model that accurately represents the collected data and helps identify the factor levels that achieve the best response. The methodology incorporates various models, including linear, quadratic, and cubic forms [26]. The quadratic model is represented by the equation provided in (2.1).

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{1 \le i < j}^{n} \beta_{ij} x_i x_j + \varepsilon \tag{2.1}$$

In this equation, $x_1, x_2, \ldots, x_n$ are independent variables, y is dependent (response) variable, β_0, β_i, β_{ii} $(i = 1,2,\ldots,n)$, β_{ij} $(i = 1,2,\ldots,n\,; j = 1,2,\ldots,n)$ are unknown model parameters and ε is a random error term [sic][26].

Various experimental designs can be implemented within the framework of Response Surface Methodology (RSM). However, Box-Behnken and Central Composite designs, which have been specifically developed for RSM and significantly reduce the number of experiments required, are frequently preferred [sic][26].

The Central Composite Design (CCD) of the RSM is a statistical experimental design approach frequently used to maximize research output with minimal operating costs, experiments, chemicals, and trial numbers. In this study, oleic acid conversion was identified as the response. The variable factors were the alcohol ratio, catalyst concentration, and temperature. These conditions and their limits are provided in Table 3. Statistical modeling was conducted using Design Expert 12 software. A total of 17 test points were determined for this study, including 3 intermediate control values. The optimization conditions have been obtained from the RSM model and were implemented in the plug flow reactor according to the specified sequence and experimental conditions.

Table 3. Limit values of CCD factors

Factors	**Symbol**	**Range/Value**		
		-1	0	+1
Temperature (^{o}C)	T	45	55	65
Alcohol: Acid Molar Ratio	N	3	6	9
Catalyst amount (%w/w)	m	2	4	6

In the experimental setup, an oleic acid and sulfuric acid mixture were added to the Reactor 1 tank, and methanol was added to the Reactor 2 tank. Flow rates of methanol and oleic acid were adjusted according to the specified alcohol/acid ratios. The reactor temperature was equilibrated according to each alcohol/acid ratio under the operating conditions. Before initiating the reaction, a 0.1-gram sample was taken from the reactant tanks to determine the initial acidity. The initial acidity value was calculated by titrating the sample with sodium hydroxide. The final acidity and conversion were calculated by repeating the same procedures at the end of the residence times.

For each experimental condition, before commencing the experiment, 0.1 g samples taken from the reactant tanks were titrated with sodium hydroxide. A drop of phenolphthalein was added to the samples, and the titration was considered complete when a color change was observed. The acidity was calculated using the amount of sodium hydroxide consumed during the titration. The acidity was determined using the formula shown in (2.2) below.

$$F(wt.\%) = \frac{N_{NaOH}\ V_{NaOH}\ MW_{OA}}{1000W} 100 \tag{2.2}$$

Here, F represents the mass of free acid, N_{NaOH} denotes the molarity of the sodium hydroxide used as the titrant, V_{NaOH} is the volume of the sodium hydroxide titrant, MW_{OA} is the molecular weight of oleic acid, and W is the mass of the sample used in the titration.

The same procedures were repeated for 0.1 g samples taken at each flow rate after the reaction was complete. The conversion values of the reactions were calculated using (2.3).

$$X = \frac{F_{A0} - F_A}{F_{A0}} \tag{2.3}$$

In (2.3), F_{A0} represents the initial molar flow rate of the limiting component, F_A denotes the molar flow rate at the end of the residence times, and X indicates the conversion value. In the experiments conducted in the batch reactor, the conversion is calculated using (2.4).

$$X = \frac{N_{A0} - N_A}{N_{A0}} \tag{2.4}$$

In (2.4), N_{A0} represents the initial number of moles of the limiting component, and N_A denotes the number of moles of the component at the end of the reaction.

2.4. Biodiesel Production in a Batch Reactor

In the batch reactor experiments, shown in Figure 3, biodiesel production was carried out in a three-necked reactor. A mechanical stirrer was used to ensure continuous mixing throughout the reaction, and a condenser was employed to facilitate condensation during the reaction. After the completion of experiments in the plug flow reactor, biodiesel production was carried out using the parameters from the 9th, 12th, and 17th trials. These trials were selected because they yielded the highest conversions in the plug flow reactor. The effect of these selected parameter values on biodiesel conversion in the batch reactor was investigated. The reaction time to reach equilibrium in the batch reactor was set at 4 hours. Under the conditions specified in the 9th trial, a mixture with an alcohol-to-acid molar ratio of 6 and a catalyst concentration of 4% was reacted in the batch reactor at 65°C for 4 hours.

Figure 3. Experimental set-up of batch reactor

3. Results and Discussion

The conversion data obtained from the conducted experiments are presented in Table 4. The effects of the investigated parameters, including temperature, catalyst concentration, and alcohol-to-acid molar ratio, on reaction conversion are evident in the experimental results. The conditions from the 9th, 12th, and 17th trials conducted in the piston flow/tubular reactor were applied to the batch reactor to study their impact on reaction conversions.

Table 4. Experimental results with PFR

Run	Catalyst amount (%w/w)	Temperature (ºC)	Alcohol/Acid Molar Ratio	Conversion (%)
1	6	45	3	93.75
2	4	55	3	92.77
3	2	45	9	94.54
4	2	65	3	94.44
5	4	55	6	93.94
6	2	45	3	92.72
7	2	55	6	92.5
8	6	45	9	95.38
9	4	65	6	95.45
10	2	65	9	97.22
11	6	65	3	96.5
12	6	55	6	97.33
13	6	65	9	96.92
14	4	45	6	92.42
15	4	55	6	93.94
16	4	55	6	93.94
17	4	55	9	94.64

3.1. Effect of Temperature on Conversion

Temperature is a significant parameter in the esterification reaction involved in biodiesel production [27]. Therefore, the effect of increasing temperature on reaction conversion was investigated while keeping other experimental parameters constant. For the experiments conducted at temperatures of 45°C, 55°C, and 65°C, the alcohol-to-acid ratio was maintained at 6, and the catalyst concentration was kept at 4. The experimental data is provided in Figure 4. The esterification reaction of methanol and oleic acid is an endothermic process. Increasing the temperature enhances the speed of the molecules, increasing the frequency of collisions between them and breaking chemical bonds, which facilitates the formation of a more homogeneous mixture of reactants [28].

According to the Arrhenius equation, the rate constant, k, increases with temperature, leading to an increase in the reaction rate. Consequently, an increase in temperature was observed to enhance biodiesel conversion [29].

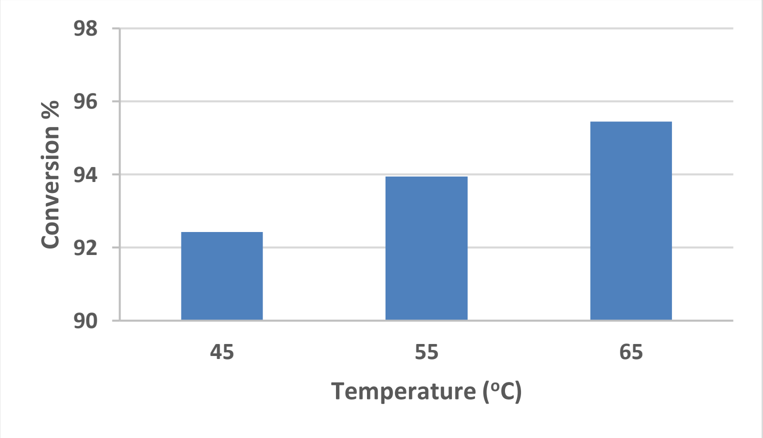


Figure 4. The effect of temperature on the conversion of the biodiesel production reaction from oleic acid in PFR (Catalyst amount: 4% w/w, alcohol/acid molar ratio: 6)

3.2. Effect of Alcohol/Acid Molar Ratio on Conversion

The alcohol-to-acid molar ratio is one of the critical parameters in the esterification reaction. In reversible reactions, one method to increase acid conversion is to raise the concentration of one of the reactants added initially. Based on Le Chatelier's principle, the effect of the alcohol-to-acid molar ratio on equilibrium conversion has been investigated. As the alcohol ratio is increased, the rate of the reverse reaction decreases concerning the equilibrium conversion, shifting the reaction towards the formation of products. Consequently, an increase in biodiesel conversion has been observed. Increasing the concentration of one reactant in the system also enhances its contact area with the other reactant, leading to an increase in oleic acid conversion [30]. In the experiments, the temperature was maintained at 55°C, and the catalyst concentration was kept at 4%, while the alcohol-to-acid ratio was adjusted to 3, 6, and 9. The experimental data are presented in Figure 5.

According to Figure 5, at an alcohol-to-oleic acid ratio of 3, the conversion was observed to be 92.77%. When the ratio was increased to 6, the conversion rose to 93.94%, and at a ratio of 9, the conversion reached 94.64%.

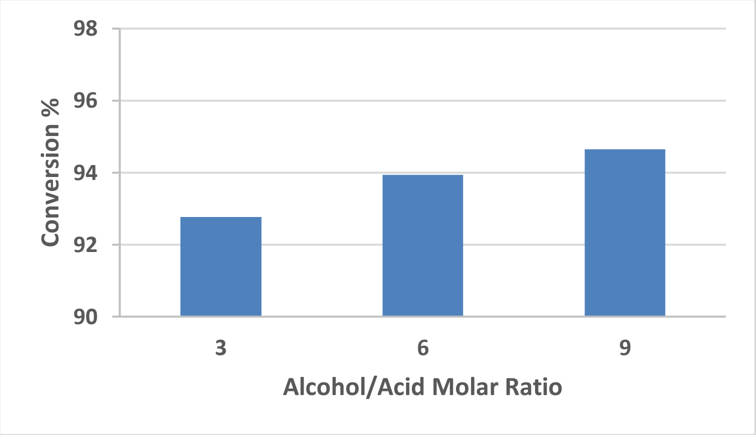


Figure 5. The effect of alcohol/acid ratio on the conversion of the biodiesel production reaction from oleic acid in PFR (Catalyst amount: 4% w/w, Temperature: 55℃)

3.3. Effect of Catalyst Amount (%w/w) on Conversion

In the esterification reaction, catalyst selection is one of the crucial parameters for increasing conversion. The catalyst concentration was calculated based on the mass percentage of oleic acid. An increase in the catalyst concentration raises the acidic area of oleic acid, leading to an increase in the active surface area of the catalyst. Consequently, oleic acid and methanol more readily reach the active sites of the sulfuric acid catalyst, resulting in increased conversion [31,32]. The catalyst reduces the activation energy, thereby increasing the reaction rate and shortening the reaction time [33]. In these experiments, the alcohol-to-acid ratio was fixed at 6 and the temperature at 55°C. The experimental data are presented in Figure 6. When the catalyst concentrations were set at 2%, 4%, and 6%, the conversions were calculated as 92.5%, 93.94%, and 97.33%, respectively.

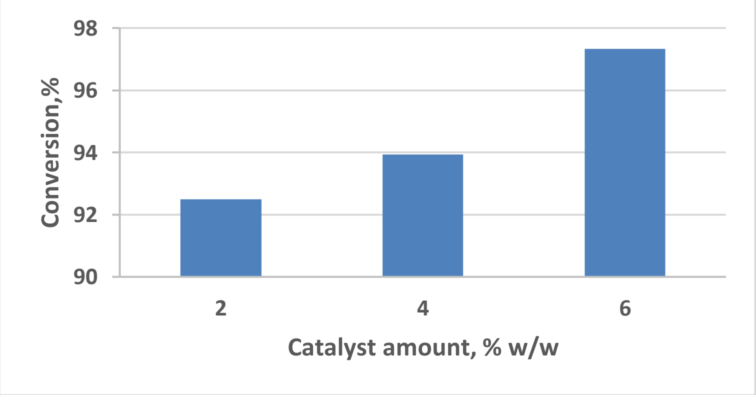


Figure 6. Effect of catalyst amount (%w/w) on the conversion of the biodiesel production reaction from oleic acid in PFR (Temperature: 55℃, alcohol/acid molar ratio: 6)

3.4. Effect of Reactor Type on Conversion

The effect of the type of reactor used on the conversion of oleic acid was investigated in the studies and the results were shown in Table 5. Reactions were initially conducted in a plug flow reactor at 65°C with an alcohol-to-acid molar ratio of 6 and a catalyst concentration of 4%, resulting in a conversion of 95.45%. Under the same conditions, the conversion in the batch reactor decreased to 52.38%, reflecting a reduction of 43.07%, shown in Figure 7. As a result of the experiments and calculations, the reaction conversion under the conditions of the 9th trial in the batch reactor was found to be 52.38%. In contrast, the conversion for the same experimental conditions in the plug flow reactor was found to be 95.45%.

In the batch reactor, a mechanical stirrer was used to ensure the homogeneous mixing of reactants. In contrast, in the piston flow/tubular reactors, the mixture is continuously mixed homogeneously due to the turbulent flow through the pipes. Since homogeneous mixing is not fully achieved in the batch reactor, the mass transfer between the catalyst and the mixture is less efficient compared to the piston flow/tubular reactor. As a result, the acid conversion in the batch reactor was found to be lower than in the PFR reactor. Additionally, it was observed that in the piston flow/tubular reactor, the temperature reaches the desired value more easily and the reaction times are shorter.

Table 5. Experiments carried out in batch reactor

Run	Catalyst amount (%w/w)	Temperature (°C)	Alcohol/Acid Molar Ratio	Conversion (%)
9	4	65	6	52.38
12	6	55	6	50
17	4	55	9	34.11

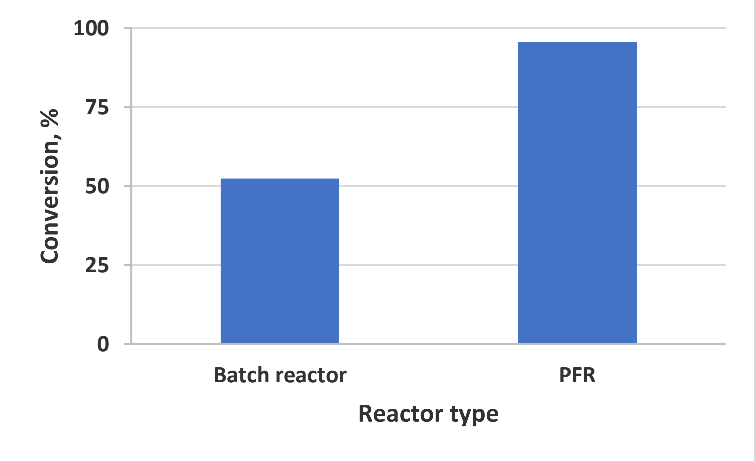


Figure 7. Conversion values for the biodiesel production reaction from oleic acid, which takes place in the PFR and batch reactor, when the alcohol/acid mole ratio is kept constant: 6, the temperature is 65 °C and the catalyst ratio is 4% w/w

3.5. RSM Model Results

The results of the experiments from the optimization conditions table provided by the RSM with a central composite design have been incorporated into the model, and the obtained results are presented in Tables 6-8 and Figures 8 and 9. A linear dependence is observed. Coefficient information is given in Table 9. Obtained equation for conversion is given in (3.1). With this dependence equation, it is possible to predict the conversion value for any parametric condition, whether within or outside the limits entered in the RSM.

$$y = 94.6118 + 0.906A + 1.172B + 0.852C \tag{3.1}$$

In (3.1), y is conversion, A is Catalyst Amount (%w/w), B is Temperature (°C) and C is alcohol/acid mole ratio. Accordingly, it is observed that the conversion is primarily dependent on temperature. In fact, since temperature increases the reaction rate constantly, both the reaction rate and the conversion are enhanced.

Table 6. Fit summary obtained from RSM

Standard Deviation	1.02	R^2	0.6832
Mean	94.61	Adjusted R^2	0.6101
C. V. %	1.08	Predicted R^2	0.4507
		Adequate Precision	11.8370

As shown in Table 8, the linear model is considered the most suitable model for the experimental data. Analyzing the F-value, the highest value is observed for temperature. Furthermore, examining the p-values of all variables confirms the significance of the factors' effects on the response in the model.

Table 8. ANOVA for linear model obtained from RSM

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	29.20	3	9.73	9.35	0.0015	significant
A- Catalyst amount (%w/w)	8.21	1	8.21	7.88	0.0148	
B-Temperature (°C)	13.74	1	13.74	13.19	0.0030	
C- Alcohol/Acid Molar Ratio	7.26	1	7.26	6.97	0.0204	
Residual	13.54	13	1.04			
Lack of Fit	13.54	11	1.23			
Pure Error	0.00	2	0.00			
Cor Total	42.74	16				

p-value shading: $p < 0.05$, $0.05 \le p < 0.1$, and $p \ge 0.1$

Figure 8 illustrates the alignment between the values predicted by the model and the actual experimental values. It can be concluded that the linear model exhibits a reasonable fit with the experimental data, which provides insight into the model's acceptability.

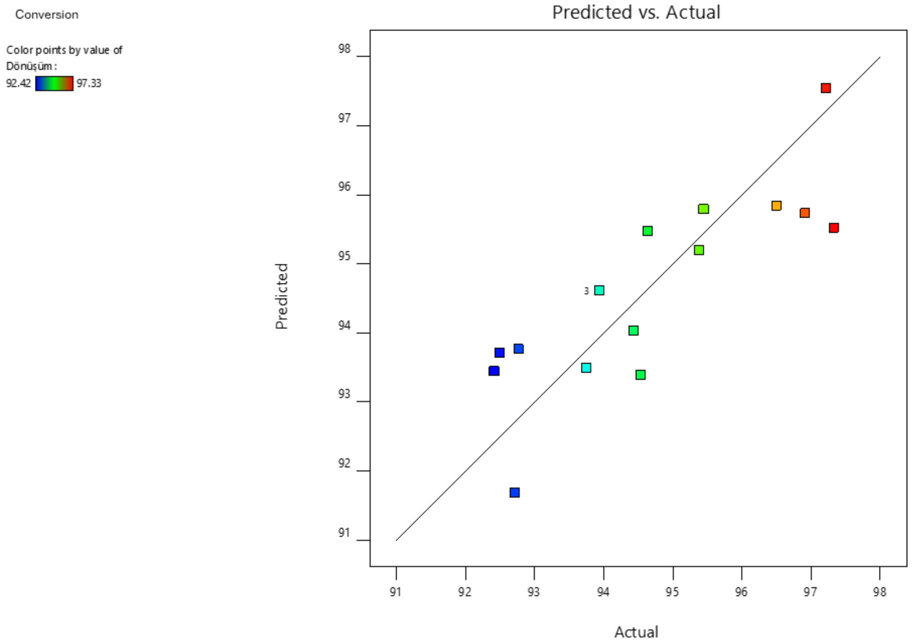
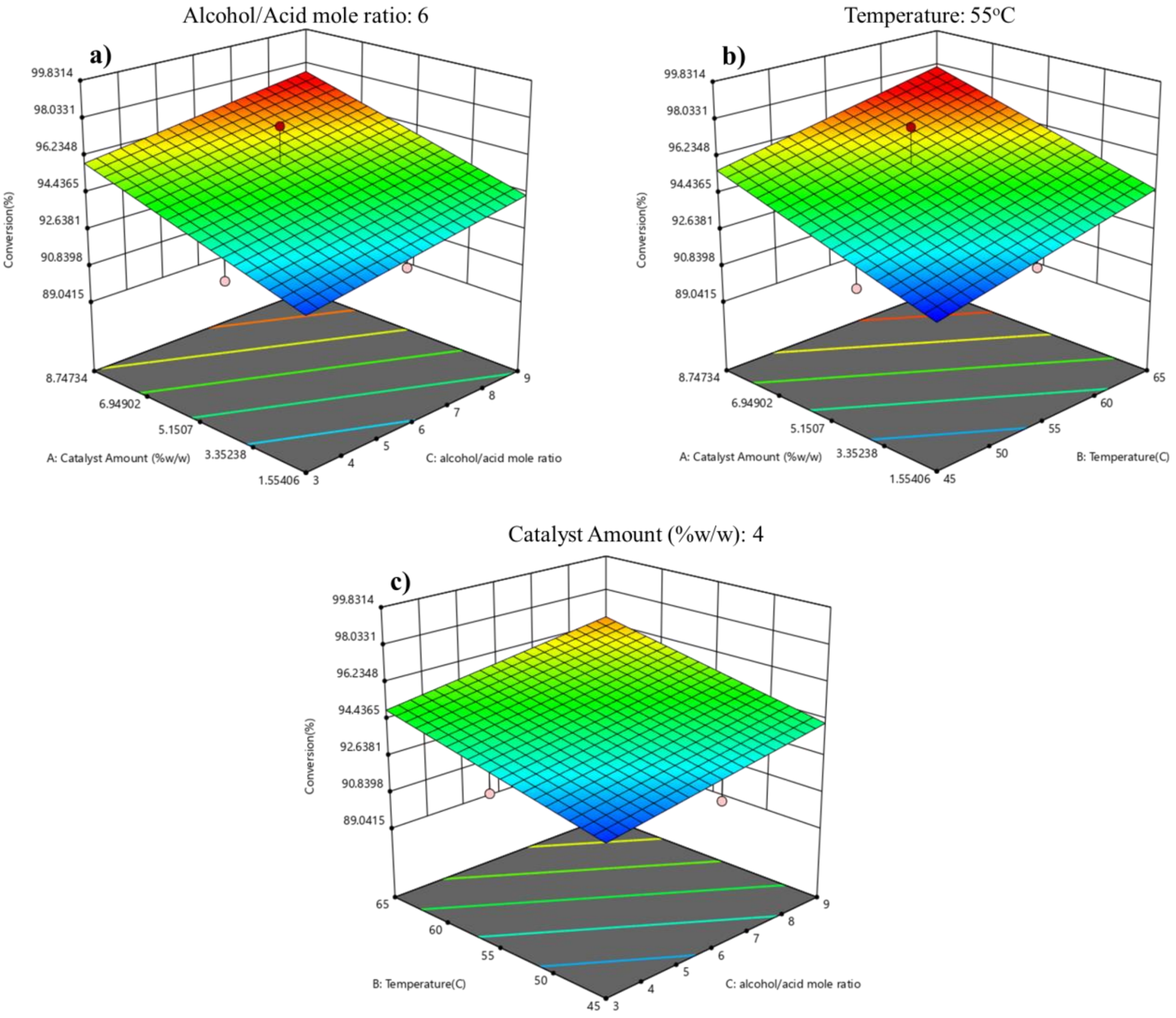


Figure 8. Comparison of experimental vs RSM results

Figure 9 demonstrates the effect of the interdependence of factors on conversion. When the alcohol-to-acid ratio is held constant at 6, the impacts of catalyst and temperature are shown in Figure 9a. When the temperature is maintained at 55 °C, the effects of the alcohol-to-acid ratio and catalyst are illustrated in Figure 9b. Additionally, when the catalyst ratio is held constant at 4%, the influences of temperature and alcohol-to-acid ratio on conversion are depicted in Figure 9c. As shown in Figure 9a, the highest conversion is achieved in the red region, which corresponds to the highest values of both temperature and catalyst ratio. Conversely, the lowest conversion occurs in the blue region, where both temperature and catalyst ratio are at their minimum levels. This indicates that the two most influential factors on the reaction are temperature and catalyst ratio. In Figure 9b, it can be observed that, at low temperatures in the PFR, the effect of the catalyst ratio is greater than that of the molar ratio. When the catalyst ratio is held constant at 4%, the effect of temperature on conversion, as inferred from the slope of the graph, is also greater than that of the molar ratio. The Arrhenius equation indicates that the rate constant, k, rises with temperature, which in turn accelerates the reaction rate. The literature indicates that both elevated temperatures and increased catalyst ratios significantly enhance the conversion of biodiesel [29, 34-36].


Alcohol/Acid mole ratio: 6

Temperature: 55°C

Catalyst Amount (%w/w): 4

Figure 9. RSM results (3D representation of the effect of catalyst amount, temperature and alcohol/acid molar ratio on conversion)

4. Conclusion

This study investigated the esterification reaction between oleic acid and methanol in both a plug flow reactor and a batch reactor. The effects of parametric factors such as alcohol-to-acid molar ratio, temperature, catalyst concentration (%w/w), and reactor type on oleic acid conversion were examined. It was observed that increases in the alcohol-to-acid ratio, temperature, and catalyst concentration (%w/w), led to higher oleic acid conversion. Among the 17 experiments conducted in the plug flow reactor, the highest conversion was observed under conditions of a catalyst concentration of 6%, a temperature of 55°C, and an alcohol-to-acid molar ratio of 6:1, achieving a conversion of 97.33%. The effects of temperature and alcohol-to-acid ratio on conversion were found to be more significant than the effect of catalyst concentration. The experimental conditions that yielded the highest conversion in the PFR were applied to the batch reactor, resulting in a conversion value of 50%. It was noted that oleic acid conversion in the batch reactor decreased by 47.33% and that the reaction times were longer compared to the piston flow reactor. Modeling of oleic acid/methanol esterification, i.e., biodiesel production, was found to follow a cubic dependence within certain boundary values. Furthermore, to enhance conversion under low operating conditions and ensure catalyst recovery, the esterification of oleic acid can be planned to use heterogeneous and high-performance catalysts as a future study.

Author Contributions

All the authors equally contributed to this work. They all read and approved the final version of the paper.

Conflict of Interest

All the authors declare no conflict of interest.

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