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Characteristics of Biodiesel Produced from Crude Palm Oil through Non-Alcohol Synthesis Route Using Dimethyl Carbonate and Immobilized Eco-Enzyme Catalyst

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Abstract: Biodiesel, an alternative to traditional diesel, is essential for the sustainability of long-term energy supplies and often synthesized through a non-alcoholic route called interesterification. The described synthesis method facilitates the modification of oil and fat by exchanging acyl radical groups between triglyceride and alcoholic acid (alcoholysis), fat (acidolysis), or ester (transesterification). Therefore, this research aimed to determine the effect of the reactant ratio between crude palm oil (CPO) and dimethyl carbonate (DMC), along with the use of an eco-enzyme catalyst, on biodiesel characteristics. The CPO:DMC ratio was 1:1.5, 1:2, 1:2.5, and 1:3, while the immobilized eco-enzyme catalyst was 2%, 3%, 4%, 5%, and 6% of CPO mass. The results showed that interesterification with a 1:3 reactant ratio using a 4%wt catalyst was the best procedure, producing biodiesel yield of 73.65%, density of 0.860 g/mL, viscosity of 4.63 mm^2/s (cSt), flash point of 113 °C, calorific value of 34.454 MJ/kg, and cetane number of 70.6%.

Keywords: biodiesel; CPO; dimethyl carbonate; immobilized eco-enzyme; interesterification

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1. Introduction

The limited availability of non-renewable fossil energy sources (coal, crude oil, and natural gas) along with the current high fuel consumption is a significant issue necessitating the development of renewable energy from nature [1]. These conventional energy sources produce large amounts of greenhouse gases, particularly carbon dioxide (CO_2), posing a severe environmental threat [2]. One strategy to mitigate CO_2 emissions from vehicles and reduce fossil fuel usage requires harnessing renewable energy and incorporating additives with high oxygen content (oxygenated compounds) into liquid fuel such as gasoline [3]. Biodiesel is considered an alternative to the current issues, serving as an economical and environmentally friendly source of renewable energy that offers effective solutions to availability problems [4]. This can be derived from vegetable oil, animal fat, and used cooking oil (waste cooking oil) [5] and applied in pure form or blended with diesel fuel without significantly modifying the fuel system. Furthermore, the production process includes converting triglyceride, the main component of vegetable oil, into fatty acid methyl ester (FAME), commonly known as biodiesel [6]. In general, biodiesel contains a higher energy density per volume, functions as a lubricant for engine pistons (since it belongs to the non-drying oil category, reduces carbon dioxide emissions alongside greenhouse gas effects, possesses clean combustion characteristics, incurs low production costs, and is renewable, biodegradable, and easily transportable [7]. Additionally, exhaust emissions from biodiesel are sulfur-free, non-toxic, and known to burn cleanly with a higher smoke number of 62, meaning they are more environmentally friendly [8].

Among vegetable oils, CPO is the most widely used, specifically in Indonesia. Palm oil mainly contains triglyceride, namely, carboxylic acid, comprising a carbon number ranging from 6 to 30, along with monoglyceride and diglyceride. CPO contains saturated fatty acids amounting to 50.3% and unsaturated fatty acids 49.7%, while VCO contains 91.3% saturated fatty acids and 8.7% unsaturated fatty acids [9]. Moreover, the higher saturated fatty acid content, such as palmitic acid, constituting 47% of the total volume, affects the cetane number [10]. In palm fruit flesh, there is 43% crude palm oil, which is composed of various types of fatty acids, i.e., palmitic acid (C16) 40–46%, oleic acid (C18-1) 39–45%, linoleic acid (C18-2) 7–11%, stearic acid (C18) 3.6–4.7% and myristic acid (C14) 1.1–2.5%. Crude palm oil (CPO) is used as industrial raw material for biodiesel production because it is a product from milling factories. After the milling process, CPO is a non-vegetable oil because it has high FFA levels and contains impurities. Therefore, CPO is usually sent to refineries for processing further processed and purified [11]. Dimethyl carbonate (DMC), a reactant considered a viable replacement for methanol, is a green chemistry option that appears to be more environmentally friendly and capable of reducing hydrocarbon, CO, NOx, and other particle emissions. Additionally, it has a relatively high oxygen content (53.3 %wt), low vapor pressure, and a high octane value [12]. DMC is an organic compound classified as carbonate ester OC (OCH3) and is highly soluble in water, biodegradable, and non-toxic. This colorless liquid can be used as a methylation agent and a solvent in biofuel production [13,14]. Additionally, both esterification and transesterification methods in biodiesel production generate glycerol as a by-product [15], making the use of eco-enzyme as a biocatalyst [16] and DMC as a reagent extremely feasible in this research. Using an eco-enzyme as a substitute for an alkaline catalyst offers several advantages, including low energy consumption, and enables glyceride esterification with high levels of free fatty acid (FFA, 85–95%), expediting the reaction by breaking down fatty acid with lipase assistance. Moreover, the eco-enzyme is derived from waste materials and known to be environmentally friendly [17], with great selectivity, high activity, the ability to operate at low reaction temperatures, and biodegradability [16].

Biodiesel synthesis using interesterification, a non-alcoholic route, includes altering the structure and composition of oil and fat through the exchange of acyl radical groups between triglyceride and alcohol (alcoholysis), fat (acidolysis), or ester (transesterification) [18]. Acyl acceptors such as DMC (an ethyl acetate) can be applied in interesterification of triglyceride, producing triacetin, which is physically similar to methyl ester [16]. Previous investigations [19–21] reported the significant influence of DMC on resulting fuel characteristics when applied as a biofuel blend for diesel engines. Similarly, this research proves that DMC can reduce vegetable oil viscosity to levels compliant with the European Biodiesel Standard (EN 590) [22] for current diesel engine use.

The application of DMC leads to lower cloud and pour points for B20SO-B40SO and B20CO-B40CO blends, specifically with the incorporation of a maximum of 40% biofuel from jatropha oil into diesel used as a straight vegetable oil (SVO) blend. The high oxygen content in DMC added to the fuel is one of the key parameters in reducing carbon emissions by approximately 97%. Other research showed that Pertamax blended fuel with diethyl carbonate and DMC components outperformed fuel without additive mixtures [23]. Therefore, this research aims to develop more effective and environmentally friendly methods for clean biodiesel production. Specifically, the objective is to understand the influence exerted on characteristics of biodiesel synthesized through interesterification method using DMC as a substitute for methanol and immobilized eco-enzyme as catalyst. The expected benefits of this research include providing an alternative solution to energy challenges by using raw materials compliant with the 12 principles of green chemistry [24].

Other advantages comprise applying waste as raw material for an immobilized eco-enzyme catalyst, facilitating green technology policies of the government, and contributing solutions to various environmental and global issues. Moreover, the quality and standard of the produced biodiesel adhered to the specified requirements applicable in biodiesel marketing region, specifically EN 590 [25], as presented in Table 1.

Table 1. The European Biodiesel Standard (EN 590).

Parameters	Unit	Value
Density at 150 °C	kg/m^3	850–900
Viscosity at 400 °C	mm^2/s (cSt)	3.5–5.0
Flash Point	°C	120
Cetane Number	min	51
Calorific Value (Gross Specific Energy)	MJ/kg	Max 45.4
Sulfur Content	mg/kg	10.0
Carbon Residue	% (m/m)	0.30
Sulfated Ash Content	% (m/m)	0.01
Water Content	mg/kg	200
Total Contamination	mg/kg	24
Oxidative Stability	g/m^3	25
Acid Value	mg KOH/g	0.50
Iodine Value	g I/100 g	130
Linolenic Acid Content	% (m/m)	0.20
Monoglyceride Content	% (m/m)	0.80
Diglyceride Content	% (m/m)	0.20
Free Glycerin	% (m/m)	0.02
Total Glycerin	% (m/m)	0.25
Alkali Metals (Na + K)	mg/kg	5.0

2. Materials and Methods

2.1. Materials

As shown in Figure 1, this research used a purposely built setup that consisted of a biodiesel reactor, separator funnel, flask, and glass beaker. As solvent material, DMC was supplied by Merck from China where the synthesis specification was described in reference [26]. Immobilized eco-enzyme and distilled water were sourced from local market in Indonesia. CPO was obtained from PT Perkebunan Nusantara (PTPN)-I Cot Girek, Aceh Utara- Indonesia. Additionally, the product adhered to biodiesel production requirements outlined in the European Biodiesel Standard (EN) and ASTM, with specified levels of FFA at 2%, water content at 0.25%, and other impurities not exceeding 0.25%.

2.2. Experimental Design

In this research, CPO served as a constant variable with a molar ratio of 1. The independent variables included molar ratio of DCM to CPO of 1:1, 1:1.5, 1:2, 1:2.5, and 1:3. The molar mass for CPO is 847.28 g/mol and the molar mass for DMC is 90.08 g/mol [26]. Additionally, an immobilized eco-enzyme catalyst varied as a percentage of the total weight of CPO (3%, 4%, 5%, 6%), along with variations in temperature (47.5 °C, 55 °C, 62.5 °C, and 70 °C) and reaction time (30, 45, 60, and 75 min). Analysis and characterization were realized through tests for biodiesel yield calculation density using a pycnometer (ASTM-D1298) [27], viscosity using a Brookfield viscometer (ASTM-D445) [28], calorific value using a bomb calorimeter (ASTM-K88890) [29], cetane number using a portable Koehler K-888 cetane octane meter (ASTM D-613) [30], and flash point using a manual Pensky–Martens closed-cup flash-point tester (ASTM-D93) [31]. Gas chromatography–mass spectrometry testing (ASTM-D5769) was also conducted [32]. GC-MS analysis is conducted to identify biodiesel components [7] by using the high volatility of esters, enabling easier conversion into gas in GC-MS devices [33]. Chromatography is based on the polarity and molecular mass differences among vaporized samples. The liquid samples are injected into the injector and vaporized. The carrier gas then transports the samples into the column for the components to be separated based on the partition between the mobile (carrier gas) and stationary phases (column). The resulting gas molecules are ionized in the mass spectrometer, causing fragmentation of the samples into positive ions, which have a specific ratio between mass and charge (m/z) [34].

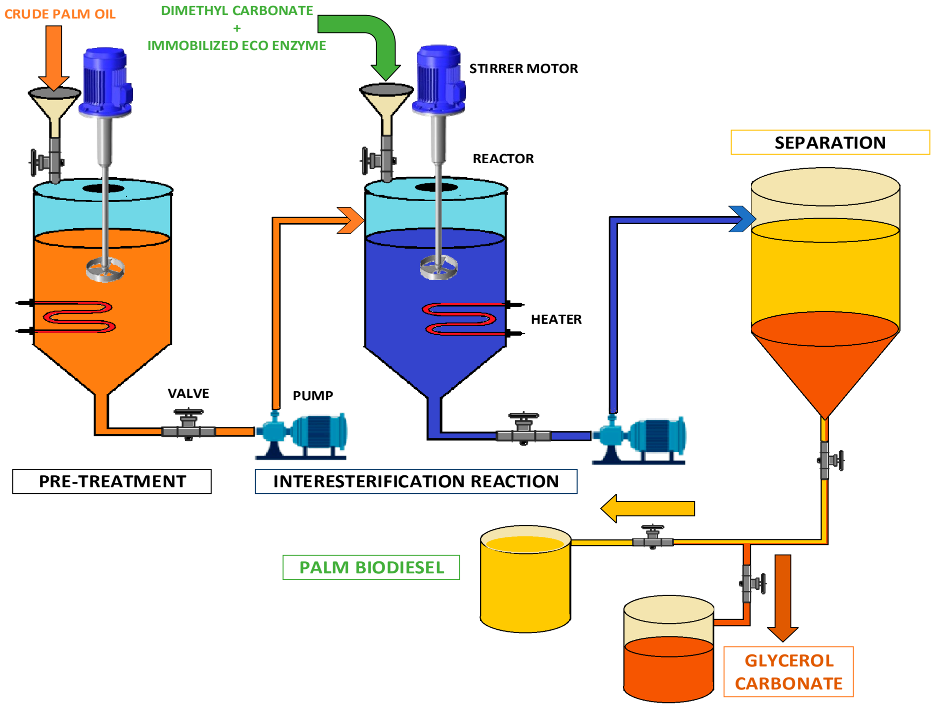

Figure 1. Biodiesel reactor setup.

CPO was used in this research as the main raw material for biodiesel production, applying DMC as solvent and immobilized eco-enzyme as catalyst. Furthermore, several variables were incorporated, namely, the concentration ratio between DMC and CPO, as well as the concentration of eco-enzyme in relation to the weight of CPO. Temperature and reaction time variations were implemented to assess the impact exerted on the biodiesel production process. This research was conducted to understand characteristics of the produced biodiesel by measuring yield, determining density, viscosity, and cetane number, as well as analyzing the calorific value, flash point, and the composition of biodiesel using gas chromatography–mass spectrometry (GC-MS) analysis. Initially, the process involved mixing DMC with the eco-enzyme catalyst in a flask simultaneously heated to a temperature of 35 °C. Subsequently, the heating of CPO was carried out in another flask before proceeding with interesterification, a biodiesel formation process without alcohol use.

This research focuses on using DMC as a solvent in the biodiesel production process by varying the composition between CPO and DMC in molar ratios. Moreover, comparisons (%wt) of the total weight between CPO and DMC were performed for the eco-enzyme catalyst to observe the influence on the biodiesel interesterification process. Furthermore, temperature and reaction time variations were conducted to determine the impact exerted on the interesterification process. The preparation required creating a solution of CPO mixed with DMC and eco-enzyme according to the research variables. The solution was prepared by mixing CPO with a solution of DMC and eco-enzyme, each preheated to a temperature of 35 °C in separate reactors and then combined into the same reactor.

2.3. Production Methods and Interesterification of Biodiesel

The experiment commenced with creating a solution of CPO mixed with DMC and the eco-enzyme based on the research variables. The solution was prepared by combining CPO with preheated mixtures of DMC and eco-enzyme, each maintained at a temperature of 35 °C in separate reactors. These were subsequently combined in the same reactor according to previous literature. The eco-enzyme, initially dissolved in DMC at a specific concentration, was poured into the reactor and the solution was heated to the desired temperature. Simultaneously, CPO was separately heated to the same temperature and poured into the previous reactor. The interesterification reaction of CPO with DMC using the eco-enzyme was conducted under different reaction times, temperatures, catalyst concentrations, and molar ratios of reactants. Catalyst concentrations ranged from 2% to 6% *w*/*w* of oil and the impact of reaction temperature was assessed at 47.5 °C, 55 °C, 62.5 °C, and 70 °C. Molar ratio comparison between CPO and DMC was set at 1:1, 1:1.5, 1:2, 1:2.5, and 1:3, while reaction time spanned from 30 to 75 min. The principle of the interesterification process is shown in Figure 2 [18].

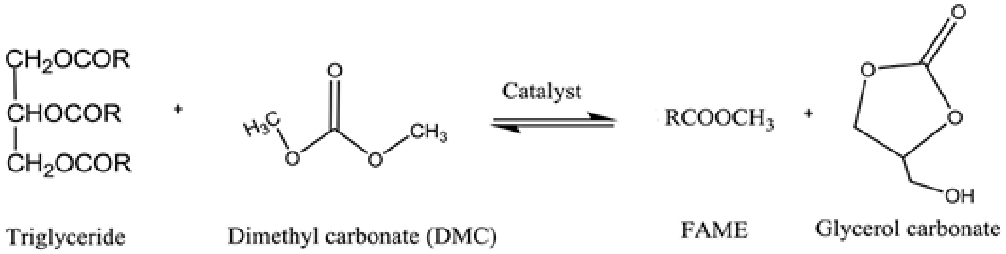

Figure 2. Interesterification process.

3. Results and Discussion

3.1. Conversion Yield of Biodiesel Interesterification

Generally, biodiesel yield obtained is determined by several factors, such as reaction time, reactant ratio, catalyst usage, and reaction temperature. In this case, the ratio between CPO as the raw material and DMC as the reactant also became a determining factor for the produced yield, where a higher molar ratio led to a larger yield [5]. As shown in Table 2, the conversion yield results from interesterification process amounted to 30 runs of samples.

The best yield obtained was 73.65% at a molar ratio between CPO and DMC of 1:3, with the catalyst ratio reaching 4% of the total weight of CPO. This showed that using a greater quantity of DMC in the biodiesel interesterification process would initiate more methyl ester formation. This was attributed to the requirement of a greater reactant quantity to break down alkyl groups into methyl ester. In this case, DMC was the excess reactant in the interesterification process, following the basic principles of biodiesel production [25]. Previously [35], the esterification of lauric acid was conducted using methanol and Amberlyst CM-4 catalyst activated with HCl. The yield of methyl ester obtained was 93.7% with a reaction time of 120 min and a temperature of 60 °C under stirring at 500 rpm. Another study [21] focused on the transesterification of biodiesel using methanol as a solvent with both DMC and KOH as catalyst. This generated methyl ester yield of 98.2%, density of 0.858 g/mL, and viscosity of 4.58 mm^2/s when DMC was used as a catalyst. For biodiesel with KOH catalyst and molar ratio of 1:6, the best results were obtained with methyl ester content of 89.0%, density of 0.883 g/mL, and viscosity of 4.91 mm^2/s. A reputable investigation [36] suggested application of a higher molar ratio of DMC to replace methanol and ethanol for in situ transesterification with DMC and diethyl carbonate or using additional solvents to enhance the surface contact between lipids and alcohol, thereby increasing the reaction rate and fatty acid ester yield.

Table 2. Biodiesel yield conversion, density and viscosity values.

Run	DMC Ratio (Mol)	Reaction Time (Minute)	Temperature (°C)	Catalyst Ratio (%)	Yield (%)	Density (g/mL)	Viscosity (mm^2/s)
1	2.5	45	47.5	3	68.82	0.87	5.06
2	2	60	50	4	66.35	0.87	5.47
3	2.5	75	47.5	5	71.63	0.87	4.63
4	1.5	75	47.5	5	63.76	0.88	6.34
5	1.5	75	47.5	3	62.68	0.88	6.80
6	2	60	55	6	66.89	0.87	5.38
7	2	60	55	2	64.55	0.87	5.99
8	2.5	45	47.5	5	70.41	0.87	4.63
9	1.5	45	62.5	3	62.87	0.88	6.80
10	1.5	75	62.5	3	63.23	0.88	6.75
11	2	90	55	4	65.83	0.87	5.47
12	2	60	55	4	66.35	0.87	5.44
13	3	60	55	4	73.65	0.86	3.73
14	2	60	55	4	65.83	0.87	5.48
15	2	60	55	4	65.48	0.87	5.48
16	1.5	45	62.5	5	63.14	0.88	6.34
17	2	60	55	4	66.22	0.87	5.47
18	1.5	75	62.5	5	63.58	0.88	6.34
19	2	60	55	4	65.48	0.87	5.48
20	2	60	55	4	66.61	0.87	5.48
21	1.5	45	47.5	5	62.87	0.88	6.34
22	1	60	55	4	58.83	0.93	6.92
23	2.5	45	62.5	3	69.28	0.87	5.06
24	2.5	75	62.5	5	72.19	0.87	4.63
25	1.5	45	47.5	3	62.14	0.88	6.80
26	2	60	70	4	67.21	0.87	5.47
27	2.5	75	47.5	3	68.46	0.87	5.06
28	2	30	55	4	66.69	0.87	5.47
29	2.5	45	62.5	5	71.71	0.87	4.63
30	2.5	75	62.5	3	68.95	0.87	5.06
European Biodiesel Standard (EN 590)						0.850–0.900 g/mL	3.5–5.0 mm^2/s (cSt)

Temperature and reaction time are other crucial factors contributing to biodiesel yield. Generally, a higher temperature and longer reaction time result in greater yields and improved characteristics of the produced biodiesel [37]. According to Table 2, the best biodiesel yield was obtained with a reaction time of 55 min at 60 °C. This showed that the optimum time and temperature for biodiesel production in the interesterification process, with the best yield of 73.65%, occurred at 60 °C and 55 min. Specifically, as the reaction time increased, the molecular interactions became more intensive, leading to a larger biodiesel yield. The result was also influenced by the appropriate ratio of reactants and catalysts, ensuring the reaction reached optimum conditions. The optimum temperature in the interesterification process increased the reaction rate associated with the kinetic energy of particles, causing particles to move faster and increasing the chances of effective particle collisions. The higher the temperature used, the faster the reaction and the greater the conversion yield, consistent with the Arrhenius equation. In previous research [36], temperature and reaction time significantly impacted the yield of methyl esters produced from the transesterification process with methanol as solvent. A higher molar ratio could be incorporated by replacing methanol or ethanol applied for in situ transesterification with DMC and diethyl carbonate or by using additional solvents to enhance the surface contact between lipids and alcohol, increasing the reaction rate and the yield of fatty acid ester.

The catalyst also played a crucial role in increasing the reaction rate, which was related to the reaction mechanism comprising a lower activation energy [38]. The use of the eco-enzyme as homogeneous catalyst was beneficial due to being easily soluble and reactive [39]. The general application of homogeneous catalysts in the biodiesel production process, such as H_2SO_4, HCl, NaOH, and KOH, has some drawbacks, including corrosiveness, difficulty of separation from the product, tendency to pollute the environment, and lack of reusability [21]. However, in the biodiesel interesterification process, the eco-enzyme was used because it did not have the disadvantages of other homogeneous catalyst types. Moreover, it is environmentally friendly and can be reused [40], adhering to the "3R" policy of the government (reduce, reuse, and recycle) [41]. This is a distinct advantage in the use of eco-enzyme catalysts in biodiesel production, specifically during the interesterification process.

In previous research [42], interesterification of soybean oil using methyl acetate with Mg-Al hydrotalcite as base catalyst led to a yield of 95.9% methyl ester and 5.3% glycerol triacetin. The optimum conditions were achieved with a molar ratio of oil to methyl acetate of 1:50, catalyst of 0.04 g/cm^3 at a temperature of 200 °C, and a reaction time of 4 h.

3.2. Characterization of Yield from Biodiesel Interesterification

The characterization conducted on the produced biodiesel included density, viscosity, cetane number, calorific value, and flash-point measurements, as well as GC-MS analysis for determining biodiesel composition.

3.2.1. Density Measurement

Density represents the mass per unit volume ratio, a characteristic related to the calorific value and power generated by a diesel engine per unit of fuel volume. Density or specific weight is measured by weighing the volume of biodiesel produced at 40 °C in a pycnometer (ASTM-D1298) [27]. The results of density measurements can be seen in Table 2. Density measurement results showed that CPO and DMC molar ratio as well as catalyst did not significantly affect density values obtained. However, the larger molar ratio used, the lower the resulting density value. This was also related to viscosity, where the larger ratio of eco-enzyme led to a greater reaction rate, causing triglyceride chains to break and release into other fatty acid chains in the oil–water phase, which became glycerol and biodiesel. Consequently, the weight of the solution decreased by one third of the initial molecular weight, leading to a reduction in viscosity and density. The slight differences in density values produced by biodiesel in all runs in this research were influenced by other factors, including impurities, residual raw material content, and glycerol present in biodiesel. Additional factors, such as temperature and reaction time, did not significantly affect the density values of biodiesel. Generally, in the biodiesel production process, the lower the temperature, the higher the density values of biodiesel produced and vice versa. The same principle applies to reaction time, where longer reaction time generates lower density values of biodiesel. However, in this research, the lowest density value obtained was 0.860 g/mL or 860 kg/m^3 at the highest molar ratio of CPO:DMC, 1:3, with temperature of 55 °C and reaction time of 60 min. This showed that molar ratio significantly determined density values produced. Despite temperature and reaction time exerting no significant effect, both were optimal for biodiesel interesterification reactions. The obtained value was considered safe and it met biodiesel characteristics according to EN 590, assessed with the ASTM D 1298 test method in the range of 850–890 kg/m^3 [25]. Therefore, it can be blended with diesel as fuel for diesel engines, following the usage policies and standards [25,43].

In a previous investigation [44], the transesterification process for synthesizing biodiesel from gurgura oil (Monotheca buxifolia) was conducted using green calcium oxide nanoparticles synthesized with Boerhavia procumbens leaf water extract as catalyst and methanol as reactant, producing a highest yield of 95%. Reaction conditions included molar ratio of methanol to oil of 9:1, catalyst concentration of 0.83% (%wt), reaction time of 180 min, and temperature of 85 °C. Biodiesel characteristics, such as density (821 kg/m^3), viscosity (5.35 mm^2/s), cloud point (−8 °C), pour point (−9 °C), and flash point (95 °C), complied with international standards ASTM D-6571 [45], EN 14.214 [46], and China GB/T 20828–2007 [47]. The density obtained in this research (860 kg/m^3 or 0.860 g/mL) was better than a value previously generated through transesterification method with methanol as reactant and it complied with EN 590 [25].

3.2.2. Measurement of Biodiesel Viscosity

Viscosity is a characteristic that reflects the resistance of a fluid to flow, and is influenced by internal friction as the fluid moves across different locations. This affects the fuel injection into the combustion chamber, forming deposits in the engine. High viscosity results in slower flow rates, delaying the atomization process of the fuel in the combustion chamber [41]. The standard kinematic viscosity for biodiesel is 3.5 mm^2/s to 5 mm^2/s, as described by EN 590 [25]. When viscosity is excessively high, friction in the pipes increases, impacting pump performance and making the filtration process difficult. There is a higher chance of sedimentation, causing fuel atomization during ignition to be challenging. Extremely low viscosity can initiate inadequate engine lubrication, leading to increased wear and tear over time. Viscosity values were tested using a Brookfield viscometer (ASTM-D445) [28] and the analysis results are presented in Table 2.

The measurement results showed that the lowest viscosity value for biodiesel was 3.73 mm^2/s at a CPO:DMC molar ratio of 1:3, with the catalyst reaching 4% of the total CPO weight. The highest viscosity was 6.92 mm^2/s with a CPO:DMC molar ratio of 1:1 and 4% catalyst proportion. This suggested that the molar ratio between CPO and DMC significantly influenced biodiesel value [1]. Specifically, a larger molar ratio between raw material and reactant would lead to a lower viscosity of biodiesel produced. The results showed that viscosity of biodiesel produced from interesterification of CPO met EN 590 (3.5–5.0 mm^2/s) [25]. When viscosity is excessively high, slower flow rates will occur, delaying the fuel atomization process in the combustion chamber. Biodiesel is a fuel that replaces traditional diesel during depletion, and hence it should share similar or approximate characteristics with traditional diesel [3]. The ratio of catalyst used in the interesterification process did not significantly affect the viscosity value of the biodiesel produced. This was because the application of the homogeneous catalyst led to easy dissolution during interesterification. The use of an eco-enzyme as catalyst in this research was considered very good due to its homogeneous and environmentally friendly characteristics [7,16]. Interesterification was more beneficial than other synthesis methods due to not requiring alcohol; hence, density and viscosity values of the produced biodiesel were unaffected [18,42,48].

In previous research [49], transesterification of biodiesel from catfish oil (CFO) was conducted using a heterogenous catalyst extracted from fish bones and calcined at 600 °C for 4 h, leading to viscosity of 9.391 mm^2/s. Another investigation [8] determined the influence of a DMC mixture on biodiesel from lauric acid by applying a used Amberlyst CM-4 catalyst. This yielded biodiesel above 80% under reaction conditions, including a methanol:oil molar ratio of 9:1, 0.83% catalyst (%wt), reaction time of 180 min, and temperature of 85 °C, with a resulting viscosity of 5.35 mm^2/s.

The interaction between temperature and reaction time factors did not significantly affect viscosity either. Both factors depended heavily on the interaction with CPO and DMC ratio as well as the percentage ratio of the catalyst. Optimum conditions yielding the best biodiesel conversion included run 13 with CPO:DMC molar ratio of 1:3 and catalyst proportion reaching 4% of the total weight of CPO. This showed that the higher the biodiesel conversion (yield), the lower the kinematic viscosity produced. Viscosity decreased further when there was a lack of unsaturation in biodiesel [2]. In this case, the interaction between temperature and reaction time had no significant effect and did not differ significantly at the 80% confidence level.

Previous research [50] synthesizing biodiesel from kesambi seed oil through transesterification was conducted using methanol as reactant. The highest biodiesel yield obtained was 92.1% under reaction conditions with a methanol:oil molar ratio of 7:2, reaction time of 45 to 90 min, and temperature of 55 °C and 60 °C, with biodiesel characteristics of density 850–873 kg/m^3, viscosity 4.41–6.01 mm^2/s, and acid number 0.481–0.681 mmKOH/g.

In another investigation [6], the best biodiesel viscosity obtained was 2.26 mm^2/s. This showed that the viscosity found in this research was better than that previously reported and compliant with EN 590 [25]. The results also show that DMC and eco-enzyme application could be an alternative to replace alcohol as reactant and alkaline catalyst in the biodiesel production processes. Additionally, the eco-enzyme was considered superior to the heterogeneous and alkali catalyst in biodiesel production. The application of the biocatalyst affected the amount of triglyceride degraded into methyl ester, thereby reducing the molecular weight of triglyceride and lowering the viscosity [18].

3.2.3. Flash-Point Test

The flash point is the temperature at which a fraction will vaporize and ignite once exposed to a spark and then extinguish rapidly in a short period [51]. This is attributed to the incapacity of fuel to sustain continuous combustion [52]. The flash point can be determined by consistently heating a fuel fraction, and when a certain temperature is reached, it vaporizes. Supposing a flame source is introduced to the vapor, ignition tends to occur, leading to a spark, which will extinguish due to vapor pressure from below. In other words, a higher flash point of a fraction leads to difficultly in ignition and vice versa. Diesel fuel has a flash point of 376 K, and biodiesel from palm oil has flash point of 431 K, equivalent to 157.85 °C. The flash point is the lowest temperature at which combustion commences when an ignition source is introduced near the surface of the liquid fuel. Additionally, it is temperature at which a brief flame is visible for less than 5 s at a point above the asphalt surface [53]. This research conducted flash-point tests on the nine best samples based on the yield, density, and viscosity analysis results using a manual Pensky–Martens closed-cup flash-point tester (ASTM-D93) [31], and the measured flash point values are presented in Table 3.

Table 3. Biodiesel flash point, calorific value and cetane number results.

Run	DMC Ratio (Mol)	Reaction Time (Minute)	Temperature (°C)	Catalyst Ratio (%)	Flash Point (°C)	Calorific Value (MJ/kg)	Cetane Number (CN)
4	1.5	75	47.5	5	103	30.1	70.6
5	1.5	75	47.5	3	100	29.3	76.7
6	2	60	55	6	108	27.9	79.3
7	2	60	55	2	110	28.1	80.5
12	2	60	55	4	105	29.7	82.9
8	2.5	45	47.5	5	106	28.1	83.3
23	2.5	45	62.5	3	109	30.1	84.3
24	2.5	75	62.5	5	110	30.7	84.6
13	3	60	55	4	113	34.4	86.1
European Biodiesel Standard (EN 590)					Min. 120 °C	Max. 45.4	Min. 51

The highest flash point generated with various CPO:DMC ratios (1:1.5 to 1:3) and eco-enzyme catalyst percentages (2% to 6%) was 113 °C at 4% and a ratio of 1:3. The lowest flash point was obtained at 100 °C with 3% and 1:1.5. Referring to EN 590, the minimum flash point of biodiesel was 120 °C. Therefore, the results were below the standard, but close to EN 590 criteria [25]. An extremely high flash point can lead to detonation or small explosions before the fuel enters the combustion chamber, leading to increased risk during storage [52]. Based on the ignition test, the flame produced was reddish orange, did not generate smoke, and could last a long time.

In previous research [54], the best result obtained was 135 °C in the transesterification of soybean oil using ladle furnace slag for fabrication of geopolymer as a catalyst for biodiesel production. This research applied a biocatalyst, specifically eugenol, at 0.75% of oil mass, showing that DMC and eco-enzyme application could be an alternative to alcohol as reactant and alkaline catalyst in biodiesel production processes.

3.2.4. Calorific Value Test

Calorific value is the amount of chemical energy contained in a unit mass or volume of fuel, with two types: high heating value (HHV) and low heating value (LHV). HHV represents the heating value and the ability of a fuel to release latent heat, producing water vapor as a combustion residue. This is also determined through experiments featuring the combustion of fuel, followed by cooling to room temperature. Under HHV conditions, there is a tendency for more complete combustion to occur. LHV is the amount of heat produced from the combustion of each unit mass of fuel by subtracting the amount of heat carried by the water vapor formed during combustion. Typically, the hydrogen content in liquid fuel is around 15%, meaning that for every unit of fuel, 0.15 parts are hydrogen. In a perfect combustion process, the water produced from the fuel is half the number of the hydrogen moles [55]. Traditional diesel fuel has a calorific value of 43.4 MJ/kg, while biodiesel possesses a calorific value of 39.07 MJ/kg. Calorific value is often interpreted as the amount of energy released from an object and a measure of the amount of heat energy that can be provided to the surrounding environment at 25 °C and a pressure of 1 atm. The magnitude of the calorific value in biodiesel is inversely proportional to density, meaning larger density leads to lower calorific value. The combustion calorific value is a figure representing the amount of heat generated during the combustion process of a specific quantity of biodiesel with air or oxygen through reduction–oxidation [56]. This research tested the best samples obtained based on viscosity and flash point only to determine the calorific values using a bomb calorimeter (ASTM-K88890) [29], and the test results can be seen in Table 3.

The combustion process of biodiesel derived from CPO generates carbon dioxide, water, oxygen, nitrogen, ash, and other products [55]. The results showed that a higher reactant ratio and amount of eco-enzyme catalyst yielded greater calorific value. This was influenced by the water content in biodiesel, which was considered an undesirable external component or impurity. In this research, the highest calorific value obtained was 34.43 MJ/kg at a CPO:DMC ratio of 1:3 with a concentration ratio of eco-enzyme reaching 4% of the total weight of CPO. The calorific value established by EN 590 for biodiesel is a maximum of 45.4 MJ/kg [25]. The calorific value of biodiesel was found to significantly affect the consumption. The lowest calorific value obtained was 27.9 MJ/kg at CPO:DMC ratio of 1:2 with eco-enzyme concentration reaching 6% of the total weight of CPO.

Other factors, such as temperature and reaction time, affected the calorific value of the biodiesel, as higher levels of both parameters led to greater calorific value [56], which was related to reaction mechanisms. However, under optimum conditions with the interaction between variables, biodiesel possessing the highest calorific value was produced at 55 °C and 60 min.

A previous investigation [57] conducted transesterification of biodiesel from palm oil with the addition of DMC as solvent. Molar ratio, temperature, and reaction time were varied, yielding a calorific value of 37.27 MJ/kg, which was still in accordance with EN 590.

3.2.5. Cetane Number Test

Cetane number measures the combustion quality of diesel fuel during compression ignition. This number is a significant expression of the overall quality of diesel fuel among various quality-determining measurements. Additionally, it shows the capability of fuel for autoignition [58] and is often interpreted as the ability to ignite quickly after injection. A low cetane number necessitates a high temperature for self-ignition, while a high number leads to the need for a lower temperature. Excessive levels of cetane in the fuel can cause detonation inside the engine, leading to increased engine noise over prolonged periods. A high cetane number also makes fuel more prone to combustion and vice versa [3]. This is one of the crucial parameters determining the usability of biodiesel as a fuel. The test to determine cetane number was only conducted on the best samples obtained from the superior density and viscosity values using the portable cetane octane meter Koehler K-888 (ASTM D2699 and D2700) [30], and the results can be seen in Table 3.

A higher molar ratio of reactants and amount of catalyst was found to initiate a greater cetane number, which led to a reduction in the flash point of fuel [59]. The highest number in this research was 86.1 for a CPO:DMC ratio of 1:3 with a catalyst concentration ratio of 4%. Molar ratio of DMC and catalyst ratio significantly influenced cetane number obtained. The cetane number of biodiesels is associated with the composition of saturated fatty acid, including 23-carbon chains such as lauric, myristic, palmitic, stearic, and arachidic acids, among other types, which generally tend to have high values [56]. Additionally, it is related to the calorific value of the fuel required to operate an engine efficiently [60]. The best analysis results with a minimum cetane number of 51 adhered to EN 590, and all values obtained were considered safe [25].

In this research, neither temperature nor reaction time significantly influenced the cetane number of the biodiesels obtained, except in specific runs of samples. Therefore, it was concluded that the ratio of reactant and catalyst affected the cetane number.

3.3. Analysis of Gas Chromatography–Mass Spectroscopy

In this research, the best biodiesel produced was analyzed using GC-MS (ASTM-D5769) [32] to confirm methyl ester derived from the interesterification reaction and determine the composition. GC-MS analysis focused on the best yield (%) and flash-point values of biodiesel obtained, and the results are presented in Figure 3 and Table 4.

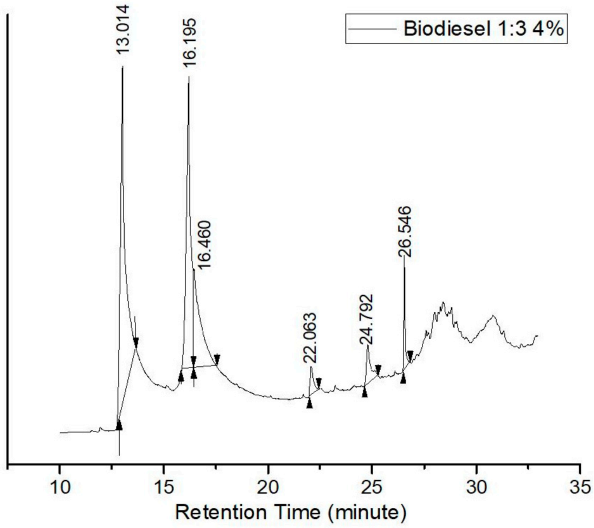

Figure 3. Chromatogram of results of biodiesel GC-MS analysis.

Table 4. Components of biodiesel derived from interesterification reaction.

Peak	Retention Time (Minutes)	Area (mg/g)	Compound Name
1	13.014	41.45	Hexadecanoic acid, ethyl ester (CAS) ethyl
2	16.195	33.36	Oleic acid
3	16.460	16.13	Ethyl oleate
4	22.063	2.19	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)
5	24.792	2.93	Oleoyl chloride
6	26.546	3.95	Squalene

In Figure 3, six peaks represent six biodiesel compounds, meaning that the interesterification reaction of CPO completely transformed fatty acid into biodiesel. The components identified from the interesterification reaction can be seen in Table 4.

The GC-MS analysis results in Figure 3 show that fatty acid composition of biodiesel from CPO was dominated by saturated fatty acids, namely, hexadecanoic acid, amounting to 41.45 mg/g with a retention time of 13.014 min, while the other composition was dominated by unsaturated fatty acids, namely, oleic acid of 33.36 mg/g, with a retention time of 16.195 min, and ethyl oleate of 16.13 mg/g, with a retention time of 16.460 min. In the manufacturing process, biodiesel samples are sometimes obtained with high fatty acid levels due to saturated fatty acids and unsaturated fatty acids not being converted into biodiesel. To determine the composition of unconverted fatty acids in biodiesel, analysis needs to be carried out using gas chromatography–mass spectroscopy (GC-MS).

The results of the GC-MS analysis of biodiesel showed that characteristics of biodiesel from saturated fatty acids from CPO are very good in terms of viscosity, pour point, acid number, iodine number and cetane number. This is important, considering the viscosity is a fuel resistance parameter to flow. A higher level of viscosity can make biodiesel difficult to be distributed, while too low can cause leaks. The pour point is important in relation to the environmental temperature conditions that the fuel can still handle when it is pumped or flowing. The pour point is the lowest temperature at which fuel can still be poured or flow. The low acid number benefits in preventing the engine corrosion. This is important, considering the corrosion that occurs on machines is related to many safety issues. The iodine number shows the number of double bonds in the methyl ester. The more double bonds the fuel has, the more unstable it is. The double bonds in methyl esters are easily oxidized and polymerized to form resin, which can settle and clog the nozzle. Another parameter that is no less important in diesel fuel is the cetane number. The cetane number is an indication of the ease with which the fuel ignites when injected into the engine. A high level of saturation has the potential to increase the cetane number. This is proven by the high cetane number in biodiesel from saturated fatty acids.

The weaknesses of biodiesel from saturated fatty acids include its low flash point. Saturated fatty acids dissolve more easily in dimethyl carbonate. It is possible that this causes the dimethyl carbonate to remain in the biodiesel, thereby lowering the flash point of the fuel. The flash point is the lowest temperature at which fuel will ignite when it comes into contact with air. This is closely related to safety in storage. Even though the flash point for biodiesel is slightly lower than the established standards, it is still relatively safe, because it is still much higher than the environmental temperature in Indonesia. Thus, to produce high-quality biodiesel, a feedstock containing high saturation level of fatty acids is needed. Biodiesel feedstock comes from oily vegetables, which tend to have low saturated fatty acid content. Thus, its unsaturated fatty acids need to be reduced. On the other hand, to enhance cetane number of biodiesel, a high levels of saturated fatty acids in the feedstock is needed [61].

In previous research [33], GC-MS was conducted to observe the formation of fatty acid and methyl ester compounds in biodiesel derived from karanja seed oil. The largest compound composition obtained was oleic acid (52.40%), linoleic acid (16.53%), and palmitic acid (9.66%). Another GC-MS [62] analysis identified the main fatty acid composition in methyl esters included 41.78% of methyl elaidate with a retention time of 24.237 min, 41.55% of methyl palmitate with a retention time of 20.130 min, 11.6% of methyl linoleate with a retention time of 23.999 min, 2.59% of methyl stearate with a retention time of 24.947 min, 1.03% of methyl myristate with a retention time of 14.983 min, 0.82% of methyl oleate with a retention time of 24.362 min, and finally, the seventh peak was 0.62% of methyl margarate with a retention time of 9.822 min. Furthermore, the biodiesel content can be calculated by comparing the area of methyl ester contained in biodiesel with the total area analyzed in the GC test. However, the biodiesel's quality is not determined by the type of compounds contained, but by the characterization of their physical and chemical properties. The total peak area (%) of all the methyl ester components made up 100% of the fuel's components [63].

4. Conclusions

This research produced environmentally friendly biodiesel by using DMC as a substitute reactant for methanol and an immobilized eco-enzyme as a biocatalyst in the interesterification process. The results showed that a higher molar ratio of DMC and immobilized eco-enzyme in the interesterification process generated a greater percentage yield. Furthermore, the molar ratio influenced the flash point, calorific value, and cetane number of the biodiesels produced. The optimum operating conditions in this research were CPO:DMC molar ratio of 1:3 and eco-enzyme catalyst ratio reaching 4% of CPO weight. Characteristics of the optimal biodiesel obtained included biodiesel yield of 73.65%, density of 0.860 g/mL, viscosity of 3.73 mm^2/s, flash point of 113 °C, calorific value of 34.4 MJ/kg, and cetane number of 86.1. The application of DMC as a green chemistry option showed the potential to replace methanol in the biodiesel synthesis process, contributing to the production of clean and environmentally friendly energy. The immobilized eco-enzyme served as an alternative to an alkali catalyst. The results for density, viscosity, calorific value, and cetane number adhered to EN 590 [25]. The biodiesel flash point in this study does not comply with EN 590. In an effort to develop biodiesel production technology that is more efficient and environmentally friendly, future research must focus on exploring novel feedstocks, reactants and biocatalysts with favorable fatty acid profiles that are better in all aspects and obviously environmentally friendly. This expansion of potential biodiesel sources will require comprehensive assessment, considering not only economic viability but also the environmental and social impacts of production, providing valuable guidance for policy and industry decisions. The authors suggest determining the right ratio of reactants and catalysts to obtain better biodiesel conversion results and purifying the resulting biodiesel.

5. Patents

We have patented this research in the form of a process for producing biodiesel from palm oil through a non-alcohol method (interesterification) using dimethyl carbonate and immobilized eco-enzymes with patent registration number P00202401603.

Author Contributions: R.N.B.: conceptualization, methodology, formal analysis, resources, data curation, writing original manuscript, visualization. A.M.S.: Conceptualization, Methodology, Analysis, Validation. M.M.: conceptualization, methodology. A.S.: writing—review and editing, supervision, project administration. H.F.: supervision, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Abbreviations

CPO	crude palm oil
DMC	dimethyl carbonate
FFA	free fatty acid
FAME	fatty acid methyl ester
HHV	high heating value
LHV	low heating value
CO	coconut oil
SO	soybean oil
SVO	straight vegetable oil
CFO	catfish oil
ASTM	American Society for Testing and Materials
EN	European Norm/European Standard
GC-MS	gas chromatography–mass spectrometry

Nomenclature

CO	carbon monoxide
CO_2	carbon dioxide
NOx	nitrogen oxide
KOH	potassium hydroxide
NaOH	sodium hydroxide
MgAl	magnesium aluminide
K	potassium
HCl	hydrogen chloride
H_2SO_4	sulfuric acid
Na	sodium

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