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A Review: Synthesis of Biodiesel from Low/Off Grade Crude Palm Oil on Pretreatment, Transesterification, and Characteristics

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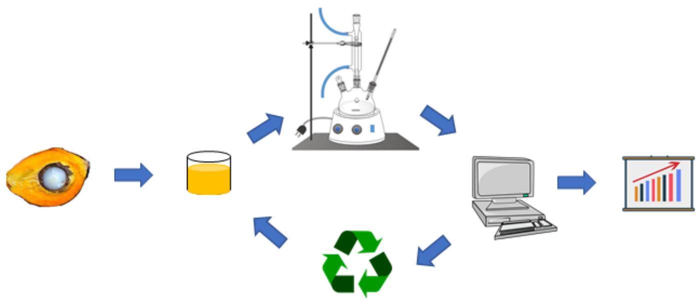
Biodiesel from natural materials has proven its contribution as a renewable energy source. Exploration of natural materials has expanded until many studies have begun to consider natural waste materials to reduce the impact of environmental damage. A natural material that is still considered waste is Low/Off Grade Crude Palm Oil (CPO). Research on this waste has begun to be projected as a raw material for biodiesel. Research on the use of various catalysts in the transesterification and esterification reaction of this waste has expanded. Then, the biodiesel produced has unique characteristics. Thus, some of these studies have been reviewed on a small scale. From that, it is proposed a route to utilize Low/Off Grade CPO which is sustainable and renewable. Therefore, this review article aims to provide a unique understanding of research on the use of Low/Off Grade CPO as biodiesel.

Graphical abstract



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1. Introduction

Biodiesel is developed on the basis of increasing energy needs and the dwindling availability of non-renewable energy. It was noted that there was a decrease in the production of petroleum products in Indonesia from 292,373.80 barrels (in 2017) to 281,826.61 barrels (in 2018) [1]. Then, continuous exploitation cannot be a solution. On the other hand, high levels of CO2 emissions and the greenhouse effect can cause climate change and environmental conditions, so that researchers have started to move towards developing renewable energy that is environmentally friendly, sustainable and renewable. The implication is that biodiesel as an alternative to unrenewable petrodiesel fuel because biodiesel has advantages such as renewable, biodegradable, low environmental toxicity, and superior combustion efficiency [2]. Until now, researchers are still developing biodiesel production from various raw materials, one of which is Crude Palm Oil (CPO) [3].

The use of CPO as raw material for biodiesel production has been widely studied in the last 15 years. The conversion

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of CPO to biodiesel has been carried out using the following methods: direct use [2], blending [4], microemulsion [4, 5], pyrolysis [6], transesterification [7, 8] and esterification-transesterification [9]. Of these methods, the transesterification method is most often used in industrial-scale biodiesel production because 1 mole of triglycerides produces 3 moles of mono-alkyl ester [4]. In a sense, transesterification converts triglycerides in CPO into biodiesel with a by-product in the form of glycerol [10]. However, the weaknesses of the transesterification method are the need for Free Fatty Acids (FFA) and low water content. Alternatively, esterification is applied to reduce levels of free fatty acids [9, 11], because high FFA levels will affect the transesterification reaction. Some of the other disadvantages of the transesterification method are that the separation and purification steps are expensive, the possibility of side reactions that can occur, and result in large wastewater [4]. Therefore, the development of the biodiesel production system continues to be developed.

The main problem during the production of CPO as raw material for biodiesel is the unfavorable yield of CPO in the form of CPO with high FFA levels due to the palm fruit factor [12]. This type of CPO is called low grade or off grade CPO which the term has been mentioned in many studies. Based on SNI 01-2901-2006, standard CPO is characterized by a maximum free fatty acid content of 5%, a maximum moisture content of 5%, and an orange color. As a result of this material condition, many producers experience loss of income. Off grade CPO is generally dark red in color, has a strong odor, and contains gum [13]. Several laboratory-scale studies in the last 15 years have taken place. The results obtained show the fluctuation of many factors during the synthesis. This has a new perspective on the complexity of the chemical events that occur in esterification-transesterification. Researchers observed the unique characteristics seen from the application of a method and the yield of alkyl esters (biodiesel).

Based on the previous description, the researcher will present a comprehensive discussion on "Synthesis of Biodiesel from Low/Off Grade CPO on Pretreatment, Transesterification, and Characteristics". This review is carried out by reviewing the relevant literature and then discussing it descriptively and analytically. With this review, the authors use the term Off Grade more often and hope to be able to describe an understanding and encouragement of biodiesel research from CPO.

2. Synthesis of Biodiesel of Low/Off Grade CPO

Crude Palm Oil (CPO) is a natural raw material that has been developed as biodiesel. The main reason is the kinematic viscosity properties that are closer to petro-diesel and has a lower fuel viscosity, so this property can be advantageous for diesel engine performance [14]. So far, CPO has been obtained from the extraction of oil palm fruit mesocarp. The parts of the oil palm fruit are shown in Figure 1. CPO which is bright orange in color can contain glycerides and impurities such as fiber, water, free fatty acids (FFA), phospholipids, phytochemicals (carotene & tocol) and trace metals [15]. The orange color of the CPO is contributed by carotenoid compounds as the highest minor compounds [16].

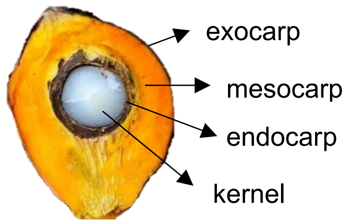

Fig. 1. Palm fruit anatomy.

Furthermore, the authors propose a classification of CPO yields shown in Table 1. Generally, CPO with 5% FFA content is considered inappropriate because FFA will cause the resulting methyl ester levels to be impure and side reactions, such as saponification and esterification (Figure 2). This is due to the presence of lipolytic enzymes that sort the fruit into free fatty acids (FFA) and glycerol [12]. The high water content of CPO will also cause side reactions such as ester hydrolysis which produces FFA back [2]. Until now, many studies that applied esterification reactions to reduce FFA levels and continued to transesterification reactions, so the two-step method is known. These side reactions will compete with the transesterification reaction as the main reaction which is expected to react completely (Figure 2). The reaction requires excess alcohol to suppress product formation [2]. However, the equilibrium reaction that takes place is capable of producing products and residues. Therefore, proper separation technique will support the recycling or reproducing process.

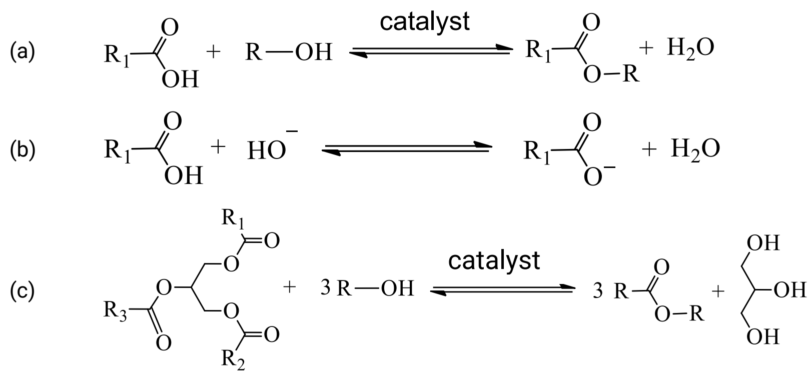

Fig. 2. Esterification (a), saponification (b), and transesterification (c).

Technical problems can also be found in a series of commonly applied laboratory equipment (Figure 3). Some of the things that concern research with this circuit, include: stable thermometer control, stable irrigation conditions both temperature and pressure, heating conditions that can maintain the reaction temperature, room conditions in the form of clean air, room temperature, and room pressure.

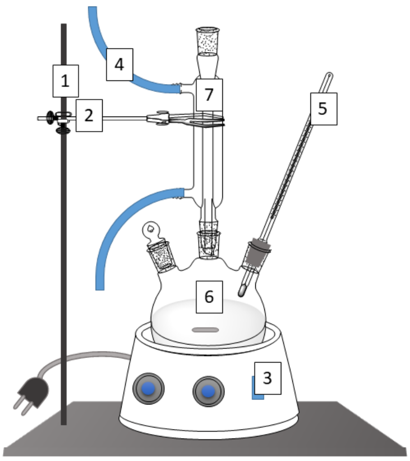

Fig. 3. Biodiesel Synthesis Equipment Series: (1) statif, (2) clamps, (3) heating mantle + stirrer, (4) irrigation hose, (5) thermometer, (6) three-neck flask + magnet stirrer, and (7) condenser.

Table 1. Classification of Crude Palm Oil (CPO).

Classification	FFA levels (%)	Remark
Low grade	>5	Many studies equate this quality with the term Off Grade
Grade	1 – 5	
High grade	0.1 – 1	

3. Pre-Treatment of Low/Off Grade CPO Before Esterification

Off Grade CPO is CPO that does not meet the standards as CPO ready for processing. Off Grade CPO contains a lot of impurities and a high free fatty acid (FFA) value. Several research articles were reviewed, many pretreatments in the form of extraction were carried out on oil palm mesocarp raw materials, but it was rare to find pretreatment on the results of extraction of palm oil or Off Grade CPO obtained. This is an implication, that since the beginning, many impurities contained in Off Grade CPO can interfere with the biodiesel synthesis process. The initial treatment that has been carried out on Off Grade CPO based on research is shown in Table 2.

Table 2. Initial treatment of ff grade CPO before esterification.

Method	Condition	Result	Reference
Heating & filtering	103°C ±2°C, 3 jam	No FFA test	[17]
Refined with HCl-activated Natural Zeolite	Heating temperature 170°C, 1 hour Centrifuge 3000 rpm, 20 minutes	FFA tested at 8.5% & 7.96%; There was a change in color from dark orange to faded orange	[13, 18]
the gumming in the oil, & filtering	H_3PO_4 0.6%, stirring 400 rpm	No FFA Test	[19]
Preheating	In oven, 70°C	FFA tested at 7%	[20]

Based on Table 2, the pretreatment of Off Grade CPO is important in terms of reducing the impurity content in it such as a change in oil color [18]. This is clearly distinguished from Off Grade CPO by preheating before esterification in Hayyan's research [20] with the characteristics of an impurity content of 0.05%, moisture content of 1.03%, an ash content of 3.2%, and a saponification number of 198% and of course this material is of low quality. Meanwhile, Off Grade CPO without pre-esterification such as containing a moisture content of 3.5% [21], the color of the CPO is still reddish-yellow [22], and iodine number 58.8464 g I_2/100g which is higher than the standard SNI-01-2901-2006 (50-55 gI_2/100g) [23]. In addition, the quality standard of CPO SNI 01-2901-2006 is reddish-orange color, the max water content is 0.5% wt, max impurity content is 0.5% wt, and free fatty acid content (palmitic acid) is max 0.5%wt.

4. Decreasing of FFA Value Through Esterification

An effort so that CPO can be good in the transesterification process, namely through the esterification process. Esterification is the reaction between free fatty acids (a carboxylic acid) and alcohol, and produces ester compounds [24]. Because of that, the FFA levels in Off Grade CPO can be lowered. The esterification method has been able to reduce the value of FFA levels to below 5%. Several methods apply research parameters. The parameters that are susceptible to changes in FFA levels in this review are time, methanol: oil ratio, and use of catalysts. So far, research using esterification on Off Grade CPO can be shown in Table 3.

Based on Table 3, the esterification process can be evaluated. The first aspect, namely the esterification temperature. Almost all studies show a temperature consistency of 60°C. 60°C is a fairly efficient temperature. Temperature is known to affect the rate and an equilibrium of the esterification reaction. The second aspect is the esterification time. The time consistency used is 0.5 hours - 2 hours. This time affects a reaction that is constant or returns to equilibrium where the equilibrium constant value is very small. The third aspect is the methanol: oil ratio in esterification. The consistency ratio of methanol: oil is shown at 10: 1 and 12: 1 ratio. The esterification reaction is recognized to be consistent using methanol reactants. The fourth aspect, the esterification catalyst aspect. H_2SO_4 catalyst has been used in esterification reactions, but it is not environmentally friendly. In addition, natural zeolite catalysts have shown promising results for reducing FFA levels. Also, no less, organic-based catalysts show good catalytic work, so they have the potential to be developed again as superior heterogeneous catalysts.

The optimum conditions for esterification reaction of Off Grade CPO that have been applied by previous studies have shown satisfactory results, because the FFA level can drop to below 1%. In addition, research with pretreatment before esterification was able to obtain satisfactory FFA reduction results [13, 20]. Some of the results of decreased FFA levels appear to be slightly fluctuating. However, this does not make a difference in results that differ greatly. Thus, research development for esterification rests on innovative types of catalysts.

Table 3. Esterification of off grade CPO.

Optimum Esterification Conditions					Decrease in FFA levels (initial to result)	% recovery	Ref.
Temperature (°C)	**time (hour/s)**	**Ratio MetOH: oil**	**Catalyst**	**Remarks**			
50	2	12:1	10%wt Ni/Natural Zeolite	-	6.2813% to 0.7278%.	88.4	[22]
50-58	1	0.26:1	H_2SO_4 1.168%	-	5.838% to 4.21 %.	27.8	[17]
60	0.5	8:1	0.75 wt% Benzenasulfonic acid	300 rpm	9.3% to less than 1%	>89.2	[25]
60	0.5	10:1	0.75% Chromosulfuric acid	200 rpm	7.0% to less than 1%	>85.7	[20]
60	0.5	10:1	Phosphonium-based deep eutectic solvent (P-DES) 1%wt	-	9.3% to less than 2%	>78.5	[26]
60	1	12:1	H_2SO_4 1%wt CPO	Making use of the difference in catalysts in transesterification	11.95% to 1.44%	87.9	[27]
					11.32% to 0.989%	91.3	[28]
					12.02% to 1.22%.	89.8	[29]
					16.18% to 0.6%	96.3	[30]
					12.47% to 0.36%.	93.5	[31]
					12.02% to 1.22%	89.8	[32]
					11.32% to 0.989%	91.3	[33]
60	1	12:1	H_2SO_4 1%wt,	400 rpm	2.87% to 0.77%	38.0	[34]
60	2	6:1	H_2SO_4 1% v/v	-	12.34% to 1.786%	85.5	[23]
60	2.83	23.41:1	1.59 % natural zeolite	300 rpm, metanol anhydrous	64.23 % to 1.59 %	97.5	[35]
60	3	12:1	H_2SO_4 % 1%wt	-	8.50% to 0.7%	91.7	[13]
60-65	1	12:1	H_2SO_4 % 1%wt		7.96% to 0.93%	88.3	[18]

Table 4. Transesterification of off grade CPO.

Optimum Transesterification Conditions					Highest Yield	Reference
Temperature (°C)	**Time (hour/s)**	**Ratio MetOH: oil**	**Catalyst**	**Remarks**		
40-50	1	6:1	KOH 1%wt	-	60%	[23]
50	2	10:1	KOH 1%wt	400 rpm	89.84%	[26]
50-58	1	6:1	KOH 1%wt	-	81.94 %	[17]
60	1	10:1	KOH 1%wt	400 rpm, esterification with catalyst BZSA	88.67%	[25]
60	1	10:1	KOH 1%wt	400 rpm, esterification with chromosulfate acid	85%	[20]
60	2	20:1	KOH 1 % b	-	80.14 %	[36]
60	2	8:1	3%wt natural zeolite /KOH	nothing data [KOH]	97.79%	[33]
60	2	8:1	4% wt zeolite/KOH	KOH 75%.	96.99%	[29]
60	2	8:1	7,36% K/natural zeolite	KOH solution 50 g/100 ml	95.84%	[28]
60	2	8:1	3%wt K/zeolite	KOH 75%	92.04%	[32]
60	2.5	18:1	KOH 2%wt	2 bar, membrane reactor	72.02%	[37]
60	3	8:1	CaO/*fly ash* 7%wt,	400 rpm	61.72%	[38]
60	3	8:1	Na_2O/*fly ash* 4% wt	*Fly ash* (SiO_2, Na_2O & $Na_2CaSi_3O_8$); 400 rpm	77.33%	[39]
60	3	8:1	Na_2O/Fe_3O_4 2%-w	-	59.92%	[27]
60	3	8:1	Na_2O/*fly ash* 4%-wt	No fly ash content data	81.2%	[40]
60	4	12:1	4% K_2O/Al_2O_3 (w/w)	200 rpm, Centrifuge: 20 minutes, 3000 rpm	85.58%	[13]
65	1.67	18:1	ZnO 2%-w	-	94.26%	[41]
65	1.67	12:1	CaO 2%-b	-	29.5%	[34]
65	2	10:1	Zeolit/KI	Conveyance Catalyst (90°C) 2,5% (b/v)	67.39%	[42]
70	2	10:1	Fe_3O_4/CaO of 6%	-	90%	[21]
70	2	11:1	CaO 2%wt	-	87.41%	[30]
70	2	11:1	$Ca_2Fe_2O_5$ 1%-wt	-	52.34%	[31]
70	2	6:1	CaO/*Wasted iron* 3%-wt	400 rpm	67.64%	[43]
70	3	6:1	CaO/*fly ash* 6%-wt	-	59.34%	[44]

5. Production of Biodiesel of Low/Off Grade CPO Through Transesterification

Transesterification is a method commonly used to produce an ester [24]. This ester is used in the category name biodiesel as a renewable energy source. For Off Grade CPO, several studies highlight the methanol: oil ratio parameter and the use of a catalyst. There are various parameters taken in several studies of transesterification of Off Grade CPO shown and the best parameters to produce the highest biodiesel yield are shown in Table 4.

Based on Table 4, the transesterification process can be evaluated. The first aspect, namely temperature. Temperature from 40ºC -70ºC, shows the contribution of biodiesel yield and is proven to be quite an effective temperature at 60ºC. The second aspect, namely time. Time will affect a reaction work efficiency. From a time span of 1-4 hours, the time consistent with high yield yields is 2 hours. The third aspect is the methanol: oil ratio. The methanol: oil ratio greatly affects the transesterification reaction process. The methanol: oil ratio is related to the feed and feeder analogy, which means that the more methanol is not necessarily, the higher yield yields, this condition is a concern to establish. The fourth aspect, namely the catalyst. The catalyst that is promising in the transesterification reaction is zeolite impregnated with KOH. It is a perspective that zeolites can be optimized superacid catalysts in the near future.

Of the four parameters of the optimum conditions for the transesterification reaction which produced the highest biodiesel content, several studies showed that the four optimum conditions were the same, but were accompanied by different yield levels. Similar research was conducted by Saputri et al. [32] and Ulfayana et al. [33] to obtain different yield levels of biodiesel. This also happened in the research of Tua et.al [39] and Arva et.al [40]. Another interesting thing is the research of Maulidan et al with a very low biodiesel yield of 29.5%, even though the CPO esterification process is with an FFA level of 2.87% (Grade category) [34] whereas the catalyst used is the same as the research of Putri et.al [30]. There was also a study with the same esterification method, then the transesterification method that was applied was almost the same, and produced different levels of biodiesel, namely 95.84% in the research of Zulfadli et al. [28] and 97.79% in the research of ulfayana et al. [33], whereas the transesterification catalyst in the research of Zulfadli et al. [28] much more than the research of ulfayana et al. [33]. In addition, the authors observed that there were not many studies that carried out replication activities for the biodiesel synthesis process. So, this fluctuation in biodiesel yield is something that is common. An interesting assumption is that the research that has been carried out has not been assisted by technology to ensure the accuracy of the amount of reactants when mixing and to control the reaction conditions by mechanical automation. So, the results of the understanding of the fluctuations in bidiesel yields can be used as information for the implication that a large-scale biodiesel production cannot be separated from yield fluctuations and the biodiesel production process is important to develop. This will relate to efficiency and cost-effectiveness during production.

6. Characteristics of the Biodiesel Synthesis Method

Some of the transesterification method processes above, variable temperature, time, methanol: oil ratio, and catalyst have unique characteristics. Some of the characteristics of the biodiesel synthesis method from Off Grade CPO are described below.

1. Temperature, the recommended temperature ranges from 50℃ to 60℃
2. Time, the recommended time ranges from 1 hour to 2 hours
3. Methanol: oil ratio, recommended ratio ranges from 8: 1 to 10: 1
4. The catalyst, the recommended catalyst, namely zeolite or acid organic catalyst can show good catalyst performance
5. The results of biodiesel content from Off Grade CPO can be said that it still does not meet the standards of SNI 7182: 2015 and EN 14214, which is a minimum of 96.5%.

The characteristics of biodiesel from Off Grade CPO are shown in Table 5. Not all studies in this review carried out all the characteristics set by the applicable standards. A simple conclusion as a result of fluctuation in research results, that Off Grade CPO can also be suspected of product defects as a material being synthesized also has certain defects such as structural defects in polyvinyl chloride [45], although the degree of defect is very small and until now there is no proper method to identify it. A defect in a product indicates a lower (favorable) free energy state in a chemical system [46]. In addition, the research conditions for Off Grade CPO have shown an increasing development, due to the emergence of research based on environmental sustainability.

Table 5. Biodiesel characteristics from SNI 7182: 2015, ASTM D6751, En 14214, and off grade CPO.

Characteristic	SNI 7182:2015	ASTM D6751	EN 14214	Off Grade CPO
Ester (% mass)	min 96.5	-	96.5	89.84%
Density (kg.m^{-3})	850-890 (40℃)	820-900 (15℃)	860-900 (15℃)	874.5
Flash point (℃)	min 100	130 min	120 min	182.9
Kinematic viscosity 40 ℃ (mm^2/s)	2.3 – 6.0	1.9 – 6.0	3.5 – 5.0	3.81
Sulfated ash (% mass)	0.02 max	0.02 max	0.02 max	0.005
Kalium (mg/kg)	-	max 5	max 5	1
Fosfor (mg/kg)	max 4	max 10	max 10	7.2
Cetane number	51	47 min	51 min	77
Acid value (mg KOH/g)	max 0.5	max 0.5	max 0.5	0.12
Free glycerol (% mass)	max 0.02	max 0.02	max 0.02	<0.01%
Total glycerol (% mass)	max 0.24	max 0.24	Max 0.25	0.04%

source of Off Grade CPO: [26]

7. Sustainability of Low/Off Grade CPO

As in the biodiesel synthesis process, Off grade CPO produced from oil palm extraction can have organic impurities. Then esterification to reduce the free fatty acid content was successfully carried out even with conventional methods. However, the esterification results still contain by-products that become impurities, so that the transesterification process competes with existing organic impurities. This is a fluctuation in the methyl ester levels obtained from the synthesis. The process route that can be proposed to improve the sustainability of Off grade CPO empowerment can be shown in Figure 4.

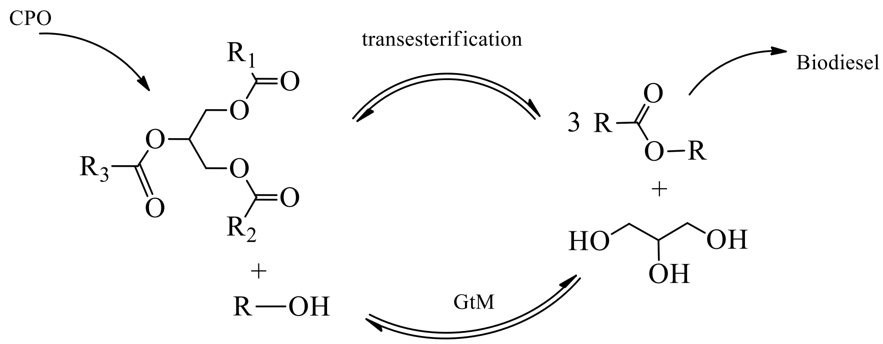

Fig. 4. Low/off grade CPO sustainable development route.

The transesterification process is carried out with a catalyst that supports the green process. then the residue that settles is subjected to analytical separation to obtain glycerol. Furthermore, glycerol is converted to methanol (GtM) using green synthesis [47]. The green process can be supported by *in situ* transesterification, which eliminates the extraction stage. The extraction solvent may not be needed in the extraction process because the alcohol in the transesterification reaction also acts as an extraction agent and the fatty acid esters formed also have good oil solvent properties, so that the efficiency of oil extraction increases [4].

Biodiesel product from CPO which is an important factor is the cetane number [14]. It is known that the cetane number affects the performance of diesel engines, that is, too high a cetane number can cause the combustion process to occur first before the fuel mixes with the air in the engine, and the cetane number is too low causing the engine to become coarse, and incomplete combustion occurs. So, many machine manufacturers are designed with cetane numbers ranging from 40-50 [48]. In addition to the cetane number, viscosity is a factor being observed, because it can affect the atomization of biodiesel when injection into the combustion vessel. The higher the viscosity, the greater the tendency for the fuel to be problematic. Viscosity increases with the length of the carbon chain and with increasing degrees of saturation. Ethyl ester viscosity is slightly higher than methyl ester. The double bond configuration factor affects the viscosity. The cis position double bond gives a lower viscosity than the transposition [49]. Thus, the higher concentration of saturated fat esters and the presence of a number of trans fat compounds are the reasons why the kinematic viscosity of biodiesel from cooking oil is higher than biodiesel from vegetable oil [49]. In addition, the oxidative stability of biodiesel is weak, so it is prone to oxidation in exposure to air, due to the presence of double bonds in the chain of fatty compounds, namely the position of bis-allylic methylene on the linoleic and linolenic esters [50].

8. Conclusions

This review on research on biodiesel synthesis from Off Grade CPO has not been able to cover all the research that has been done. However, this review is intended to answer a need for research direction on green process Off Grade CPO raw materials. That is, several important things that can be conveyed, namely: (1) pre-treatment of materials before esterification needs to be considered to reduce the number of unprofitable compounds, (2) the esterification and transesterification processes show reaction results with fluctuating performance. However, the unique characteristic of biodiesel of Off Grade CPO is that it does not meet the standards of SNI 7182: 2015 and EN 14214. Furthermore, a future study that puts forward green processes and high efficiency is an interesting challenge so that the residue from biodiesel synthesis does not endanger environmental sustainability.

Author Contributions

Sumari Sumari contributed with conceptualization, formal analysis, investigation, methodology and writing – original draft. Aman Santoso contributed with investigation, visualization, writing – original draft and writing – review & editing. Muhammad Roy Asrori contributed with writing – review & editing.

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