RiCE: Research in Chemical Engineering

Volume 3 No. 1, 2024

Journal homepage: https://ejournal.ump.ac.id/index.php/rice

Impact of Adsorbent Weight, Time, and Temperature on Purification Efficiency with Activated Carbon

Rusly Ma'arief[1], Abdul Haris Mulyadi[2*], Yeti Rusmiati Hasanah[3]

[1,2,3]Department of Chemical Engineering, Faculty of Engineering and Science,
Universitas Muhammadiyah Purwokerto.
Purwokerto, Indonesia, 53182

Corresponding author: harismulyadi@yahoo.com

Article Info

Submitted:
11 October 2024

Revised:
9 November 2024

Accepted:
10 November 2024

ABSTRACT

Based on data from the *Indonesian Biofuel Producers Association* 2022, biodiesel production will reach 10.8 billion liters, producing crude glycerol of 10-20% of the total product volume in the transesterification process. Crude Glycerol is a by-product of making biodiesel with low purity because it still contains impurities such as methanol, free fatty acids, KOH catalysts, and water. These impurity compounds must be removed so that the quality of glycerol increases and has a high selling value. Adsorption is one method that can be used to absorb these impurity compounds. This research aims to determine the effect of adsorbent weight, adsorption time, and temperature on glycerol purity levels. This experimental research uses an exploratory factorial design method to determine the most influential factors. The low level of adsorbent weight used is 9%, while the high level of adsorbent weight is 15%. The low-level adsorption time is 60 minutes and the high level is 90 minutes. The adsorption temperature used is a low level of 40℃ and a high level of 80℃. The research results showed that the weight of the adsorbent was the factor that had the most influence on the purity level of glycerol

Keywords: crude glycerol; adsorption, factorial design; activated carbon;

1. INTRODUCTION

The rapid growth of technology is inextricably linked to societal progress. The evolution of technology is growing more complex, notably in the automotive industry. Rapid technical development, along with economic expansion, has had a negative influence on people's purchasing power around the world, particularly in Indonesia. According to statistical data from 2020, the number of motor vehicles in Indonesia reached 136,137,735 units, and it is expected to reach 148,212,865 units by 2022. It may be stated that the number of motor vehicle owners in Indonesia has risen dramatically in recent years [1].

However, the increased number of motor vehicles is expected to negatively influence fuel demand. As more individuals buy automobiles, the demand for fuel (oil fuel) rises. This causes an imbalance between the number of motor vehicles and the amount of gasoline consumed, resulting in fuel depletion and price variations. According to data from the Central Statistics Agency, Indonesia's oil reserves are expected to reach 4.17 trillion barrels in 2020 [2], and the Ministry of Energy and Mineral Resources forecasts that these stocks will endure for 9.5 years if no new oil deposits are discovered [3]. This should cause worry as we investigate and create alternative renewable fuels such as biodiesel.

Fatty acid methyl ester (FAME) is a type of alternative fuel derived from diverse natural materials. Biodiesel can help to minimize sulfur, non-reactive hydrocarbon, and carbon monoxide emissions. The depletion of global fuel stocks (fuel and gasoline), air pollution, and changes in fossil fuel costs will drive up demand for biodiesel. Transesterification is the method of producing biodiesel by reacting alcohol and triglycerides to form monoesters. Transesterification converts triglyceride chains into monoesters and glycerol [4].

Crude glycerol is a waste or byproduct of the transesterification of oils and fats used to make biodiesel. Ten to twenty percent of the entire product volume comes from this product [5]. According to a report released by the *Indonesian Biofuel Producers Association*, 10.8 billion liters of biodiesel were produced in Indonesia between January and November 2022. This production

volume is the highest recorded since it started keeping data. Approximately 1 billion liters of crude glycerol will be produced annually from this quantity of biodiesel [6]. Because of its high impurity percentage, the crude glycerin generated has not yet been used in the biodiesel production industry. Glycerin, water, inorganic salts, catalysts, and non-glycerin organic matter, which includes alcohol (mostly methanol or ethanol), free fatty acids, residual fatty acid methyl esters, and glycerides, are the main contaminants of crude glycerin. Crude glycerin can be used as a raw ingredient for the food, chemical, pharmaceutical, and cosmetic industries as well as an additive in gasoline once it has been distilled [7].

Therefore, crude glycerin must be refined. This will not only reduce waste generated during the biodiesel production process, but it will also increase revenue for the biodiesel industry. Because, in addition to the main product, biodiesel, there are still economically significant byproducts. Crude glycerol can be purified via distillation, ion exchange, and various physicochemical processes such as filtration, saponification, acidification, neutralization, extraction, and adsorption [8]. Based on this, this paper is developed to investigate the influence of adsorbent weight, adsorption time, and adsorption temperature on glycerol purity.

Glycerol is one of the simplest glyceride molecules, with a hydrophilic and hygroscopic hydroxyl group. Glycerin, a clear and hygroscopic liquid, boils at 290°C. This chemical, with a molecular weight of 92.09 g/mol, has a high boiling point due to the extremely strong hydrogen bonds between glycerin molecules [9] [10].

2. MATERIALS AND METHODS

2.1 Materials

The materials used in this glycerol purification research are raw glycerol, KOH, methanol, Aquades, H_3PO_4, H_2SO_4, NaOH, sodium acetate, and activated carbon

2.2 Production of Crude Glycerol [11]

The first step is to heat 1 liter of used cooking oil to 60°C, then add a solution of 10 g KOH in 250 ml of methanol to the cooking oil and homogenize with a stirrer at 700 rpm for 60 minutes. After homogenization, let it sit for around 8 hours to create two layers: biodiesel and crude glycerol. The resulting glycerin solution serves as the starting material for the glycerin purification process.

2.3 Process of Raw Glycerol Acidification [12]

Mix phosphoric acid (H_3PO_4) and glycerol in a molar ratio of 1:0.6 into an Erlenmeyer flask. After that, the mixture is homogenized with a magnetic stirrer for one hour at a speed of 250 rpm while being heated on a hot plate until it reaches a temperature of 70°C, covered. Then, the mixture is poured into a separating funnel and left for a while until three layers are formed, with the salt settling at the bottom, glycerol in the middle, and the free fatty layer on top. Next, the precipitated salts are filtered out and neutralized with 5 M NaOH. Then, the glycerol is evaporated to remove its water content. After that, the purity level of the glycerol is analyzed.

2.4 Adsorption Process with Activated Carbon [13]

Activated carbon with a size of 250 µm and glycerol were mixed with weight/volume ratios (w/v) of 9% and 15% into a beaker. The mixture was then stirred at 250 rpm at temperatures ranging from 40℃ to 80℃. After that, an adsorption process was carried out with each treatment for 60 minutes and 90 minutes. Then, filtration was performed. After that, the purity level of glycerol was analyzed.

2.5 Glycerol Content Analysis

Analysis of glycerol content using the SNI method, 0.5 grams of glycerol is dissolved in 50 ml of water, then 5 drops of bromothymol blue indicator are added. The solution is then acidified with 0.2 N H2SO4 until a yellow-green color is formed. The solution is carefully neutralized with 0.05 N NaOH until a blue color is formed. Then, 50 ml of Sodium Acetate is added and stirred gently. The solution is then covered and left at room temperature for 30 minutes in a dark room. Then, 10 ml of ethylene glycol is added to the solution, covered, and placed in a dark room at room temperature for 20 minutes. Then, add 3 drops of bromothymol blue indicator to the solution. The resulting solution is slowly titrated with 0.5 N NaOH until a blue color forms. The same process applies to the blank treatment. The glycerol purity content is calculated using the following equation (Naibaho, 2019):

[the glycerol purity level (%) = $(T_1 - T_2) \times N \times 9{,}209 / W$]

T_1 = mL NaOH for sample titration
T_2 = mL NaOH for blank titration
N = normality of NaOH for titration
9.209 = glycerol factor

2.5 Water Content Analysis [ISO 2097-1972]

Water content analysis using the heating of 1 gram of glycerol in a pre-dried and weighed dish. Next, the sample along with the dish is placed in an oven at a temperature of 105℃ for 120 minutes.

The water content calculation uses the following equation:

$$\text{Moisture content} = \frac{T_2 - T_1}{T_1} \times 100\%$$

T_1 = Weight of the cup + sample before heating (g)
T_2 = Weight of the cup + sample after heating (g)

2.6 Analysis of Ash Content [Method ISO 2098-1972]

To analyze the ash content, one gram of glycerol is burned for three hours at a temperature of 750 degrees Celsius in a porcelain cup with a specific weight. After cooling, weigh. The ash content is calculated using the following formula:

[Ash content (%) = $W1/W_2\ x$ 100%]

W1 = Mass of Ash (g)
W2 = Mass of Sample (g)

2.7 Analysis of *Matter Organic Non Glycerol* (MONG) Levels [12] [13]

The following formula is used to determine the difference in glycerol content, water content, and ash content to analyze the MONG content:

[MONG = (100 – (% glycerol results + % air + % ash)]

2.8 Density Analysis [14]

The pycnometer is cleaned with HCl, then rinsed three times with distilled water, once with alcohol, and then dried in an oven for 5 minutes. After that, it is placed in a desiccator for 10 minutes, and the pycnometer is weighed until a constant mass (W_1) is obtained. The pycnometer is filled with a crude glycerol solution, the outer part is wiped dry, and it is weighed until a constant mass (W_2) is obtained. The calculation of the density of crude glycerol is done using the equation:

$$(\text{density}) = (W_1 - W_2)/V$$

W_1 = mass of the empty pycnometer (g)
W_2 = mass of the pycnometer + crude glycerol (mL)

2.9 Data Analysis

In this research, the statistical data analysis used was Factorial Design analysis. Statistical analysis was carried out using the Minitab 16 application [15].

3. RESULTS AND DISCUSSION

3.1 Glycerol Content

The results obtained from the purification of Crude Glycerol are shown in **Table 1.** It can be concluded that glycerol obtained with an adsorbent weight of 15% has a higher purity level compared to glycerol obtained with an adsorbent weight of 9%; Furthermore, the longer the adsorption time, the higher the purity level of the obtained glycerol; and the higher the temperature, the higher the purity level of the glycerol.

Table 1. Observation Results

No	Absorbent mass (w/v)	Time (minute)	Temperature (℃)	The glycerol purity level (%)
1	9	60	40	39.67
2	15	60	40	41.73
3	9	90	40	50.83
4	15	90	40	52.68
5	9	60	80	40.22
6	15	60	80	74.59
7	9	90	80	40.42
8	15	90	80	62.25
9	9	60	40	38.84
10	15	60	40	41.08
11	9	90	40	49.93
12	15	90	40	52.66
13	9	60	80	39.60
14	15	60	80	75.69
15	9	90	80	41.42
16	15	90	80	63.35

3.2 Factorial Design Analysis

The results of the foregoing analysis show that the equation produced from the independent variable has a considerable influence. The p-value of 0.00 indicates significance, as it is less than 0.05. Furthermore, the results show that the most influential variable is adsorbent weight, which has a higher effect value than the time and temperature factors. The adsorbent weight has a substantial effect (value = 15.387). The coefficient of determination (R-squared) of 99.88% exceeds the expected R-squared of 99.51%.

It is shown by the results of the previous analysis that the equation derived from the independent variable has significant effects. This is clear from the obtained p-value of 0.00, which indicates significance (p-value < 0.05). Furthermore, The results indicate that the adsorbent weight has the greatest influence, with a higher effect value than the temperature and time factors. With a value of 15.387, the adsorbent weight significantly influences the result. Compared to the expected R-squared of 99.51%, the coefficient of determination (R-squared) of 99.88% is greater. This shows that the model captures 99.88% of the overall variation in the findings that were collected.

The first-order linear equation obtained to predict the purity level of glycerol is:

$Y = 50.310 + 7.694\ X_1 + 1.383\ X_2 + 4.383\ X_3 - 1.651\ X_1*X_2 + 6.584\ X_1*X_3 - 4.215\ X_2*X_3 - 1.686\ X_1*X_2*X_3$

Where:

Y = Glycerol purity level (%)
X_1 = Adsorbent Weight
X_2 = Adsorption Time
X_3 = Adsorption Temperature

The percentage of glycerol purity produced at a 15% adsorbent concentration exceeds the percentage of glycerol content produced at a 9% adsorbent concentration **(Figure 1)**. The weight of the adsorbent and the percentage of glycerol purity produced are linearly related, meaning that the heavier the adsorbent, the higher the percentage of glycerol purity produced. This could be because the adsorbent's surface area and the number of active sites that can interact with the adsorbate grow with concentration or mass, improving the ability to absorb contaminants from glycerol [16].

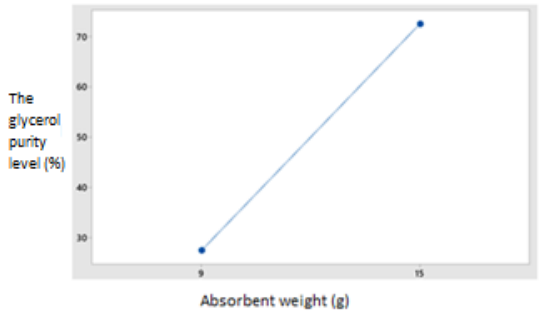

Figure 1. The Effect of Adsorbent Weight on the percentage of glycerol purity

It is clearly shown in **Figure 2** that the higher the percentage of purity achieved, the longer the adsorption period. This is due to the extended adsorption period, which allows more time for the adsorbent and impurities to interact. As a result, the increased amount of adsorbed impurities leads to a higher concentration of glycerol produced. However, the increase in glycerol purity eventually decreases because an excessively long adsorption time can cause activated carbon to absorb most of the glycerol [11].

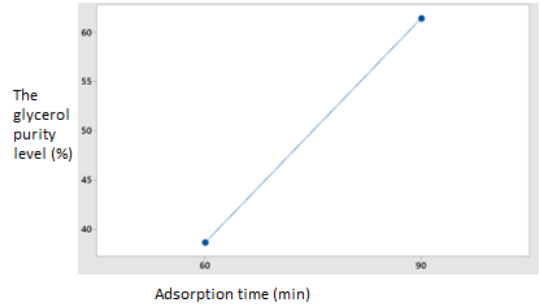

Figure 2. The Effect of Adsorption Time on % the percentage of glycerol purity

The percentage of purity gained grows with increasing adsorption temperature (**Figure 3**). The influence of adsorption temperature demonstrates that the adsorption capacity of activated carbon increases as the temperature rises. The reason could be that when the temperature rises, the particles in the system travel faster and with higher kinetic energy, resulting in more collisions between those particles and the adsorbent (the absorber) and the adsorbate (the material being absorbed) [11].

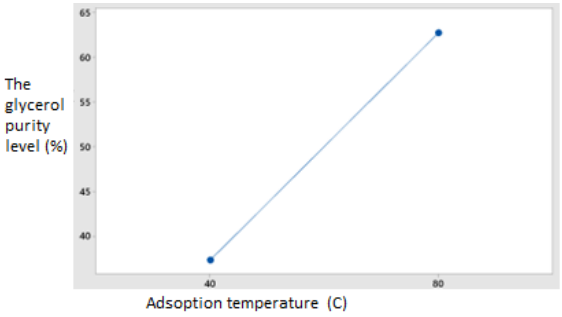

Figure 3. The Effect of Adsorption Temperature on the percentage of glycerol purity

3.3 Factors and Conditions of the Most Influential Variables

After determining the influence of each variable, the following step is to select the ideal parameters and conditions for the variable that has the greatest impact on glycerol purity throughout the adsorption process. According to the research, the most important component is the mass of the adsorbent. The design table for varying adsorbent weights is provided below.

Table 2. Results of Observations on Influential Variable Factors

Adsorption mass (%w/v)	Time (mins)	Temperature (°C)	Glycerol purity level (%)
10	60	80	70.35
10	60	80	72.1
15	60	80	74.59
15	60	80	75.6
20	60	80	83.15
20	60	80	82.69
25	60	80	80.76
25	60	80	81.31
30	60	80	79.19
30	60	80	78.37

The optimization process analysis data resulted in the equation y=0.425 X +69.391; R-square 0.5025. The result shown that the optimum point is 20% adsorbent weight, which results in a glycerol content of 82.92%. This means that as additional adsorbent is applied, more contaminants are trapped within it, resulting in a larger glycerol concentration. Glycerol content decreases when

concentrations rise above 20%. This is because the number of active sites is greater than the amount of adsorbate, causing the adsorbent to absorb the majority of the glycerol [11].

3.4 The characteristics of glycerol

The quality of the acidified crude glycerol was assessed, including glycerol content, water content, ash content, MONG content, and density. Table 3 shows the analysis results for crude glycerol after acidification

Table 3. The characteristics of sample

No	Characters	*The initial sample (Crude)*	After adsorption	SNI 06-1564-1995
1.	Glycerol content (%)	34.90 %	82,92 %	> 80 %
2.	Ash content (%)	20.50 %	3 %	< 10 %
3.	Water content (%)	1.,28 %	4,5 %	< 10 %
4.	*Matter Organic Non Glycerol* (MONG) (%)	28.32 %	9,58 %	< 2,5 %
5.	Density	1.162 gr/ml	1,253 gr/ml	1,267 gr/ml

Crude glycerol still contains a significant amount of water (16.28%) due to the glycerol dehydration reaction that occurs during the acidification process. The ash percentage (20.50%) indicates the presence of inorganic elements, such as potassium salts from the transesterification catalyst. In addition to water and ash levels, crude glycerol contains contaminants known as MONG (Non-Glycerol Organic Matter). Based on the computation (100%-(%glycerol+%water+%ash), the MONG content is 28.32%. These findings show the amount of pollutants obtained throughout the biodiesel production process, including soap, methanol, and methyl ester [17].

The results of the Crude Glycerol quality analysis in Table 3 show that Crude Glycerol after the adsorption process under optimum conditions meets the SNI 06-1564-1995 standard. This indicates that the quality of crude glycerol can be improved through the adsorption process using activated carbon adsorbent. A glycerol content of 82.92% was obtained. This indicates that most of the impurities in crude glycerol, including water, ash, and other organic molecules, can be absorbed by activated carbon. The glycerol content obtained from adsorption using coconut shell activated carbon is still lower compared to the glycerol content in the study by Aziz [11], which used rice husk adsorbent, amounting to 97.29%.

4. CONCLUSION

The most influential variable among the three (adsorbent mass, adsorption duration, and adsorption temperature) is adsorbent mass, with an impact value of 15.387. The ideal concentration for the adsorbent weight is 20%, resulting in a content of 82.92%. This means that the more adsorbent used, the more contaminants are bound within it, resulting in a larger glycerol concentration.

The analysis of the quality of glycerol obtained through adsorption under optimal conditions did not fully comply with SNI 06-1564-1995 standard, with glycerol content of 82.92%, water content of 4.5%, ash content of 3%, density of 1.253, and MONG (Matter Organic Non Glycerol) content of 9.58%. According to Indonesian national norms, SNI has set a maximum MONG content of 2.5%.

ACKNOWLEDGMENT

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CONFLICT OF INTEREST

No potential conflict of interest was reported by the author(s).

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Rusly Ma'arief: conceptualization, investigation, writing—original draft preparation.
Abdul Haris Mulyadi: conceptualization, methodology, writing—review and editing, supervision.
Yeti Rusmiati Hasanah: data analysis, writing—review, and editing.
All authors have read and agreed to the published version of the manuscript.

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