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The characteristics of waste, cooking oil biodiesel by non-catalytic methods

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Abstract. The research investigates the properties of biodiesel produced from waste cooking oil (WCO) through a non-catalytic transesterification process. This approach eliminates the need for chemical catalysts, reducing costs and offering a sustainable solution to waste disposal and energy needs. The process involves reacting WCO with methanol at varying molar ratios of 160, 170, and 180, with 200 mL of WCO processed in a column reactor. The reactor temperatures were set at 70 °C, 170 °C, and 150 °C for heaters one, two, and three, respectively. The properties of the biodiesel, including density, kinematic viscosity, cetane number, and iodine value, were analysed to ensure compliance with the standards outlined by the Indonesian Directorate General of New, Renewable Energy, and Energy Conservation Regulation EBTKE No. 195.K/EK.05/DJE/202. The highest biodiesel yield of 51% was achieved at a molar ratio of 160. The characterization tests confirmed that the biodiesel met all specified requirements, with cetane number, density and kinematic viscosity (both at 40 °C), also iodine value (below the 115%-mass threshold) falling within acceptable ranges. This research highlights the potential of WCO as a viable feedstock for high-quality biodiesel production.

1 Introduction

Biodiesel has become a key alternative to traditional fossil fuels, motivated by the pressing need to mitigate environmental issues and the depletion of non-renewable energy resources. The use of WCO for biodiesel production is especially attractive due to its availability and low cost, positioning it as a sustainable feedstock for biofuel production. Recent research emphasizes the potential of utilizing WCO through non-catalytic methods, which streamline the production process, lower associated costs, and maintain high efficiency in biodiesel yield [1].

The non-catalytic transesterification process involves the direct reaction of WCO with methanol without the use of catalysts, which can complicate and increase the cost of biodiesel production. This method not only streamlines the production process but also enhances the

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economic feasibility of biodiesel derived from waste oils. Research indicates that optimizing parameters such as methanol to oil ratios and temperature are critical for maximizing biodiesel quality and yield [2]

Characterizing the physicochemical properties of biodiesel produced from WCO is essential for assessing its suitability as a fuel alternative. Key parameters include density, cetane number, kinematic viscosity, and iodine value. These characteristics significantly influence the performance, and emissions of biodiesel when used in diesel engines. For instance, a higher cetane number indicates better ignition quality, while appropriate viscosity ensures proper fuel atomization during combustion [2]. Research has shown that biodiesel from WCO can meet or exceed standard specifications for these critical parameters, making it a viable option combined with conventional diesel fuels [3, 4]. The emphasis on understanding these characteristics is crucial for enhancing the operational efficiency of engines running on biodiesel, thereby promoting its adoption in various applications [1].

Furthermore, as global energy demands continue to rise, exploring alternative energy sources like biodiesel becomes increasingly important. The transition towards renewable energy solutions not only helps mitigate environmental impacts but also contributes to energy security by reducing dependency on fossil fuels. Therefore, investigating the characteristics of biodiesel produced from WCO is vital for advancing its commercial viability and ensuring compliance with regulatory standards [2, 5].

Recent research on biodiesel production in Indonesia has increasingly focused on non-catalytic methods to address economic and environmental challenges. A key advancement involves the subcritical water-methanol mixture technique for in situ biodiesel production from rice bran, which eliminates pretreatment steps and achieves high yields (96.4% fatty acid methyl esters) under optimized conditions (290°C, 160:1 methanol-to-oil ratio) [6]. This method leverages Indonesia's abundant rice milling byproducts while avoiding catalyst-related costs and waste [7]. The primary objective is to produce biodiesel from waste cooking oil (WCO) as a substitute for diesel fuel and to identify optimal processing conditions. From a scientific perspective, this study aims to provide insights into the most effective and efficient methods for processing vegetable oils with high FFA content into biodiesel

Studying the characteristics of biodiesel derived from waste cooking oil, particularly focusing on density, cetane number, kinematic viscosity, and iodine value, is imperative for optimizing its performance in diesel engines. This research not only supports environmental sustainability but also paves the way for integrating renewable energy sources into mainstream fuel markets [1]

2 Methodology

WCO was collected from households in Surabaya to be used as a feedstock for triglycerides. The process involved methanol, which was used as a reagent with a purity of 99.8% by weight, and nitrogen gas with 99.5% purity. The design of the column reactor system is depicted in Figure 1. The column reactor features an inner tube and is equipped with two perforated plates at the top and bottom, each containing 30 holes with the diameter of 4 mm. The inner tube measures 43 mm in diameter and 90 mm in height, while the column reactor itself has an outer diameter of 71 mm, an inner, diameter of 55 mm, and a height of 210 mm. The system is designed to maintain a nominal oil volume of 200 ml. Both the column reactor and the inner tube are made from stainless steel 316. Additionally, components VR, SH, and R1 are fitted with five electric heaters (H1–H5) and five temperature controllers. B1 includes an inner pipe (O3), while F1 has one pipe at the bottom (O2) and another at the top (O1).

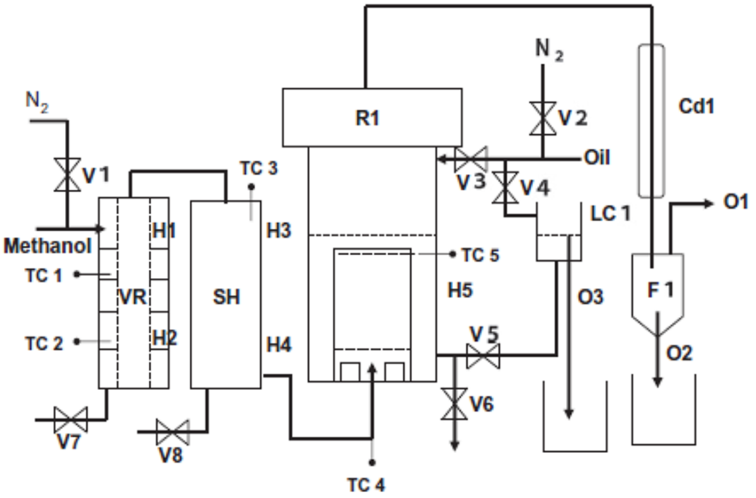

Fig. 1. The schematic of the column reactor test equipment includes the following components: VR represents the vaporizer, SH indicates the superheater, R1 refers to the column reactor, LC1 is the level controller, Cd1 denotes the condenser, and F1 serves as the glass, container for sample collection. The setup also includes valves labelled V1–V8, electrical heaters marked as H1–H5, and temperature controllers identified as TC1–TC5. Additionally, O1 corresponds to the pipe at the top of F1, O2 is the pipe at the bottom of F1, and O3 signifies the inner pipe within LC1.

The semi-batch systems, V3 and V4, remain closed throughout the process. Reactor R1 is initially filled with 200 ml of waste cooking oil (WCO) through B1 and V5, which will be processed into biodiesel. During and prior to the WCO filling, nitrogen gas (N_2) is flowed to purge the oil pipeline, preventing backflow into the methanol area. The N_2 gas exits through pipe O1, which ends in a water-filled glass container. The WCO in R1 is then heated to the required temperature. Methanol is pumped from a glass tank at a specific flow rate into a vaporizer and superheater for evaporation (with N_2 flow stopped). The effect of methanol flow rate on productivity can be studied at a consistent reaction temperature of 175°C.

Being a semi-batch system, the reaction is limited to the initial 200 ml of oil at the bottom of the reactor. The vapor-phase reaction products are condensed and collected in F1. The initial reaction time is noted when liquid begins to drip into F1. Every hour, the reaction product is withdrawn from F1 via O2 and weighed as sample A. Over a reaction period of approximately six hours, three samples are collected. Sample A contains methanol, methyl ester (ME), and glycerol (GL). Methanol is then evaporated from Sample A to obtain Sample B, which consists only of ME and GL. ME and GL are subsequently separated using a burette. The recovered methanol, ME, and GL are measured for volume and mass to facilitate analysis.

Operating the column reactor for, biodiesel production through non-catalytic transesterification of triglycerides (TG) is a complex process involving methanol gas diffusion in oil, liquid-phase transesterification, and distillation. Kinetics and mechanics of the transesterification reaction indicate a series of reversible reactions.

In this reaction, methanol not only serves as a reactant but also acts as a gas transporter, functioning similarly to steam in steam distillation. Methanol vapor extracts ME and GL, the reaction products, and removes them from the liquid-phase reaction zone, shifting the reaction equilibrium to the right and enhancing the conversion rate. Consequently, achieving a complete reaction depends on parameters such as methanol flow rate, reaction temperature, pressure, reaction duration, and the properties of the feedstock and components in the reaction mixture. Optimizing operating conditions requires comprehensive evaluation of these parameters.

The complexity of the column reactor system can be mitigated for biodiesel production for two reasons: (1) the significant difference in boiling points between the reaction products (GL and ME) and TG facilitates easy separation of the products, and (2) the transesterification reaction occurs exclusively in the liquid phase.

The biodiesel produced from WCO is then tested to determine its density at 40°C, kinematic viscosity at 40°C, and cetane number. Testing is conducted at the Energy and Environmental Laboratory of the Institut Teknologi Sepuluh Nopember, Surabaya. An analysis is performed to evaluate the effect of molar variations on biodiesel quality. The results are compared with biofuel quality standards as outlined in the Decree of the Director General of EBTKE.

The iodine number is an empirical measure of the degree of unsaturation in biodiesel, expressed as the mass of iodine absorbed per gram of the sample. In accordance with SNI 7182:2015, the testing procedure begins by weighing a sample of biodiesel and dissolving it in carbon tetrachloride before adding Wijs solution and allowing it to react in the dark for one hour. After the reaction, potassium iodide and distilled water are added, followed by titration with sodium thiosulfate until a color change indicates the endpoint. A blank determination is also performed for accuracy, ensuring consistent results across biodiesel samples

3 Results and discussion

The transesterification reaction between WCO and methanol was carried out using 200 mL of WCO with varying methanol volumes: 1758.788 mL for a molar ratio of 160, 1868.702 mL for 170 molar ratio, and 1978.625 mL for 180 molar ratio. The resulting biodiesel production outcomes are presented in Table 1. A high molar ratio in the transesterification reaction tends to increase glycerol production, as the reaction is more inclined to yield glycerol as a by-product. This is due to the excessive amount of methanol used beyond the ideal requirement for converting WCO into biodiesel, thereby resulting in a higher glycerol output. The highest biodiesel yield was obtained at the lowest molar ratio, despite such ratios typically being regarded as large for biodiesel production.

Density in Table 3 is a measure of mass per unit volume of a substance, indicating that the higher the density, the greater the mass of the material. According to EBTKE No. 195.K/EK.05/DJE/2022, the ideal density range for biodiesel is 850-890 kg/m^3, and testing revealed that molar ratios of 160, 170, and 180 resulted in densities of 889.6 kg/m^3, 888.6 kg/m^3, and 885.2 kg/m^3, respectively, all meeting the required standards EBTKE No. 195.K/EK.05/DJE/2022. Of these, the highest density was recorded at a molar ratio of 160, whereas the lowest was observed at a molar ratio of 180. The molar ratio of WCO to methanol plays a vital role in the transesterification reaction. Studies have shown that an increase in this ratio can lead to higher glycerol production. For instance, when the molar ratio exceeds optimal levels, it can shift the equilibrium back towards reactants, thereby reducing biodiesel yield and affecting its density [8]. Glycerol has a higher density compared to biodiesel. Therefore, as more glycerol is produced, it can dilute the biodiesel phase, leading to an overall decrease in the density of the final biodiesel product. This phenomenon was observed in various studies where increasing glycerol production negatively impacted biodiesel density [9].

Table 1. The results of the biodiesel production

RM	Temperature	Methanol	Condensate	Column Reactor Residual	Methanol Recovery	Glycerol
	°C	ml/minute	ml	ml	ml	ml
160	150	4,885	1030	98	900	28
170	150	5,19	1180	121	998	103
180	150	5,496	1270	133	1075	128

Table 2. The biodiesel yield value

RM	ME		WCO		Yield
	ml	gr	ml	gr	%
160	102	93,524	200	183,380	51,00
170	79	72,435			39,50
180	67	61,432			33,50

Raising the molar ratio of alcohol to oil in the1transesterification process generally results in a reduction in the kinematic viscosity of the biodiesel produced. This phenomenon is substantiated by various studies focused on optimizing biodiesel production, which demonstrate that elevated molar ratios enhance fuel properties like reducing kinematic viscosity [10, 11]. Furthermore, studies utilizing advanced optimization techniques, such as hybrid genetic programming and gray wolf optimizers, highlight the significant effect of the alcohol-to-oil molar ratio in reducing biodiesel viscosity [10].

Table 3. The characteristics of biodiesel

Test Parameters	Unit	Requirements*		Test Results (Molar Ratio)		
		Min	Maks	160	170	180
Density (40 °C)	kg/m^3	850	890	889,6	888,6	885,2
Kinematic,Viscosity (40 °C)	mm^2/s (cSt)	2,3	6,0	5,76	5,27	5,15
Cetane Number	-	51	-	>74,7	>74,6	>73,5
Iodium Number	%-massa ($g\text{-}I_2/100$ g)	-	115	55	56	115

The cetane number, which reflects ignition delay and combustion quality, indicates that WCO biodiesel possesses considerable potential as a fuel. Gas chromatography analysis showed a high level of unsaturation in both WCO and its biodiesel, with linoleic and oleic acids as the predominant fatty acids [12]. This underscores the substantial impact of fatty acid composition on the cetane number.

Iodine value is a crucial indicator for assessing the degree of unsaturation in biodiesel, reflecting its oxidative stability and degradation potential. According to research, a higher iodine value correlates with increased unsaturation, which can enhance the biodiesel's susceptibility to oxidation and degradation over time [13, 14]. The stability of biodiesel is significantly influenced by its composition; polyunsaturated fatty acid methyl esters (FAMEs) contribute to a higher iodine value, while saturated and monounsaturated FAMEs lower it [14].

Studies have shown that biodiesel with a low iodine value tends to exhibit better combustion properties and efficiency, making it preferable for various applications [14, 15]. In addition, environmental factors such as temperature and light exposure during storage can impact the oxidative stability of biodiesel, potentially causing a reduction in iodine value over time [15]. For instance, samples of biodiesel stored at elevated temperatures showed a more significant decrease in iodine value compared to those stored at lower temperatures or with antioxidants. Furthermore, the transesterification process's efficiency plays a vital role; inefficient reactions can leave unsaturated fatty acids in the final product, resulting in higher iodine values. This highlights the importance of optimizing production conditions to achieve desired biodiesel characteristics. Overall, understanding the relationship between iodine value and biodiesel properties is essential for improving its quality and performance in practical applications.

4 Conclusions

The biodiesel yield from WCO was highest at a molar ratio of 160, reaching 51%, followed by 39.50% at a molar ratio of 170, and 33.50% at 180. The optimal yield in this research was achieved with a molar ratio of 160. The density values (at 40 °C) for molar ratios of 160, 170, and 180 complied with the standards specified by the Indonesian Directorate General of New, Renewable and Conservation Energy Regulation EBTKE No. 195.K/EK.05/DJE/2022. The kinematic viscosity values (at 40°C) for all three molar ratios also met the specified requirements. Additionally, the cetane numbers for molar ratios of 160, 170, and 180 satisfied the regulatory standards. The iodine values for the tested molar ratios were within the acceptable range of the specified criteria.

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