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Purification of Residual Glycerol from Biodiesel Production as a Value-Added Raw Material for Glycerolysis of Free Fatty Acids in Waste Cooking Oil

K. A. Viraj Miyuranga [1], Udara S. P. R. Arachchige [1], Randika A. Jayasinghe [1] and Gamunu Samarakoon [2,*]

[1] Department of Civil and Environmental Technology, University of Sri Jayewardenepura, Pitipana 10206, Sri Lanka
[2] Department of Process, Energy and Environmental Technology, University of South-Eastern Norway, 3918 Porsgrunn, Norway
* Correspondence: gamunu.arachchige@usn.no

Abstract: The crude glycerol produced as a byproduct of transesterification synthesis has very few applications because it comprises of significant amounts of methanol, catalyst, and soap. On the other hand, transesterifications of highly acidic oil in the presence of an alkaline catalyst are problematic due to the presence of high amounts of free fatty acids. In this study, the free fatty acid level of high acid oil, which was initially determined to be 19.25%, was decreased to permit the direct production of biodiesel via glycerolysis with pure glycerol, making direct transesterification feasible. Through a process of purification, crude glycerol was refined to 92.5% purity. It was revealed that the physiochemical parameters of density, moisture content, ash content, matter organic non-glycerol content, pH, and Na/K concentrations of generated purified glycerol are equal to those of commercially available glycerol. In contrast, glycerolysis treatment successfully decreased the free fatty acid level to less than 2% under optimal conditions, which were determined to be 200 °C, a glycerol-to-oil molar ratio of 4:1, and a KOH catalyst concentration of 1.6 wt.% at 350 rpm. The inclusion of hexane as a co-solvent accelerated the glycerolysis process, and the weight ratio of oil-to-hexane was 8:1. Moreover, it was viable to use waste methanol for biodiesel synthesis and purified crude glycerol as a raw material in a variety of industries, including biodiesel production. In addition, compared to acid esterification, the FFA concentration of oil with a high acid value fell significantly.

Keywords: biodiesel; biofuel; free fatty acid; glycerol; glycerolysis; purification; renewable energy; sustainability; value-added; waste cooking oil

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Citation: Miyuranga, K.A.V.; Arachchige, U.S.P.R.; Jayasinghe, R.A.; Samarakoon, G. Purification of Residual Glycerol from Biodiesel Production as a Value-Added Raw Material for Glycerolysis of Free Fatty Acids in Waste Cooking Oil. *Energies* **2022**, *15*, 8856. https://doi.org/10.3390/en15238856

Academic Editor: Nadir Yilmaz

Received: 21 October 2022
Accepted: 21 November 2022
Published: 23 November 2022

1. Introduction

Biofuels are non-toxic and have low emissions of hydrocarbons, which can be used to offset the energy crisis and the dependency on fossil fuel [1]. Biofuels are gaining tremendous attention due to the economic instability of the fossil fuel market and, as a result, of international agreements to reduce greenhouse gas emissions by limiting the use of non-renewable energy sources [2,3]. For decades, biodiesel has been produced using various raw materials, including edible and non-edible oils, animal fat, and algal oil [4,5]. Due to of its simplicity and ease of operation, the transesterification reaction has been widely used to produce biodiesel. The most frequently used catalyst for optimal performance is a homogeneous catalyst such as potassium hydroxide or sodium hydroxide [6]. On the other hand, multiple homogeneous and heterogeneous catalysts are available and have been used by numerous researchers worldwide [7].

Typically, biodiesel is produced using short-chain alcohol, such as methanol, to convert the triglycerides to methyl ester. Three moles of methanol and one mole of triglycerides react at a temperature of approximately 60 °C to produce three moles of biodiesel and one mole of glycerol, as illustrated in Figure 1.

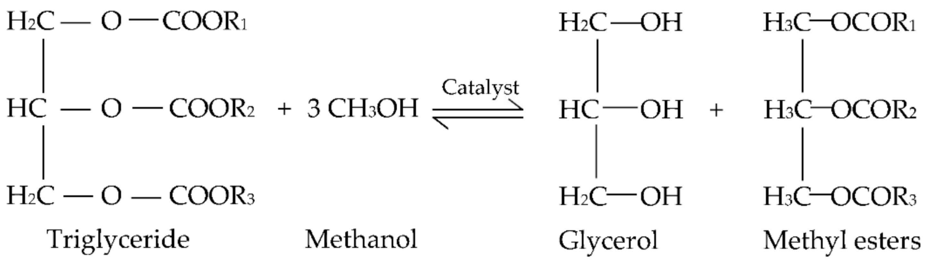

Figure 1. A schematic representation of the transesterification reaction.

Once the reaction is completed, two distinct layers are visible and separated the methyl ester by decanting or centrifugation [8]. At the separation step, the production of biodiesel from oils with a free fatty acid (FFA) content of less than 2% is not difficult, as there will be two layers. The bottom layer is glycerol, and the top layer is fatty acid methyl ester (FAME) [9]. Therefore, the oil quality, such as the FFA percentage or acid value (AV), is essential for biodiesel production to achieve a higher yield [10].

As saponification reaction dominates the biodiesel production process [11], the yield of biodiesel is drastically reduced if it is produced from oils with a higher FFA content. It should be noted that the feedstock for biodiesel production accounts for a substantial portion of the final cost of biodiesel [12]. Therefore, these raw material costs can be significantly reduced if inexpensive waste cooking oil (WCO) or non-edible oils, such as jatropha and rubber seed oil, are used for the esterification. The problem is that the transesterification reaction can only be performed successfully if the acid value of the oil is less than 4%, which translates to an FFA percentage of less than 2%. For biodiesel production, it is difficult for oils with a high FFA content to follow the alkaline esterification reaction, which leads to saponification, as illustrated in Figure 2. In order to reduce the cost of biodiesel, the reduction of FFA is important. The present study uses a byproduct of the biodiesel production process, such as glycerol, to reduce higher FFA levels. Glycerolysis is the name given to the reaction that occurs when glycerol is present, as shown in Figure 3 [13].

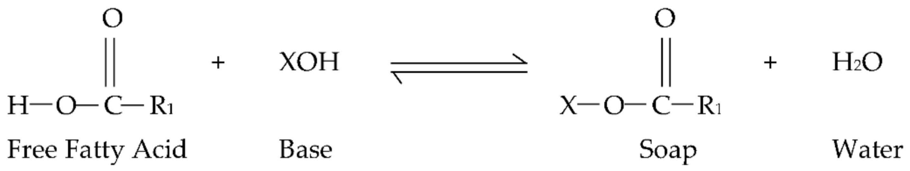

Figure 2. A schematic representation of the saponification reaction.

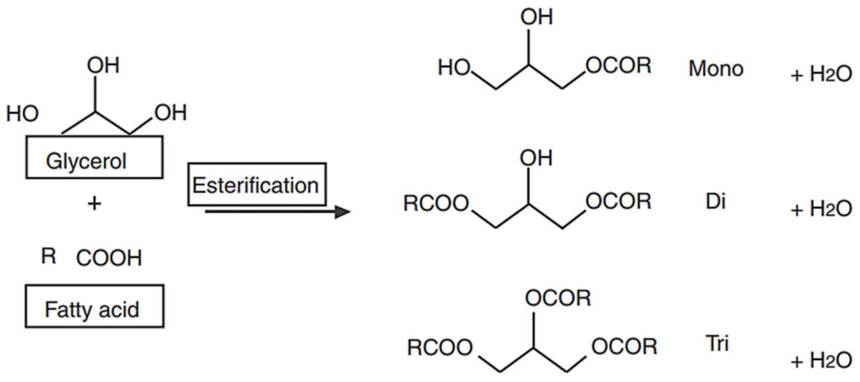

Figure 3. A schematic representation of the glycerolysis reaction.

While glycerol is the primary byproduct of transesterification, it degrades biodiesel quality [14]. According to the American Society for Testing and Materials (ASTM) Standard for biodiesel [15], glycerol must constitute less than 0.0002 mass fraction of the purified biodiesel (ASTM, 2002). Additionally, the residual glycerol produced by transesterification is of poor quality and purity due to impurities such as free fatty acids, excess alcohol, water, organic compound, catalyst, and soap residue [16]. The alkyl esters (ethyl or methyl) and triglycerides are concentrated in the alkyl ester-rich phase, whereas the glycerol and monoglycerides are concentrated in the glycerol-rich phase. Diglycerides are distributed evenly between the two phases. Vegetable colorants give this glycerol phase a brown color [17]. As a result, its commercial market as a raw material is limited. Due to its low purity for industrial applications, glycerol residue from the biodiesel process is frequently disposed of in landfills or waste. Numerous techniques have been used to purify glycerol, which has a market value in multiple ways [1,18,19]. Numerous technologies are widely used to purify glycerol, including methanol and activated carbon treatment, weak acid treatment followed by alkaline solution pH adjustment and filtration, vacuum evaporation to remove moisture, and unreacted excess methanol, ion exchange resins, membrane separation, and filtration [20–22].

However, acidification does not completely eliminate impurities and additional purification is required to remove excess methanol, free fatty acids, and water. Typically, distillation or vacuum distillation is required to remove the methanol and water, which consumes a large amount of energy [23,24]. However, industrial-grade glycerol must be highly pure to be used as a raw material in various industries. Numerous industries use glycerol as raw material, including the paint, food, soap, and pharmaceutical industries [25].

Previous experiments have been conducted to determine the effect of glycerolysis on FFA reduction [12,26–28]. However, compared to the acid esterification process, the glycerolysis approach has a number of upsides. Glycerolysis is more profitable than acid esterification treatment since it does not need an excessive amount of methanol throughout the process, unlike acid treatment. Moreover, an excessive amount of catalyst is required for the acid treatment, while an inadequate amount is employed for the glycerolysis treatment [29]. Its implementation is safer since it does not need the removal of alcohol or the use of corrosive acids as a catalyst [30]. Glycerolysis is a quick reaction that occurs in less than one hour, while acid treatment is a slow reaction that may take more than three hours [31].

However, the process of glycerolysis utilizing alkaline catalysis and the kinetics of the reaction are not yet fully understood and are thus the subject of ongoing research. According to Ochoa-Gómez et al. [31], the glycerolysis reaction needed the synthesis of the glyceroxide anion in the first stage in order to proceed. If there were no mass transfer constraints to the catalytic sites and the glycerol and basic catalytic sites would come into close proximity and create a glyceroxide anion. They also established that the strength of the catalytic base must be sufficient to extract a proton from the hydroxyl group of glycerol, hence KOH was utilized. The following are the stages hypothesized for the glycerolysis mechanism [30].

- The glycerol interacts with three moles of the base catalyst to generate free radical anion and three moles of the protonated catalyst, as shown in Figure 4.
- Three molecules of protonated catalyst attack three molecules of substrate FFAs to generate free radicals, as seen in Figure 5.
- The glyceroxide anion reacts with the FFAs cations to generate an intermediate molecule, as seen in Figure 6.
- As demonstrated in the equation, the intermediate chemical decomposes into water and triglycerides, as shown in Figure 7.

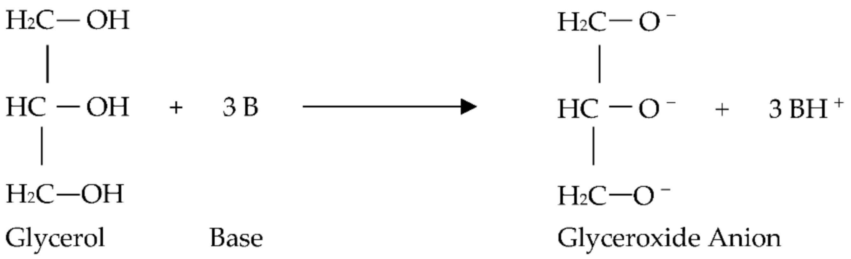

Figure 4. A schematic representation of the glycerolysis reaction first step.

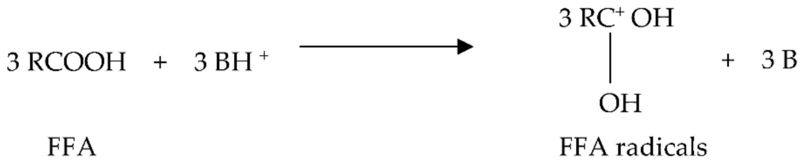

Figure 5. A schematic representation of the glycerolysis reaction second step.

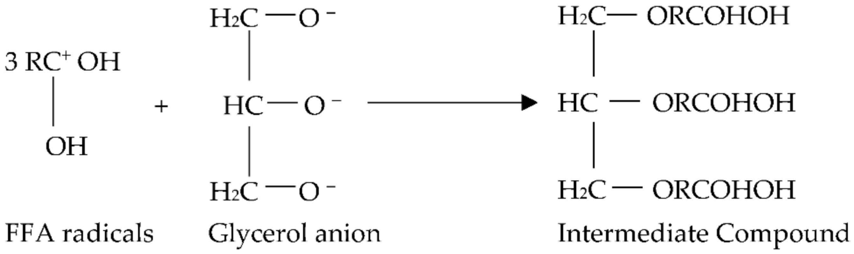

Figure 6. A schematic representation of the glycerolysis reaction third step.

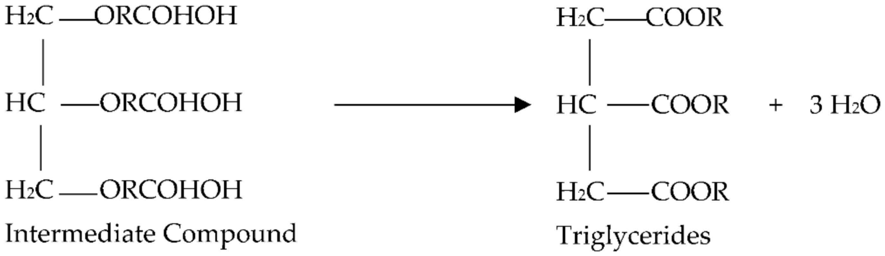

Figure 7. A schematic representation of the glycerolysis reaction fourth step.

As a backward reaction commences, the water produced during the reaction will reduce the yield. Several methods, such as introducing an inert gas or air [12], maintaining a vacuum [12], and introducing silica beads [13] to absorb moisture, have been reported.

The glycerolysis process can be carried out by enzyme-catalyzed, alkaline-catalyzed, or acid-catalyzed reactions [32]. According to the vast majority of previous research on glycerolysis, the procedure requires high temperatures but relatively low pressures. It also demonstrates that the temperature of the reaction, the type and amount of catalyst, the molar ratio of oil-to-glycerol, the mixing intensity, and the reaction time are significant variables in the glycerolysis reaction [13,33–35]. Table 1 displays a variety of parameter values extracted from various publications.

Table 1. A variety of parameter values, each of which was taken from a different publication.

Catalyst	Temperature	Oil-To-Glycerol Ratio	Time	Speed	FFA Conversion	Reference
zinc acetate 0.6 wt.%	200 °C	1:2 molar ratio	240 min	350 rpm	9.1 to 0.6 wt.%.	[35]
ZnO 0.6 wt.%	150 °C	50 wt.%	180 min	600 rpm	20 to 1.5 wt.%	[36]
Lipase 0.5 wt.%	40 °C	1:6 molar ratio	1440 min	250 rpm		[37]
NaOH 1.75 wt.%	65 °C	224 wt.%	73 min	800 rpm	4.6 to 0.07 wt.%	[38]
NaOH 1.75 wt.%	56 °C	234 wt.%	85 min	800 rpm	6.50 to 0.06 wt.%	[39]
NaOH 1.3 wt.%	65 °C	1:2 molar ratio	20 min	600 rpm	6.1 to 0.5 wt.%	[26]
NaOH 0.875 wt.%	65 °C	1:1 molar ratio	150 min	600 rpm	5.7 to 0.45 wt%	[40]
$SO_4^{2-}/ZrO_2–Al_2O_3$ 0.3 wt.%	200 °C	1:4 molar ratio	240 min	200 rpm	44.2 to 0.66 wt%	[41]
metallic zinc 0.1 wt.%	220 °C	1:10 molar ratio	120 min	300 rpm	50 to 5 wt.%	[13]

This research attempts to produce purified glycerol using a unique process that incorporates several different purification procedures, such as simple distillation, acidification followed by neutralization, and activated carbon, whereas many earlier studies have focused on a single technique. In addition, this paper details the advantages of using waste methanol recovered during the crude glycerol purification process for biodiesel production as opposed to using fresh methanol. In addition to these evaluations, this study optimizes the glycerolysis parameters to decrease the reaction time and the FFA level of high acid oil, allowing for direct transesterification. Even though multiple steps are used in the present study, higher purity is vital to gain the market approach with an economic value. In order to generate economic value, it is envisaged that purified glycerol with a high acid value will be added as a raw material to WCO. This action will be carried out to achieve the goal of acquiring economic value. As a result, the acid value of the WCO will drop, and it will be converted into a high-quality oil that has the potential to be used in biodiesel production.

2. Materials and Methods

2.1. Pre-Treatment

A representative sample of WCO was obtained at a market in Colombo, Sri Lanka, where it was being prepared for disposal alongside the other garbage. Filtration and preheating at 110 °C were used to remove the WCO's suspended matter and moisture content, respectively.

2.2. Determination of Acid Value and FFA Content

The acid value and FFA% were calculated as described by Miyuranga et al. [42], as follows: 1 g of pre-treated WCO was added to a titration flask containing 125 mL isopropyl and 5–6 drops of phenolphthalein as an indicator. Titration with 0.1 M KOH was performed, and the volume required for a colorless solution to turn pale pink was determined (V1). A similar procedure was used for the blank sample devoid of WCO, and the KOH consumption was recorded (V2). The entire titration procedure was conducted three times to decrease the possibility of human errors. The acid value and FFA content of WCO were then determined using the formulas indicated in (1) and (2) for the acid value and FFA content of WCO, respectively.

$$\textbf{Acid value}\ (\textbf{mg KOH}/\textbf{g}) = \frac{56.1 \times 0.1 \times (\textbf{V}1 - \textbf{V}2)}{1} \tag{1}$$

$$\textbf{FFA}\% = \frac{\textbf{Acid value}\ (\textbf{mg KOH}/\textbf{g})}{2} \tag{2}$$

where **V**1 is the 0.1 M KOH volume required for the sample, **V**2 is the 0.1 M KOH volume required for the blank sample

2.3. Transesterification

Miyuranga et al. [42] described the procedure for transesterification. The transesterification of waste cooking oil was carried out in a closed container. Methanol (6: 1 molar ratio by molar of oil) was combined with a potassium hydroxide (KOH) catalyst (1 wt.% by oil weight). When the methoxide solution was added to the WCO, the transesterification reaction was initiated. The reaction was conducted at a speed of 600 rpm for 30 min at a temperature of 60 °C. After 30 min, the solution was poured into a separatory funnel and allowed to cool to room temperature for 4 h to allow the glycerol and biodiesel layers to separate. The bottom layer containing crude glycerol was collected. The FAME phase was rinsed with hot water to remove any remaining KOH and methanol. Using a 20-min heating procedure at a temperature of 110 °C, any remaining water was eliminated. Washing and drying were carried out until the pH of the biodiesel reached approximately 7. The percentage of biodiesel yield was calculated as shown in (3).

$$\boldsymbol{Biodiesel\ yield}\ (\%) = \frac{\boldsymbol{Dry\ weight\ of\ biodiesel}}{\boldsymbol{Dry\ weight\ of\ WCO}} \times 100 \tag{3}$$

2.4. Methanol Recovery

The crude glycerol was distilled at 70 °C in a simple distillation unit to remove any excess methanol that had dissolved during the extraction process. To absorb any remaining water molecules, distilled methanol was kept for 24 h in 3A molecular sieves.

2.5. Glycerol Purification

Under gentle stirring, approximately 200 mL of distilled crude glycerol was acidified with Phosphoric acid (H_3PO_4), to a 1 pH level in a 500 mL beaker set on a magnetic hot plate and held for an extended period of time to allow the formation of three distinct layers. The top layer is composed of fatty acids, the middle layer is composed of glycerol, and the bottom layer is composed of inorganic salts. Simple decantation was used to separate the bottom phase. A separator funnel was used to separate the fatty acid-rich top phase from the glycerol-rich bottom phase. The extracted glycerol was neutralized with a solution of 12 M NaOH, followed by two hours of evaporation at 110 °C. The 0.45 µm filter was used to remove the inorganic salts that formed during the neutralization stage under vacuum filtration. Glycerol was purified further using a solvent extraction process with methanol as the solvent to aid in the precipitation of dissolved salts. Under vacuum filtration, the 0.45 µm filter was used to remove the inorganic salts, which were then combined with activated carbon to remove color, odor, and some metal ions, and silica beads to absorb any remaining water molecules for several hours. Thereafter, activated carbon and silica beads were removed through filtration and the final glycerol sample was heated at 70 °C to remove methanol.

2.6. Glycerolysis

As a catalyst for the glycerolysis reaction, KOH was selected. However, the catalytic effect of glycerolysis must be studied later in this investigation.

According to Elgharbawy et al., to enhance its solubility in the viscous glycerol, KOH was pulverized into minute particles first. To ensure complete solubility of KOH in glycerol, the glycerol and KOH were mixed in a baker at a high stirring speed (600 rpm) and a temperature of 70 °C for five minutes to produce the potassium glyceroxide solution [30]. Frequently, the elevated temperature was required to reduce the viscosity of glycerol and facilitate the stirrer's motion. To increase the catalyst's solubility in glycerol, a little amount of hexane was added as a solvent. The potassium glycerol solution was added to the preheated high FFA oil sample in a separate reactor. According to Felizardo et al., the reaction was conducted at 200 °C and 350 rpm for 240 min as the baseline condition for the experiment [13]. Glycerol samples were obtained through the aforementioned laboratory experiments, while the high FFA oil was purchased on the market. The methanol and KOH were obtained from an analytical-grade chemical supplier. The chosen oil-to-glycerol molar ratio for the experiments was 1:4. Co-solvent of hexane was added concurrently at a weight ratio of 8:1 of oil-to-hexane. These ratios were later optimized in this study after these values were selected for the base case experiment. At the end of the stipulated reaction period, the mixture was put into the separating funnel to separate low-quality feedstock from unreacted glycerol based on the large density difference between the two substances. Allowing the mixture to settle for three hours ensured a complete phase separation. During separation, two layers formed; the top layer was the treated feedstock, which had a pale yellow hue. In contrast, the lower layer was the unreacted glycerol, which was extracted from the bottom of the separating funnel and subsequently purified for the glycerolysis procedure. To evaluate the effect of glycerolysis, the ultimate FFAs concentration of the upper layer was determined.

2.7. Acid Esterification

Utilizing a batch reactor, the esterification reaction was carried out. 100 g of oil were poured into the flask, which was then heated. After adding the acid catalyst of H_2SO_4 0.5 wt.% to this mixture, the reaction was allowed to continue for 4 h. Based on the findings of Encinar et al. [43], the reaction temperature was set to 60 °C and the methanol-to-oil molar ratio was set to 6:1. After the completion of the reaction, the contents of each reactor were poured into a separating funnel and left to settle for two hours. After that, a clear separation between the various layers was observed. According to Kombe et al. [44], the upper layer contained unreacted methanol, the middle layer contained fatty acid methyl ester (a small amount obtained from the conversion of free fatty acids to esters), and esterified oil and the lower layer primarily contained water, acid, and other impurities.

2.8. Statistical Analysis

Using Minitab 2016 software, the mean value of biodiesel production created from commercial methanol (Fresh methanol) and recovered methanol was statistically examined using a two-sample T-test. A confidence level of 95% was used. In addition, a two-sample T-test was conducted to assess the co-solvent effect of acetone and hexane.

3. Results and Discussion

3.1. Methanol Recovery

Transesterification promotes the formation of two distinct compounds in the biodiesel production process, such as methyl ester (biodiesel) and crude glycerol. Previous research [9,45,46] revealed that optimizing the methanol-to-oil molar ratio during the transesterification process was critical in increasing biodiesel yield. Due to the fact that transesterification is an equilibrium reaction, it requires an excessive amount of alcohol to enhance the biodiesel yield by shifting the reaction equilibrium towards higher yields of biodiesel. As a result, excess methanol (methanol-to-oil molar ratio of 6:1) was used in this experiment to advance the chemical equilibrium, despite the fact that a 3:1 methanol-to-oil molar ratio is required theoretically. As a result, once the reaction has reached equilibrium, the excess methanol is uniformly distributed across the two products [47,48]. However, due to the polarity of methanol, it dissolves more readily in crude glycerol than methyl ester [49]. Therefore, after the biodiesel synthesis process is complete, a significant amount of methanol is created for recovery and reuse. As a result of its toxicity in the majority of chemical applications, excessive unreacted methanol is seen as an impediment [48]. Apart from its toxicity, unreacted methanol acts as a phase stabilizer, slowing phase separation [47]. Therefore, Excess methanol must be removed in order to meet ASTM D6751 or EN214214 requirements. Almost every biodiesel standard allows for a finished product methanol level of 0.2% [50]. Apart from the methyl ester phase, crude glycerol contained a large amount of methanol, which could be utilized in the methanolysis of oil to produce biodiesel. Due to of methanol's low boiling point (64.5 °C), simple distillation is the most often used method of extracting it from the solution.

The crude glycerol was distilled at 70 °C until the methanol was recovered, then the isolated methanol was analyzed using GC-MS to determine its methanol content. The recovered methanol sample was determined to contain 92.5% of methanol. It was determined that when recovered methanol was used as alcohol instead of commercial methanol, a reduction in biodiesel yield occurred, biodiesel yield of commercial methanol and recovered methanol were found to be statistically equivalent based on a two-sample T-test, as the p value of the samples was greater than 0.05. As a result, the null hypothesis cannot be rejected. Nonetheless, the numerical reduction in biodiesel output may be mostly related to the fact that less methanol was present than in commercial methanol, which was shown to contain 98.5% methanol, as shown in Figure 8.

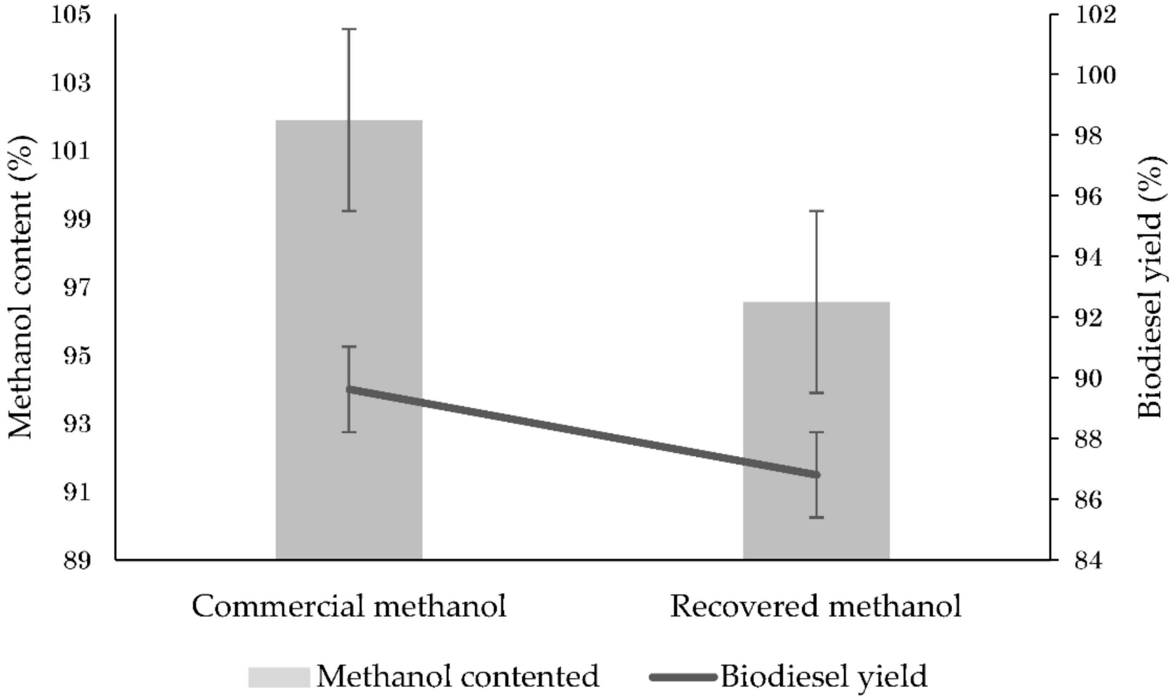

Figure 8. Methanol content and biodiesel yield of commercial methanol and recovered methanol.

3.2. Crude Glycerol and Methanol Removed Glycerol

The crude glycerol had a pH of 10 and was a dark brown liquid. Crude glycerol has a higher pH value and lower density (1.036 g/mL) than commercially available pure glycerol. According to Table 2, crude glycerol consists of a negligible amount of glycerol (16.25 wt.%) and a substantial amount of ash, water, and Matter Organic Non-Glycerol (MONG). MONG is found to be the predominant contaminant in crude glycerol (75.588 wt.%). MONG consists of contaminants, such as soap, alcohol, and methyl esters, in the glycerol resulting from biodiesel production processes [51]. The liberated fatty acids will be released in the form of a soluble soap. In addition, during the phase separation procedure, the methyl esters will be suspended in the glycerol phase [51]. These organic compounds can also reconstruct soap by reacting with the excess alkaline catalyst of KOH in the glycerol solution. During the transesterification process, alkali catalyst of KOH was used, resulting in the creation of inorganic compounds that constitute ash (5.982 wt.%). The presence of 2.18% water in the crude glycerol sample may be attributable to the hygroscopic nature of glycerol, which absorbs moisture from the surrounding environment during the transesterification procedure.

Table 2. Properties of crude glycerol and methanol-free glycerol.

Property	Test Method	Crude Glycerol	Methanol-Free Glycerol
Glycerol (wt.%)	ASTM D 6584	16.25	23.28
Moisture (wt.%)	ASTM D 4377-00 (2011)	2.18	2.16
Methanol (wt.%)	Simple distillation	8	0
Ash (wt.%)	ASTM D 482-19	5.982	6.260
Total salt (w/v%)	AOAC 965. 01	5.2	5.2
MONG content (wt.%) [1]	ISO 2464	75.588	68.300
pH at 25 °C	pH meter	10	9.4
Density (at 25 °C g/mL)	ASTM D891-95 (2004)	1.036	1.152
Color	Naked eye observation	Dark brown	Deep dark brown

[1] MONG = 100 − [glycerine content (%) + water content (%) + ash content (%)].

3.3. Crude Glycerol Purification

In the initial phase of the purification process, H_3PO_4 was used to acidify crude glycerol. This occurs when the acid reacts with the molecules of soap to form free fatty acids and less soluble monopotassium phosphate (KH_2PO_4), as demonstrated in the below reaction (4). Under conditions when the pH is extremely low, such as 1, the acid neutralizes nearly all of the alkali species present in the crude glycerol, causing the salt to precipitate out at the bottom while reacting with the soap to produce FFAs as the upper phase. Therefore, the acidity led to the creation of three distinct phases. The middle glycerol-rich phase was successfully obtained after the decantation of the solid residues and subsequent separation of the fatty acid layer from the glycerol-rich phase. Figure 9 depicts the FFA layer and glycerol layer after removing solid residues.

$$\mathrm{RCOOK} + \mathrm{H_3PO_4} \rightarrow \mathrm{RCOOH} + \mathrm{KH_2PO_4} \quad (4)$$

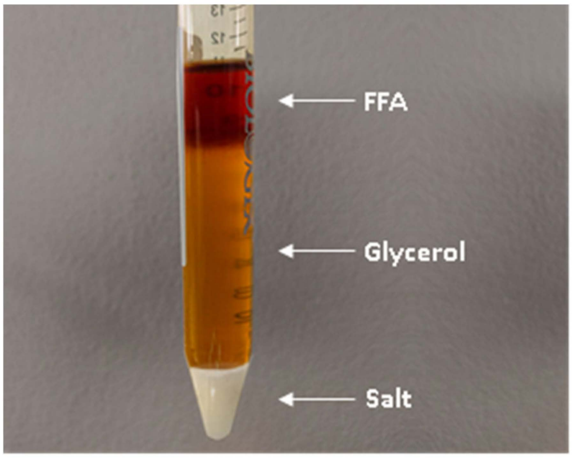

Figure 9. Acidified glycerol with three layers the FFA layer, glycerol layer, and salt residues.

A portion of the fatty acids was converted into a water-soluble soap during the acidification process, while a portion of the methyl esters was dissolved or suspended in the glycerol solution. During the subsequent neutralization phase, free fatty acids and methyl esters interacted with excess NaOH to form soap, which was left in the glycerol residue. Therefore, some sodium phosphate (Na_3PO_4) salts and water were produced as a result of NaOH neutralization with excess H_3PO_4. Neutralization was necessary because the PH of the crude glycerol had to be adjusted so that it was neither acidic nor basic, similar to pure glycerol. In consequence, the pH level was raised from 1 to 7. After the neutralization procedures, the generated water was removed by evaporating the solution at 110 °C.

The solution was then filtered through a 0.45 µm filter to remove the inorganic salts that formed during the neutralization stage while it was being processed under a vacuum. Utilizing activated carbon, the pure glycerol was stripped of its color, odor, and a number of the metal ions it contained. Figure 10 demonstrates the process of vacuum filtering of activated carbon-treated pure glycerol. In order to absorb any leftover water molecules, the purified glycerol was treated with molecular sieves for a specified period of time. The activated carbon and molecular sieves were then removed by filtering, and the final sample of glycerol was heated to 70 °C to eliminate any remaining methanol. Figure 11 depicts how the color of the sample changed throughout the various phases of the purification procedure. After the purified glycerol was treated with activated carbon, it was necessary to treat the sample twice in order to achieve complete color removal. Even though the treatment resulted in a substantial reduction in color, it was essential to treat the sample twice in order to completely eliminate color as shown in Figure 11.

Figure 10. The process of vacuum filtering of activated carbon-treated glycerol.

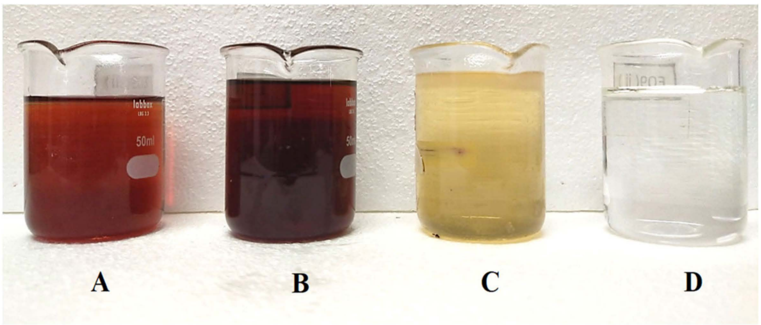

Figure 11. The color of the glycerol sample at various phases of the purification procedure. (**A**) Crude glycerol; (**B**) Methanol-free glycerol; (**C**) Neutralized purified glycerol; (**D**) Activated carbon treated purified glycerol.

Table 3 presents the results of a comparison between the outcome of this research and commercially available glycerol. The comparison table reveals that the purification approach employed in this study successfully produced glycerol with a higher purity that is very close to commercially available glycerol. According to the findings of this experiment, 94.0% of the retrieved crude glycerol was refined. Other measurements confirmed that a substantial decrease had occurred, and their values were extremely close to those of commercially available glycerol.

Table 3. Properties of purified glycerol and commercially available glycerol.

Property	Test Method	Purified Glycerol in This Study	Commercially Available Glycerol
Glycerol (wt.%)	ASTM D 6584	94.0	99.9
Moisture (wt.%)	ASTM D 4377-00 (2011)	0.20	0.01
Methanol (wt.%)	Simple distillation	0	0
Ash (wt.%)	ASTM D 482-19	<0.001	0.000
Total salt (*w*/*v*%)	AOAC 965. 01	2.1	0.0
MONG content (wt.%) [1]	ISO 2464	5.800	0.000
pH at 25 °C	pH meter	6.99	6.98
Density (at 25 °C g/mL)	ASTM D891-95 (2004)	1.26	1.27
Color	Naked eye observation	Colorless	Colorless

[1] MONG = 100 − [glycerine content (%) + water content (%) + ash content (%)].

3.4. Economic Analysis of Glycerol Purification and Commercially Available Glycerol

Each stage of glycerol purification needed a unique combination of chemicals and labor-intensive procedures. Consequently, it is crucial to compare the economic analysis of crude glycerol purification with that of commercially available glycerol. Table 4 depicts the comparative cost analysis between the purification of crude glycerol and commercially supplied glycerol. According to Table 4, the cost of purifying crude glycerol was $11.787 per liter, while the price of commercially supplied glycerol was $19.68 per liter. Some components, however, such as methanol and molecular sieves (3A), can be recycled and reused. Consequently, the expense of these items contributes nothing to the process. In addition, the cost of purifying crude glycerol is considerably less than the cost of purchasing pure glycerol, as indicated by the table's data.

Table 4. Properties of purified glycerol and commercially available glycerol.

Item	CAS Number	Unit Price	Quantity	Crude Glycerol Purification	Commercially Available Glycerine
H_3PO_4 (90%)	7664-38-2	$1.04/L	5 L	$5.2	
NaOH (99%)	1310-73-2	$0.74/Kg	2 L	$1.48	
Silica beads (99%)	7631-86-9	$1.04/Kg	2 Kg	$2.08	
Activated carbon (99%)	7440-44-0	$2.58/Kg	0.05 Kg	$0.129	
Electricity		$0.069/kWh	2 kWh	$0.138	
Operational cost		$0.69/h	4 h	$2.76	
Commercial glycerol (99.6%)	56-81-8	$19.68/L	1 L		$19.68
Total cost			1 L	$11.787	$19.68

3.5. Glycerolysis

Using purified glycerol as a raw material, the FFA concentration of a waste cooking oil sample was reduced by a method known as glycerolysis, which is expected to have a high acid value for biodiesel production. In the analysis of the impact of the factors on the glycerolysis process, the experimental outcomes from the base case are utilized. The experiment was conducted at 200 °C for 2 h using KOH as an alkaline catalyst while rotating at 350 rpm under the conditions of the base case. 0.5 wt.% hexane was utilized as a co-solvent, which enhanced phase solubility and overcame mass transfer resistance. During the operation, the molar ratio of oil-to-glycerol was fixed to 1:4.

It was determined that the initial FFA content of the oil sample was 19.25%, and its acid value was 48.50 mg KOH/g. Figure 12 depicts the outcomes of tests conducted utilizing the baseline situation.

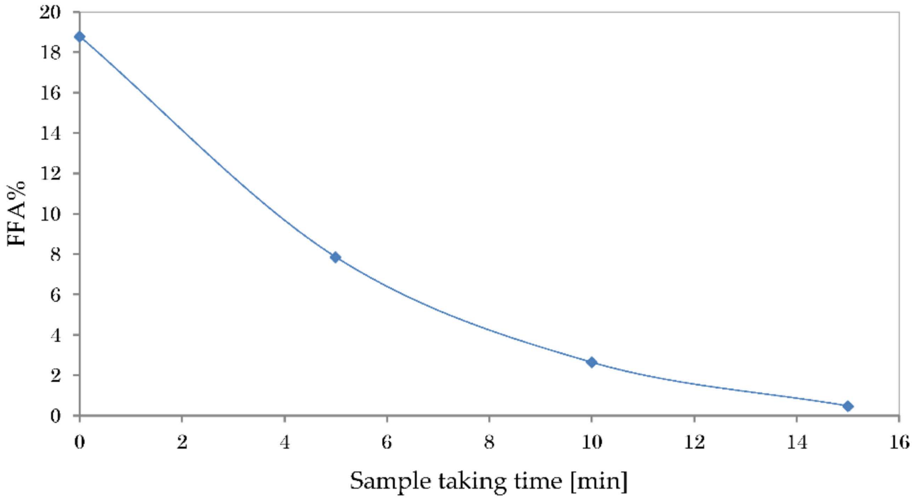

Figure 12. FFA variation during the glycerolysis reaction (Temperature: 200 °C, Stirring speed: 350 rpm, Time: 2 h, Catalyst: 1 wt.% KOH, Co-solvent: 0.5 wt.% hexane, Oil-to-glycerol molar ratio: 1:4).

The FFA content of the feedstock was monitored every five minutes throughout the duration of the reaction, which lasted for a total of two hours. However, according to Figure 12, the amount of FFA in the oil sample decreased dramatically over time, falling below 2% after 15 min and the FFA content of the feedstock remained unchanged between 15 min and two hours of reaction time. Consequently, the remaining of the rection was conducted for a duration of 30 min, as the baseline situation revealed a significantly lower FFA% after only 30 min. The value of less than 2% is desirable enough for alkaline esterification to be considered. As a result, sample collection was halted at that time.

Nevertheless, the influence of the glycerolysis process parameters was examined by altering each crucial parameter while holding the levels of the other parameters constant. When optimizing the glycerolysis reaction, the most important parameters were considered, including operating temperature, reaction time, rpm value, catalyst effect, and co-solvent influence.

3.5.1. Impact of Reaction Temperature on Glycerolysis

The influence of operating temperature on the system was evaluated at five different temperatures, such as 120, 150, 180, 200, and 250 °C, as shown in Figure 13. It should not come as a surprise that the temperature at which the glycerolysis reaction was conducted has a discernible effect on the outcome of the procedure. However, the selected temperature for the base instance was the optimal temperature for operation, as the FFA % reached 0.5 within the allotted 15 min time frame. This was due to the fact that the temperature was appropriate for operating. If the temperature is below 200 °C, the process of reducing FFA will take a significantly longer time, resulting in a greater demand for energy. Temperatures beyond 200 °C required less time to achieve the same FFA % reduction; nevertheless, the temperature returned to its original level within 15 min after the reduction was accomplished. As a direct result, based on Figure 13, one can conclude that an increase in temperature makes the reaction more favorable, and that the reaction's kinetics increase at a much faster rate due to the increase in temperature. The temperature of 200°C can be determined to be the best temperature for the glycerolysis reaction based on the cost of energy and the time required to achieve an FFA % of less than 2 min.

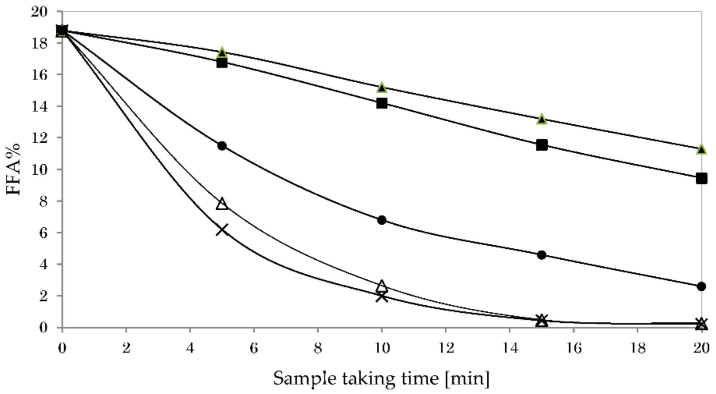

Figure 13. Impact of the operating temperature on glycerolysis reaction (▲: 120 °C, ■: 150 °C, ●: 180 °C, Δ: 200 °C, ×: 250 °C), (Stirring speed: 350 rpm, Time: 30 min, Catalyst: 1 wt.% KOH, Co-solvent: 0.5 wt.% hexane, Oil-to-glycerol molar ratio: 1:4).

3.5.2. Impact of Stirring Speed on Glycerolysis

As this was the desired outcome, it was hypothesized that increasing the speed at which the mixture was being stirred would accelerate the rate of glycerolysis. In order to test the hypothesis, this aspect of the experimental design emphasized the effect of the stirring speed as a significant variable. To evaluate the effect of stirring seed, the stirring speed was varied across five distinct speeds: 200, 300, 350, 400, and 500 rpm. Stirring speed was the only variable that varied over the course of the experiment. All other variables remained constant. Figure 14 illustrates the totality of the findings in its entirety. According to these data, there was no discernible improvement in situation when the stirring speed was increased from 200 to 500 rpm. Despite the fact that the increase was intended to result in this improvement, it did not occur as expected, refuting the hypothesis of glycerolysis. In contrast, when the stirring speed increased to a range between 300 and 400 rpm, the FFA percentage dropped substantially. Compared to other values, the FFA % reduction decreased more slowly at 200 rpm after the sample was obtained 5 min, compared to other values.

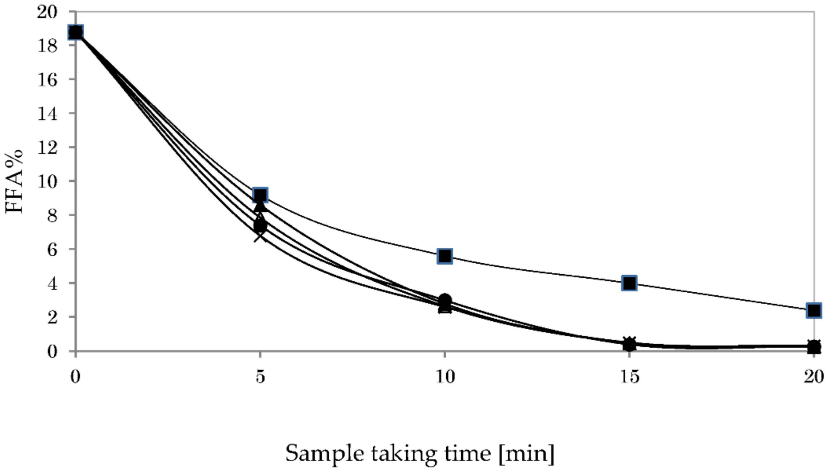

Figure 14. Impact of the stirring speed on glycerolysis reaction (■: 200 rpm, ▲: 300 rpm, Δ: 350 rpm, ●: 400 rpm, ×: 500 rpm), (Temperature: 200 °C, Time: 30 min, Catalyst: 1 wt.% KOH, Co-solvent: 0.5 wt.% hexane, Oil-to-glycerol molar ratio: 1:4).

3.5.3. Impact of Catalyst Type on Glycerolysis

The purpose of the catalyst is to remove the proton from the glycerol, convert it into a free radical, and then have the free radical attack the molecule of FFAs to produce the glyceride molecule (Figure 4). Increasing the weight of the catalyst improves the outcome since it produces a greater amount of glyceroxide radicals. These radicals convert FFA molecules into glycerides, which leads to a higher drop in FFA concentration. The glycerolysis process uses two distinct catalysts, including KOH and NaOH, to determine which catalyst is the most effective for this procedure. Increasing the amount of catalyst should be conducted with care since doing so might expedite soap production if an excessive amount is employed. Therefore, both catalysts were applied at 1% by weight. The percentage drop in FFA that has happened over time is depicted in Figure 15. According to Figure 15, the reduction of FFA percentage was highest with a KOH catalyst as opposed to a NaOH catalyst. However, NaOH was also effective in reducing the FFA %. KOH was selected as the catalyst because it is inexpensive, stable, and can be dissolved in glycerol. In addition, it can remove hydrogen atoms from the hydroxyl groups of alcohols, such as methanol, ethanol, and glycerol. This is an extremely valuable property [52].

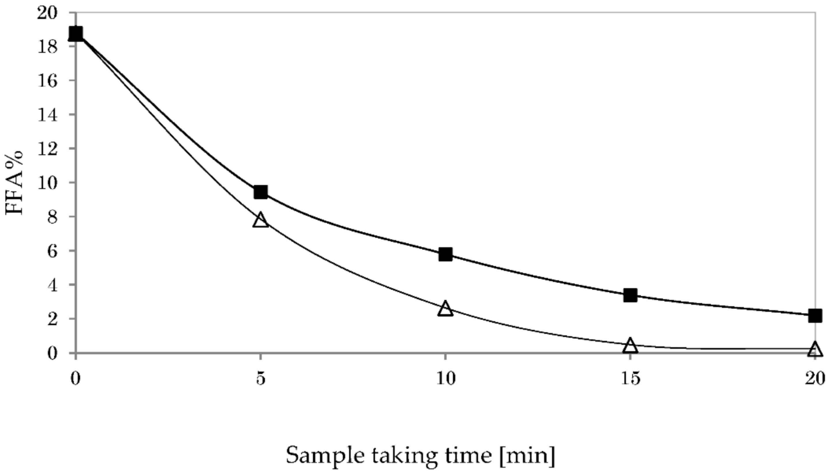

Figure 15. Impact of the catalyst type on glycerolysis reaction (■: NaOH, Δ: KOH), (Temperature: 200 °C, Time: 30 min, Stirring speed: 350 rpm, Co-solvent: 0.5 wt.% hexane, Oil-to-glycerol molar ratio: 1:4).

3.5.4. Impact of Co-Solvent Type on Glycerolysis

When it comes to glycerolysis, the immiscibility of glycerol and oil may slow the mass transfer process and limit the reaction’s rate. In the majority of instances, this issue can be resolved by vigorously agitating the reaction mixture. However, this will increase the total cost of energy needed during the production process. To reduce the reaction temperature while retaining high reaction yields, a glycerolysis process intensification procedure must be designed. This will also assist lower the quantity of energy required for the process and the total cost of processing. Utilizing one-phase reactions is one way to bypass the challenges associated with mass transfer limitations. It can be created by mixing oil and glycerol with a co-solvent to increase their solubility in water. In this study, a homogeneous potassium hydroxide base catalyst was combined with low temperature glycerolysis to decrease the amount of FFAs in waste cooking oil. Therefore, it was necessary to investigate the effect of the co-solvent on the glycerolysis reaction in order to determine the most effective co-solvent. Hexane, toluene, and acetone were chosen as the co-solvents to be utilized in the glycerolysis reaction so that it could be conducted under optimal conditions. Figure 16 clearly demonstrates that acetone performed better than hexane and toluene during the glycerolysis process, resulting in a more rapid decrease in FFA %. This was the direct result of acetone’s enhanced performance. This can be attributed that, acetone is an aprotic solvent that dissolves both polar and nonpolar FFAs, and polar glycerol, creating a homogenous reaction environment that facilitates the glycerolysis reaction between glycerol and FFA compared to the hexane and toluene [53,54]. Hexane is a nonpolar solvent with a low water solubility and polarity index, would extract longer-chain free fatty acids more efficiently than shorter-chain acids such as C6:0 and C8:0. It was thought that toluene, which is much more polar than hexane, would extract shorter-chain acids [40]. However, waste cooking oil was a sample of coconut oil, which contained abundant non-polar long chain Lauric acid (C12; 0). Therefore, hexane is more capable than toluene of dissolving a larger number of FFAs in the waste cooking sample. However, it was not as intense as acetone. Furthermore, acetone is more expensive than hexane, as demonstrated by their relative prices of $40.34 per liter and $22.64 per liter, respectively. Moreover, as the *p* value of the samples was more than 0.05, a two-sample T-test indicated that reducing FFA content with acetone and hexane had statistically equal results. Therefore, it is impossible to reject the null hypothesis. Therefore, hexane is preferred as a co-solvent for glycerolysis due to its inexpensive cost and statistically equivalent performance.

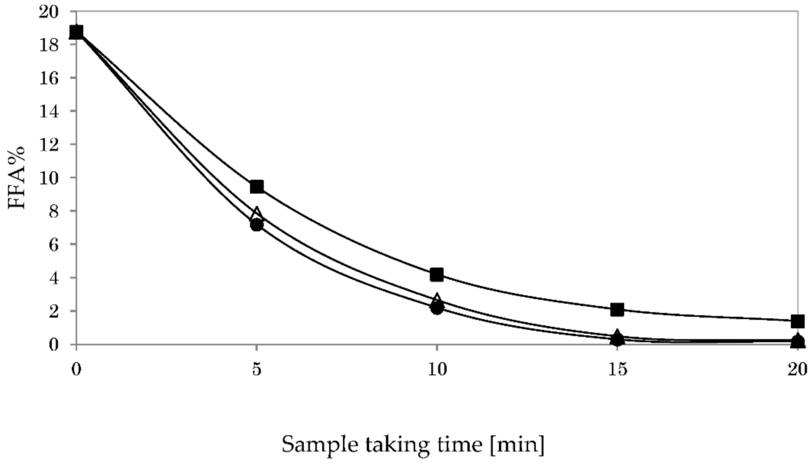

Figure 16. Impact of the type of the Co-Solvent on glycerolysis reaction (■: toluene, Δ: hexane, •: acetone), (Temperature: 200 °C, Time: 30 min, Stirring speed: 350 rpm, Catalyst: 1 wt.% KOH, Oil-to-glycerol molar ratio: 1:4).

3.5.5. Impact of Oil-To-Hexane Ratio on Glycerolysis

When mixing oil with hexane as a co-solvent, a weight-based ratio of 8:1 was maintained. Co-solvents must be combined in order to be utilized. For the subsequent study, the co-solvent ratio was modified, such as 4:1, 6:1, 8:1, and 10:1. Figure 17 depicts the influence of the ratio of oil to co-solvent on the glycerolysis process.

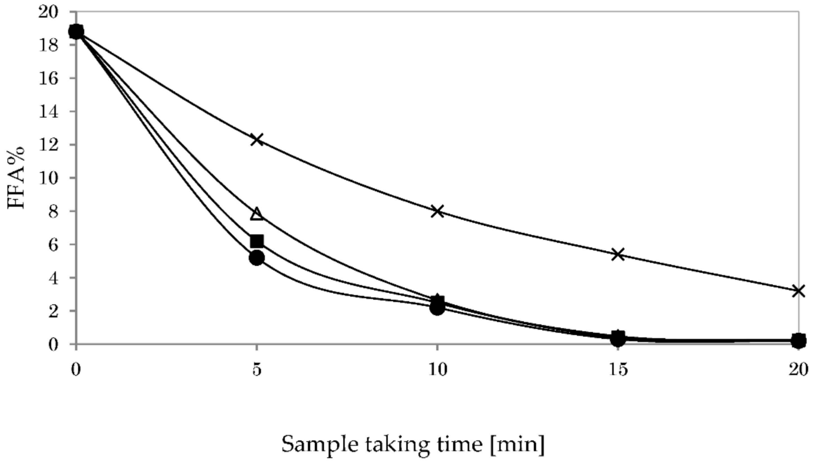

Figure 17. Impact of the amount of the Co-Solvent on glycerolysis reaction (×: 10:1, Δ: 8:1, ■: 6:1, •: 4:1), (Temperature: 200 °C, Time: 30 min, Stirring speed: 350 rpm, Catalyst: 1 wt.% KOH, Oil-to-glycerol molar ratio: 1:4, Co-solvent: hexane).

Considering Figure 17, it was abundantly clear that an increase in the weight ratio of oil-to-co-solvent decreased the glycerolysis reaction kinetics. The co-solvent was added to the reaction in order to dissolve the glycerin effectively in the alcohol solution. Therefore, if a smaller proportion of the co-solvent is present, it may not dissolve properly in the alcoholic solution. The weight ratio of 4:1 was preferred for reducing the FFA percentage because it can be achieved more quickly than other ratios. However, after 15 min, the FFA percentages for the 4:1, 6:1, and 8:1 weight ratios were identical. In order to reduce the amount of solvent required, the mixing weight ratio of 8:1 oil-to-co-solvent was determined to be optimal.

3.6. Acid Esterification and Glycerolysis

At this stage, the objective was to reduce the FFA content of the high acid oil to less than 1% using two distinct approaches. At the initial step, the FFA content of the oil was determined to be 19.25%. A number of studies were conducted in order to compare the effects of glycerolysis and acid esterification. The acid esterification procedure was conducted at a temperature of 60 °C, with a reaction time of 4 h and a H_2SO_4 as the acid catalyst concentration of 0.5 wt.%. In each instance, the FFA content of the product was determined using a chemical titration method in accordance with the Section 2.2 standards.

The same oil was also subjected to glycerolysis treatment, and the established reaction parameters from this experiment are supplied. This requires a temperature of 200 °C, a glycerol-to-oil molar ratio of 4:1, a KOH catalyst concentration of 1.6 wt.% at a speed of 350 rpm, reaction time was 30 min, hexane as a co-solvent with 0.5 wt.%, and the weight ratio of oil-to-hexane was 8 to 1. Figure 18 illustrates the complete findings. According to the findings, the FFA concentration at the completion of glycerolysis is 0.48%, while the acid esterification content is 3.23%. Consequently, it was evident that glycerolysis was able to fulfill the need in lieu of acid esterification. Furthermore, glycerolysis demanded less time than acid esterification.

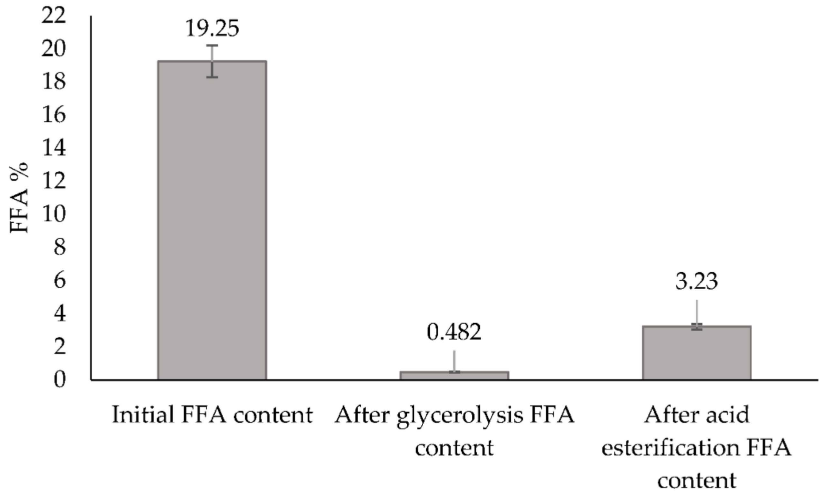

Figure 18. Impact of glycerolysis and acid esterification on feedstock FFA content.

3.7. Practical Implications of the Study

Today, promoting the United Nations sustainable goal of affordable and clean energy will lead to increased biodiesel production due to its renewability. However, biodiesel synthesis boosts crude glycerol production which the primary byproduct of transesterification which must be managed. Since crude glycerol has little commercial value, it is discarded in an environmentally damaging manner. Significant quantities of crude glycerol must be disposed of, which needs processing, land, and disposal. This increases the cost of biodiesel production. Utilizing the byproducts of biodiesel production to create value products is one strategy to reduce the cost of biodiesel manufacturing.

Recycling is essential to sustainability because it prevents reusable materials from being dumped in landfills. Therefore, recycling crude glycerol through the purification and glycerolysis of high acid value oil for biodiesel synthesis creates a sustainable solution that will eventually result in the attainment of the United Nations sustainable development goal 12 of ensured sustainable consumption and production patterns. The glycerolysis of oil with a high acid value resulted in a successful reduction of the FFA level, allowing the feedstock to undergo transesterification without acid esterification. Therefore, the purification of crude glycerol and the glycerolysis treatment resulted in a number of advantages that encourage sustainability.

The challenges associated with the utilization and purification of crude glycerol necessitate the development of new techniques and alternatives [55]. This is necessary to ensure the long-term viability of biodiesel-producing industries. The current situation regarding the purification of glycerol is exemplified by the extensive efforts made to identify cost-effective means of transforming waste into valuable products. The incorporation of glycerol purification into biodiesel plants is an excellent illustration of this effort [56]. One of the primary challenges is the purification of crude glycerol, which involves converting crude glycerol to a more usable state for both existing and emerging applications [57–60]. Even though the 'waste' has numerous applications, crude glycerol purification is one of the greatest challenges because refined glycerol is used to produce the vast majority of industrial raw materials [61]. Therefore, it is crucial to develop a feasible method for purifying crude glycerol. However, the majority of current techniques have numerous drawbacks such as high energy consumption and less quality. This research is able to overcome these obstacles.

Even though the current technology is capable of producing high-quality biodiesel, it has a number of drawbacks that necessitate a new approach in the production of biodiesel from feedstock with a high acid value. Both the alcohol and the vegetable oil must contain a high concentration of anhydrous fatty acids and a low concentration of free fatty acids [62]. Utilizing a base catalyst, which leads to the formation of soap in the presence of a high FFA content in the feedstock, decreased biodiesel yield. This is due to the fact that the presence of water, free fatty acid, or both, facilitates the production of soap [62], resulting in an enormous amount of salt being produced in the waste stream, high operating costs, and costly separation procedures are all disadvantages of biodiesel production. However, the findings of this study demonstrated a straightforward method for the production of biodiesel from feedstocks with a high FFA content, which required less reaction time and yielded a greater overall yield than acid esterification.

4. Conclusions

This study aims to purify the crude glycerol generated as a byproduct of waste cooking oil methanolysis. This will enable the purified glycerol to be utilized as a raw material for the glycerolysis process, with the ultimate objective of reducing the FFA content of high acid value oil prior to its conversion into biodiesel. In the process of purifying crude glycerol, waste methanol was extracted and shown to have the potential to be utilized in biodiesel production. It was observed that distillated methanol has a 92.5% methanol concentration and accounts for 91.5% of biodiesel production by validating the feasibility of recycling waste methanol in crude glycerol for transesterification. In order to obtain purified glycerol, biodiesel-derived crude glycerol was subjected to acidification, neutralization, and decolorization processes. These processes yielded glycerol with a purity level of 94 wt.%. When the density, moisture content, ash content, MONG content, pH, and Na/K contents of purified glycerol products were compared to those of commercially available pure glycerol, it was revealed that they were remarkably close.

Waste cooking oil with a high FFA percentage was treated with glycerolysis using purified glycerol to reduce the FFA content to below 2%. Upon first examination, it was discovered that the oil had 19.25% FFA. According to the results of the study, after 15 min of reaction, purified glycerol was able to effectively decrease the FFA level of oil to less than 2%. This allows biodiesel to be produced by direct transesterification without the requirement for an esterification step. It has been determined that the ideal conditions for glycerolysis for effective FFA reduction are as follows: 200 °C, a glycerol-to-oil molar ratio of 4:1, and a KOH catalyst concentration of 1.6% by weight at 350 rpm. The glycerolysis process was accelerated in the presence of hexane as a co-solvent at an oil-to-hexane weight ratio of 8:1.

According to the study's findings, the FFA level can be successfully lowered via glycerolysis of high acid oil obtained from purified crude glycerol, which subsequently permits direct transesterification for the production of biodiesel. The purification of crude glycerol and the treatment of glycerolysis therefore contribute directly to the concept of sustainability.

On the basis of the experimental findings, it is possible to conclude that it was feasible to use waste methanol for biodiesel synthesis and purified crude glycerol as a raw material in numerous sectors, including biodiesel manufacturing. In addition, it was determined that the FFA level of oil with a high acid value decreased significantly compared to that of acid esterification.

Author Contributions: Conceptualization, G.S., K.A.V.M. and U.S.P.R.A.; methodology, G.S., K.A.V.M. and U.S.P.R.A.; software, K.A.V.M.; validation, G.S., K.A.V.M. and U.S.P.R.A.; formal analysis, K.A.V.M.; investigation, U.S.P.R.A. and R.A.J.; data curation, K.A.V.M.; writing—original draft preparation, G.S. and K.A.V.M.; writing—review and editing, G.S. and U.S.P.R.A.; visualization, R.A.J.; supervision, U.S.P.R.A.; project administration, U.S.P.R.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by the AHEAD project of the world bank, grant number 8743–LK.

Conflicts of Interest: The authors declare no conflict of interest.

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