Performance Analysis of Biodiesel Derived from Alkali Catalyzed Transesterification of Waste Cooking Oil

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Abstract- Biodiesel is a promising renewable energy source due to its comparable properties with petroleum diesel and is reported to be friendly environmental. One way to prepare affordable biodiesel is through the transesterification of waste cooking oil. Utilization of biodiesel from waste cooking oil needs a low cost of production and gives a great profit. This paper aims to investigate the synthesis of biodiesel using potassium hydroxide catalyzed transesterification of waste cooking oil in a continuously stirred tank reactor and the performance evaluation of biodiesel-petroleum diesel blend to fuel an unmodified diesel engine. The optimum conditions for the transesterification were at 60°C using a catalyst loading of 2% wt. of waste cooking oil. The biodiesel obtained from this work has met the existing Indonesian regulatory standards for biodiesel. Based on the consumption, acceleration, and opacity tests, up to 10% volume substitution of petroleum diesel with biodiesel can satisfactorily fuel diesel engines without modification.

Keywords Biodiesel, blend, diesel engine, performance, waste cooking oil.

1. Introduction

The world's demand for renewable energy resources has been experiencing a steady increase in recent decades. In addition to the inevitable increase in oil consumption, the severe depletion of fossil energy reserves, fluctuating global oil prices, and increasingly strict regulation of the environmental impact have contributed to the occurrence of this situation [1]. Most countries consider renewable energy resources an efficient solution to the global energy crisis [2]-[4]. Renewable biofuels are considered the fourth energy source to fulfill the world's energy requirement [5]. By 2030, biofuels will contribute approximately 4-7% of the world's total energy consumption [6]. Renewable fuels and biofuels have been of great interest in recent decades as a significant replacement for fossil fuels. Several models to predict biomass supply chain for commercial production of biofuels has been presented. The biomass can be a vegetable oil, agricultural waste, or specific lignocellulosic biomass [7]. Various vegetable oils such as soybean, corn, palm, and

sunflower oil are raw materials for making biodiesel [8]-[13]. Biodiesel derived from vegetable oils is generally less volatile and more viscous than petroleum diesel [14]-[15]. Biodiesel can be made by a simple pyrolysis process [16] or a trans-esterification reaction. As one of the biofuels, biodiesel offers numerous advantages compared to petroleum diesel, such as high flash point and cetane numbers, high lubricity, excellent biodegradability, and lower carbon monoxide and sulfur dioxide emissions [17]. Therefore, biodiesel can be a promising renewable energy source [18]-[19].

Palm oil and its derivatives are the most promising raw material for commercial-scale biodiesel production. However, palm oil bears some shortcomings rooted in its high fatty acid content. Palm oil is naturally easy to oxidize and vulnerable to microbial degradation. One alternative to producing biodiesel at a low cost is by utilizing waste cooking oil as the raw material. Biodiesel production from waste cooking oil (WCO) is not only environmentally friendly but is also an effective method of managing waste cooking oil [18]; [20]-[21]. However, the total cost of biodiesel production from vegetable oil remains higher than petroleum diesel due to the high raw materials cost.

The pre-treatment and the use of WCO for biodiesel production can be conducted using several methods by employing different reactors and catalysts, alcohol, and operating conditions [22]-[24]. Roy et al. [25] synthesized biodiesel from waste cooking oil and castor oil mixture using the modified potassium oxide catalyst. Meanwhile, Binhayeeding et al. [26] prepared biodiesel by applying single and lipase cocktails immobilized on polyhydroxyalkanoate. Uprety et al. [27] and Bhatia et al. [28] employed heterogeneous catalysts for biodiesel manufacturing. Astuti and Mufrodi [29] investigated the optimum conditions for continuous biodiesel production from waste cooking oil. Recently, Gad and Ismael [30] studied the effect of mixing biodiesel with gasoline and kerosene.

A comprehensive study of the performance of a new fuel candidate to drive the engine is extremely crucial before its actual implementation. As a preliminary study, biodiesel is usually mixed with petroleum diesel in various compositions to fuel diesel engines. Many studies have been carried out to investigate biodiesel performance to fuel diesel engines [31]-[33]. An off-road engine application testing was conducted to examine the performance of various fuels, namely exhaust emission, power engine, and specific fuel consumption tests [34]. Said et al. [31] described the biodiesel yields based on a combination of performance, emissions, injection, and combustion characteristics. Later, Prasutiyon and Zuhdi [35] also conducted a biodiesel performance investigation through a diesel engine reliability test, performance analysis, engine damage level analysis, exhaust emission, particulate removal, and separators. The objective of this work was to investigate the effect of temperature and catalyst loading on the production of biodiesel from waste cooking oil in a continuously stirred tank reactor and to examine the performance of biodiesel to fuel an unmodified diesel engine installed on a testing car by conducting the consumption, acceleration, and opacity tests.

2. Material and Method

All The materials used were WCO from household waste with a mass density of 0.99 g/ml and free fatty acid content of 1.43, methanol with a mass density of 0.792 g/ml and potassium hydroxide with purity of 98%, density of 2.04 g/cm^3, molar mass of 56.11 g/mol and acidicmetric (KOH ≥ 85.0%) from Merck.

Initially, waste cooking oil and potassium methoxide solutions were continuously fed into the three-necked flask that served as a continuously stirred tank reactor (CSTR) with a residence time of 1.5 hours. The studied variables were the reaction temperature (55ºC to 65ºC) and catalyst loading (1% wt to 3% wt) with time process of 1.5h. For each experiment, the product continuously exited the reactor and was collected in a container. Then, it was left to stand overnight to allow complete separation of biodiesel and glycerol. Furthermore, the properties of the biodiesel samples were analyzed according to the test method SNI 7182:2015 set by Ministry of Energy and Mineral Resources of the Republic of Indonesia. All biodiesel samples were examined for their performance through consumption, acceleration, and opacity tests, as done by Attia and Hassaneen [36]. The equipment for producing biodiesel continuously is shown in Fig. 1.

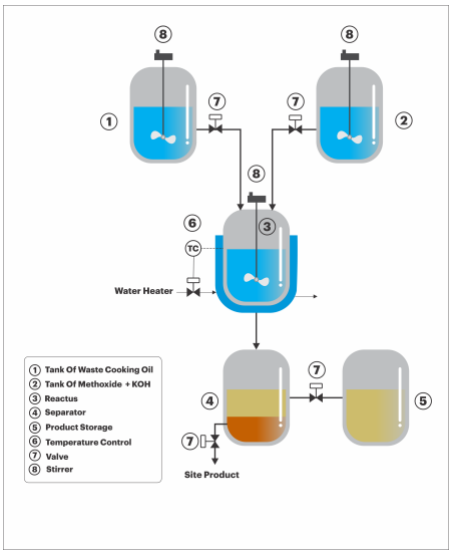

Fig. 1. The experimental set-up for continuous production of biodiesel.

3. Result and Discussion

3.1. Operating Conditions for Continuous Process of Biodiesel Production

A4 Waste cooking oil is a highly potential raw material for biodiesel synthesis due to its high fatty acids content. To examine the presence of fatty acids in biodiesel derived from waste cooking oil, a gas chromatography-mass spectrometry (GCMS) analysis was performed. The result of the GCMS analysis of biodiesel is presented in Table 1.

Table 1. Fatty acids composition of waste cooking oil

No	Component	% Area	Molecular weight, g/mole
1	Octadecanoic acid	0.08	184
2	Hexadecanoic acid	5.72	256
3	Octadecenoic acid	1.01	282
4	Hexanedioic acid	10.94	146
5	Octadecane	1.20	254
6	Heptacosane	1.24	380
7	9-Octadecenoic Acid	1.10	284
8	Tricosane	1.08	324
9	Beta-Carotene	0.08	536
10	2,6,11 trimethyldodecane	0.91	212
11	Beta-Farnese	1.68	402
12	Methanol (Carbinol)	44.1	32
13	Water	23.12	28
14	Others	7.74	

The types of fatty acids involved in the transesterification reaction for biodiesel manufacturing strongly depend on the botanical source of the vegetable oil used as raw material and the respective treatments. Taufiqurrahmi et al. [37] explained that fatty acids of biodiesel from cooking oil consist of palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, palmitic acid, lauric acid, and other types of acids. In this study, the biodiesel produced contains hexanedioic acid, hexadecanoic acid, octadecanoic acid and octadecenoic acid.

This research used WCO and methanol to produce biodiesel continuously. Astuti and Mufrodi [29] have made biodiesel with various reaction temperatures shown in Fig. 2.

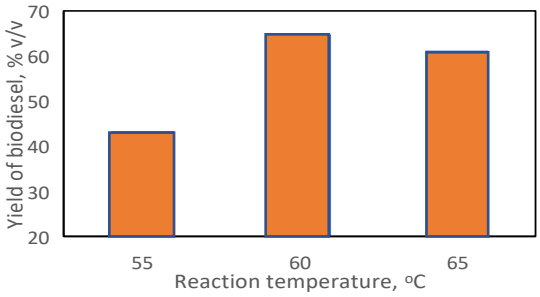

Fig. 2. Yield of biodiesel at difference temperature [29]

The maximum biodiesel yield, 64.8 %v/v, from transesterification of waste cooking oil using methanol was achieved at a reaction temperature of 60°C. At a temperature of 65°C biodiesel yield decreased become 61.2 %v/v. This finding is plausible because the boiling temperature of methanol is 64.7°C, so that at 65°C some of the methanol evaporates. As a result, the biodiesel yield was lower compared to that at 60°C.

Generally, the alkaline catalysts used for the transesterification of triglycerides are sodium methoxide ($NaOCH_3$), potassium hydroxide (KOH), and sodium hydroxide (NaOH). They are loaded to the reaction system between 0.5% wt. to 1% wt. [38]. Potassium hydroxide is more reactive than sodium hydroxide; therefore, potassium hydroxide was chosen in this work to catalyze the transesterification of waste cooking oil to achieve a higher biodiesel yield. The biodiesel yields at various catalyst loadings biodiesel yield on catalyst weight variations based on this research is shown in fig 3 biodiesel yield on catalyst weight variations based on this research are depicted in Fig. 3.

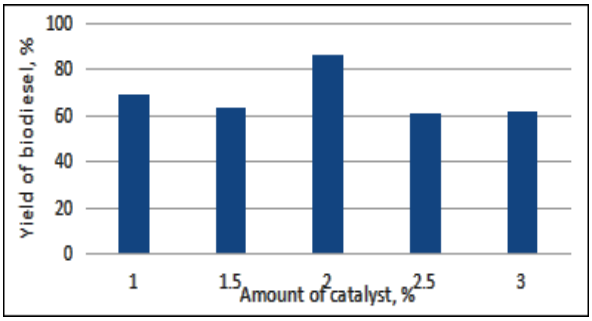

Fig. 3. Biodiesel yield on various catalyst concentrations

However, biodiesel yields were lower at higher catalyst loadings. This phenomenon is likely due to the excess potassium hydroxide in the reaction system triggering triglyceride saponification.

3.2. Properties of Biodiesel at Various Catalyst Loadings

Biodiesel properties, namely the specific gravity 60/60°F, kinematic viscosity at 40°C, flash point PM.cc, cloud point, and moisture content were examined to biodiesel samples obtained from transesterification of waste cooking oil at various catalyst loadings (1%,1.5%, 2%, 2.5%, and 3% wt.) with the temperature of 60°C and a reaction time of 90

minutes. The results properties of biodiesel samples obtained are shown in Table 2.

Table 2. Properties of Biodiesel Samples Obtained from Transesterification at Various Catalyst Loadings

No	Parameter	Unit	Catalyst Loading, wt					Indonesian National standard/ ASTM
			1%	1.5 %	2%	2.5%	3%	
1	Density at 40°C	kg/m^3	890.9	883.2	883.5	875.2	874.0	650 - 890
2	Kinematic Viscosity at 40°C	mm^2/s	10.37	7.298	5.990	4.712	4.564	2.3 - 6.0
3	Flash Point PM.cc	°C	192.5	148.5	165.0	165.5	172.5	Min 130
4	Cloud Point	°C	21	19	22	18	19	-
5	Moisture Content	Ppm	200	100	Trace	160	100	Max 350

The results in Table 2 confirm that the density of the four biodiesel samples has met the biodiesel standard, namely in the range of 0.85 to 0.89. For the lowest specific gravity value obtained in the biodiesel sample with a variation of 3% wt. of a catalyst with a value of 0.8740 and for the highest value obtained at a variation of 1% wt. with a value of 0.8909. From the data, it can be seen that the higher catalyst loading resulted in a lower value of specific gravity. Specific gravity values that meet the criteria are obtained using a catalyst of 1.5% wt. to 3% wt. The kinematic viscosity value of biodiesel gets lower with more catalysts. Viscosity values that meet the standards and quality of biodiesel marketed domestically were obtained using 2% wt. to 3% wt. of catalyst. The flash point value of biodiesel is at least 130°C. All samples met these criteria. In the previous regulation regarding the Indonesian National standard of biodiesel, there was a cloud point limit. Now that this limit has been removed, there is no limit to the cloud point value in the standard and quality of biodiesel marketed in Indonesia. The water content that meets the requirements is obtained at 2% wt., so a catalyst of 2% wt is used.

Shi dan Liang [39] describe the biodiesel yield with pampas grass stick (solid acid) catalysts and fried cooking oils as a resource. The solid acid produced from three maturity levels of pampas grass stick (newly-formed, young, and old) at the temperature of 150°C and reaction time of 12h shows a microtube yield value below 50%. Then biodiesel was produced using a synthesis microtube above 0.05g in 5g waste oil. The temperature of 70°C and reaction time of 9h shows a yield value above 99%. The catalyst amount was the essential factor. The experiment can provide insight for this research to get better results by paying attention to the same temperature of 70°C, considering time as a criterion for the optimization. Niju et al. [40] showed a heterogeneous catalyst from eggshells as CaO used for transesterification WCO in biodiesel production. There were three kinds of CaO catalysts: CaO commercial, eggshell CaO-900, and eggshell CaO-900-600. The biodiesel yield at the temperature of 65°C and reaction time of 1h shows a value of 94.52% with eggshell CaO-900-600 catalyst of 5% wt. This yield result is higher than this research. The essential feature in this research is the catalyst's ability to be recycled. Mathiarasi et al. [41] explain the transesterification of soap nut oil using a new heterogeneous catalyst, a coal-burned boiler. The new catalyst can be used to produce biodiesel, and the catalyst cost is meager. It will be interesting if a new catalyst can produce biodiesel with WCO as a resource for subsequent research.

However, considerable research regarding biodiesel production has been carried out due to discussions of the same or different material resources and catalysts. It should have been discussed more directly about biodiesel performance analysis in diesel engines.

3.3. Biodiesel Performance Analysis

The biodiesel obtained from the experiment was mixed with petroleum diesel fuel at various compositions (0%; 2.5%; 5%, 7.5%, and 10%), as presented in Table 3. This percentage value indicates the volumetric percentage of biodiesel in the biodiesel-petroleum diesel mixture. The performance of these fuel blends was tested by filling them into the fuel tank of a 2016 Toyota Dyna car with an unmodified diesel engine installed. Many parameters may be considered in a preliminary energy audit: performance characteristics, emission characteristics, heat flow analysis, and lubricity [42]. The biodiesel performance tests carried out were consumption, acceleration, and opacity tests.

3.3.1 Consumption Test

The driving cycle aims to the vehicle's fuel consumption. Table 3 summarizes the results of the consumption test of the fuel blends.

Table 3. Consumption Test of Biodiesel-Petroleum Diesel Mixture Samples at Various Compositions

No	Biodiesel composition	Petroleum diesel	Distance, m	Volume (cc)		Average Volume, cc	Distance (S): Volume (V)		Average S:V	Description Engine
				V_1	V_2		$S:V_1$	$S:V_2$		
1	0 %	100%	1000	124	112	118	8.06	8.93	8.50	run normally
2	2.5%	97.5%	1000	128	118	123	7.81	8.47	8.14	run normally
3	5 %	95.0%	1000	134	108	121	7.46	9.26	8.36	run normally
4	7.5 %	92.5%	1000	128	122	125	7.81	8.20	8.00	run normally
5	10 %	90.0%	1000	101	107	104	9.90	9.35	9.62	run normally

The consumption test results proved that the car engine usually ran when fueled by biodiesel-petroleum diesel blends at various compositions. However, the most economical fuel was a mixture of fuel containing 10% volume of biodiesel. As presented in Table 3, the diesel engine required the lowest volume of this fuel and the lowest average volume to reach the same distance. In addition, the volume/distance ratio for fuel containing 10% volume biodiesel is the largest, namely 9.9 and 9.35, indicating that this type of fuel provides the farthest distance compared to the fuels with other biodiesel compositions. This observation aligns with previous studies, which reported that fuel consumption and exhaust temperature increase with the ratio of biodiesel to petroleum diesel [35]-[36];[43]. Meanwhile, research conducted by Gharehghani [44] showed a reduction in fuel consumption when the simultaneous application of water and cerium oxide nanoparticles in the diesel-biodiesel fuel mixture was added..

The measurement results as shown in Table 3 show that the fuel consumption of the mixture below 10% is more than the mixture of 0%. or pure biodiesel. This research is supported by Shen's [45] research which found that blending biodiesel into traditional fossil diesel will increase fuel consumption at a percentage below 12.5%.

3.3.2 Acceleration Test

Acceleration is the change in speed in a given unit of time. A higher acceleration value the vehicle possesses reflects a more significant increase in the vehicle's speed. Diesel fuel blends with various biodiesel compositions were tested for their acceleration, and the results are presented in Table 4.

Table 4. Acceleration test results for various biodiesel compositions

No	Biodiesel composition	Petroleum diesel	Acceleration (10 s)	Description Engine
1	0 %	100%	50 km/h	run normally
2	2.5%	97.5%	50 km/h	run normally
3	5 %	95%	55 km/h	run normally
4	7.5 %	92.5%	55 km/h	run normally
5	10 %	90%	50 km/h	run normally

The acceleration test results proved that diesel fuel blends containing 0%, 2.5%, and 10% volume biodiesel exhibited the same acceleration of 50 km/hour. Surprisingly, diesel fuels containing 5% and 7.5% volume biodiesel demonstrated the same acceleration, which was each 55 km/hour. Thus, considering that a higher substitution of petroleum diesel with biodiesel is expected to solve the problems related to the depletion of fossil fuel resources and environmental protection, the preferred diesel fuel blend is a blend of petroleum diesel and 7.5% volume of biodiesel.

The results of the acceleration measurements in Table 4 show that the mixture of 5% and 7.5% has higher acceleration than the mixture of 2.5 & and 10%. or pure biodiesel; this is supported by the research of Agarwal et al. [46] who found that the acceleration characteristics of biodiesel-fueled vehicles are as good as diesel-fueled vehicles up to a speed of 90 km/hour.

3.3.3 Opacity Ratio

Opacity is the ratio of the rate of light absorption by smoke, expressed in percent. The test was carried out by a smoke opacimeter, as depicted in Fig. 4.

Fig. 4. Opacity test using smoke opacimeter

The results of the opacity test are tabulated in Table 5.

Table 5. Opacity Test of Diesel Fuel at Various Biodiesel Compositions

No	Biodiesel composition	Petroleum diesel	Opacity (%)					Description Engine
			1	2	3	4	Average	
1	0 %	100%	13.0	17.1	13.1	10.5	13.4	run normally
2	2.5%	97.5%	9.7	1.,2	*	*	10.0	run normally
3	5 %	95%	12.5	10.3	*	*	11.4	run normally
4	7.5 %	92.5%	13.2	13.6	*	*	13.4	run normally
5	10 %	90%	14.3	14.8	13.7	12.7	13.9	run normally

*not detected

The regulation of the Minister for the Environment of the Republic of Indonesia Number 5 of 2006 concerning the exhaust emission threshold for old motorized vehicles states that for the M, N, and O motor categories with the GVW category 3,5 years with the year of manufacture 2010, the maximum opacity is 40 %. All diesel fuel blends studied in this work demonstrated far below the opacity threshold. Dhar and Agrawal [47] stated that the smoke opacity of Karanja biodiesel is lower than that of diesel. Smoke opacity was also found to decrease with a mixture of 10%, 20%, and 30% biodiesel [48]. Biodiesel has a lower carbon-to-hydrogen ratio compared to diesel. The lower carbon count reduces the smoke formation and opacity [49]. As expected, the engine was still running normally. Hence, the diesel fuels tested in this work fulfilled the specified opacity. Research conducted by Hoang [50] found that biodiesel containing CeO_2 nanoparticles will cause fuel atomization and micro-explosion, thereby reducing engine exhaust gas opacity.

4. Conclusion

Biodiesel can be produced from waste cooking oil using potassium hydroxide-catalyzed transesterification continuously. The optimum condition for manufacturing of biodiesel was at 60^{o}C using a catalyst loading of 2.0% wt. for 1.5h. The driving cycle test proved that a diesel fuel blend containing a 10% volume of biodiesel exhibits the best performance compared to biodiesel with other compositions. Diesel fuel blends containing 5% and 7.5% volume of biodiesel provided the best acceleration. All biodiesel compositions complied with the % opacity threshold.

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