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Glycerolysis-Based Reduction of Free Fatty Acids in Crude Palm Oil (CPO) for Cost Effective Biodiesel Pre-Treatment

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Abstract

The high content of free fatty acids (FFA) in crude palm oil (CPO) presents a significant challenge for biodiesel production. This study investigates the glycerolysis pretreatment method using crude glycerol and potassium hydroxide (KOH) to reduce FFAs. Experiments were performed at varying molar ratios (1:3 to 1:9) and temperatures (60°C to 80°C). Results showed optimal FFA reduction at a 1:7 molar ratio and 80°C, reducing FFA below 5% within 60 minutes. FTIR analysis confirmed FFA conversion. The reaction followed a pseudo-second-order kinetic model (R^2 = 0.9832). Viscosity and density of the oil improved to 41.2 mPa·s and 0.886 g/cm^3, respectively. These findings demonstrate that glycerolysis is a promising, eco-friendly, and cost-effective solution for pretreating high-FFA feedstock in biodiesel production.

1. Introduction

The push for renewable fuels has spurred interest in biodiesel production from non-edible oils such as crude palm oil (CPO). However, the high free fatty acid (FFA) content in CPO reduces yield and complicates transesterification due to soap formation and catalyst deactivation [1-5]. Traditional methods to reduce FFA levels, such as esterification, involve using acid catalysts, high temperatures, and excess alcohol, which increase operational complexity and environmental concerns. These processes also demand substantial energy input to remove reaction by-products like water and excess alcohol [6-10]. As a result, there is a need for a more efficient, cost-effective, and sustainable pretreatment approach that can handle high FFA feedstocks while minimizing resource use and environmental impact [11-13].

Glycerolysis is an alternative pretreatment method that addresses many of these challenges. It reduces the FFA content by converting FFAs into neutral glycerides through their reaction with glycerol. This process removes the need for alcohol, streamlines by-product handling, and enables the use of crude glycerol—a by-product of biodiesel production—as an affordable reactant. Despite its potential, the industrial adoption of glycerolysis is hindered by the lack of comprehensive kinetic models, which are critical for maximizing reaction conditions, designing processes, and scaling up for industrial applications [14-19].

This study evaluates the effectiveness of glycerolysis for FFA reduction under varying conditions and explores the reaction kinetics and quality enhancement of treated oil.

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2. Methodology

Glycerolysis involves the reaction of triglycerides present in crude palm oil (CPO) with glycerol. This reaction occurs in the presence of a catalyst, typically an acid or base, and aims to break down ester bonds in the triglycerides. One of the primary objectives of this process is to reduce the free fatty acid (FFA) content in the oil. Lowering the FFA levels enhances the oil's stability and usability, making it more suitable for both food and industrial applications. The glycerolysis treatment is particularly beneficial for low-quality feedstocks, which often have higher FFA content. In this process, glycerol is used alongside a base catalyst, such as potassium hydroxide (KOH), to facilitate the reaction. The treatment effectively lowers the FFA levels, improving the overall quality of the oil, as shown in Fig. 1 [20-27].

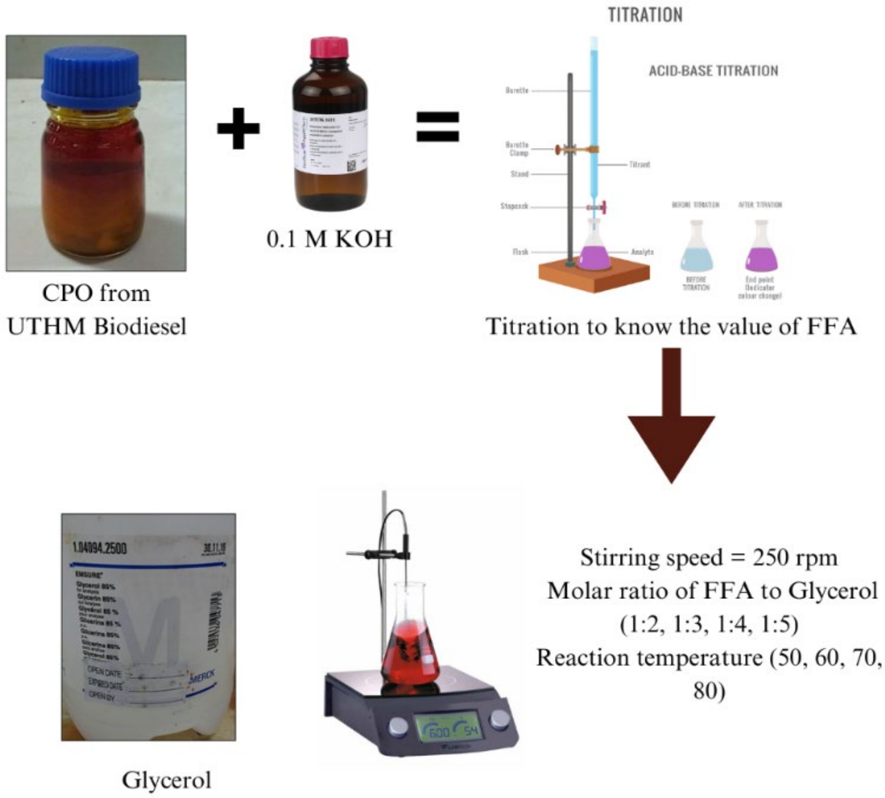

Fig. 1 *Experimental setup of FFA reduction by using Glycerolysis*

2.1 Materials

The crude palm oil (CPO) used in this study was sourced from the UTHM Biodiesel Plant. The initial free fatty acid (FFA) content of the CPO was approximately 25%. Crude glycerol, a by-product from the biodiesel production process, was used as the reactant. Potassium hydroxide (KOH) was selected as the homogeneous alkaline catalyst due to its higher solubility in glycerol and better catalytic performance in saponification reactions compared to sodium hydroxide (NaOH).

2.2 Experimental Design

The experimental procedure was conducted using a batch process setup. Molar ratios of FFA to glycerol varied from 1:3 to 1:9, and the reaction temperatures were set at 60°C, 70°C, and 80°C. Each batch was stirred at a consistent rate of 250 rpm for 60 minutes. These parameters were selected to determine their influence on the FFA reduction efficiency and to identify the optimal reaction conditions for effective pretreatment.

2.3 Characterization

FFA content was quantified using standard acid-base titration techniques. Fourier Transform Infrared (FTIR) spectroscopy was employed to analyze changes in the functional groups of CPO before and after treatment, providing molecular-level evidence of FFA conversion. Physical properties, including viscosity and density, were measured using standard ASTM methods to assess improvements in oil quality post-treatment.

3. Results and Discussion

The initial FFA content of untreated CPO was determined through titration analysis. Results showed a high FFA concentration of approximately 25%, far exceeding the acceptable industrial limit of 5%. This elevated level is often due to the enzymatic hydrolysis of triglycerides during improper storage or delayed processing of oil palm fruit. Such high acidity necessitates an effective pretreatment method to make the oil viable for further use.

3.1 Effect of Molar Ratio on FFA Reduction

Fig. 2 shows a clear trend: increasing the amount of glycerol leads to a greater reduction in free fatty acid (FFA) content. At a molar ratio of 1:3 (oil to glycerol), the FFA dropped from about 24.8% to 4.6% after 120 minutes. While this is a good reduction, it just missed the target of under 5%, which is needed to avoid soap formation during biodiesel production. When the molar ratio was increased to 1:5, the FFA level went down further to 3.2%, showing better reaction performance. However, the best result came from the 1:7 ratio, where FFA was reduced to 3%, meeting the requirement for biodiesel processing.

All tested ratios reduced FFA over time, especially in the first 60 minutes. The 1:7 ratio was the most efficient, reaching below 5% FFA within that time. The 1:5 and 1:9 ratios also worked well, though not quite as effectively. The 1:3 and 1:4 ratios were less effective—even after 120 minutes, FFA levels stayed slightly above 5%, likely due to not enough glycerol. On the other hand, while the 1:9 ratio did lower FFA, using too much glycerol might cause issues in separating it later, making it less practical for large-scale use. Overall, the 1:7 ratio gave the best balance between efficiency and practicality. This agrees with other studies, such as by Mujtaba et al. (2021), showing that a moderate excess of glycerol improves FFA conversion without creating too much waste.

The graph also shows that FFA levels drop quickly in the first 20–30 minutes, then more slowly as the reaction nears equilibrium. This shows how glycerol reacts with FFAs to form monoglycerides and water, reducing FFA over time. In summary, the 1:7 glycerol-to-oil molar ratio at 80°C worked best, reducing FFA below 5% within an hour and going down to about 3%. It offers a good mix of speed, effectiveness, and economic feasibility for biodiesel production. This matches past research and supports using this ratio for treating high-FFA feedstocks. This result also fits with Le Chatelier's Principle—adding more glycerol (a reactant) pushes the reaction forward, helping convert more FFAs into useful products.

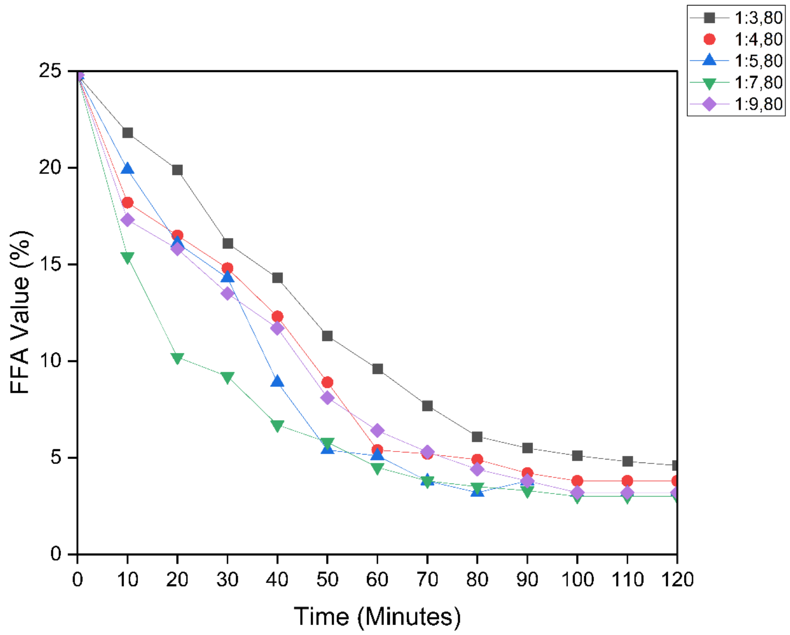

Fig. 2 *FFA reduction at variable ratio of Glycerolysis*

3.2 Effect of Temperature on FFA Reduction

Fig. 3 shows that temperature greatly affects how fast FFAs are reduced. At the start, the FFA content was about 24.8% for all temperatures tested. The fastest drop happened at 80°C, where FFA fell below 5% within 60 minutes, meeting the industrial standard for biodiesel pretreatment. At 70°C, the FFA also dropped below 5%, but it took almost 100 minutes, so it was slower. The slowest was at 60°C, where FFA stayed above 5% even after 110 minutes. This makes sense because higher temperatures speed up reactions by making molecules move and collide more often. More heat helps the reaction between glycerol and FFAs happen faster, turning FFAs into safer compounds like mono- and diglycerides.

Higher temperatures also make the mixture less thick (less viscous), helping the reactants mix better. According to Tan et al. (2022), good mixing between the oil and glycerol is important since they don't naturally mix well, especially in crude palm oil (CPO). Micic et al. (2019) also found that temperatures between 75°C and 85°C result in the best FFA conversion. But going too high can cause glycerol to break down, create unwanted by-products, and increase costs. That's why 80°C is the best temperature here.

So, 80°C with a 1:7 molar ratio works best, balancing fast reaction, product quality, and cost. Still, it's important to watch the process carefully to avoid overheating, which can spoil the product. In summary, at a 1:7 ratio, 80°C reduced FFA below 5% in just 60 minutes, making the process efficient and economical. Lower temperatures needed more time and didn't reduce FFA as consistently.

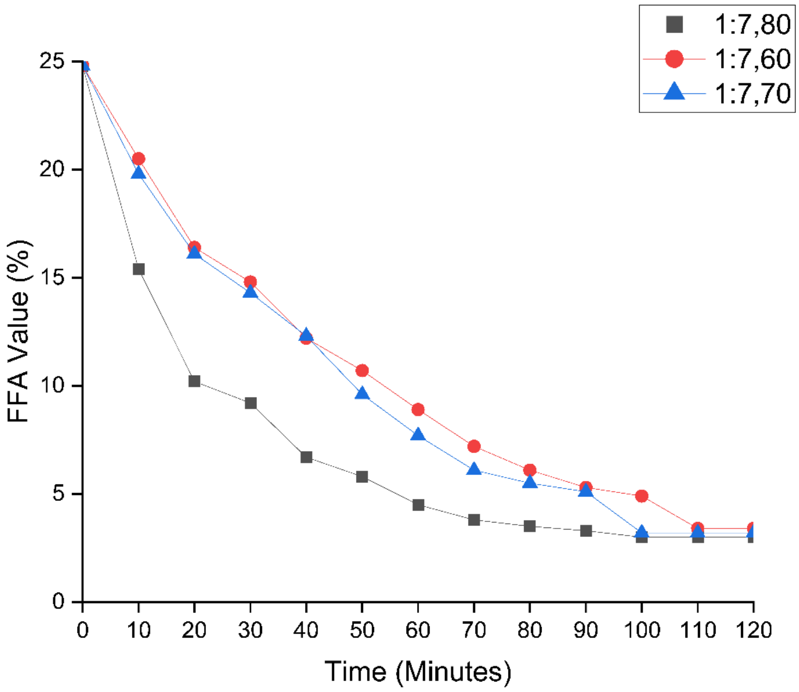

Fig. 3 *FFA Reduction at different temperatures*

3.3 FTIR Analysis

FTIR spectra showed the disappearance of peaks associated with carboxylic acid groups, confirming the transformation of FFAs into glycerides. Characteristic peaks for hydroxyl and ester groups further validated the successful chemical modification of the oil, consistent with glycerolysis reactions, as shown in Table 1 and Fig. 4. Fig. 4 shows the FTIR spectra of crude palm oil (CPO) before and after glycerolysis treatment. This treatment reacts free fatty acids (FFAs) in the oil with glycerol to form mono- and diglycerides, which improves the oil's quality by reducing FFAs. Comparing the spectra before and after treatment, several key changes show that the reaction worked: Around 3300 cm^{-1} (O–H stretching region), the treated samples at 1:7 ratio and 80°C or 70°C show a stronger signal than untreated oil. This means more hydroxyl (–OH) groups are present, coming from the glycerol and the new glyceride compounds. The 80°C sample shows a slightly stronger signal, meaning more reaction happened. Near 1750 cm^{-1} (C=O stretching), there is a slight decrease in signal in treated samples. This band relates to ester carbonyl groups found in FFAs and triglycerides. The peak remains due to leftover triglycerides and new glycerides, but the drop means some FFAs were used. Between 1000–1200 cm^{-1} (C–O stretching), the treated samples show increased signals, indicating the formation of new ester bonds and more hydroxyl groups. Again, the 80°C sample shows a slightly higher increase, suggesting better conversion. In the 900–700 cm^{-1} fingerprint region, the treated samples look similar to untreated oil, with only small changes. These are likely minor changes in the fatty acid structure due to the reaction. Overall, the spectral changes prove that glycerolysis successfully reduced FFAs and formed more stable glyceride compounds. The increase in O–H and C–O signals, along with the decrease in carbonyl signals, confirms this chemical transformation.

Table 1 *Summary of key functional groups identified from FTIR of crude palm oil*

Wavenumber (cm^{-1})	Functional Group	Assignment	Untreated CPO	1:7, 80°C	1:7, 70°C
~3300	O–H stretching	Alcohols / Hydroxyl groups	Weak	Moderate	Strong
~2920 & ~2850	C–H stretching	$-CH_2$ / $-CH_3$ groups (alkyl)	Weak	Strong	Strong
~1750	C=O stretching	Esters / Free fatty acids	Strong	Slightly less	Less
~1450	O–H stretching	Alcohols / Hydroxyl groups	Weak	Moderate	Strong
~1100	C=O stretching	Esters / Free fatty acids	Strong	Slightly less	Less
~1000	C–O stretching	$-CH_2$ / $-CH_3$ groups (alkyl)	Weak	Strong	Strong

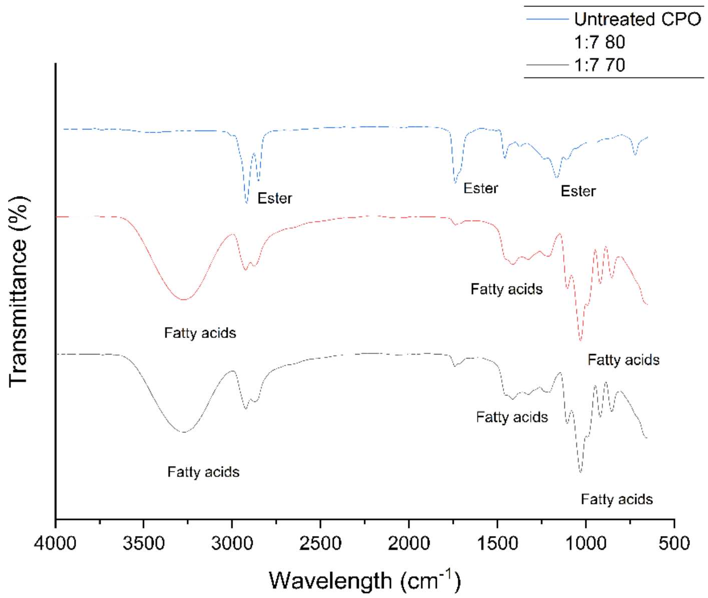

Fig. 4 *FTIR spectra*

3.4 Oil Quality

Viscosity and density measurements confirmed improvements in oil quality post-treatment. The viscosity decreased from its initial high value to 41.2 mPa·s, and the density dropped to 0.886 g/cm^3. These values fall within acceptable limits for biodiesel feedstocks, making the treated CPO suitable for downstream processing.

3.5 Reaction Kinetics and Rate Analysis

The kinetics of the glycerolysis reaction is critical for understanding the mechanism of free fatty acid (FFA) reduction in crude palm oil (CPO). By investigating the rate at which FFAs are converted into neutral glycerides, it becomes possible to optimize the process for industrial applications. The experimental data were analyzed using various kinetic models, and the pseudo-second-order model provided the best fit to the observed behavior.

Based on Fig. 5, FFA content at various time intervals was plotted as $\frac{1}{[FFA]_t}$ versus time. The plot yielded a strong linear relationship with a high correlation coefficient of R^2 = 0.9832, indicating that the pseudo-second-order model accurately represents the kinetics of FFA reduction under the tested conditions.

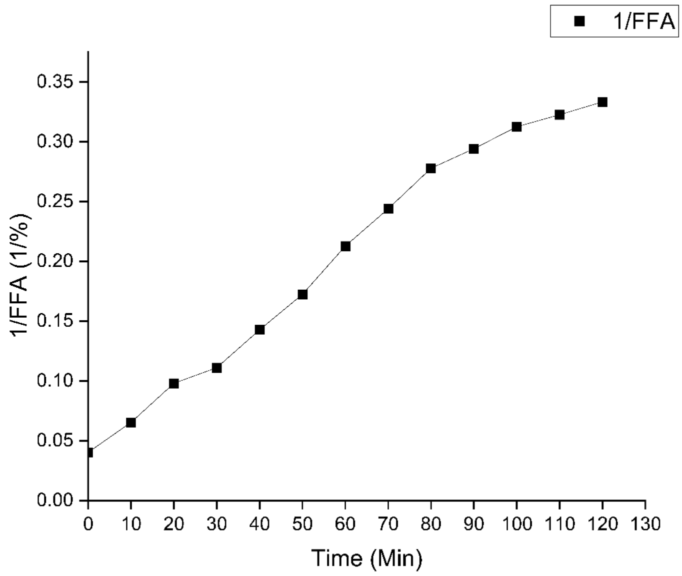

Fig. 5 *Pseudo-second-order model*

4. Conclusion

The study demonstrates that glycerolysis using crude glycerol and KOH is an effective method for reducing FFA content in crude palm oil. Optimized at a 1:7 molar ratio and 80°C, the process significantly lowers FFA levels and enhances oil quality. The reaction kinetics align with a pseudo-second-order model, which facilitates process scale-up and optimization. Glycerolysis improves biodiesel feedstock quality and promotes sustainability by utilizing biodiesel by-products.

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Conflict of Interest

Authors declare that there is no conflict of interest regarding the publication of the paper.

Author Contribution

The authors confirm their contribution to the paper, as follows: ***study conception and design:*** *Mursyid Musa;* ***data collection:*** *Mursyid Musa, Rais Hanizam Madon;* ***analysis and interpretation of results:*** *Mursyid Musa, Rais Hanizam Madon, Rais Mohd Hazri Madon;* ***draft manuscript preparation:*** *Mursyid Musa, Rais Hanizam Madon, Rohaizam Roslan, Zuliazura Mohd Salleh, MZahar Abd Jalal, Nurasyikin Misdan, Mohamad Alif Hakimi Hamdan, Rais Mohd Hazri Madon. All authors reviewed the results and approved the final version of the manuscript.*

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