



OPTIMIZATION OF REACTION TIME FOR SULFURIC ACID-CATALYZED PRE-ESTERIFICATION OF PALM OIL FATTY ACID DISTILLATE IN BIODIESEL PRODUCTION

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Producing biodiesel from palm oil fatty acid distillate (PFAD) offers a sustainable, cost-effective, and eco-friendly way to manage waste and generate energy. However, direct base-catalyzed transesterification of PFAD is not feasible because its high acid value (AV) leads to saponification, creating an undesired by-product that cannot be reversed. To avoid this, acid-catalyzed esterification is used to reduce the AV to a suitable range, allowing soap-free biodiesel production. Further, optimizing reaction conditions at the laboratory scale is a crucial step in determining the parameters needed for large-scale production. The purified PFAD was pre-esterified by applying 30% and 3% methanol and sulfuric acid, respectively by PFAD weight. Further, the reaction mixture temperature (45^o C) and stirring speed (3000 rpm) were maintained at a constant level throughout the reaction period. The reaction was carried out for a continuous period of 6 hours, with aliquot samples being taken every 30 min. The AV of each sample was measured using the titrimetric method according to ASTM D 974 standards. The oil obtained under optimal conditions underwent transesterification, according to the reported condition to produce the final biodiesel product. The quality parameters of the refined biodiesel were then evaluated using standard ASTM procedures. According to the results, the AV was reduced by 89 % (from 35.50 to 4.00 mg KOH g⁻¹) after a couple of cycles with 2.5 hours and 2 hours of reaction times, reaching a level that was considered suitable. Moreover, no soap was detected in the final raw biodiesel product. The refined biodiesel met the standard values set by ASTM D6751. This study identifies the optimal conditions for the sulfuric acid-catalyzed pre-esterification process, enabling biodiesel production from PFAD waste in a way that meets international standards and achieves a soap-free product.

Keywords: biodiesel, pre-esterification, optimization

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1. INTRODUCTION

The exploration of renewable, sustainable, and clean energy sources has intensified in response to the pressing issues associated with traditional energy sources. Biodiesel has emerged as a promising alternative, offering a potential solution to mitigate environmental concerns and reduce dependency on petroleum-based diesel fuels. Moreover, biodiesel presents a viable option for powering engines currently reliant on conventional diesel, addressing a critical need for sustainable transportation solutions [1].

The utilization of waste feedstocks for biodiesel production has gained traction due to economic viability, with feedstock accounting for approximately 70% of the total production cost [2]. However, waste and non-edible feedstocks often pose challenges, notably high acidity levels primarily in the form of free fatty acids[3], [4].

Out of numerous potential waste feedstocks for biodiesel production, Palm Oil Fatty Acid Distillate (POFAD) stands out as a promising candidate. It emerges as a by-product during the palm oil refining process, offering accessibility, affordability, and avoiding competition with food sources. POFAD consists mainly of free fatty acids, supplemented by tocopherols, sterols, and minor impurities [5].

Direct conversion of such feedstocks into biodiesel via base-catalyzed transesterification is hindered by irreversible saponification reactions, leading to reduced biodiesel yields. While acid-catalyzed transesterification offers an alternative, it requires higher energy input and extended reaction times, increasing production costs. To overcome these challenges, a two-step approach involving acid-catalyzed pre-esterification followed by base-catalyzed transesterification has emerged as the most suitable pathway for feedstocks with high acidity levels. The pre-esterification step aims to reduce acid levels to a desired threshold, thereby minimizing soap formation during subsequent transesterification [6], [7].

However, the pre-esterification step poses energy-intensive challenges, necessitating optimization of reaction conditions to minimize energy input. Additionally, comprehensive optimization studies at the laboratory scale are essential before transitioning to large-scale production processes.

This study introduces a methodology centered on optimizing the reaction time of the pre-esterification reaction of a high acid-value waste feedstock to improve biodiesel production efficiency.



Additionally, we assess the quality parameters of the resulting refined biodiesel to gauge the potential of POFAD for sustainable biodiesel production.

2. METHODOLOGY

2.1. Materials

Palm oil fatty acid distillate (POFAD) was obtained from the waste oil pit of a local palm oil production facility. Subsequently, the POFAD was purified through centrifugation, separating the upper oil layer from the deposited heavy sludge. All chemicals employed for chemical analysis and conversions were of analytical grade.

2.2. Pre-esterification Reaction

2.2.1. Procedure

A predetermined quantity of purified POFAD was placed into a glass reaction vessel submerged in a constant-temperature water bath and connected to a magnetic stirrer. The mixture was stirred continuously until reaching the desired temperature. Following this, a specified volume of methanol was introduced, and the stirring speed was adjusted to ensure a thorough blending of the oil and methanol phases. Subsequently, a predetermined amount of sulfuric acid was added drop by drop to the reaction mixture while stirring at the designated temperature.

At specific intervals, 5 mL aliquots were withdrawn into test tubes. Each aliquot was promptly cooled in a cold-water bath to halt the reaction and facilitate phase separation of the oil and methanol. The methanol layer was then carefully decanted using a dropper, and the test tube was subsequently placed in a boiling water bath to evaporate any remaining dissolved methanol. The resulting oil sample underwent centrifugation to remove suspended solid particles and polar aqueous components, including any unreacted sulfuric acid. The clarified oil sample obtained was utilized for determining the reaction progress.

2.2.2. Experimental Design

The experimental setup aimed to refine the reaction duration under specified reaction conditions. Throughout the optimization phase, methanol and sulfuric acid concentrations were held constant at 30% and 3% respectively, relative to POFAD weight. Meanwhile, the reaction mixture temperature (45 °C) and stirring speed (3000 rpm) remained consistent throughout the experiment. The reaction proceeded continuously for 6 hours, with aliquot samples collected every 30 minutes.

Each aliquot was analysed by performing a single titration and two separate experiments were conducted under identical conditions as described above.

2.2.3. Evaluate the progress

The percentage reduction of acid value ($\Delta AV\%$) was used to evaluate the progress of the pre-esterification reaction and determined as per Eq. (1) shown below.



$$\Delta AV\% = \left[\frac{AV_i - AV_f}{AV_i} \right] \times 100\% \text{ ---- Eq. (1)}$$

Where, AV_i and AV_f are acid values of initial and final products, respectively.

The acid value of the oil product was assessed using the titrimetric method by ASTM D 974 standards [7]. This method quantifies the quantity of a specified base (alcoholic potassium hydroxide) required to titrate a sample in a specific solvent (toluene, water, and anhydrous isopropyl alcohol in a ratio of 100:1:99) to a defined endpoint using a specified detection system (p-Naphtholbenzein Indicator).

Acid value determination was done using Eq. (2) shown below.

$$\text{Acid value (mg KOH g}^{-1}\text{)} = [(A - B) \times M \times 56.1] / W \text{ ---- Eq. (2)}$$

A = KOH solution required for titration of the sample/cm³.

B = KOH solution required for titration of the blank/cm³.

M = Concentration of the KOH solution/mol dm⁻³.

W = Weight of sample used for the titration/g.

2.3. Transesterification of pre-esterified PFAD

The product obtained from the pre-esterification of PFAD under the conditions of 45°C, a stirring speed of 3000 rpm, methanol content at 30% by PFAD weight, and sulfuric acid content at 3% by PFAD weight, with reaction times of two successive cycles lasting 2.5 hours and 2 hours, was transesterified using a base (NaOH) catalyzed pathway, following the procedure reported by A. Soly Peter *et al.*, [8].

2.4. Separation and Purification of Crude Biodiesel

The trans-esterified reaction mixture was transferred to a separatory funnel and allowed to undergo gravity-based separation for 24 hours. This process yielded an upper layer (crude biodiesel) and a lower layer (crude glycerine). The separated crude biodiesel was then subjected to three rounds of washing with hot water (in a ratio of 1 part oil to 3 parts water by volume) until the resulting washing water reached a neutral state. Subsequently, the biodiesel sample was left to stand for an additional 24 hours to facilitate the removal of any separated water. The resulting refined biodiesel sample was then analyzed for its fuel parameters.

3. RESULTS AND DISCUSSION

Figure 1 depicts the progression of the reaction over time, expressed in terms of the percentage reduction of the acid value. According to the results obtained under specific reaction conditions (30% methanol and 3% sulfuric acid by POFAD weight, with a reaction mixture temperature of 45° C and stirring speed of 3000 rpm), the reaction can reach completion within 2.5 hours. A 68% reduction in acid value was achieved after 3 hours, with no significant increase observed after that. This plateau effect is primarily due to the saturation of the reaction mixture with products. Additionally, after 2.5



hours, the acid value of the sample was measured at 11.52 mg KOH g⁻¹, which exceeds the suitable level for healthy transesterification, surpassing the risk of saponification reaction. Typically, a 4 mg KOH g⁻¹ level is considered safe for effective transesterification. Hence, the pre-esterified mixture undergoes another round of esterification under identical conditions. Within 2 hours, the acid value was observed to decrease to the desired level. As a result, after a couple of conversion cycles, AV was able to decrease by 89% from its initial value.

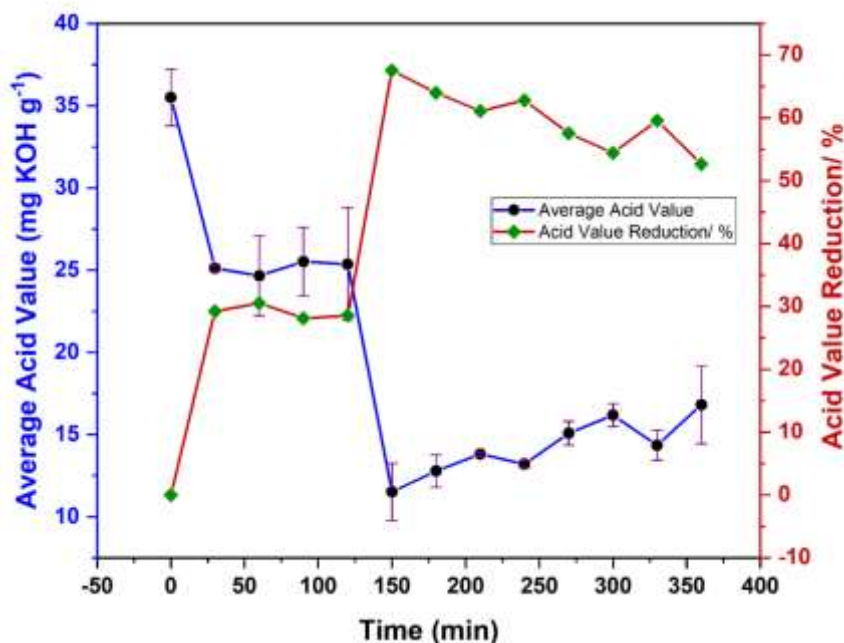


Figure 1 – Variation of average acid value and percentage acid value reduction of pre-esterification reaction mixture with time.



Figure 2 - B100 palm oil biodiesel

The fuel quality parameters of the refined biodiesel, obtained under optimal conditions, were assessed. All parameters were found to meet internationally defined ASTM standards. The values are presented in the table below.



Table 1: Quality of Biodiesel

Test	Test Method	Unit	Experimental value	Standard Specification of B100 as per ASTM D6751-07b
Calorific value	-	kJ/kg	40.23	N/A
Kinematic viscosity at 40 °C	ASTM D7042	mm ² /s	5.3835	1.9 – 6.0
Density at 25 °C	ASTM D7042	g/cm ³	0.863	0.860 – 0.900
Flash point	ASTM D93	°C	145	Minimum 130

The FT-IR spectral analysis (Figure 3) of the oily product at each stage of biodiesel production elucidates the purity of the product.

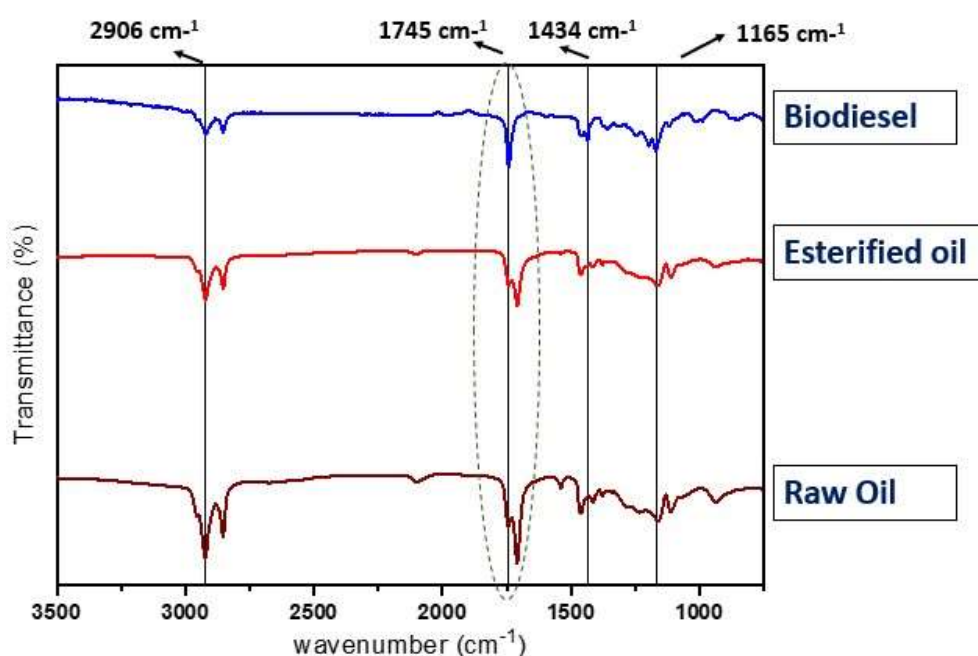


Figure 3 – FTIR spectra of POFA, Esterified oil, and final biodiesel samples.

The peak observed at 1745 cm⁻¹ in the FTIR spectrum corresponds to the stretching vibration of the carbonyl group (C=O), signifying the presence of ester functional groups within the molecule. Peak broadening may occur due to the association of various functional groups with the ester molecule, contributing to a diverse chemical environment. In the raw oil and esterified oil, a broad peak is evident due to the presence of different esters. Such compounds may be present in minor quantities as impurities. However, during transesterification, these impurities may be separated, potentially accumulating in a glycerine phase. Consequently, the sharpening of this peak indicates an improvement in the oil's purity, serving as an additional indicator of biodiesel quality.



4. CONCLUSION

The study presents an environmentally friendly method for converting palm oil fatty acid distillate (PFAD) into biodiesel, achieving an 89% reduction in acid value through acid-catalyzed esterification. This process yields high-quality biodiesel that complies with international ASTM requirements, thus providing a sustainable, eco-friendly alternative to traditional biodiesel production.

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