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Innovative Use of Fly Ash as a Free Fatty Acid Reducer in Used Cooking Oil for Enhanced Biodiesel Production

Heni Anggorowati[1*], Perwitasari[2], Muhammad Syukron[3], and Yusmardhany Yusuf[4]

[1] Faculty of Industrial Engineering, Universitas Pembangunan Nasional Veteran Yogyakarta, 55283, Indonesia
[2] Faculty of Industrial Engineering, Universitas Pembangunan Nasional Veteran Yogyakarta, 55283, Indonesia
[3] Faculty of Mineral and Energy Technology, Universitas Pembangunan Nasional Veteran Yogyakarta, 55283, Indonesia
[4] Faculty of Industrial Engineering, Universitas Pembangunan Nasional Veteran Yogyakarta, 55283, Indonesia
* Correspondence: heni.anggorowati@upnyk.ac.id

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Abstract: High free fatty acid (FFA) levels in used cooking oil (UCO) hinder biodiesel production by reducing yield and complicating purification due to soap formation during transesterification. Traditional FFA reduction methods, such as acid-catalyzed esterification, have environmental and cost drawbacks. This study explores the use of activated fly ash, a coal combustion byproduct, as an eco-friendly, low-cost adsorbent for FFA reduction. Fly ash was treated with NaOH to enhance adsorption capacity, with effects of reaction time (1–4 hours) and adsorbent mass (1–5 grams) evaluated. Results showed that longer reaction times and higher fly ash masses significantly reduced FFA content, reaching equilibrium at extended times and higher masses. A power-law kinetic model (R^2 = 0.9895) confirmed the accuracy of FFA degradation data. The study concludes that activated fly ash offers a viable solution for improving biodiesel efficiency by repurposing industrial waste, supporting both renewable energy production and waste management.

Keywords: Fly ash; free fatty; used cooking oil; biodiesel; adsorption kinetics

1. Introduction

The quest for sustainable and renewable energy sources has intensified, with biodiesel emerging as a promising alternative to fossil fuels due to its biodegradability, lower greenhouse gas emissions, and potential production from waste materials, such as used cooking oil (UCO) [1, 2]. Among various feedstocks, UCO is particularly advantageous due to its cost-effectiveness and contribution to waste reduction, making it an ideal candidate for biodiesel production [3, 4]. However, a major challenge with UCO is its high free fatty acid (FFA) content, which reacts with alkaline catalysts to form soap during the transesterification process, thus reducing biodiesel yield and complicating purification [5, 6]

Traditional methods for FFA reduction in UCO, such as acid-catalyzed esterification using sulfuric acid, are widely used but present high operational costs, corrosion issues, and environmental concerns due to hazardous waste [3, 7]. Alternatively, adsorbents like activated carbon can be used, but high costs and limited reusability challenge large scale applications [1, 8]. Consequently, the search for sustainable and cost-effective alternatives has driven research into the use of industrial byproducts, such as fly ash [6, 9]. Fly ash, a waste product from coal combustion, is abundantly available and has gained attention due to

its potential in various applications, including as a catalyst or adsorbent in environmental and industrial processes [6, 8]. Its composition, including oxides like silica, alumina, and iron oxides, and its porous structure make it suitable for reducing FFAs in biodiesel feedstocks [2]. Recent studies suggest that fly ash can effectively remove pollutants and contaminants, thus improving the quality of processed materials. However, its specific application for FFA reduction in UCO is still underexplored, indicating a promising research area[1, 3].

Current research into fly ash utilization in biodiesel production shows mixed results. Some studies report that untreated fly ash can significantly reduce FFAs in UCO, enhancing biodiesel yield, while others suggest that untreated fly ash may lack sufficient catalytic sites and may require modifications like acid or base treatments to optimize its performance [5, 9]. This variation highlights the need for further investigation into the catalytic properties of fly ash, particularly to determine effective treatment methods for biodiesel applications. This study aims to explore the application of activated fly ash as a free fatty acid (FFA) reducer in used cooking oil (UCO) to improve biodiesel production. Specifically, it evaluates the effectiveness of modified fly ash in reducing FFAs by examining the influence of contact time and adsorbent mass on FFA adsorption. By identifying optimal conditions for fly ash application such as reaction time and fly ash quantity this research provides a comprehensive understanding of its potential as a sustainable solution in biodiesel feedstock processing.

The significance of this study lies in its potential to contribute to more sustainable biodiesel production practices by incorporating industrial byproducts like fly ash. This approach not only addresses technical challenges associated with high FFA content in UCO but also supports broader environmental goals of waste management and resource efficiency, ultimately advancing the field of renewable energy.

2. Materials and Methods

2.1 Material

This study employed various equipment, including an analytical balance, oven, magnetic stirrer, heating stove, beaker, measuring cylinder, stirring rod, watch glass, stopwatch, filter paper, Erlenmeyer flask, and burette. The materials utilized were fly ash from the steam power plant (PLTU) Cirebon, used cooking oil, distilled water, ethanol, and phenolphthalein indicator. Interventional studies involving animals or humans, and other studies that require ethical approval, must list the authority that provided approval and the corresponding ethical approval code.

2.2 Methods

Fly ash was washed with hot distilled water to remove impurities. The fly ash was then dried in an oven at 100°C until its mass was constant to remove moisture content. Subsequently, the fly ash was activated using a NaOH solution with a mass-to-volume ratio of 1:5 for 6 hours. The fly ash was then separated from the NaOH solution using filter paper and washed with distilled water until its pH was neutral. The fly ash was dried in an oven at 100°C until its mass was constant to remove moisture content. The next step involved adding 30 ml of used cooking oil into a glass beaker. 1-5 grams of fly ash were then added to the beaker. The mixture was stirred using a magnetic stirrer for 0 - 240 min. The used cooking oil was separated from the fly ash using a centrifuge at 3000 rpm for 20 minutes, and the FFA content was analyzed.

3. Results and Discussion

3.1 Effect of Reaction Time on %FFA Reduction

Figure 1 indicates that %FFA reduction improves significantly with increased reaction time across all tested adsorbent masses. As the reaction time extends from 1 to 4 hours, each adsorbent mass shows a consistent increase in %FFA reduction, highlighting the importance of adequate contact time for effective FFA adsorption. This trend is well-aligned with adsorption kinetics principles, which state that longer contact times enhance the interaction between FFA molecules and the adsorbent surface, leading to improved adsorption efficiency[10]

For lower adsorbent masses, such as 1 gram, %FFA reduction begins at approximately 20% after 1 hour and gradually reaches around 35% at the 4-hour mark. In contrast, for higher adsorbent masses like 5 grams, the %FFA reduction exceeds 60% after 4 hours, demonstrating that both reaction time and adsorbent mass play crucial roles in maximizing FFA removal. Manuale et al. (2013) observed similar results, noting that

increased adsorbent mass provides more active sites for FFA adsorption, which amplifies FFA reduction rates as reaction time increases[11].

Interestingly, the rate of increase in %FFA reduction begins to stabilize at longer reaction times, particularly for higher adsorbent masses. This behavior suggests that the adsorption process is nearing equilibrium, where most active sites on the adsorbent become occupied, leading to a plateau in FFA reduction. Such equilibrium phenomena are typical in adsorption processes, as additional reaction time contributes little to further reduction once the active sites are saturated [12].

The stabilization of %FFA reduction at extended reaction times implies that optimal adsorption time is crucial for efficient biodiesel production. Rezayan & Taghizadeh (2018) emphasize that optimizing reaction time not only enhances FFA reduction but also conserves resources, making the process more viable for industrial applications[13].

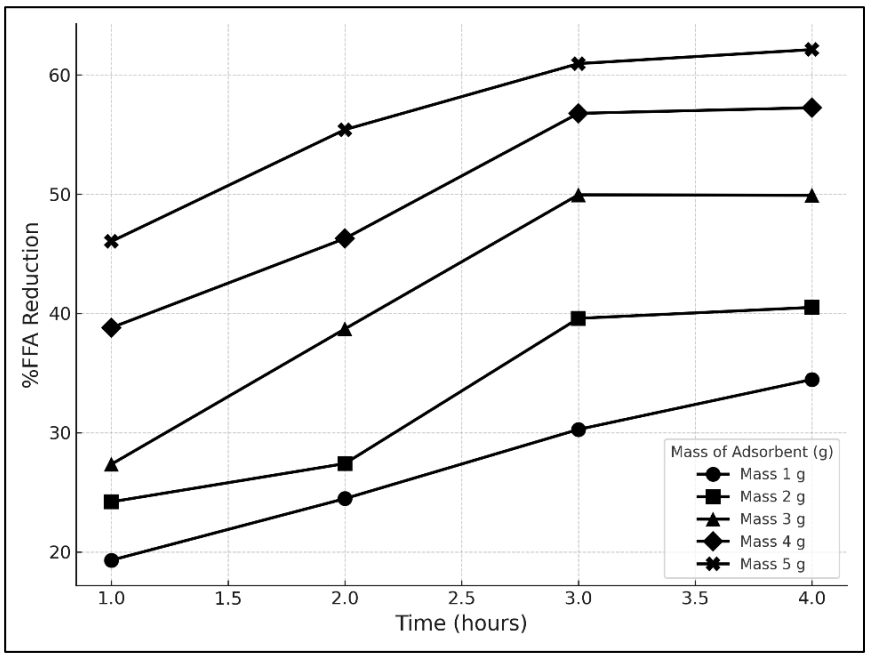

Figure 1. Effect of Reaction Time on % FFA Reduction

3.2 Effect of Adsorbent Mass on %FFA Reduction

The influence of adsorbent mass on the percentage reduction of free fatty acids (FFA) over a range of reaction times is illustrated in **Figure 2**. The data in this figure show a positive relationship between adsorbent mass and %FFA reduction, with higher masses resulting in greater FFA removal across various time intervals. This trend suggests that as the adsorbent mass increases, the availability of active sites also rises, enhancing the adsorption capacity and overall efficiency of FFA reduction. This observation aligns with findings by Hasan et al. (2019), who noted that using larger amounts of activated coal ash improved FFA reduction due to increased adsorption surface area [14].

In longer reaction times, the effect of adsorbent mass on %FFA reduction becomes more substantial. For example, at a reaction time of 4 hours, %FFA reduction reaches its peak with the highest adsorbent mass, indicating a synergistic effect of time and adsorbent quantity. This finding is consistent with Díaz et al. who reported similar improvements in FFA reduction when using energy crop shells as adsorbents, as increased mass provides a greater number of active sites for adsorption [10].

However, the trend toward equilibrium is evident at the highest adsorbent masses and longest reaction times, where %FFA reduction begins to plateau. This plateau effect indicates that additional adsorbent mass yields diminishing returns as the adsorption sites become saturated. Shafizah et al. observed this saturation effect in their optimization study, noting that beyond a certain adsorbent mass, the efficiency of FFA removal levels off [15].

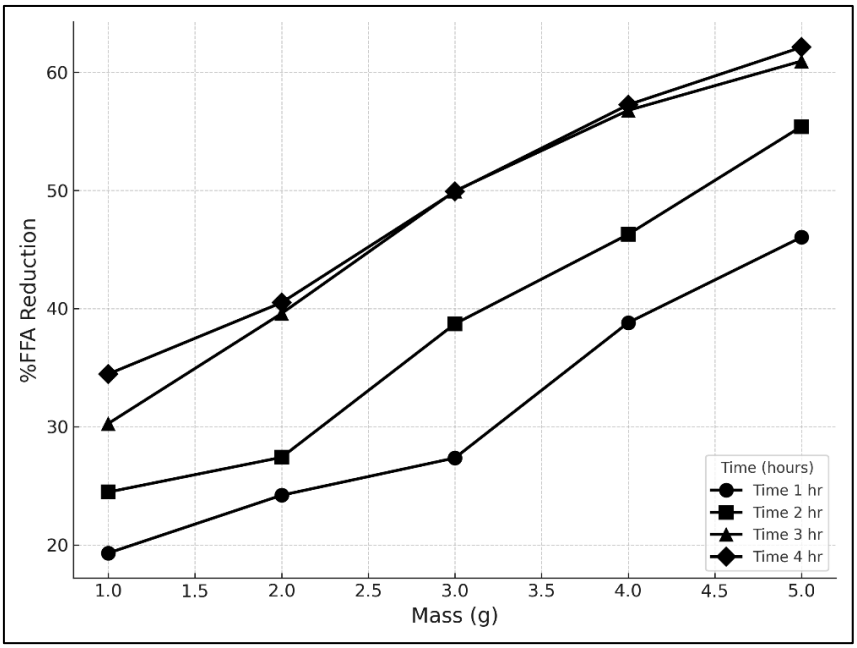

Figure 2. Effect of Adsorbent Mass on %FFA Reduction

4. Kinetic Model of Adsorption

The degradation kinetics of free fatty acids (FFA) were analyzed in this study using the kinetic model. $\frac{dC}{dt} = -kC^n$, where C is the FFA concentration, $k = 0{,}1027$ is the rate constant, and $n = 4.7834$ is the reaction order. These values were derived by fitting the experimental data to this kinetic model, capturing the behavior of FFA degradation over time.

Figure 3 illustrates the %FFA concentration over time, showing an initial rapid decline in FFA concentration that gradually slows as the reaction proceeds. This pattern is typical of reactions that follow power-law kinetics, particularly those with higher reaction orders, such as $n = 4.7834$. A high reaction order indicates that the reaction rate is initially susceptible to the concentration of FFA, decreasing significantly as the concentration diminishes. This trend is consistent with other studies where degradation reactions were modeled with power-law kinetics and high reaction orders, such as in the degradation of pollutants in water, where the rate constant k and reaction order n were found to have significant impacts on the reaction rate.

Figure 4, labeled "Data vs Estimated," further confirms the model's accuracy by comparing experimental %FFA data to estimated %FFA values, yielding a high coefficient of determination $R^2 = 0.9895$. This strong correlation between experimental and estimated values indicates that the kinetic model with k = 0.1027 and n = 4.7834 provides a good fit to the observed data. The high R^2 value aligns with findings from previous studies that used similar kinetic models, such as those investigating the degradation of organic compounds with rate constants in the range of k = 0.1 - 0.15 and reaction orders between 4 and 5, which yielded high correlation coefficients as well.

In conclusion, the kinetic model with parameters k = 0.1027 and n = 4.7834 accurately describes the degradation of FFA, as evidenced by the high correlation between experimental and model-predicted values. The high reaction order reflects a strong concentration dependency, particularly at higher initial concentrations, and the model's accuracy, supported by the high R^2 value, demonstrates its potential applicability for predicting degradation kinetics in similar systems.

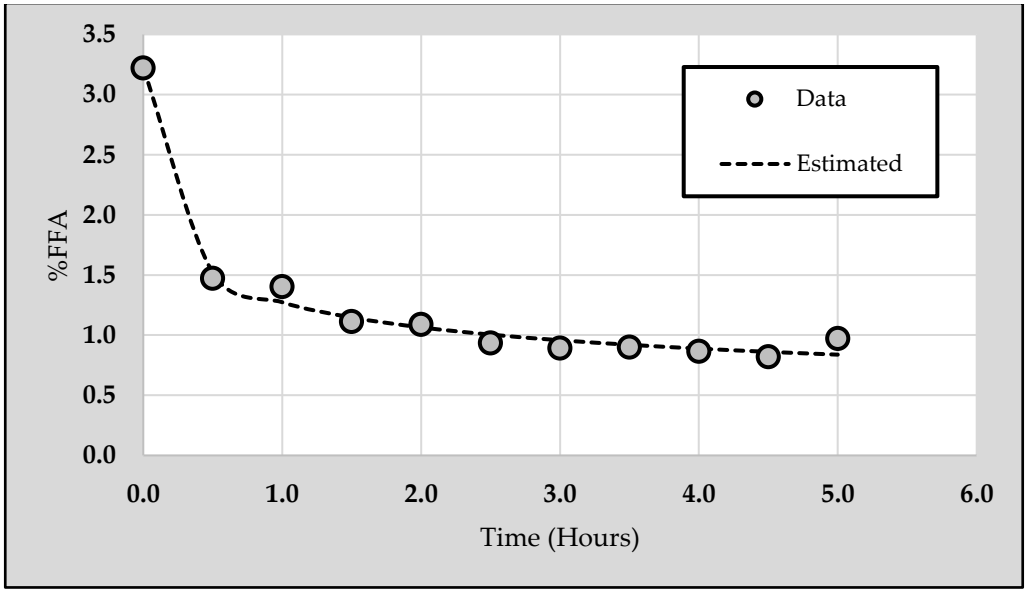

Figure 3. Plotting Time vs Concentration (%FFA)

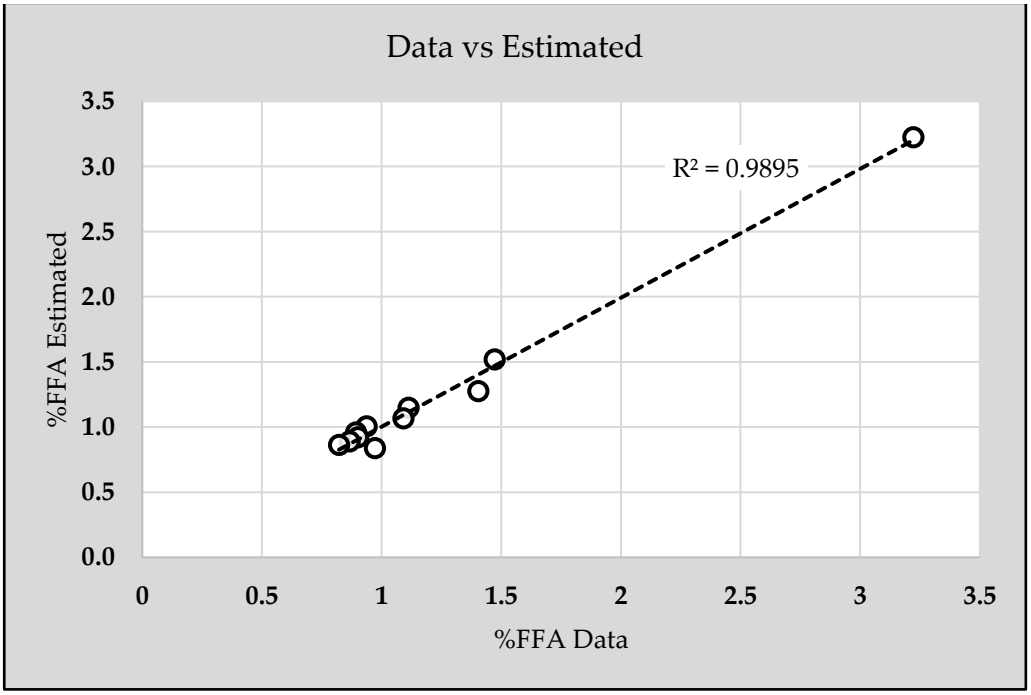

Figure 4. Plotting Data vs Estimated

4. Conclusions

Increasing reaction time and fly ash mass significantly enhances the reduction of free fatty acids (FFA) through adsorption. Extending the reaction time from 1 to 4 hours and using more fly ash improves FFA removal, but a saturation point is reached where additional time or fly ash yields minimal benefits due to occupied active sites. The kinetic model accurately described FFA degradation, confirming strong dependence on FFA concentration. Optimizing these parameters is crucial for efficient FFA reduction in biodiesel production..

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Conflicts of Interest: The authors declare no conflict of interest

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