

Biodiesel Production from Rubber Seed Oil as An Alternative Energy Source – A Review

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ABSTRACT

Biodiesel is one of the alternative energies that can be used to overcome the problem caused by the limited amount of fossil fuels reserved. Biodiesel can be made from rubber seed oil that has high potencies in Indonesia. The availability of rubber seed is quite much, with more than 3-million-hectare rubber plantation area. The production of biodiesel from rubber seed oil has been carried out by several researchers using various methods. Therefore, this study was conducted as a review to obtain optimum operation conditions and the effect of antioxidant addition in biodiesel production. Production methods of biodiesel from rubber seed oil observed in this study are esterification-transesterification, one-stage transesterification, and in situ transesterification methods. Types of antioxidants added to biodiesel from rubber seed oil observed are TBHQ, D-TBHQ, BHA, BHT, PG, and OG. Esterification-transesterification was chosen as the most effective method in producing biodiesel with a minimum yield of 96.4%. Antioxidant addition of TBHQ with 1000×10^{-6} (ω) dosage was selected as the most effective to increase the biodiesel induction period to become 6.41 hours, fulfilling the SNI 7182-2015 standard, which is minimum of 6 hours. The Standard used as the reference for observing biodiesel parameters is SNI 7182-2015.

KEYWORDS

Literature review
Biodiesel
Rubber seed oil
Operation Condition
Antioxidant

INTRODUCTION

Energy is one of the most important human needs, which continues to increase. Most of the energy comes from non-renewable fossils or better known as fossil fuels. Fossil fuels account for 94% of Indonesia's national energy needs [1]. However, its availability, particularly petroleum, has decreased since 1995 due to exploration constraints. The Government of Indonesia, through the Regulation of the Minister of Energy and Mineral Resources No. 12 of 2015, stipulates the obligation to use alternative energy in the form of biodiesel by 30% (B30) as of January 2020.

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Biodiesel can be made from a wide variety of vegetable resources, one of which is the seeds of rubber plants. The area of rubber plantations in Indonesia reaches more than 3 million hectares, making rubber seeds become one of the high-potential biodiesel raw materials [2]. Several studies have been conducted to utilize the potential of these rubber seeds, but some have not met SNI 7182-2015 standards. Discussion on oxidation stability and the addition of antioxidants in biodiesel rubber seed oil is also rare in previous studies.

This research is focused on reviewing the operating conditions and the effect of antioxidant addition in previous studies of manufacturing biodiesel from rubber seed oil. The operating methods reviewed include manufacturing methods, catalyst concentrations, the molar ratio of methanol to oil, reaction temperatures, reaction time, and its effect on the produced products based on SNI 7182-2015 standards.

LITERATURE REVIEW

Rubber seeds are underutilized byproducts from rubber plants (*Hevea brasiliensis*). Rubber seeds are large and hard-shelled, weighing between 3 – 5 grams depending on the type, age, seed, and moisture content [3], [4]. Rubber seeds consist of 45 – 50% shell and 50 – 55% seed flesh [4]. Fresh rubber seeds contain 24.5% water which can cause triglyceride hydrolysis into fatty acids [5], [6].

Rubber Seed Oil

Rubber seed oil has an iodine number of 130, which is categorized as drying oil. This causes rubber seed oil to oxidize into a thick and viscous layer when stored in the open air [7]. Rubber seeds contain 45 – 50% oil with a composition of 14.1% saturated fatty acids and 85.9% unsaturated fatty acids [8]. The composition of fatty acids in rubber seed oil is summarized in Table 1 [8].

Table 1. Fatty acid composition in rubber seed oil

Saturated Fatty Acid		Unsaturated Fatty Acid	
<i>Composition</i>	<i>Percentage (%)</i>	<i>Composition</i>	<i>Percentage (%)</i>
Myristate (C14)	0.09	Oleic (C18-1)	20.6
Palmitate (C16-o)	7.41	Linoleic (C18-2)	36.6
Stearate (C18-o)	6.60	Linolenic (C18-3)	28.7

Biodiesel

Biodiesel is an alternative fuel of methyl ester compounds from the esterification/transesterification of vegetable oils or animal fats using short-chain alcohol [9], [10]. Biodiesel has physical properties that are not much different from solar and have advantages

such as easy to decompose, being derived from renewable natural materials, being non-toxic, and producing a very small amount of CO₂ and sulfur gas. Biodiesel can be made through esterification reactions, transesterification, or a combination of both (two-stage reactions). The selection of this reaction depends on the type of oil used [11].

Biodiesel Production

Esterification is the process of making biodiesel from oils that have free fatty acid content (FFA) of more than 2%. Oils with high FFA levels are not suitable to use as raw materials for transesterification reactions as they can lead to soap formation and complicate the separation process of base catalysts [12], [13]. Therefore, the esterification process is done to lower the FFA levels contained in the oil. Esterification reactions usually use the strong acid catalyst H₂SO₄ or HCl. This reaction produces water, so it needs to be separated. The esterification reaction is shown in Figure 1 [14].

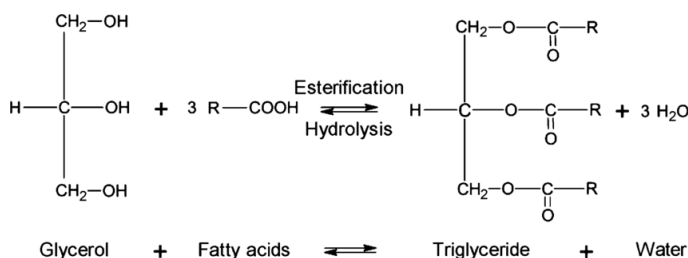


Figure 1. Esterification Reaction Mechanism

Transesterification is the process of reacting triglycerides with alcohol to form glycerol and ester compounds. This reaction was performed on rubber seed oil with an FFA content of less than 2%. A commonly used type of alcohol is methanol because it is more reactive than ethanol. Transesterification generally uses base catalysts because the yield is higher than that of acid catalysts [15]. The transesterification reaction is shown in Figure 2 [16], [17].

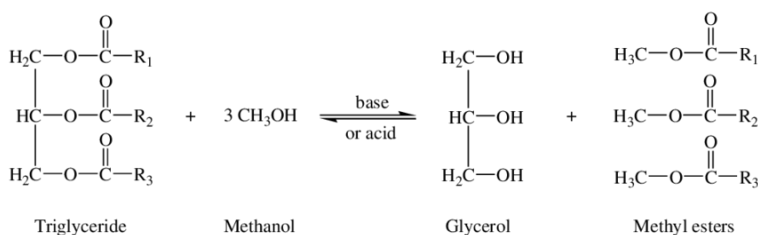


Figure 2. Transesterification Reaction Mechanism

Quality Standards

The national scale biodiesel quality standard is SNI 7182-2015. The SNI 7182-2015 quality standard was used in this study as a reference to analyze biodiesel products produced.

RESULTS AND DISCUSSION

In the implementation of this literature review, the methodology used is the systematic review. Stages of research on literature review with systematic review include designing, article selection, analysis, review writing, and conclusion making [18].

Gate Logic

Designing the review includes the determination of the topic to be discussed, the purpose of the literature review, as well as the scope set out in the literature review. The topic chosen is the manufacture of biodiesel from rubber seed oil. The scope of this literature review includes the manufacture of biodiesel based on rubber seed oil, the influence of operating conditions, and the influence of antioxidant additions.

Article

Research related to the manufacture of biodiesel from rubber seed oil was collected and selected. The selection process was done by reading abstracts of the research articles and grouping them based on the scope that has been set. The selection was also carried out based on the focus of the review.

Analysis

Quantitative analysis was carried out by taking the resulting yield into account, as well as qualitative analysis referring to SNI 7182-2015. Thus, the optimum operating conditions, as well as the optimum amount of antioxidant addition in the manufacture of biodiesel from rubber seed oil, were obtained.

Optimum Operating Condition Determination

The results of the analysis will lead to optimum operating conditions for biodiesel rubber seed oil production in which product characteristics are in accordance with SNI 7182-2015. At this stage, a complete and in-depth discussion of the results of the analysis was carried out to obtain results that were in accordance with the objectives.

Conclusion Making

From the determining the optimum operating conditions stage, the conclusion of all reviews that have been done can be made. From this conclusion, suggestions can be withdrawn and can be proposed for the improvement of the implementation of further research. The stages of the research methodology are listed in Figure 3.

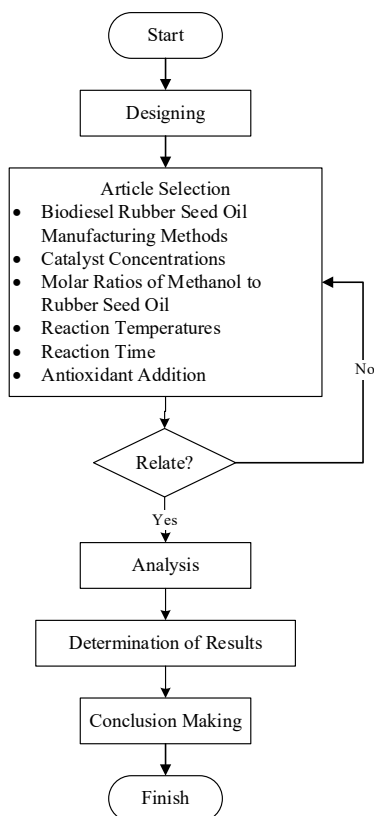


Figure 3. Literature Review Flow Diagram

DISCUSSION

From the search, selection, and analysis of the related journals, fifteen journal articles related to the focus of this literature review were collected. There are three different biodiesel production methods from the 15 journal articles, namely esterification-transesterification, one-stage transesterification, and in situ transesterification.

Quantitative Result of Esterification-Transesterification Methods

The manufacture of biodiesel by the esterification-transesterification method involves a two-stage reaction. The maximum yield obtained by this method varies from 75.6% to 99.7%. Table 2 presents quantitative data on biodiesel obtained with various operating conditions.

Table 2. Operating condition and resulting yield of biodiesel from rubber seed oil by esterification-transesterification methods

Reference	Esterification					Transesterification				
	Catalyst	Ratio Oil: Methanol	T (°C)	Time (mins)	FFA (%)	Catalyst	Ratio Oil: Methanol	T (°C)	Time (mins)	Yield (%)
[9]	3 %-w H ₂ SO ₄	1 : 2 (mass)	60	180	69.1	2 %-w KOH	1 : 2 (mass)	60	120	95

Reference	Esterification					Transesterification				
	Catalyst	Ratio Oil: Methanol	T (°C)	Time (mins)	FFA (%)	Catalyst	Ratio Oil: Methanol	T (°C)	Time (mins)	Yield (%)
[19]	0.5 %-v H ₂ SO ₄ 98%	5 : 1 (vol.)	50	60	-	1 %-w KOH	4 : 1 (vol.)	60	60	81.7
[20]	2.5 %-w H ₂ SO ₄	1 : 6 (molar)	60	30	2.9	1.5 %-w KOH	1 : 9 (molar)	60	-	96.4
[21]	5 mL/L H ₂ SO ₄	1 : 9 (molar)	60	60	3.2	3.7 g/L NaOH	1 : 6 (molar)	60	60	88
[22]	2 %-w H ₂ SO ₄ 18M	1 : 20 (molar)	60	60	1.8	1 %-w KOH	1 : 8 (molar)	65	120	-
[23]	10 mL 5 %- (w/v) H ₂ SO ₄	1 : 6 (vol.)	60	120	2.1	50 mL 0.5 %- (w/v) NaOH	1 : 9 (vol.)	60	120	-
[18]	18 M H ₂ SO ₄	1 : 8*	60	60	-	1 %-w KOH	5:57 : 1 (mass)	65	120	-
[24]	0.5 %-w H ₂ SO ₄	1 : 6*	-	-	-	1 %-w KOH	1 : 6*	55	30	80
[24]	0.5 %-w H ₂ SO ₄	1 : 6*	-	-	-	1 %-w NaOH	1 : 6*	55	30	75.6
[25]	3 %-v H ₂ SO ₄	1 : 15 (molar)	65	120	-	4 %-w CaO	1 : 12 (molar)	-	120	99.7

*Not Mentioned

Quantitative Result of One-Stage Transesterification Methods

There are three studies that observed the operating conditions in the manufacture of biodiesel rubber seed oil with one-stage transesterification method. Quantitative results in the form of yields from the three studies vary from 86.79% to 98.7% and can be seen in Table 3.

Table 3. Operating condition and resulting yield of biodiesel rubber seed oil product by one stage transesterification methods

Ref	One Stage Transesterification				
	Catalyst	Ratio oil: methanol	T (°C)	Time (mins)	Yield (%)
[26]	CaO 6%-w	1 : 4 (molar)	65	240	96.9
[27]	BaCl ₂ /CaO 200 mm	1 : 12 (molar)	60	120	98.7
[28]	KF/CaO-Fe ₃ O ₄ -Al 1.5%-w	1 : 28 (molar)	220	49	86.79

Quantitative Result of In-Situ Transesterification Methods

In situ transesterification is a method where the raw material in the form of seed is directly contacted with alcohol and acid or alkaline catalysts. In this method, the process of oil extraction and transesterification reaction occurs simultaneously in one process [29]. Table 4 contains the yield data produced by this method. The yield varies from 74% to 91.05%.

Table 4. Operating condition and resulting yield of biodiesel rubber seed oil product by in situ transesterification methods

Ref	In Situ Transesterification				
	Catalyst	Ratio oil : methanol	T (°C)	Time (mins)	Yield (%)
[30]	H ₂ SO ₄ 0.5%-v	1 : 3 (w/v)	60	120	91.05
[31]	3 g KOH/g rubber seed	1 : 6 (w/w)	60	120	96
[32]	1 mL NaOH p.a 0.1 N	1 : 2.38 (w/v)	60	120	74

Quantitative Result Based on SNI 7182-2015

Qualitative analysis was conducted by comparing biodiesel products from the reference literature to SNI 7182-2015. Qualitative analysis is done to reference literature which results with the highest yield in each method. This is done to facilitate the conclusion of the most effective method and optimum operating conditions in the process of producing biodiesel. In Table 5, it can be seen that almost all characteristic testing data meet the standards, except carbon residues in Thaiyasuit, et al. [20] and density studies in Abdulkadir, et al. [32].

Table 5. Qualitative comparison of biodiesel produced to sni 7182-2015

Parameters	Units min, max	[19]	[20]	[25]	[27]	[31]	SNI 7182- 2015
Density	kg/m ³	887.4	878.9	-	890	897	850 – 890
Kinematic viscosity	mm ² /s (cSt)	4.456	5.67	4.49	4.8	4.68	2.3 – 6.0
Cetane Number	Min	51.2	51.23	-	56	-	51
Flash point	°C, min	187	179	140	160	-	100
Cloud Point	°C, max	3.4	-	-	12	4.8	18
Copper plate corrosion	Max	-	-	-	-	-	1
Carbon residue	%-w, max	0.22	0.043	-	-	-	0.05
Water and sediment	%-volume, max	-	0.026	-	0.02	-	0.05
Distillation Temperature	°C, max	-	345	-	-	-	360
Phosphor	mg/kg, max	-	-	-	-	-	4

Table 6. Qualitative comparison of biodiesel produced to sni 7182-2015

Parameters	Units min, max	[20]	[33]	[25]	[27]	[34]	SNI 7182- 2015
Acid value	mg- KOH/g, max	0.18	-	0.26	0.42	0.65	0.5
Free Glycerol	%-w, max	-	-	-	0.009	-	0.02
Total Glycerol	%-w, max	0.23	-	-	0.13	-	0.24
Methyl ester content	%-w, min	96.4	-	-	-	-	96.5
Iodine value	%-w, max	82.9	-	-	115	-	115
Oxidation Stability	Hours	7.82	-	-	-	-	6

Effect of Operating Conditions

Methods of biodiesel manufacturing with the combination of esterification-transesterification reactions are more desirable than the other two methods. This is due to FFA levels in rubber seed oil that is more than 2% which can cause soaping and complicate the process of separation of products so that the FFA levels need to be lowered by esterification reactions [25], [35]. One-stage transesterification methods are also desirable for the limestone (CaO) catalyst used that is heterogeneous, reusable, non-corrosive, and has a high tolerance to water and FFA in oil. Meanwhile, the advantage of in situ transesterification method is in the short pretreatment process because the oil extraction process is not done separately. Thus, the cost of oil extraction and refining solvents will be cheaper, and the manufacturing process will be easier [36]. The highest yield from all reference libraries is found in research by Bharadwaj, et al. [25], with a yield of 99.7% using a two-stage reaction method. Although the methods used are the same, there is still a difference in the amount of yield. The resulting yield difference is caused by other effecting factors, such as catalyst concentration, temperature, oil-to-methanol ratio, and different times.

The catalyst used as well as the amount of the use, will affect the biodiesel produced [37], [38]. In esterification reactions, catalysts are needed to accelerate the reaction and increase the number of esters. H₂SO₄ catalysts are more desirable due to low prices and high catalytic activity [39]. In addition, more concentrations of H⁺ ions in H₂SO₄ than HCl cause the formation of more active intermediate compounds, and the reaction rate will be faster [13], [24], [39]. The H₂SO₄ catalyst also serves as a water puller because the esterification reaction is an equilibrium reaction that produces water [40]. In Thaiyasuit et al. [20] research, the addition of H₂SO₄ catalysts of 2.5 %-w was shown to lower FFA levels from 20% to 3%. More than 2.5 %-w, decrease in FFA content is not significant. However, Devi et al. [33] research finds that the use of the heterogeneous acid catalyst Fe₂(SO₄)₃ can reduce FFA more than the H₂SO₄ catalyst. KOH catalysts are more desirable for transesterification reactions because they are more stable and can produce biodiesel with better characteristics [41]. Based on Wicakso et al. [24] research, KOH catalyst also produce biodiesel with a higher yield and smaller acid values than NaOH catalysts. The addition of 0.5 %-w KOH resulted in a biodiesel yield of 89.3% [20]. While in other studies, the addition of 1 %-w KOH produced a biodiesel yield of 81.69% [19]. The addition of too many

KOH catalysts can cause side reactions in the form of saponification so that soap products block methanol contact with oil and cause yields to decrease. The CaO catalyst was chosen to support the reaction in the one-stage transesterification method. Buasri and Loryuenyong [27] obtained a maximum yield of 98.7% with the use of a 200 mm BaCl₂/CaO catalyst bed. This selection is based on the fact that Ba²⁺ ions are highly alkaline when added to Ca²⁺ ions, resulting in high yields under low reaction conditions [42], [43]. Additions of too much catalyst do not show a significant increase in yield, it can even lower the yield as reported by Gimbut, et al. [26]. This is because the characteristics of the transesterification reaction is reversible, allowing for a reverse reaction [44]. In the in situ transesterification method, the maximum biodiesel yield achieved is 96% with the use of KOH catalyst as much as 3 g [34]. The base catalyst in this method also serves to help break down the seed cell wall so that methanol can come into contact with the oil in the cotyledon cell [45].

The methanol-to-rubber-seed-oil molar ratio plays an important role in affecting biodiesel conversion efficiency [46]. Esterification and transesterification reactions are reversible reactions that require excessive amounts of methanol from their stoichiometry needs to increase solubility, contact between alcohol and oil molecules, and shift reactions toward products [47], [48]. Thaiyasuit, et al. [20] examined the effect of increasing the ratio of methanol to oil on esterification reactions. the most significant decrease occurred in the molar ratio 6:1 where the FFA rate dropped to 2.92% from 20%. The increase in the ratio of methanol to oil is directly proportional to the decrease in FFA content that occur, but the excessive amount of methanol can cause methanol to move to the product phase making it difficult to separate and decrease viscosity, density, and flash point [13], [41], [49]. In line with the esterification reaction, the addition of excess methanol to the transesterification reaction also increases the yield of biodiesel produced. Thaiyasuit, et al. [20] reported that the highest yield of biodiesel was obtained by 90.1% when the molar ratio was 4.5:1. Research by Rusmaningtyas, et al. [22] and Siswani, et al. [6] showed that the molar ratio was directly proportional to density. Qualitatively, the molar ratio 4: 1 and 5: 1 has not provided biodiesel quality that met SNI 7182-2015 standards. In the one-stage transesterification method, Buasri and Loryuenyong [27] reported that the increase in biodiesel yield occurred at a ratio of 6: 1 to 12: 1. A further increase in the ratio will increase the yield, but a stable emulsion will be formed that is difficult to separate from biodiesel [50]. Gimbut, et al. [26] research shows that excessive amounts of methanol in reversible reactions will decrease conversions due to increased solubility of byproducts [51]. In the insitu transesterification method, the ratio used is the volume of oil to the mass of rubber seeds. This is due to the rubber seeds which are not extracted in advance is difficult to determine the molar amount of the raw material. The most optimum mass ratio for producing biodiesel is 6 : 1, with a yield of 96.1% [31]. However, with this ratio, the density of biodiesel produced is higher than the specified standard. To overcome this, the mass ratio can be more increased.

Reaction temperature is one of the factors that affect the reaction rate. Generally, the increase in temperature leads to an increase in kinetic energy resulting in a faster reaction rate. When the kinetic energy of the reactant molecule increases, more inter-reactant collisions result in the product [52]. For esterification reactions, commonly used temperatures range from 50°C – 65°C. Esterification at 50°C results in a relatively smaller biodiesel yield than higher temperature esterification. Bharadwaj research, et al. [25] used esterification reaction temperature of 65°C and obtained the highest biodiesel yield of 99.7%. Kusumaningtyas and Bachtiar [19] reported that a temperature of 60°C was most appropriate for transesterification reactions. In line with Darnoko and Cheryan's theory [53], the reaction rate will continue to increase to 60°C but higher

temperatures will not provide maximum conversion [54]. The increase in temperature will result in a decrease in viscosity and density of fluid because the particles becoming stretched and their molecular coherence reduced [55], [56]. In the one-stage transesterification method, the reported optimum reaction temperature of Buasri and Loryuenyong [27] is 60°C. Lower temperatures lead to low conversion due to limited mass transfer as well as the solubility of both reactants, while higher temperatures decrease conversion presumably because methanol evaporation decreases catalyst activity. Despite, temperatures above 60°C are not recommended. Yoswathana [28] uses a temperature of 220°C which performed on methanol subcritical conditions. The reaction temperature for the most suitable in situ transesterification is 60°C with a yield of 96% [40].

Reaction time that continues to increase will also increase biodiesel production to balance, but further increasing will only lead to a decrease in methyl ester products [9], [57]. In the study by Arita, et al. [9] products increase significantly at a 2-hour esterification reaction time. Meanwhile, the reaction time of 1 hour yielded only 11% because the reactants have not yet reacted perfectly meanwhile the 3-hour reaction time yielded 95%. Transesterification reactions generally use a reaction time of 2 hours, but Kusumaningtyas and Bachtiar [18] use a 1-hour reaction time and produce a relatively lower biodiesel yield. In one-stage transesterification, Buasri and Loryuenyong reported a 2-hour reaction time can yield 98.7%, while a 3-hour reaction time only gives a yield increase of 0.28% so it is considered less effective. Rahim and Prihatiningtyas [32] performed temperature variations on in situ transesterification and obtained a reaction time of 2 hours as the most optimum but the characteristics of biodiesel produced have not met SNI 7182-2015 standards. Abdulkadir, et al. [31] and Widayat, et al. [30] also used a 2-hour reaction time for in situ transesterification.

Effect of Operating Conditions

Given the properties of rubber seed oil that is easily oxidized when stored in the open air for it is a drying oil, it is necessary to add antioxidants to its biodiesel products [4], [7], [58]. Primary antioxidant types of TBHQ, D-TBHQ, BHA, BHT, PG, and OG are added to biodiesel to break reactive radical chains and convert them into stable compounds. Antioxidants inhibit oxidation by lowering the energy bond by releasing H molecules to be donated to lipid radicals in order to stabilize and make it uneasy to react [59], [60]. She, et al. [61] obtained biodiesel rubber seed oil by esterification-transesterification method. The physical and chemical properties also the induction period of biodiesel produced are then determined. Before the addition of antioxidants, the biodiesel induction period was valued 0.81 hours due to the high content of linoleic acid, oleic acid, and linolenic acid which causes biodiesel to be easily oxidized. Standard biodiesel induction period in SNI 7182-2015 is 6 hours. Each antioxidant is added in a dosage of $1000 - 6000 \times 10^{-6}$ (ω). The addition of TBHQ antioxidants as much as 1000×10^{-6} (ω) showed the most significant effect in increasing the biodiesel induction period from 0.81 hours to 6.41 hours. Meanwhile, BHT antioxidants need to be added as much as 4000×10^{-6} (ω) to be able to achieve the standard induction period. TBHQ antioxidants are superior to BHT because they can donate two hydrogen atoms to radicals and have better resonancing capabilities. Antioxidants D-TBHQ, PG, and OG need more than 5000×10^{-6} (ω) addition to reach the standard. Meanwhile, BHA antioxidants cannot increase the induction period to reach the standard. The addition of antioxidant BHA more than 1000×10^{-6} (ω) even decreases the induction period. The BHA antioxidants are no more effective than other antioxidants because the number of hydroxyl groups in their benzene rings

is only one, while PG has three hydroxyl groups. However, the addition of BHA and PG when combined with other antioxidants can increase its antioxidation effect. It is proven that the combination of BHA – D-TBHQ, BHA – PG, D-TBHQ – PG, and OG – PG will increase the induction period values more than when the antioxidant is added by itself.

CONCLUSION

From the literature review that had been conducted, it can be concluded that the esterification-transesterification method is the most effective method for producing biodiesel. Quantitative analysis was done based on yield obtained and qualitative analysis was done by comparing to SNI 7182-2015 standards. The use of H_2SO_4 catalysts as much as 2.5%-w, methanol-to-oil molar ratio of 6: 1, reaction temperature of 60 – 65°C, and a reaction time of 2 hours is the optimum operating condition for esterification reactions. Meanwhile, the use of KOH catalyst as much as 0.5%-w, methanol-to-oil molar ratio of 4.5: 1, reaction temperature of 60°C, and reaction time of 2 hours are the optimum operating conditions for transesterification reactions. It can also be concluded that the addition of antioxidant TBHQ at a dose of 1000×10^{-6} (ω) can increase the biodiesel induction period to become 6.41 hours, fulfilling the SNI 7182-2015, which is 6 hours.

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