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Optimizing Operating Conditions for Maximum Biodiesel Production from Salmon Fish Oil

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In Loving Memory of Late Professor Doctor ""Mohamed Refaat Hussein Mahran""

Abstract

Petroleum-based diesel is a significant contributor to greenhouse gas emissions, including carbon oxides, methane, and other greenhouse gases. The depletion of fossil fuel reserves, coupled with their increasing prices, has prompted the global oil industry to seek alternative sources. Biodiesel has emerged as a clean alternative fuel and a means to reduce pollutants from combustion equipment. Fish oil, obtained from fish processing waste, is a sustainable, abundant, and cost-effective raw material for biodiesel production. In this study, salmon fish waste oil was utilized as the raw material for biodiesel production. The oil underwent transesterification using methanol and sodium hydroxide as an alkaline catalyst to facilitate the conversion of oil to methyl ester. The study focused on four process parameters: reaction time, reaction temperature, and the amounts of methanol and catalyst. The results demonstrated that the highest mass yield of fatty acid methyl esters (FAME) was accomplished at reaction temperature of 100 °C, 20 wt.% methanol concentration with 0.75 wt. % NaOH concentration for 30 minutes. A comparison was made between the physicochemical properties of the produced biodiesel and ASTM biodiesel standards, indicating the high quality of the optimized methyl ester derived from salmon fish waste oil.

Keywords: Alkali homogeneous catalyst, Environmental pollution issue, Oil fish waste, Transesterification reaction.

1. Introduction

Overreliance on fossil fuels drains the reserves and poisons the environment. Therefore, seeking a sustainable future, researchers are dedicating their efforts to developing and integrating renewable energy solutions [1][2]. Bio-based energy or biofuel has become significantly crucial within the spectrum of renewable energy sources (including solar, wind, water, and nuclear energy) owing to its utilization as a fuel and in the production of additional value-added chemicals [3][4]. As concerns about fossil fuel depletion and environmental pollution escalate, biodiesel has entered the scene as a compelling answer, offering a renewable and less harmful fuel option. Biodiesel's near-identical properties to diesel allow for effortless blending, making it a convenient and effective way to reduce our reliance on fossil fuels [5][6]. Abundant efforts have been made to investigate potential resources containing substantial oil/lipids which could also lead to economic production of biodiesel. The fact that these resources do not compete with food supplies has drawn a lot of attention to microalgae, waste cooking oil (WCO), and animal and fish fats and oil waste [7][8][9].

Currently, Fish waste is becoming more widely acknowledged as a useful for biodiesel production. This is because numerous fish components, including the head, spine, skin, stomach, and tail, are typically discarded after consumption [10]. Most fish, accounting for over 60-70%, is utilized by humans and the production of fishmeal and fish oil for medicinal applications. However, this extensive use of fish generates a significant amount of waste, which poses a severe environmental threat if not properly managed. It is crucial to treat and dispose of fish waste responsibly to minimize potential harm to human health and the environment [11][12].

Andersen and Weinbach (2010) highlighted the potential of utilizing waste triglycerides derived from the poultry and fishing industries as a significant contributor to global biodiesel production [13]. Their research on marine fish oil revealed that the optimal conditions for maximizing FAME yield were a reaction temperature of 60°C, a reaction time of 180

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minutes, and a methanol-to-oil molar ratio of 15:1, resulting in yields of 80.16%, 80.03%, and 80.39%, respectively. Kara et al. (2018) conducted research in Morocco, exploring the conversion of waste fish oil into biodiesel employing a two-stage acid-base esterification-transesterification process. This methodology sought to minimize the high free fatty acid (FFA) content in fish oil following a rapid purification technique. The outcomes obtained through GC/MS analysis confirmed the presence of substantial amounts of crucial biodiesel components, including palmitic acid, oleic acid, and linolenic acid [14]. Aditya et al. (2018) extracted fats from fish waste and subjected it to saponification with sodium hydroxide to lower the fatty acid content. Utilizing approximately 1% KOH at 60°C, a transesterification reaction resulted in a remarkable yield of biodiesel, which was 92%[15] [16]. In Egypt, the fish processing industry yields a substantial amount of salmon fish oil as a by-product. Currently, a significant portion of these oils are disposed of in an inefficient and environmentally detrimental manner. Consequently, there is a consideration to address this issue by safely disposing of the oils, recycling them, and converting them into biofuel. Considering these considerations, this study aimed to evaluate the feasibility of biodiesel production from fish oil waste using sodium hydroxide as a catalyst. The investigation focused on assessing the impact of reaction temperature, methanol, and catalyst concentrations, as well as reaction time on the mass yield of biodiesel. Furthermore, the resulting biodiesel derived from fish oil waste was subjected to a characterization analysis and compared to standard biodiesel and diesel samples.

2. Material and methods

2.1. Materials

This fish oil was obtained from Waste Industries salmon fish in Egypt and had the following characteristics: an acid value of 5.6 mg KOH/g oil, and a viscosity of 31.76 (mm^2/s) which calculated according to ASTM D664 and ASTM D94, respectively. Methanol (99.8%) and sodium hydroxide (99%) were procured from Sigma Aldrich. Gas chromatography, an analytical technique that separates and quantifies compounds within a sample, was employed to analyze the raw waste fish oil, providing detailed insight into its chemical composition and the specific compounds present within the oil.

2.2. Production process

The most suitable method for producing biodiesel involves the transesterification reaction, as illustrated in Figure 1, using an alcohol and a catalyst. Biodiesel production from non-edible oils utilizes both one-step and two-step procedures, employing both homogeneous and heterogeneous catalysts. This process is essential for transforming non-edible oils, such as those derived from fish waste, into biodiesel, offering a sustainable and environmentally friendly alternative to traditional fossil fuels [17]. The selection between base and acid catalysts in one-step processes depends on the non-edible oil's FFA concentration or acid value. The traditional method of biodiesel production involves usage of homogeneous catalyst but requires a larger amount of water for purification [18]. In the current study, sodium methoxide was employed as the catalyst. Transesterification with a base catalyst occurs 4000 times faster than with an acid catalyst. However, the base catalyst has a higher tendency to generate soap in the presence of FFA and water [19].

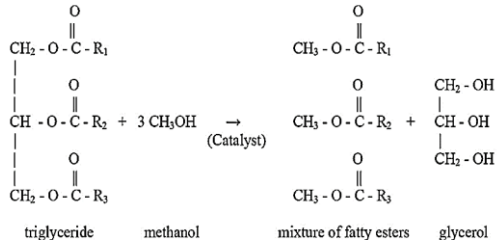

Figure 1: Transesterification reaction of triglycerides

The experiments were carried out using a 250 cm^3 round glass reactor positioned on a magnetic stirrer with a hot plate, operating under atmospheric pressure. Initially, a 100 ml portion of waste fish oil (WFO) was introduced into the reactor and preheated. Following this, methanol and the catalyst NaOH were added to the preheated oil. The study focused on exploring various factors to establish the optimal reaction conditions, including reaction temperature, reaction time, catalyst concentration, and methanol concentration. These parameters were crucial in determining the efficiency and effectiveness of the transesterification process for converting waste fish oil into biodiesel.

After the reaction concluded, the mixture was moved to a separating funnel to discreet the biodiesel phase from the glycerol phase. The biodiesel phase underwent several washes with warm water until the wash water became colorless. To eliminate any remaining water, the biodiesel was dried on a stirring hot plate at a temperature of 110 °C. The biodiesel mass yield was calculated by Equation (1) [20][21][7].

$$\text{Yield}, \% = \frac{\text{mass of biodiesel,g}}{\text{mass of oi,g}} \qquad \text{eq. (1)}$$

2.3. Characterization of the optimum WFO biodiesel sample

Comprehensive physicochemical property tests were conducted on the optimal sample of waste fish oil (WFO) biodiesel. The properties examined included kinematic viscosity, density, flash point, and pour point. These tests aimed to assess the suitability of the biodiesel sample for use as an alternative to diesel fuel. A detailed comparison was made between the properties of the biodiesel and traditional diesel fuel.

3. Results and discussion

3.1. GC- chromatography technique for raw waste fish oil

Gas chromatography is a widely used analytical technique that separates and analyzes compounds within a sample. It is particularly useful for determining the chemical composition for each oil. In this case, WFO sample was analyzed using gas chromatography as shown in figure 2 to identify and quantify its various chemical components. This process helps in understanding the composition of the oils and is essential for optimizing the conditions required for studying temperature, reaction time, methanol and catalyst concentration needed for the transesterification reaction in biodiesel production.

Table 1 provides detailed insights into the levels of various fatty acids present within the sample. The content levels of Myristic acid (C14:0), Linolenic (C18:3), Linoleic (C18:2), Palmitic (C16:0), Docosahexaenoic (C22:6), Eicosapentaenoic acid (C20:5), Palmitoleic (C16:1), and Oleic (C18:1) were measured at 7.85, 9.98, 11.4, 10.213, 13.15, 13.79, 14.8, and 24.35, respectively. These findings align with previous reports [22] [23], confirming the presence of these compounds in fish oils. This data underscores the composition of fatty acids within the waste fish oil sample, providing valuable insights for the biodiesel production process

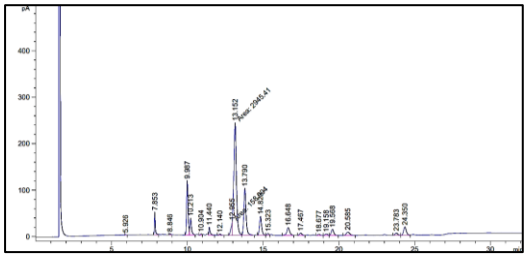

Figure (2) GC chromatography for raw waste fish oil

Table (1) Fatty acid composition of waste fish oil

Fatty acid	Carbon Number	Retention time
Myristic acid	C14:0	7.85
Linolenic	C18:3	9.98
Linoleic	C18:2	11.4
Palmitic	C16:0	10.213
Docosahexaenoic	C22:6	13.15
Eicosapentaenoic acid	C20:5	13.79
Palmitoleic	C16:1	14.8
Oleic acid	C18:1	24.35

3.2. influence of reaction temperature on biodiesel yield

The result of the temperature impact on the biodiesel mass yield is shown in figure 3. It investigated the effect of different temperatures (60 to 130°C) by step 10 with varying methanol concentrations (10%, 15%, 20%) on transesterification using a 1 wt.% NaOH catalyst for 1 hour. At the beginning, the mass yield reduced at low temperature because of low kinetic energy of reaction molecules and then increasing when increased temperature and finally decreased. Elevating the reaction temperature results in a higher mass yield due to the heightened energy of the molecules participating in the reaction. This increased energy facilitates improved compatibility between the polar alcohol and the non-polar oil, accelerating the reaction kinetics and leading to faster reactions. The temperature plays a crucial role in enhancing the efficiency of the transesterification process, ultimately impacting the yield and conversion rates of biodiesel production from waste fish oil [8][24]. However, at temperatures exceeding 100 °C, the mass yield decreased, potentially due to alcohol evaporation at higher temperatures [25][26]. In addition, it was observed that increasing methanol concentration increased the biodiesel mass yield. At 100^{o}C and 20% wt. methanol, the mass yield increased with 7.1% of the mass yield at 10% wt. methanol. Results showed that the optimum mass yield was at 100^{o}C at 20% wt. methanol.

3.3. Influence of catalyst concentration on biodiesel yield

Figure 4 illustrates the impact of varying catalyst amounts on the mass yield of biodiesel. The impact of NaOH catalyst concentration (0.25 to 1.25) wt.% by step 0.25 was examined with varying methanol concentrations (10%, 15%, 20%) on transesterification at an optimal temperature of 100 °C for 1 hour. Initially, the

mass yield was 52% at 0.25% NaOH concentration and increased with increasing catalyst wt.% to 0.75% due to increasing active sites presence in the transesterification reaction. Finally, a sharp decline in mass yield was observed at 1% wt. NaOH due to the formation of soap [27]. Furthermore, increasing methanol concentration increased the biodiesel mass yield. It was observed that at 0.75% wt. NaOH and 20% wt. methanol, the biodiesel mass yield increased with 9.7% of the mass yield at 10% methanol. From an economic perspective, the costs associated with a significant amount of catalyst make it undesirable. Consequently, the findings indicated that the best mass yield occurred at a concentration of 0.75% weight with 20% weight methanol [7].

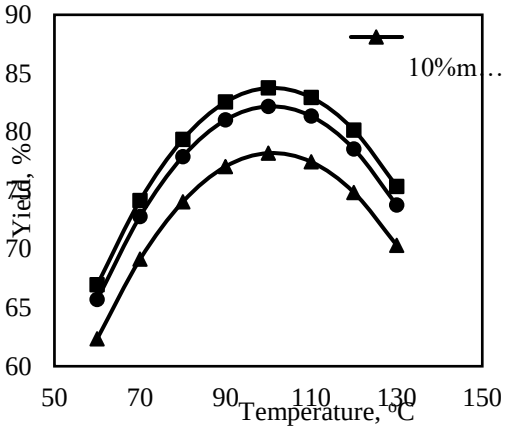

Figure 3: Impact of temperature on biodiesel mass yield

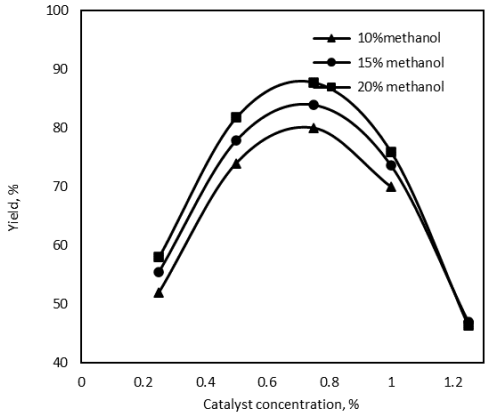

Figure 4: influence of catalyst concentration on biodiesel yield

3.4. Influence of reaction time on biodiesel yield

Figure 5 illustrates the impact of reaction time on the biodiesel mass yield. Different reaction time (15 to 90) mins by step 15 were investigated with varying methanol concentrations (10%, 15%, 20%) were investigated on transesterification at the optimal temperature of 100 °C and 0.75% wt. NaOH. It was observed that the reaction proceeded rapidly, with a noticeable increase in the mass yield of fatty acid esters once the reaction commenced. At the first 30 minutes of the reaction, the mass yield reached its maximum. However, as the reaction time increased, the mass yield of biodiesel decreased. This can be attributed to the evaporation of alcohol and the reversible nature of the transesterification reaction, which led to a decrease in the content of FAME. An increase in the amount of methanol resulted in an augmented mass yield due to an increase of molecules which react with oil particles which make the reaction complete. At 20% wt. methanol for 30 min. time reaction, the mass yield increased with 50% of the mass yield at 10% methanol

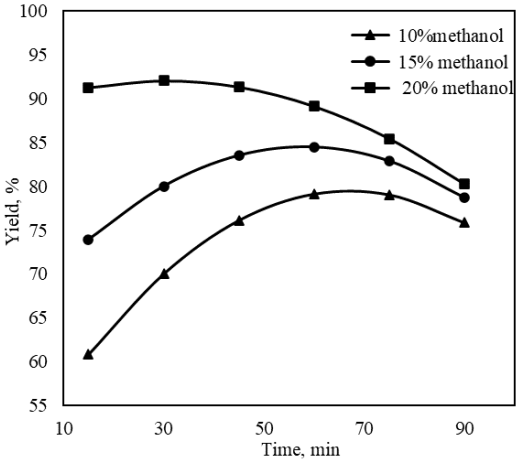

Figure 5: the impact of reaction time on biodiesel mass yield

3.5. Analysis of produced biodiesel

Pure biodiesel was synthesized under optimal conditions, with a temperature of 100 °C, 20% wt. methanol, and 0.75 wt.% NaOH catalyst for a reaction time of 30 minutes. The resulting biodiesel underwent comprehensive analysis, as outlined in Table 1 [20][28]. Key attributes of the biodiesel, including density, kinematic viscosity, acid value, pour point, and flash point, were determined in accordance with the appropriate ASTM guidelines [29][30][31]. These values were then compared to the properties of diesel fuel. The findings suggest that the generated biodiesel demonstrates comparable qualities to commercially available biodiesel and is appropriate for utilization in diesel engines. The obtained values demonstrate promising compliance with engine combustion standards, suggesting the potential of this biodiesel to meet the requirements for efficient engine performance.

Table 1: Comparison of physical properties between raw waste fish oil, commercial diesel, produced biodiesel and its standard.

Parameter	WFO	Commercial diesel fuel (D100)	Pure biodiesel prepared (B100)	ASTM Standards biodiesel D6751
Density at 15 ^{o}C g/ml	0.92	0.82	0.84	0.86-0.9
Viscosity at 40 ^{o}C (mm^2 /s)	29,76	1.3-2.4	9.5	1.9-6
Pour point ^{o}C	10	6	-2	-5– 10
Acid value mg KOH/g biodiesel	5.6	0.07	0.09	Max. 0.5
Flash point ^{o}C	140	90	120	Min. 100
Water content % wt.	0.03	0.05	0.03	Max. 0.05

4. Conclusion

This study aimed to address the need for alternative energy sources by examining the process of converting fish waste into biodiesel. The oil extracted from discarded fish, characterized by a reduced omega-3 content, was recognized as a favorable raw material for the manufacturing of biodiesel. The influence of transesterification process conditions, including temperature, methanol amount, catalyst amount, and reaction time, on both the mass yield and fuel properties of the biodiesel were assessed. Optimization experiments revealed that the optimum biodiesel sample achieved a maximum yield of 91.25% when the transesterification process was conducted at 100 °C, with 20% wt. methanol and 0.75% NaOH catalyst for 30 minutes. The characteristics of the biodiesel were assessed according to the ASTM guidelines. The results demonstrated that the produced biodiesel exhibited properties that met the requirements for combustion engines, indicating its potential as a suitable fuel alternative.

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