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Transesterification reaction time impacts on oxidation stability and acid number of biodiesel production from waste cooking oil

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Abstrak: The scarcity of fossil fuels, environmental concerns, and the sharp rise in fossil fuel prices have driven scientists to search for alternative fuels. The characteristics of biodiesel have made the quest for high-quality biodiesel production particularly appealing. The use of waste cooking oil is a key component in reducing biodiesel production costs by 60-90%. Researchers have employed various types of transesterification reactions with both homogeneous and heterogeneous catalysts for biodiesel production; in this study, a 0.5% NaOH catalyst is used. The objectives of this study are to produce biodiesel fuel based on waste cooking oil, evaluate the impact of reaction time variation on the oxidation value and acid value of biodiesel produced from waste cooking oil, and statistically test the effects of reaction time on the oxidation value and acid value of biodiesel produced from waste cooking oil using analysis of variance (ANOVA). The optimum yield was obtained at a reaction time of 90 minutes, achieving 97%. The results for acid number and oxidation value for various reaction times complied with ASTM, EN, and SNI standards. Linear regression analysis of ANOVA for the acid number concluded that the P-value t3 is 0.399, which is greater than Alpha = 0.05, indicating that the variation in reaction time does not have a significant effect on the acid number. Linear regression analysis of ANOVA for the oxidation number concluded that the P-value t3 is less than Alpha (0.047 < 0.05), indicating that reaction time has a significant effect on the oxidation number.

Keywords: Biodiesel; waste cooking oil; oxidation number; acid number; linear regression analysis

1. INTRODUCTION

This study focuses on the production of biodiesel from waste cooking oil [1], which is a widely available vegetable oil source [2] in the food industry. The use of waste cooking oil as a feedstock for biodiesel has several advantages [3], including waste reduction and lower costs [4]. However, before biodiesel can be utilized as a fuel [5], it is necessary to evaluate the quality of the waste cooking oil to ensure it is suitable for use [6]. One important characteristic of biodiesel that must be considered is its oxidation number and stability [7], [8]. In addition to the oxidation number, the acid value is also a crucial parameter to consider when using waste cooking oil in biodiesel production. According to the research by [9] the acid value indicates the amount of free fatty acids in the biodiesel [10]. A high free fatty acid content can cause corrosion in the fuel system and reduce the combustion quality of biodiesel [11].

This research employs an experimental approach to test the oxidation value, stability, and acid value of biodiesel produced from waste cooking oil [12], with reaction time as a key parameter influencing the outcomes [13]. According to the research methodology includes the stages of esterification [14], transesterification, and biodiesel purification. The produced biodiesel samples will be analyzed using relevant standard methods to measure oxidation stability and acid value [15].

2. METHOD

The research was conducted at the Mechanical Engineering Laboratory of Universitas Medan Area and the Renewable Energy Laboratory (EBT) of Politeknik Negeri Medan over a period of four months. The materials used in this study included methanol solution (CH3OH), waste cooking oil, distilled water, and sodium hydroxide (NaOH). The equipment used included filter paper, thermometers, funnels, gloves, a triator, a Stabinger Viscometer SVM 3001, and a Pensky Martens Flash Point Tester.

The research procedure consisted of five stages: raw material preparation, transesterification process, oxidation number testing, acid number testing, and data analysis. The first stage, raw material preparation, involved collecting waste cooking oil to be used as the raw material for biodiesel production. It was ensured that the waste cooking oil samples represented variations in source or processing methods.

The next stage, the transesterification process, was carried out on waste cooking oil to convert it into biodiesel. The transesterification method used in this study was either the alkaline method or the acid method. During the transesterification process, biodiesel samples were prepared with reaction times of 60, 70, 80, 90, and 100 minutes for each experiment.

The subsequent stage involved testing the oxidation number by taking samples from each biodiesel produced with different reaction times. The Rancimat oxidation number analysis method was used by placing the biodiesel sample in a heated Rancimat reactor. Air was then passed through the biodiesel sample, and the time required to reach a certain change in electrical current was recorded. This recorded time was used to calculate the oxidation value of the biodiesel.

The next stage, acid number testing, was performed by taking samples from each biodiesel with different reaction times. The acid number analysis was conducted on these biodiesel samples by dissolving each sample in a neutral solvent such as hexane. The acid number of the biodiesel was determined using an acid titration method. The biodiesel solution was titrated with a basic solution such as sodium hydroxide, and the volume of the base solution required to reach the equivalence point was recorded.

The final stage, data analysis, was conducted using statistical methods such as analysis of variance (ANOVA) to determine whether there were significant differences between samples with different reaction times. If significant differences were found, further tests were conducted to determine specific differences between sample groups.

3. RESULTS AND DISCUSSION

In this study, we examined the impact of reaction time on the oxidation and acid numbers in biodiesel production using waste cooking oil as the feedstock. The reaction times tested were 60, 70, 80, 90, and 100 minutes. The oxidation numbers, acid numbers, and their respective standards were measured at each interval Table 1).

The results indicate that as the reaction time increases, the oxidation number also increases, peaking at 90 minutes before slightly declining at 100 minutes. This suggests an optimal reaction time around 90 minutes for maximum oxidation stability. Conversely, the acid number demonstrates less variation, fluctuating around the standard value of 0.4 mg KOH/g. The acid number decreases notably at 80 minutes but does not show significant change beyond that point. These findings highlight the critical balance between oxidation stability and acid number in optimizing biodiesel production processes. The optimal reaction time identified in this study can inform future biodiesel production protocols, ensuring enhanced fuel quality and stability.

The study investigates the impact of reaction time on two critical parameters in biodiesel production from waste cooking oil: oxidation number and acid number. The results are depicted in Figure 1 and Figure 2, illustrating the relationship between reaction time and these parameters compared to their respective standard values.

Table 1. the effect of varying reaction times on the oxidation, number acid number standadr number of each

Reaction Time (minutes)	Oxidation Number (min)	Standard Oxidation Number (min)	Acid Number (mg KOH/g)	Target Acid Number (mg KOH/g)
60	4.64	4	0.21	0.4
70	5.17	4	0.27	0.4
80	6.32	4	0.17	0.4
90	7.24	4	0.18	0.4
100	6.55	4	0.21	0.4

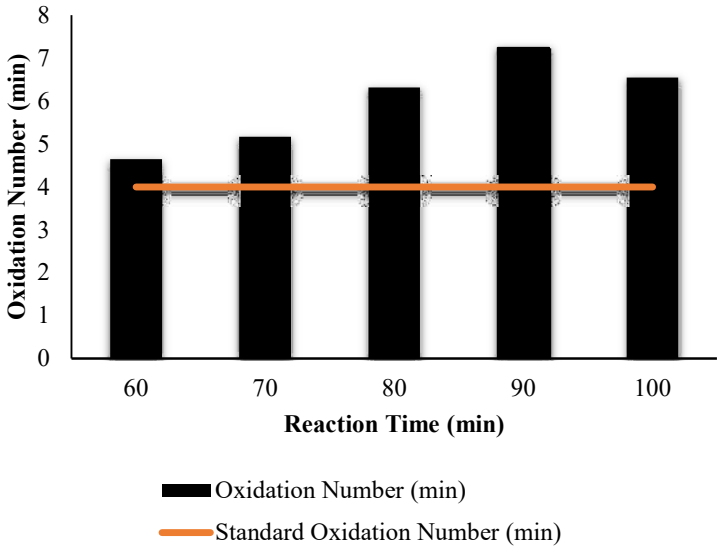

Figure 1. The reaction time effect on oxidation number comparing with standard number

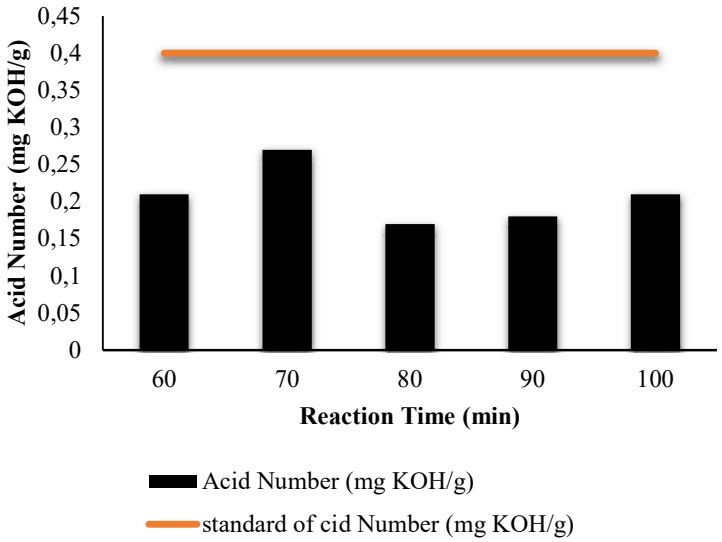

Figure 2. The reaction time effect on the acid number and comparing with standard number

Oxidation Number Analysis, Figure 1 shows that the oxidation number increases with reaction time, peaking at 90 minutes. This trend suggests an optimal reaction time around 90 minutes for achieving the highest oxidation stability, exceeding the standard oxidation number of 4. This increase aligns with findings. Who identified optimal conditions for biodiesel production from palm fatty acid distillate, noting significant improvements in oxidation stability with extended reaction times [16]. highlighted the importance of reaction time in optimizing biodiesel yield and stability, supporting the observed trend in our study [17].

Acid Number Analysis, Figure 2 illustrates the acid number at various reaction times, compared to the standard value of 0.4 mg KOH/g. The acid number decreases significantly at 80 minutes, indicating an effective reduction in free fatty acids at this interval. However, beyond 80 minutes, there is no substantial improvement. This behavior is consistent with the findings of who noted that specific reaction conditions are crucial for maintaining low acid values in biodiesel [18]. Additionally, emphasized the significance of optimizing catalyst concentration and reaction time to achieve desirable acid numbers in biodiesel production [19].

Linear regression analysis was conducted to examine the relationship between reaction time and the oxidation number in the transesterification of biodiesel. The regression equation derived is:

$$\text{Oxidation Stability} = 1.27 + 0.0589 \times \text{Time} \quad (1)$$

The results of the hypothesis testing and multicollinearity analysis are shown in Table 2. The coefficient of determination (R-sq) for the regression model is summarized in Table 3. Number From the hypothesis test, the p-value is 0.049, indicating a significant influence of reaction time on oxidation number since it is less than 0.05. The VIF value is 1.00, demonstrating no multicollinearity among the variables, ensuring the regression model's validity.

Table 2. Hypothesis testing and multicollinearity for reaction time on oxidation

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	1.27	1.49	0.85	0.456	-
Time	0.0589	0.0184	3.21	0.049	1

Table 3. Coefficient of determination for reaction time's impact on oxidation number

S	R-sq	R-sq(adj)	R-sq(pred)
0.58038	77.44%	69.92%	17.39%

The R-sq value of 77.44% indicates that 77.44% of the variability in the oxidation number can be explained by the reaction time, with the remaining 22.56% influenced by other factors. These findings align with other studies demonstrating significant relationships between reaction time and biodiesel properties. For example, the study by found optimal conditions for reducing acid values in biodiesel production by adjusting reaction times and catalyst amounts [16]. Similarly, optimized biodiesel yield by fine-tuning reaction times and other variables [20]. A linear regression analysis was also conducted for the acid number, yielding the following equation:

$$\text{Acid Value} = 0.281 - 0.00092 \times \text{Time} \quad (2)$$

The hypothesis test and multicollinearity results are shown in Table 4. The p-value of 0.54 indicates no significant influence of reaction time on the acid number. The VIF value of 1.00 confirms no multicollinearity.

Table 4. Hypothesis testing and multicollinearity for reaction time on acid number

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.281	0.108	2.59	0.081	-
Time	-0.0009	0.00134	-0.69	0.54	1

The coefficient of determination (R-sq) for the regression model is summarized in Table 5. The R-sq value of 13.66% indicates a very weak relationship, suggesting that reaction time does not significantly affect the acid number, with 86.34% of the variability influenced by other factors.

Table 5. Coefficient of determination for reaction time's impact on acid number

S	R-sq	R-sq(adj)	R-sq(pred)
0.042225	13.66%	0.00%	0.00%

These results are consistent with findings from other studies. For instance, the work on biodiesel synthesis with pyridinium and aminotriazolium ionic liquids found significant variability in acid values dependent on reaction conditions [18]. Additionally, Optimized acid values in biodiesel production using novel catalysts, demonstrating how different variables, including catalyst type and concentration, can significantly impact acid values [19].

4. CONCLUSION

This study provides a comprehensive analysis of the impact of reaction time on the oxidation and acid numbers in biodiesel production using waste cooking oil. The findings indicate that the optimal reaction time for maximizing oxidation stability is approximately 90 minutes. At this interval, the oxidation number peaks, significantly surpassing the standard oxidation number. In contrast, the acid number shows notable reduction at 80 minutes but exhibits minimal variation beyond this point, maintaining values close to the standard acid number. The regression analysis further supports these observations, revealing a strong correlation between reaction time and oxidation number, with 77.44% of the variability explained by the reaction time. Conversely, the reaction time's influence on the acid number is minimal, with only 13.66% of the variability explained, suggesting other factors play a more significant role in determining acid values. These findings align with previous research, such as

which emphasize the critical role of reaction time in optimizing biodiesel quality. The consistency of these results with the literature underscores the importance of precise reaction time management in biodiesel production to achieve desirable fuel properties.

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