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Acid-Catalyzed Esterification for Biodiesel Production from Acid Oil

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Highlights

- Acid-catalyzed esterification was employed to produce biodiesel from acid oil.
- Biodiesel yield increased with increasing methanol content, catalyst concentration, and reaction time.
- Conversion of acid oil to biodiesel decreased viscosity and refractive index, while increasing density.

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Abstract

In this study, acid oil (AO), a by-product of oil refinery waste, was utilized as a feedstock for biodiesel production through acid-catalyzed esterification. The reaction variables included the methanol-to-acid oil molar ratio 1:1, 5:1, and 10:1, catalyst concentration 1%, 2%, and 3%, and reaction time 5, 30, and 60 minutes. Conversion yield, mass yield, free fatty acid (FFA) content, and physical properties including viscosity, density, refractive index, and color attributes were evaluated for all biodiesel samples.

As the methanol-to-acid oil molar ratio, catalyst concentration, and reaction time increased, conversion yield and density increased, whereas free fatty acid content, viscosity, and refractive index decreased, exhibiting an asymptotic approach toward equilibrium. At a methanol-to-acid oil molar ratio of 10:1, catalyst concentration of 3%, and reaction time of 60 minutes, a near-maximum conversion yield of 95.3% was obtained. These conditions were identified as the practical optimum, providing a balance between biodiesel yield and operational and economic feasibility. The final biodiesel yield under these practical optimum conditions was 84.25%, confirming that acid oil is a suitable feedstock for biodiesel production.

Keywords: Acid oil; Biodiesel; Esterification; Waste

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1. Introduction

In the modern energy landscape, fossil fuels remain the primary source of energy; however, their nonrenewable nature poses significant environmental challenges. The growing industrial demand for these fuels increases the risk of depletion in the foreseeable future (Zhu et al., 2024; Yazdani and Saeedi Dehaghani., 2022). In light of declining fossil fuel reserves (Kosuru et al., 2024), rising crude oil prices, global warming, and increasing global energy demand, the development of clean, environmentally friendly, and sustainable renewable energy sources has become increasingly urgent (Golmakani et al., 2024; Ebrahimi et al., 2019). Transitioning from a fossil fuel-based energy system to renewable technologies is therefore essential to achieve long-term environmental and economic sustainability (Yusuf et al., 2024).

Biodiesel, defined as the ethyl or methyl ester of fatty acids, is recognized as an environmentally friendly, biodegradable, non-toxic, sulfur-free, and oxygenated alternative to conventional diesel fuel. Its use reduces emissions of particulate matter, hydrocarbons, and carbon monoxide in diesel engine exhaust, thereby mitigating air pollution and associated health risks compared with petroleum-based diesel (Zhou et al., 2021; Math et al., 2010).

Vegetable oils are widely used as feedstocks for biodiesel production; however, they account for approximately 70–85% of the total production cost. Moreover, the use of edible vegetable oils for biodiesel production intensifies the food–fuel competition, which may lead to increased food prices (Shibasaki-Kitakawa et al., 2015). A promising strategy to address this challenge is the utilization of low-cost waste materials, such as industrial and waste frying oils, animal fats, and non-edible vegetable oils, which have attracted increasing attention in recent years (Zhou et al., 2021).

Acid oil (AO), a by-product of vegetable oil refining, contains free fatty acids, acylglycerols, and other lipophilic compounds (Alishahi et al., 2021). The production of AO can represent up to ten percent of the total output of refined vegetable oils in a processing plant, while its market value is typically less than twenty percent of that of edible oils. If not properly utilized, AO may pose environmental concerns. The absence of appropriate treatment and management strategies for AO can ultimately threaten ecosystems and human health. Therefore, the use of AO as a feedstock for biodiesel production is advantageous from both environmental protection and energy conservation perspectives (Zou and Chai, 2017).

Transesterification is the most commonly employed reaction for biodiesel production. In this process, triglyceride molecules in oils or fats react with alcohol in the presence of an alkaline catalyst to produce biodiesel, with glycerol formed as a by-product (Rajkumari and Rokhum, 2020). However, this reaction is sensitive to the presence of free fatty acids. The alkaline catalyst reacts with free fatty acids to form soap, which inhibits biodiesel formation and complicates product separation (Talavari et al., 2021).

For feedstocks with high free fatty acid (FFA) content, acid-catalyzed esterification is recommended as a more suitable conversion route. In this reaction, free fatty acids react with methanol to form biodiesel (Baig and Ng, 2010). This approach can reduce production costs (Nisar et al., 2024) while achieving high conversion yields. Homogeneous acid catalysts are effective under relatively mild operating conditions and maintain activity even at elevated free fatty acid concentrations (Oyekunle et al., 2024). These catalysts generate additional hydrogen species that protonate the carboxylic groups of free fatty acids. Furthermore, acid catalysts exhibit stability in the presence of water during the esterification process (Valizadeh et al., 2024).

The esterification process, as shown in Figure 1, involves the conversion of free fatty acids and alcohol into fatty acid monoalkyl esters using a catalyst (Cerón Ferrusca et al., 2023). Sulfuric acid is commonly

employed as a homogeneous acid catalyst because of its high catalytic activity and stability. The efficiency of the esterification reaction is enhanced by the formation of high-density Brønsted acid sites, primarily associated with sulfonic acid groups (–SO_3H) (Valizadeh et al., 2024).

Recent waste management policies emphasize the reintegration of by-products and waste streams into production cycles. Although numerous studies have examined waste frying oils and animal fats for biodiesel production, relatively few investigations have focused on by-products of vegetable oil refinery plants, such as acid oil (Wei et al., 2023; Pali et al., 2023; Binhweel et al., 2023). In response to this research gap, the objective of the present study was to evaluate the use of acid oil for biodiesel production through a single-step acid-catalyzed esterification process. The effects of key reaction variables, including reaction time, methanol-to-free fatty acid molar ratio, and catalyst concentration, on the physicochemical properties, mass yield, free fatty acid content, and conversion yield of the produced biodiesel were systematically investigated.

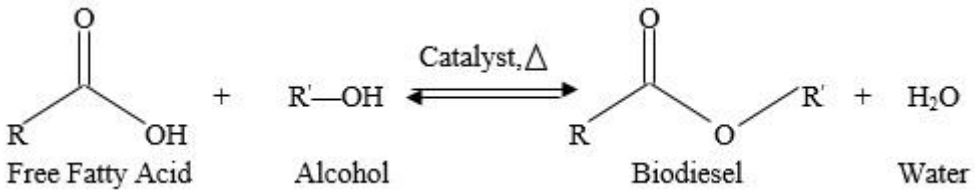

Figure 1

Esterification reaction of free fatty acids.

2. Materials and methods

2.1. Preparation of acid oil

Oil refinery waste containing acid oil with 64.00% free fatty acid content was obtained from Narges Shiraz Oil Company. To remove impurities, two centrifugation steps were performed at 50 °C for 15 minutes at 700 g. The supernatant layer was collected as acid oil, after which a hydrolysis reaction was carried out for 24 hours to convert acylglycerols into free fatty acids.

An equal volume of distilled water and acid oil was mixed with 2% concentrated sulfuric acid (98%) and 200 ppm tertiary butylhydroquinone. Sulfuric acid and tertiary butylhydroquinone were added to prevent soap formation and fatty acid oxidation, respectively (Suen and Chien, 1941; Beker et al., 2016). Upon completion of the hydrolysis reaction, centrifugation was performed again to separate distilled water from the hydrolyzed acid oil. The centrifugation conditions were 15 minutes, 700 g, and 50 °C. Finally, residual moisture in the hydrolyzed acid oil (HAO) was removed using a magnetic stirrer at 60 °C. The agitation speed and duration for moisture removal were 400 rpm and 1 hour, respectively.

2.2. HAO physicochemical properties

The free fatty acid content, purity, acid value, saponification value, iodine value, density, fatty acid composition, color attributes, and kinematic viscosity of the hydrolyzed acid oil were determined according to the method described by Dehghan et al., 2019.

To reduce the dark color of the hydrolyzed acid oil, 1 mL of sample was diluted with 9 mL of ethanol. The refractive index of the diluted samples was then measured in accordance with the AOCS Cc7-25 method (AOCS, 2000).

2.3. Acid-catalyzed esterification of HAO

Different levels of catalyst concentration (1%, 2%, and 3%, based on hydrolyzed acid oil weight), reaction time (5, 30, and 60 minutes), and methanol-to-hydrolyzed acid oil molar ratio (1:1, 5:1, and 10:1) were applied in the acid-catalyzed esterification experiments. The appropriate methanol-to-hydrolyzed acid oil molar ratio was determined based on the molecular weight of the hydrolyzed acid oil, calculated using the mass fraction (X_i) and molecular weight (MW_i) of the fatty acids present, as shown in Equation 1.

$$Molecular\ weight\ of\ HAO = \sum (MW_i \times X_i) \quad (1)$$

Hydrolyzed acid oil, methanol, and sulfuric acid, with a total mass of 30 g, were introduced into a flat-bottom flask. The flask was placed on a magnetic stirrer to heat and mix the reactants at a constant temperature of 60 °C and an agitation speed of 400 rpm. A condenser was connected to the flask during the reaction to prevent methanol evaporation.

Immediately after completion of the esterification reaction, the samples were cooled to room temperature. The biodiesel phase was separated using a separatory funnel. Residual impurities and catalyst were removed by washing the biodiesel with distilled water at 60 °C. Each sample was washed three to five times. The purified biodiesel was then transferred to an Erlenmeyer flask for drying. During drying, the temperature was maintained at 60 °C, and the magnetic stirrer operated at 250 rpm. The conversion yield was calculated according to Equation 2, and the mass yield was determined using Equation 3 (Zhang et al., 2012; Lin et al., 2014).

$$Conversion\ yield\ (\%) = \left(\frac{T_b - T_e}{T_b}\right) \times 100 \quad (2)$$

Where $T_b$represents the initial free fatty acid content (%) at the beginning of the reaction, and $T_e$represents the free fatty acid content (%) at the end of the reaction.

$$Mass\ yield\ (\%) = \left(\frac{Weight\ of\ produced\ biodiesel\ (g)}{Weight\ of\ HAO\ (g)}\right) \times 100 \quad (3)$$

2.4. Physical properties of biodiesel

Density, refractive index, color attributes, and kinematic viscosity of the produced biodiesel samples were evaluated as described in Section 2.2.

2.5. Evaluation of biodiesel under optimum condition

The purity and fatty acid composition of biodiesel under the optimum conditions were investigated as described in Section 2.2. The pour (D97), fire, flash (D92), and cloud (D2500) points of biodiesel were determined according to the ASTM Official Methods (American Society for Testing and Materials, 2013). The final yield was calculated using Equation 4. Energy consumption for the esterification reaction, washing, and drying steps was calculated using Equation 5. To monitor power usage, a wattmeter was installed at the entrance of each electrical circuit, and energy consumption was tracked using the developed software (Golmakani et al., 2024). Additionally, the specific energy consumption for the production of 1 kg of biodiesel was determined based on Equation 6 (Dehghan et al., 2019; Lin et al., 2014).

$$Final\ yield\ (\%) = \frac{Mass\ yield\ (\%)\ \times\ Purity\ of\ biodiesel(\%)}{100} \quad (4)$$

$$Energy\ consumption\ (kWh) = Time\ (h)\ \times Power\ consumption\ (kW) \quad (5)$$

$$Specific\ energy\ consumption\ (kWh/kg) = \frac{Total\ energy\ consumption\ (kWh)}{Weight\ of\ final\ biodiesel\ (kg)} \quad (6)$$

2.6. Statistical analysis

All experiments were conducted at least in triplicate, with each experiment repeated three times. The results are presented as mean values ± standard deviation. Analysis of variance (ANOVA) was performed using SAS (Statistical Analysis Software, version 9.1; SAS Institute Inc., Cary, NC). Duncan's Multiple Range Test was applied with a significance level of $P < 0.05$ to evaluate the differences between mean values.

3. Results and discussion

3.1. HAO physicochemical properties

As shown in Table 1, HAO contained 50.21% palmitic acid and 27.31% oleic acid, indicating that the purchased waste was primarily a by-product of the palm oil refining process. These results are consistent with the study by Hayan et al. (2011), who used palm oil sludge for esterification and reported 42.84% palmitic acid and 39.85% oleic acid in the sludge. The purity and free fatty acid content of HAO were 91.59% and 91.55%, respectively, confirming that the hydrolysis reaction was complete. These findings also align with previous studies by Wang et al. (2007) and Kulkarni et al. (2008), which reported that wastes and sludges contain impurities—such as unsaponifiable matter, inert materials, and phytosterols—that cannot be removed by centrifugation.

Table 1

The physicochemical properties of the hydrolyzed acid oil

Physicochemical property	Value
Free fatty acid (%)	91.55 ± 0.09**
Purity (%)	91.59 ± 0.32
Acid value (mg KOH/g)	182.28 ± 0.00
Saponification value (mg KOH/g)	207.78 ± 0.52
Refractive index	1.3737 ± 0.0002
Density (kg/m^3)	872.2863 ± 0.0671
Moisture and volatile matters (%)	0.05 ± 0.00
Iodine value	56.26 ± 0.53
Kinematic viscosity (mm^2/s; 40 ˚C)	41.309 ± 0.008
Color attribute	
*L**	26.60 ± 0.89
*a**	22.00 ± 2.00
*b**	48.00 ± 1.73

Physicochemical property	Value
Fatty acid composition (%)	
Lauric acid	0.48 ± 0.07
Myristic acid	1.66 ± 0.05
Palmitic acid	50.21 ± 0.35
Stearic acid	2.31 ± 0.08
Oleic acid	27.31 ± 0.11
Linoleic acid	16.93 ± 0.10
α-Linolenic acid	1.51 ± 0.03

** Mean ± standard deviation (n = 3).

3.2. Effect of different acid-catalyzed esterification variables on biodiesel yield

3.2.1. Methanol-to-HAO molar ratio

Table 2 presents the effect of different variables on the conversion yield, FFA content, and mass yield of biodiesel. As the methanol-to-HAO molar ratio increased, the conversion yield increased, while the FFA content decreased, as shown in Figures 2 and 3, respectively. The highest conversion yield (95.92%) was obtained at a molar ratio of 10:1. According to the stoichiometry of the reaction, 1 mol of methanol reacts with 1 mol of FFA to produce biodiesel and water; however, the reversibility of the reaction limits biodiesel production. To achieve higher efficiency, excess methanol is required to drive the acid-catalyzed esterification of FFA toward complete biodiesel formation (Gole and Gogate, 2013).

The trend observed in Table 2 and Figure 2 indicates that the conversion yield approaches a plateau, consistent with the equilibrium behavior of reversible esterification reactions. Optimizing the methanol-to-oil molar ratio is essential to reduce biodiesel production costs and maximize yield. High methanol concentrations increase the solubility of glycerol in the ester phase, complicating its separation. Moreover, excessive alcohol consumption introduces challenges related to processing, equipment costs, and energy requirements during methanol recovery (Yusuf et al., 2024). Therefore, a 10:1 molar ratio was selected as the optimum practical condition, as further increases are likely to yield only marginal improvements.

Similar to our results, Akinfalabi et al. (2020) investigated methanol-to-palm fatty acid distillate ratios ranging from 3:1 to 11:1 and reported that the optimum reaction condition was a molar ratio of 9:1 at 60 °C for 90 minutes, achieving a biodiesel yield of 95%. These findings support our conclusion that excess methanol beyond a certain threshold does not proportionally increase yield and may complicate downstream processing.

At 60 minutes and a catalyst concentration of 3%, the mass yields were 99.14%, 99.05%, and 96.63% for methanol-to-HAO molar ratios of 1:1, 5:1, and 10:1, respectively. As the methanol-to-HAO molar ratio increased from 1:1 to 10:1, additional washing steps were required until the separated water became clear. It has been noted that glycerol remains in the biodiesel phase at higher methanol-to-oil ratios (Yusuf et al., 2024). Excessive washing caused some biodiesel to be lost along with the water, leading to a decrease in mass yield as the molar ratio increased.

These findings are consistent with those of Phan et al., who reported that the yield of methyl esters increased with the methanol-to-oil molar ratio from 5:1 to 8:1, achieving an optimum yield of 90% at a ratio of 8:1 after approximately 90 minutes. However, they observed a decrease in yield when the methanol-to-oil ratio exceeded 9:1 under the same conditions (Phan and Phan, 2008).

3.2.2. Catalyst concentration

Increasing the catalyst concentration from 1% to 3% significantly enhanced the conversion yield and reduced the FFA content, while the mass yield remained unchanged, as shown in Table 2. These results suggest that the reaction approaches equilibrium, as higher catalyst concentrations beyond 3% would not substantially shift the final conversion. Therefore, 3% was selected as the optimum practical concentration. Several studies have recommended a catalyst concentration of 0.5–3% for the acid-catalyzed esterification of high-FFA feedstocks, with 3% sulfuric acid being commonly applied in biodiesel production (Litinas et al., 2020). Similarly, Peng et al. (2008) reported that the optimum acid catalyst concentration for biodiesel production was 3%.

The acid-catalyzed esterification reaction is reversible, and the catalyst (sulfuric acid) promotes the reaction. Increasing the catalyst concentration enhances the conversion yield; however, the final equilibrium of the reaction is not affected by the catalyst. Excess sulfuric acid beyond 3% does not improve efficiency. Moreover, using additional catalyst above the optimal concentration not only fails to increase yield but also complicates mixing of the reactants, products, and catalyst (Niu et al., 2018). Strong interactions among the various compounds can lead to higher byproduct formation, ultimately reducing biodiesel yield. Another concern is the corrosive nature of the catalyst at elevated concentrations, which can pose operational challenges (Sajjadi et al., 2014).

3.2.3. Reaction time

As the reaction time increased from 5 minutes to 60 minutes, the FFA content decreased, resulting in a corresponding increase in the conversion yield, as shown in Table 2. However, reaction time had no significant effect on the biodiesel mass yield. The most rapid increase in conversion occurred within the first 30 minutes, after which the reaction rate slowed, indicating that the system was approaching equilibrium. At 60 minutes, the conversion yield reached 95.92%, beyond which only negligible increases are expected.

Consistent with previous studies, the esterification reaction proceeded rapidly during the initial minutes, but after 30 minutes, the rate remained relatively constant (Figure 4) due to the reversible nature of the acid-catalyzed esterification reaction (Veillette et al., 2017; Leung et al., 2010). According to Litinas et al. (2020), biodiesel production can reach approximately 80% within the first minute of the reaction, while after 1 hour, the yield attains 93–98%. Our results are also in agreement with the study by Veljković et al. (2006), who reported that the esterification reaction reduced the FFA content from approximately 35% to less than 2% within 50 minutes at a methanol-to-tobacco seed oil molar ratio of 13:1.

Table 2

Effect of different variables on acid-catalyzed esterification of hydrolyzed acid oil.

Methanol-to-HAO molar ratio	Catalyst concentration (%)	Reaction time (min)		
		5	30	60
		Free fatty acid (%)		
1:1	1	$76.06 \pm 1.63^{a**}$	51.97 ± 0.79^{d}	37.05 ± 1.01^{f}
	2	70.49 ± 0.90^{b}	44.93 ± 1.04^{e}	$36.27 \pm 1.52f^{g}$
	3	72.38 ± 0.92^{b}	47.11 ± 1.46^{e}	30.94 ± 1.62^{i}

Methanol-to-HAO molar ratio	Catalyst concentration (%)	Reaction time (min)		
		5	**30**	**60**
5:1	1	55.52 ± 0.55^{c}	21.03 ± 0.73^{j}	16.57 ± 1.38^{k}
	2	38.02 ± 0.48^{f}	16.46 ± 0.93^{ek}	13.96 ± 0.48l
	3	33.163 ± 0.96^{hi}	13.65 ± 0.45^{l}	$11.50 \pm 1.39l^{m}$
10:1	1	56.74 ± 0.93^{c}	13.23 ± 2.95^{l}	9.46 ± 1.91^{mn}
	2	35.60 ± 0.85^{fg}	8.29 ± 0.90^{n}	3.74 ± 1.22^{o}
	3	34.26 ± 1.59^{gh}	6.97 ± 0.47^{n}	4.29 ± 1.01^{o}
		Conversion yield (%)		
1:1	1	16.97 ± 1.78^{o}	43.26 ± 0.86^{l}	57.92 ± 3.90^{f}
	2	22.05 ± 0.43^{n}	50.95 ± 1.14^{k}	60.40 ± 1.66^{ij}
	3	20.98 ± 1.01^{n}	48.57 ± 1.59^{k}	66.22 ± 1.77^{h}
5:1	1	39.38 ± 0.60^{m}	77.12 ± 0.10^{g}	81.96 ± 1.58^{f}
	2	58.50 ± 0.53^{j}	82.03 ± 1.02^{f}	84.76 ± 0.53^{ef}
	3	63.80 ± 1.04^{hi}	85.09 ± 0.49^{ef}	87.45 ± 1.52^{ed}
10:1	1	38.06 ± 1.03^{m}	85.70 ± 3.03^{e}	89.65 ± 2.12^{cd}
	2	61.13 ± 0.93^{ij}	90.95 ± 0.98^{c}	95.92 ± 1.33^{a}
	3	62.60 ± 1.73^{i}	92.39 ± 0.51^{bc}	95.32 ± 1.10^{ab}
		Mass yield (%)		
1:1	1	98.87 ± 0.25^{abc}	99.63 ± 0.52^{a}	99.25 ± 0.50^{a}
	2	98.84 ± 0.23^{abc}	99.47 ± 0.75^{a}	99.56 ± 0.14^{a}
	3	99.08 ± 0.05^{ab}	98.97 ± 0.93^{ab}	99.14 ± 1.21^{ab}
5:1	1	97.88 ± 0.18^{abcd}	98.23 ± 1.38^{abc}	98.58 ± 0.54^{abc}
	2	98.16 ± 1.10^{abc}	98.45 ± 0.72^{abc}	97.86 ± 1.36^{abcd}
	3	98.74 ± 0.43^{abc}	98.77 ± 1.75^{abc}	99.05 ± 1.34^{ab}
10:1	1	95.86 ± 0.71^{de}	95.16 ± 0.96^{e}	95.15 ± 1.15^{e}
	2	96.91 ± 0.03^{bcde}	95.43 ± 0.82^{e}	95.17 ± 1.47^{e}
	3	95.47 ± 1.46^{e}	95.78 ± 1.50^{de}	96.63 ± 0.96^{cde}

** Mean ± standard deviation ($n = 3$). For each response, means with different superscript letters are significantly different ($P < 0.05$).

3.3. Biodiesel physical properties

With increasing catalyst concentration, methanol-to-HAO molar ratio, and reaction time, the kinematic viscosity of the biodiesel samples decreased significantly, as shown in Table 3 and Figure 5. The conversion yield (y) exhibited a negative correlation with kinematic viscosity (x), expressed as $y = -6.208x + 125.8$ ($R^2 = 0.95$). After 60 minutes of reaction time, at a methanol-to-HAO molar ratio of 10:1 and 3% catalyst concentration, the kinematic viscosity of biodiesel decreased to 6.005 mm²/s, which falls within the acceptable ASTM standard range of 1.9–6.0 mm²/s (Mishra and Goswami, 2018).

The molecular weight of vegetable oils ranges from 600 to 900, which is three times or more higher than that of diesel fuel. Acid-catalyzed esterification alters the molecular structure of vegetable oils,

reducing the molecular weight of the resulting methyl esters to approximately one-third of that of the original oils. Consequently, the viscosity decreases, enabling the produced biodiesel to serve as an alternative diesel fuel (Kulkarni et al., 2008; Srivastava and Prasad, 2000). Viscosity is a critical parameter for the operation of injection systems and the atomization of fuel sprays. Elevated viscosity can impede fuel flow, potentially compromising the mechanical integrity of injection pump drive systems (Atabani et al., 2012). High biodiesel viscosity also increases the energy required to pump the fuel, which may result in engine problems (Alptekin and Canakci, 2008; Mohemmadi et al., 2019). These issues are particularly pronounced in cold weather, where viscosity rises at low temperatures (Alptekin and Canakci, 2008). Conversely, lower viscosity improves the flow of biodiesel into fuel filters over time, alleviating flow resistance (Osorio-González et al., 2020).

According to Table 3 and Figure 6, the density of biodiesel samples increased with increasing catalyst concentration, methanol-to-oil ratio, and reaction time. A positive correlation was observed between conversion yield (y) and density (x), expressed as $y = 4.774x - 4151$ ($R^2 = 0.98$). Our density results are in good agreement with the study by Alptekin and Canakci (2008), who reported that biodiesel density typically ranges from 860 to 900 kg/m³. Density is a key fuel property, influencing several aspects of engine performance, including cetane number and heating value (Alptekin and Canakci, 2008). Additionally, fuel injection systems measure volume rather than mass, so changes in density affect the actual mass of fuel injected, thereby influencing engine output power (Bahadur et al., 1995). Biodiesel density also impacts the performance of compression-ignition engines and overall engine efficiency; higher density can lead to incomplete vaporization and combustion of the injected fuel, reducing engine efficiency (Kosuru et al., 2024).

The refractive index is an important physical property of biodiesel that can be used to monitor the progress of the esterification process (Dehghan et al., 2019) and to assess the degree of ester saturation. It also provides insights into the presence of microemulsions during biodiesel production, facilitating fuel characterization and the modeling of thermodynamic properties (Cunha et al., 2017). The refractive index values of the produced biodiesel samples are presented in Table 3. Although all values fell within a narrow range (1.3719–1.3738), which is typical for biodiesel, statistical analysis revealed a consistent, though slight, decreasing trend with increasing reaction time, sulfuric acid concentration, and methanol-to-HAO ratio. The highest refractive index was observed under the mildest reaction conditions (1:1 ratio, 1% catalyst, 5 minutes), while the lowest value was obtained under the most severe conditions (10:1 ratio, 3% catalyst, 60 minutes). This slight decrease is likely due to the increased conversion of FFAs into esters, as esters exhibit marginally different refractive properties compared to the parent acids. A strong negative correlation was observed between conversion yield (y) and refractive index (x), expressed as $y = -4.346 \times 10^4 x + 5.972 \times 10^4$ ($R^2 = 0.98$), confirming that a decreasing refractive index corresponds to FFA conversion into biodiesel.

The color attributes of HAO ($L^* = 26.60$, $a^* = 22.00$, $b^* = 48.00$) indicated a dark brown appearance (Table 1). HAO contains FFAs, mineral acids, sterols, and phospholipids, which contribute to its dark brown color (Kulkarni et al., 2008). With increasing methanol-to-HAO molar ratio, catalyst concentration, and reaction time during acid-catalyzed esterification, L^* values increased, while a^* and b^* values decreased significantly (Table 4). These results demonstrate that esterification substantially reduces the darkness of HAO. Although color is not a primary indicator of biodiesel quality, an increase in L^* values reflects successful biodiesel production (Bello, 2016).

Table 3

Effect of acid-catalyzed esterification of hydrolyzed acid oil on the physical properties of biodiesel

Methanol-to-HAO molar ratio	Catalyst concentration (%)	Reaction time (min)		
		5	30	60
		Kinematic viscosity (mm^2/s)		
1:1	1	$18.533 \pm 0.003^{a**}$	12.046 ± 0.002^{f}	9.951 ± 0.027^{l}
	2	18.109 ± 0.007^{b}	11.968 ± 0.004^{g}	9.003 ± 0.001^{n}
	3	17.907 ± 0.004^{c}	11.011 ± 0.002^{h}	8.905 ± 0.002^{o}
5:1	1	13.324 ± 0.015^{d}	7.958 ± 0.001^{p}	6.844 ± 0.001^{t}
	2	10.360 ± 0.014^{i}	7.077 ± 0.003^{q}	6.622 ± 0.003^{u}
	3	10.204 ± 0.007^{k}	7.017 ± 0.007^{r}	6.380 ± 0.006^{v}
10:1	1	12.898 ± 0.011^{e}	6.897 ± 0.005^{s}	6.364 ± 0.003^{vw}
	2	10.277 ± 0.003^{j}	6.347 ± 0.012^{w}	6.265 ± 0.003^{x}
	3	9.421 ± 0.001^{m}	6.273 ± 0.010^{x}	6.005 ± 0.004^{y}
		Density (kg/m^3)		
1:1	1	873.0923 ± 0.0598^{r}	878.4131 ± 0.0006^{o}	882.8386 ± 0.0087^{k}
	2	874.3364 ± 0.0215^{q}	880.0065 ± 0.0074^{m}	882.8794 ± 0.0059^{k}
	3	874.2774 ± 0.0083^{q}	879.0194 ± 0.0081^{n}	884.0100 ± 0.0156^{i}
5:1	1	877.0196 ± 0.0055^{p}	885.3297 ± 0.0006^{h}	885.6004 ± 0.6974^{h}
	2	882.3473 ± 0.0209^{l}	886.0475 ± 0.0653^{g}	886.4530 ± 0.0257^{f}
	3	883.4865 ± 0.0218^{j}	886.6665 ± 0.0216^{ef}	887.0672 ± 0.0767^{e}
10:1	1	877.1269 ± 0.0074^{p}	887.0036 ± 0.0026^{e}	888.4134 ± 0.0002^{d}
	2	882.3865 ± 0.0067^{l}	888.4196 ± 0.0024^{d}	889.9702 ± 0.0241^{b}
	3	883.5197 ± 0.0105^{j}	888.8614 ± 0.0202^{c}	890.4759 ± 0.7343^{a}
		Refractive index		
1:1	1	1.3738 ± 0.0000^{a}	1.3730 ± 0.0001^{c}	1.3728 ± 0.0001^{d}
	2	1.3737 ± 0.0001^{a}	1.3728 ± 0.0002^{d}	1.3728 ± 0.0001^{d}
	3	1.3737 ± 0.0001^{a}	1.3728 ± 0.0001^{d}	1.3726 ± 0.0000^{de}
5:1	1	1.3732 ± 0.0001^{b}	1.3725 ± 0.0001^{e}	1.3723 ± 0.0001^{f}
	2	1.3728 ± 0.0001^{d}	1.3722 ± 0.0001^{f}	1.3721 ± 0.0001^{fg}
	3	1.3726 ± 0.0001^{d}	1.3722 ± 0.0001^{f}	1.3721 ± 0.0001^{fg}

Methanol-to-HAO molar ratio	Catalyst concentration (%)	Reaction time (min)		
		5	**30**	**60**
10:1	1	1.3732 ± 0.0001^{b}	1.3722 ± 0.0001^{fg}	1.3721 ± 0.0001^{fg}
	2	1.3727 ± 0.0001^{d}	1.3721 ± 0.0001^{gh}	1.3720 ± 0.0001^{gh}
	3	1.3727 ± 0.0001^{d}	1.3720 ± 0.0001^{gh}	1.3719 ± 0.0002^{h}

** Mean ± standard deviation ($n = 3$). For each response, means with different superscript letters are significantly different ($P < 0.05$).

Table 4

Effect of acid-catalyzed esterification of hydrolyzed acid oil on the color attributes of biodiesel

Methanol-to-HAO molar ratio	Catalyst concentration (%)	Reaction time (min)		
		5	**30**	**60**
			L*	
1:1	1	$28.00 \pm 1.00^{k**}$	40.33 ± 1.53^{ghij}	40.00 ± 1.00^{hij}
	2	29.67 ± 0.58^{k}	42.67 ± 1.15^{ef}	40.33 ± 1.15^{ghij}
	3	28.67 ± 0.58^{k}	41.33 ± 1.53^{fghi}	39.00 ± 1.00^{j}
5:1	1	39.00 ± 0.82^{j}	44.33 ± 2.081^{e}	47.33 ± 0.58^{cd}
	2	41.00 ± 1.00^{fghij}	47.00 ± 1.00^{d}	47.67 ± 0.58^{bcd}
	3	41.67 ± 1.53^{fgh}	47.67 ± 0.58^{bcd}	48.67 ± 1.15^{abcd}
10:1	1	39.33 ± 0.58^{ij}	48.33 ± 1.53^{abcd}	49.33 ± 0.58^{abc}
	2	41.00 ± 1.00^{fghij}	49.67 ± 1.15^{ab}	50.33 ± 0.58^{a}
	3	42.33 ± 0.58^{fg}	49.67 ± 0.58^{ab}	50.33 ± 1.53^{a}
			a*	
1:1	1	20.00 ± 1.00^{a}	17.67 ± 0.58^{b}	16.67 ± 0.58^{bcd}
	2	19.33 ± 1.53^{a}	17.00 ± 1.00^{bc}	16.33 ± 0.58^{bcde}
	3	20.33 ± 1.15^{a}	17.33 ± 0.58^{b}	16.67 ± 0.58^{bcd}
5:1	1	17.33 ± 0.47^{b}	15.33 ± 0.58^{defg}	15.33 ± 0.58^{defg}
	2	16.33 ± 0.58^{bcde}	15.67 ± 0.58^{cdef}	15.00 ± 0.00^{efgh}
	3	16.50 ± 0.71^{bcd}	15.33 ± 0.58^{defg}	14.00 ± 1.00^{ghi}
10:1	1	17.33 ± 0.58^{b}	15.67 ± 0.58^{cdef}	14.67 ± 0.58^{fgh}
	2	16.33 ± 0.58^{bcde}	14.00 ± 1.00^{ghi}	13.67 ± 0.58^{hi}
	3	16.67 ± 0.58^{bcd}	13.67 ± 0.58^{hi}	13.00 ± 1.00^{i}
			b*	
1:1	1	47.67 ± 0.58^{a}	44.33 ± 0.58^{bc}	42.67 ± 0.58^{de}
	2	47.33 ± 0.58^{a}	43.67 ± 0.58^{cd}	41.00 ± 1.41^{f}
	3	47.00 ± 0.00^{a}	44.33 ± 0.58^{bc}	41.50 ± 0.71^{ef}

Methanol-to-HAO molar ratio	Catalyst concentration (%)	Reaction time (min)		
		5	30	60
5:1	1	45.33 ± 0.94[b]	39.67 ± 0.58[g]	39.50 ± 0.71[g]
	2	42.33 ± 0.58[e]	38.67 ± 0.58[gh]	38.67 ± 0.58[gh]
	3	41.00 ± 1.00[f]	38.67 ± 0.58[gh]	37.67 ± 0.58[h]
10:1	1	45.33 ± 0.94[b]	38.67 ± 0.58[gh]	37.50 ± 0.71[h]
	2	42.33 ± 0.58[e]	37.50 ± 0.71[h]	37.67 ± 0.58[h]
	3	42.33 ± 0.58[e]	37.50 ± 0.71[h]	37.50 ± 0.71[h]

[**] Mean ± standard deviation ($n = 3$). For each response, means with different superscript letters are significantly different ($P < 0.05$).

3.4. Properties of biodiesel under optimum condition

According to Tables 2–4, the FFA content, conversion yield, mass yield, kinematic viscosity, density, refractive index, and color parameters (L^*, a^*, b^*) of biodiesel produced under the optimum practical conditions (3% catalyst concentration, methanol-to-HAO molar ratio of 10:1, and 60 minutes reaction time) were 4.29%, 95.32%, 96.63%, 6.005 mm²/s, 890.476 kg/m³, 1.3719, 50.33, 13.00, and 37.50, respectively. Table 5 presents additional effects of acid-catalyzed esterification of HAO on biodiesel production under the same conditions. The energy consumption and specific energy consumption for the acid-catalyzed esterification reaction of HAO were 0.070 kWh and 6.642 kWh/kg, respectively.

Based on the ASTM Official Method D6751, which specifies a minimum biodiesel flash point of 130 °C, the biodiesel produced in this study met the required specification. The final yield and purity of biodiesel were 84.25% and 87.18%, respectively, confirming that HAO is a promising feedstock for biodiesel production. These findings are consistent with those reported by Dehghan et al. (2019), who compared microwave-assisted esterification with the conventional magnetic stirrer method. In their study, the magnetic stirrer method yielded biodiesel with a conversion of 77.28% and a purity of 87.17%.

Table 5

Effect of acid-catalyzed esterification of hydrolyzed acid oil on selected properties of biodiesel under optimum practical conditions*

Parameter	Value
Final yield (%)	84.25 ± 0.55[**]
Purity (%)	87.18 ± 0.10
Heating property (°C)	
Flash point	169.0 ± 1.4
Fire point	187.0 ± 4.2
Cloud point	4.5 ± 0.6
Pour point	–1.7 ± 0.6
Fatty acid profile (%)	
Lauric acid	0.64 ± 0.08
Myristic acid	1.65 ± 0.00

Parameter	Value
Palmitic acid	50.67 ± 0.28
Stearic acid	2.01 ± 0.01
Oleic acid	26.36 ± 0.15
Linoleic acid	17.53 ± 0.10
α-Linolenic acid	1.41 ± 0.00
Energy consumption	
Esterification reaction (kWh)	0.070
Washing and drying (kWh)	0.018
Total (kWh)	0.088
Specific energy consumption (kWh/kg)	6.642

* Optimum practical condition was a catalyst concentration of 3%, a methanol-to-hydrolyzed acid oil molar ratio of 10:1, and a reaction time of 60 min.

** Mean ± standard deviation ($n = 3$). For each response, means with different superscript letters are significantly different ($P < 0.05$).

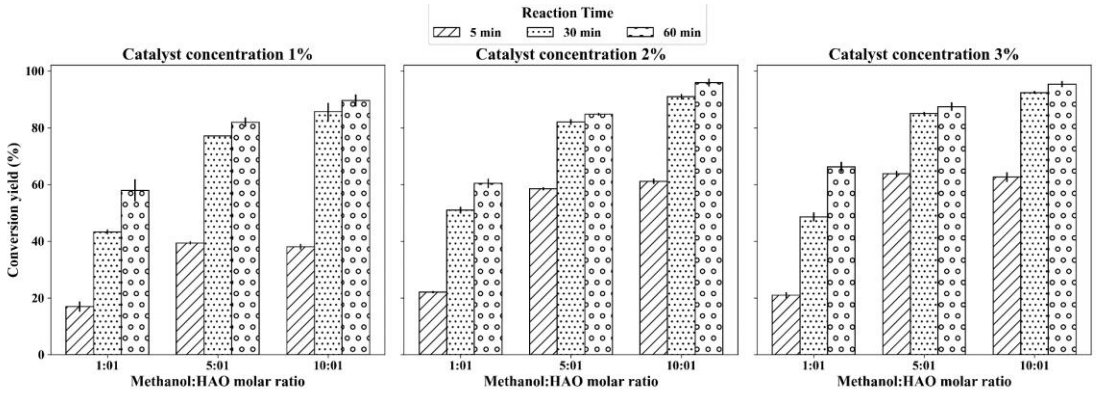

Figure 2

Effect of the methanol-to-HAO molar ratio on the conversion yield (%) of hydrolyzed acid oil

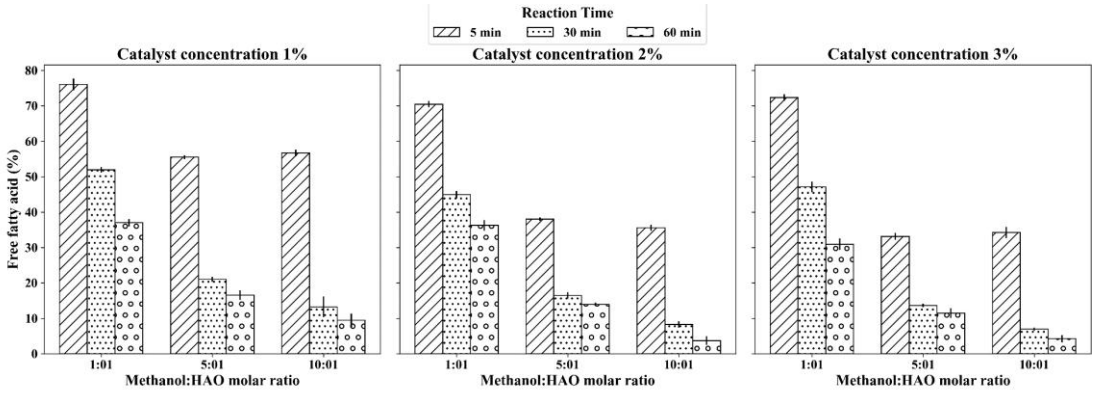

Figure 3

Effect of the methanol-to-HAO molar ratio on the free fatty acid content (%) of hydrolyzed acid oil

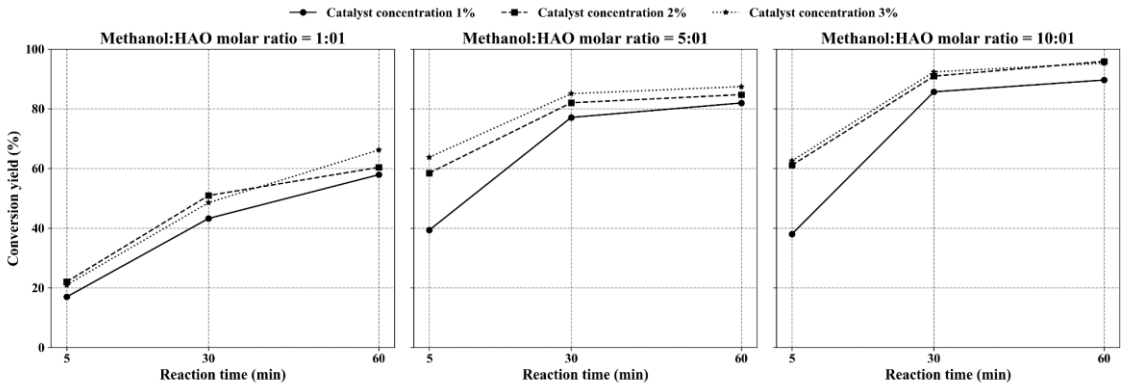

Figure 4

Effect of reaction time on the conversion yield (%) of hydrolyzed acid oil

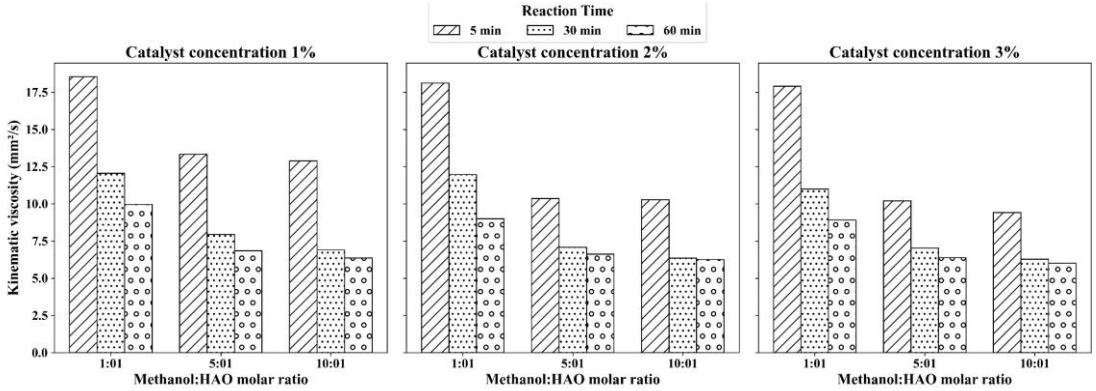

Figure 5

Effect of acid-catalyzed esterification of hydrolyzed acid oil on the kinematic viscosity of biodiesel

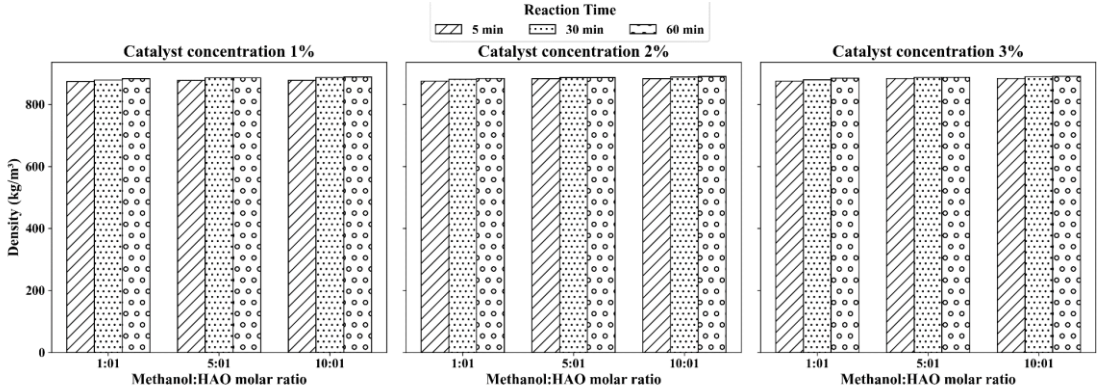

Figure 6

Effect of acid-catalyzed esterification of hydrolyzed acid oil on the density of biodiesel

4. Conclusions

Oil plant waste containing acid oil (AO) poses environmental hazards if it is not utilized for beneficial purposes. However, AO represents an inexpensive feedstock for biodiesel production. Unlike restaurant waste cooking or frying oils, AO does not require collection from multiple locations, as it is generated in situ as a by-product of the alkali refining process in oil plants. Utilizing AO for biodiesel production also reduces transportation costs, providing an economic advantage.

The aim of this study was to convert free fatty acids in hydrolyzed acid oil into biodiesel via acid-catalyzed esterification under varying methanol-to-HAO molar ratios, catalyst concentrations, and reaction times. Conversion yield increased with all three variables, reaching a maximum of 95.9% at a methanol-to-HAO ratio of 10:1, 3% catalyst concentration, and 60 minutes reaction time. These conditions represent practical optima, as the reaction trends indicated an asymptotic approach to equilibrium. Further increases in these variables would likely yield negligible improvements while increasing processing costs, separation difficulties, and equipment corrosion risks. Conversion yield exhibited negative correlations with kinematic viscosity and refractive index, and a positive correlation with density. Biodiesel samples also demonstrated higher brightness (L^*) compared to HAO, confirming quality improvements through esterification.

For industrial-scale applications, several challenges must be addressed, including catalyst recovery, methanol recycling, equipment durability, and efficient purification systems. Acid catalysts are corrosive and require resistant equipment, while recovery of catalyst and methanol is critical for cost reduction and environmental sustainability. Process intensification strategies, such as employing multiple continuous stirred-tank reactors in series and counterflow water-washing systems, can enhance process efficiency. The quality of biodiesel must comply with specifications outlined in EN 14214 and ASTM D6751. Key parameters, including sulfated ash, copper strip corrosion, cetane number, carbon residue, and oxidation stability, are essential for evaluating fuel performance. Under the optimal conditions identified in this study, the biodiesel quality is comparable to various types of biodiesel reported in the literature and to the properties of petroleum-derived diesel. Given the existing knowledge gaps, we recommend conducting comprehensive studies in the future to further optimize production and industrial application.

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Nomenclatures

Abbreviations	
ANOVA	Analysis of Variance
AO	Acid oil
ASTM	American Society for Testing and Materials
FAMEs	Fatty acid monoalkyl esters
FFA	Free fatty acids
HAO	Hydrolyzed acid oil
SAS	Statistical Analysis Software
TBHQ	Tertiary butylhydroquinone
Units and Symbols	
°C	Degree Celsius
g	Gram
h	Hour(s)
kg	Kilogram
kg/m³	Kilogram per cubic meter (unit for density)
kWh	Kilowatt hour

kW	Kilowatt
mg	Milligram
mg KOH/g	Milligrams of potassium hydroxide per gram of sample
min	Minute(s)
mL	Milliliter(s)
mm^2/s	Square millimeter per second (kinematic viscosity)
mol	Mole
n	Number of replicates
P	Probability value (statistical significance)
rpm	Revolutions per minute

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