# Optimization of Process Parameters for the Valorization of Crude Glycerol into Triacetin

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**Abstract:** The typical biodiesel production process generates glycerol as a byproduct due to the use of alcohol as an acyl acceptor. The rising necessity for biodiesel production has resulted in an excess of crude glycerol, surpassing market needs and often being treated as waste. For the enhancement of the economic sustainability of the industry, an efficient valorization strategy is required. This study explores the optimization of the process parameters that influence the conversion of crude glycerol into triacetin. The research focuses on optimizing process parameters to maximize triacetin selectivity. A "Box–Behnken Design (BBD)" was employed within the framework of "Response Surface Methodology (RSM)" to investigate the effects of key parameters, including reaction time, temperature, and molar ratio. The optimization results showed that the highest triacetin selectivity was achieved under optimal conditions of 60% at M:O molar ratio of glycerol to ethyl acetate 1:2.59, Reaction time of 2.05 h, and reaction temperature of 27°C The developed process offers an efficient and scalable approach to crude glycerol valorization, supporting the economic viability of biodiesel production while reducing waste.

**Keywords:** Crude glycerol, Valorization, Parametric Optimization, Triacetin, Design Expert.

## 1. Introduction

Shifting towards renewable energy sources caused a highly noticed increase in the production of biodiesel globally. Biodiesel is the result of transesterification of animal fat and vegetable oil, and it is recognized for its environmental value. It aids in lowering greenhouse gas emissions and offers biodegradability. It was found that for the production of 10 kg biodiesel, crude glycerol of 1 kg is produced. Glycerol production creates economic and environmental challenges as it needs to either be disposed of correctly or ~~to be~~ valorized [1]. This research is focused on examining the process variables to upgrade and valorize crude glycerol to produce triacetin. Crude glycerol is mainly composed of 40-80% glycerol along with various contaminants depending on feedstock and process of production. The contaminants can include methanol (5-15%) which is a residual reactant of transesterification, and it should be removed as it is a hazard. Free fatty acids (5-10%) are also included which are formed by incomplete reactions and affect the purity of glycerol. Salts and catalysts (1-5%) also contaminate glycerol as they contain traces of sodium or potassium hydroxide. Those impurities highlight the need for purification of crude glycerol to expand its uses and achieve sustainability [2].

The only way to utilize this crude glycerol and eliminate its hazard is to valorize it. The value of the valorization will eventually end in a pure product with high value that can be used in many aspects. Different methods for valorization were investigated such as biological conversion in which microbial fermentation is used to result in bio-based chemicals such as 1,3-propanediol and hydrogen. Another method is thermochemical conversion where processes like pyrolysis and gasification are performed to

produce syngas and bio-oil [3]. Chemical and catalytic conversion can also be used to convert glycerol into valuable chemicals such as glycerol carbonate and triacetin. Catalytic conversion is considered the most promising procedure to follow as it has higher yield and efficiency to scale up into industrial sector [4].

The chemical and catalytic conversion processes include the usage of acid or base catalysts whose aim is to facilitate and speed up chemical transformations and reactions. Types of catalysts include homogenous and heterogenous catalysts. Homogenous catalysts involve acids like $H_2SO_4$ (Sulfuric acid) and bases such as sodium hydroxide where they speed up reaction rates [5]. The issue is that the process requires excessive purification. Heterogenous catalysts are solids like metal oxides and zeolites that have the privilege of recyclability and can be easily separated [6]. The most important catalytic conversion process for valorizing glycerol is the transesterification process in which glycerol reacts with esters to form acetins [7]. The method usually produces triacetin, which is a high-value chemical that has applications in pharmaceuticals, food and fuels [8].

When an acid catalyst is present the transesterification process leads to formation of acetins including mono, di or triacetin [9]. Triacetin which is glyceryl triacetate is usually used in pharmaceutical field as it is used as solvent in formulation of drugs. It can also be used as an additive in the food industry and as a combustion enhancer in fuel industries [10]. The transesterification process' efficiency depends on numerous factors such as molar ratios, time and temperature of reactions and the selection of catalyst. Those parameters should be optimized to achieve high selectivity and minimize side reactions [11].

## 2. Methodology

### *2.1 Process description*

The purification of crude glycerol prior to its conversion into triacetin is a crucial step to remove impurities that may hinder the catalytic process and reduce product yield [12]. Crude glycerol, a by-product of biodiesel production, typically contains impurities such as methanol, soap, salts, water, free fatty acids, and traces of unreacted oils. The purification process involves several sequential steps to obtain high-purity glycerol suitable for chemical conversion. Figure (1) shows the sequence of steps with their associated chemical reactions [13].

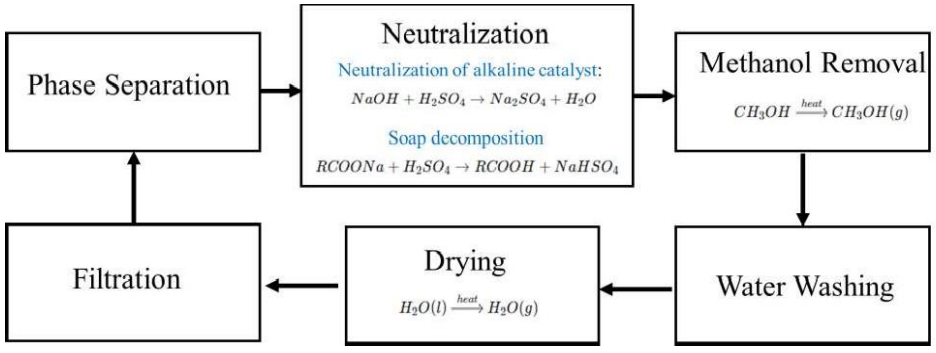


**Figure 1.** Crude glycerol purification steps associated with chemical reactions

The initial step, phase separation, involves allowing the crude glycerol to settle, promoting the separation of organic phase by density differences. Acidic and basic impurities are then neutralized using diluted acids and converts soap into free fatty acids. In the methanol removal step, any remaining methanol is removed by heating due to its low boiling point. Multiple stages of water washing are employed to remove residual salts, methanol and other impurities. The purified glycerol is subjected to

vacuum drying to remove residual water content. Final filtration step is carried out to remove suspended solids, yielding refined glycerol [14].

*2.2 Process variables*

The conversion of glycerol into triacetin involves catalytic transesterification or esterification of glycerol with acetic acid or acetic anhydride, or acetylation of glycerol in the presence of acidic catalyst. In the later case, the reaction proceeds through sequential esterification of glycerol's three hydroxyl groups, yielding monoacetin, diacetin and triacetin as can be shown in reaction (1):

$$C_3H_8O_3+3CH_3COOH \rightarrow C_9H_{14}O_6+3H_2O \quad (1)$$

The primary side products of the conversion process of crude glycerol into triacetin are mainly due to incomplete acetylation or water formation. During the stepwise acetylation process, monoacetin and diacetin can be formed as intermediate by-products as can be shown in reactions (2) and (3).

$$CH_2OH-CHOH-CH_2OH+CH_3COOH \rightarrow CH_2OCOCH_3-CHOH-CH_2OH+H_2O \quad (2)$$

$$CH_2OCOCH_3-CHOH-CH_2OH+CH_3COOH \rightarrow CH_2OCOCH_3-CHOCOCH_3-CH_2OH+H_2O \quad (3)$$

The production of triacetin is influenced by multiple factors such as reaction temperature, reaction time, molar ratio and catalyst concentration. According to Arrhenius equation, reaction rates increase by increasing temperature. The ranges varied from room temperature to around 90-100$^o$C. Studies showed that the highest yield was obtained at 100$^o$C but beyond it, decline occurs. Reactants molar ratios were also found to be effective. The higher acidic concentrations shift equilibrium towards triacetin formation as per Le Chatelier's principle, however the acid concentration was kept constant throughout the runs at 5.43 mmol, 0.1 equivalent. Upper boundaries ratios for glycerol to ethyl acetate were around 1:3 while lower ratios were 1:1. The time of the reaction varies starting from 2 hours to about 12 hours as studies showed [15].

*2.3 Design of experiment*

The selection of independent parameters for the catalytic transesterification of glycerol with ethyl acetate using $H_2SO_4$ as a catalyst was guided by a detailed investigation of previous work along with the physicochemical properties of the reactants. The experimental design integrated three key independent parameters: reaction time (denoted as A), reaction temperature (denoted as B), and molar ratio (denoted as C), as presented in Table (1). To optimize the transesterification process, the experimental runs were systematically planned to use "Response Surface Methodology (RSM)" along with a "Box–Behnken Design (BBD)". This structured approach allowed for a comprehensive evaluation of reaction parameters, facilitating the determination of optimal conditions for enhanced efficiency. The results derived from RSM and BBD were subjected to rigorous assessment and validation to ensure their reliability and practical applicability.

**Table 1.** Process variables and their coded levels

| Independent Variable | Code | Levels | | |
|---|---|---|---|---|
| | | **-1** | **0** | **1** |
| **Time** | A | 2 | 7 | 12 |
| **Temperature** | B | 25 | 57.5 | 90 |
| **Molar ratio** | C | 1 | 2 | 3 |

A total of eighteen randomized experimental runs were generated using "Design Expert Software V14" to systematically evaluate the process parameters. The study aimed to examine the effect of all three independent variables on triacetin selectivity. All variables were investigated at three distinct levels to

comprehensively explore the parameter's space Based on the predefined upper and lower margins of the independent variables, as outlined in Table (1), the matrix of the design along with the predicted selectivity values is presented in Table (2), where the selectivity ranged from 7% to 58% based on varying conditions.

The calculation for selectivity is shown in equation (1).

**Equation 1.** Selectivity equation

$$Selectivity\ (\%) = \frac{mol\ desired\ product}{mol\ starting\ compound - mol\ starting\ compound\ after\ reaction} * 10$$

**Table 2.** Experimental design matrix with predicted selectivity

| Run | A: Time (h) | B: Temp. (ºC) | C: Molar Ratio | Predicted selectivity |
|---|---|---|---|---|
| 1 | 12 | 57.5 | 3 | 10 |
| 2 | 7 | 57.5 | 2 | 16 |
| 3 | 2 | 90 | 2 | 58 |
| 4 | 7 | 25 | 1 | 15.6 |
| 5 | 7 | 90 | 3 | 17 |
| 6 | 12 | 25 | 2 | 17.5 |
| 7 | 7 | 57.5 | 2 | 16 |
| 8 | 7 | 57.5 | 2 | 15 |
| 9 | 2 | 25 | 2 | 55 |
| 10 | 7 | 25 | 3 | 15 |
| 11 | 7 | 57.5 | 2 | 16 |
| 12 | 12 | 90 | 2 | 58 |
| 13 | 7 | 90 | 1 | 7 |
| 14 | 2 | 57.5 | 3 | 54.5 |
| 15 | 2 | 57.5 | 1 | 54 |
| 16 | 7 | 57.5 | 2 | 15 |
| 17 | 12 | 57.5 | 1 | 10 |
| 18 | 7 | 57.5 | 2 | 16 |

*2.4 Model Adequacy and Regression Analysis*

Regression Analysis was used to develop statistical models with response surface methodology (RSM). This provided a quadratic polynomial equation which fits the experimental data. In equation (2), the regression model equation is shown.

**Equation 2.** Regression model equation

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x^2{}_i + \sum_{i=1}^{j-1} \sum_{j=2}^{n} b_{ij} x_i x_j + \varepsilon$$

In this model, ($\gamma$) represents the selectivity, while $b_o$ the constant model coefficient. The coefficients $b_i$, $b_{ii}$, $b_{ij}$ correspond to the linear, quadratic, and interaction terms, respectively. Also, $x_i$ and $x_j$ denote independent variables, and $\varepsilon$ accounts for random error [16].

## 3. Results and process optimization

### *3.1 Development of the model and statistical analysis*

Design Expert software generated four models for each response which are linear, two-factor interaction (2FI), quadratic, and cubic polynomial models. The most appropriate model for each response was selected based on statistical evaluations, including lack-of-fit analysis, adjusted coefficient of determination, predicted coefficient of determination, and aliased coefficients. Based on these criteria, the software identified the quadratic model as the best fit for predicting triacetin selectivity. Equation (3) below illustrates the quadratic model developed to describe the relationship between triacetin selectivity and process variables at specific levels.

**Equation 3.** Triacetin selectivity regression model equation

$$\gamma = 15.67 - 15.75A + 4.61B + 1.24C + 9.37AB - 0.125AC + 2.65BC + 24.97A^2 + 6.49B^2 - 8.51C^2$$

Where ($\gamma$) is selectivity, (A) is reaction time in hours, (B) is reaction temperature in degree Celsius and (C) is molar ratio of glycerol to ethyl acetate. The coefficients indicate that reaction time has the highest impact on selectivity with negative linear effects and strong quadratic effects. $R^2$ was found to be 0.8981. This regression equation highlights the impact of reaction variables on triacetin selectivity. A positive coefficient suggests a direct proportional relationship, while a negative coefficient signifies an inverse effect. The linear terms represent the individual influence of each variable, the interaction terms indicate the combined effect of two variables, and the quadratic terms describe the nonlinear influence of increasing a variable on the response.

According to Equation (2), reaction time negatively affects triacetin selectivity, as denoted by the negative coefficients. This implies that prolonging reaction time leads to a decrease in selectivity. On the other hand, the positive coefficients for the Glycerol: Ethyl acetate molar ratio and catalyst concentration suggest that increasing these variables enhances glycerol yield.

### *3.2 Effect of Process Variables on Selectivity*

The variables have different effects on yielded triacetin. The molar ratio significantly affects triacetin selectivity. Its increase enhanced selectivity initially to a certain point but beyond it, yield is negatively affected due to side reactions. Reaction temperature has a non-significant effect. However, higher temperatures reduce viscosity and improve mass transfer which slightly increases selectivity. At extreme temperatures, ethyl acetate evaporates causing a reduction in the yielded triacetin. Reaction time affects the yield highly. Selectivity increases as time increases to an optimal level; beyond this level no improvements occur due to limitations in equilibrium. Figure (2) illustrates the interaction between reaction time and Glycerol:EA ratio. While a higher ratio generally improves yield due to enhanced mass transfer and faster oil conversion, its effect is time dependent.

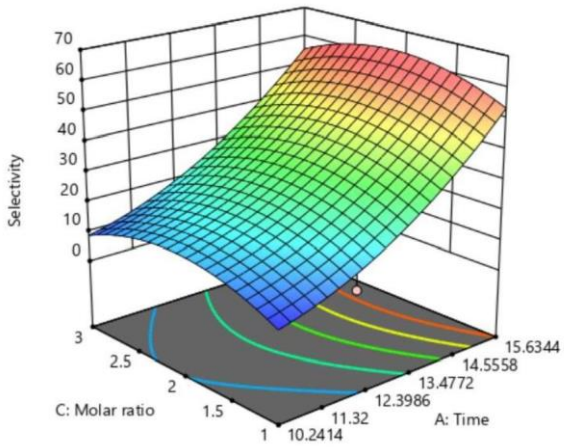


**Figure 2.** Surface plot for effect of time and molar ratio on triacetin selectivity

A comparable interaction effect was observed between the molar ratio and temperature presented in figure (3). The surface plot illustrating the interaction between the molar ratio and reaction temperature at a constant reaction time of 7 hours shows a negative effect on triacetin selectivity. Specifically, triacetin selectivity increases as reaction temperature decreases. When reaction time remains constant but both temperature and molar ratio increase, triacetin selectivity decreases. Conversely, at higher reaction times with a lower molar ratio, selectivity improves. Under the same conditions, an increase in reaction temperature leads to a decline in triacetin selectivity, while a decrease in temperature enhances selectivity. However, when reaction time decreases, regardless of whether molar ratio and temperature increase or decrease, triacetin selectivity remains nearly constant with only minor variations.

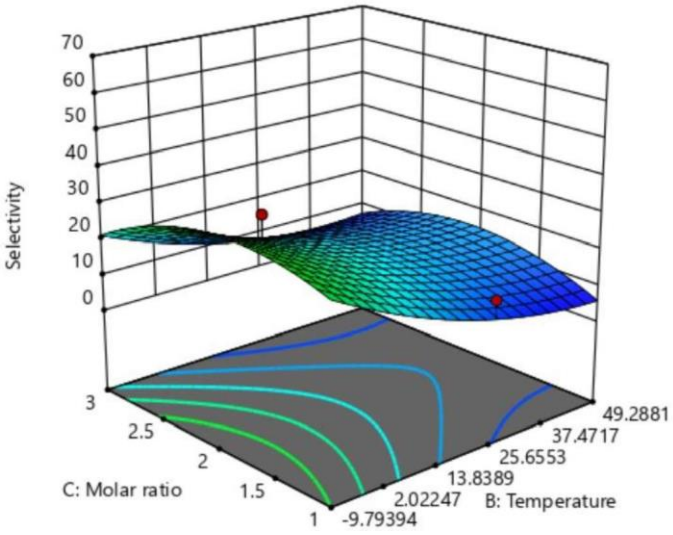


**Figure 3.** Surface plot for effect of temperature and molar ratio on triacetin selectivity

The surface plot shown in figure (4) depicting the interaction between reaction temperature and reaction time at a constant molar ratio of 1:2 demonstrates a negative effect on triacetin selectivity. When both the molar ratio and reaction time increase, triacetin selectivity decreases. Conversely, in the same conditions, an increase in molar ratio with a decrease in reaction time enhances triacetin selectivity. However, when the molar ratio increases while reaction temperature fluctuates, triacetin selectivity remains relatively constant. Furthermore, a decrease in both molar ratio and temperature results in lower triacetin selectivity, whereas a decrease in molar ratio combined with an increase in reaction temperature improves selectivity. Additionally, prolonged reaction time enhances triacetin selectivity, whereas shorter reaction times lead to a decline in selectivity.

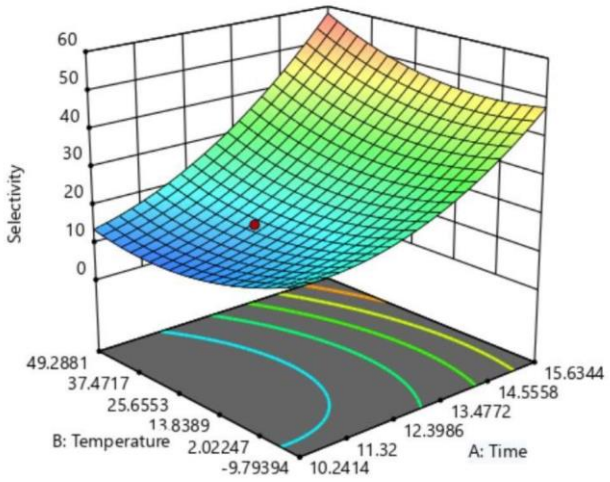


**Figure 4.** Surface plot for effect of temperature and time on triacetin selectivity

## 4. Environmental Impact

### *4.1 Waste Reduction and Resource Utilization*

There is no doubt that the valorization process is essential to ensure industrial development. On the other hand, the process has an environmental impact presented in the large percentage of impurities found in it. If crude glycerol is released to water, the organic matter will increase, leading to oxygen depletion which disrupts the Eco life under water bodies. Land disposal can also alter pH levels and disrupt soil quality. The valorization process presents a sustainable approach to reducing the environmental impacts of crude glycerol while promoting circular economy and offering pollution control [17]. The efficient utilization of crude glycerol to triacetin is an essential process that reduces waste disposal and minimizes waste. Turning the low value waste into a valuable chemical that can be used in the food industry, pharmaceuticals and cosmetics.

### *4.2 Carbon Footprint Mitigation and Contribution to a Circular Economy*

The process of transforming crude glycerol to triacetin has a large effect in reducing greenhouse gas emissions associated with waste glycerol disposal. Conventional waste disposal methods such as incineration release harmful pollutants. On the other hand, utilization of crude glycerol as a feedstock for production of triacetin not only mitigates the emissions but also reduces the reliance on fossil-based raw materials thus decreasing the overall carbon footprint of industrial processes. The integration of crude

glycerol valorization into industrial applications aligns with the principles of a circular economy by promoting resource efficiency and waste minimization [18]. The production of triacetin from a biodiesel byproduct exemplifies industrial symbiosis, where waste from one process serves as a valuable input for another. This approach fosters sustainable manufacturing practices and enhances the economic viability of biodiesel production by creating additional revenue streams.

## Conclusion

The overwhelming surplus of crude glycerol from petrochemical processes, often discarded as waste, brought challenges regarding its discharging. This study successfully discussed the catalytic conversion of crude glycerol into triacetin, providing an efficient approach to valorization of glycerol. By employing "Response Surface Methodology (RSM)" and a "Box–Behnken Design (BBD)", the effects of key process parameters which are reaction time, temperature, and molar ratio were systematically analyzed and optimized. The results showed that the highest triacetin selectivity (60%) was achieved at a glycerol-to-ethyl acetate molar ratio of 1:2.59, a reaction time of 2.05 hours, and a reaction temperature of 27°C. Regression analysis confirmed the quadratic model as the best fit for predicting selectivity, with a high coefficient of determination ($R^2 = 0.9548$), which indicates strong agreement between the experimental and predicted values. ANOVA analysis results identified reaction time and molar ratio as statistically significant factors, while reaction temperature had a minimal effect. The interaction between reaction time and molar ratio showed the most significant impact on triacetin yield. Overall, this study presents a scalable and economically viable method for crude glycerol valorization. By enhancing product selectivity, the proposed process contributes to the sustainability of the biodiesel industry while promoting the production of high value biochemicals.

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