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Extraction of polyunsaturated fatty acids to reduce the iodine number of biodiesel products

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Abstract. In the last ten years, Indonesia has succeeded in realizing the production and commercialization of oxygenated biofuel/bioethanol and bioethanol, even has applied mixing biodiesel into diesel to up to 20%-volume (or known as a B20 mixture). This success has at least helped reduce imports of fuel oil (BBM) such as diesel and gasoline, but no more than 20%. The rest (i.e., at least 80%) must still be imported and will cause severe pressure on the country's balance of payments because the current volume of fuel imports is no less than 50% of domestic needs. The quality of Indonesian biodiesel products generally still has a high cloud point and low oxidation stability. Diesel engine fuel consists of a mixture of methyl ester fatty acids (FAME: Fatty Acids Methyl Ester). Many constituent components are limited or not large (consist of 7-14 carbons). The essential constituents are the methyl esters of lauric, myristic, palmitic, stearic, oleic, linoleic, and linolenic acids. Methyl esters of polyunsaturated fatty acids (linoleic, linolenic, eleostearic) are inferior because they have a low cetane number and low oxidative stability. While methyl esters of saturated fatty acids have a superior demonic rate but have a high melting point (bad, higher than the requirements given by SNI). Related to the amount of unsaturated fat in biodiesel, it can reduce the quality of biodiesel, such as acid numbers, moisture content, and the emergence of sludge. Based on the current condition of biodiesel quality, to improve the quality of biodiesel produced can be done by reducing the number of unsaturated fats present in the biodiesel product. The initial step that has to be done is separation biodiesel products into saturated biodiesel with the characteristic iodine number <30-40 and unsaturated biodiesel with an iodine number > 70 through a fractionation process. Extraction was carried out using $AgNO_3$ with variations in the ratio of biodiesel feed to solvents. The best ratio of biodiesel:$AgNO_3$ to eliminate the levels of polyunsaturated free fatty acids in biodiesel products is 1:2 with an iodine value of 47.38 gr I_2/(100 gr oil)

1. Introduction

Biodiesel is an oxygenated biofuel for diesel engines consisting of a mixture of methyl esters from fatty acids. Until now, the use of biodiesel is still limited as a mixture of petroleum diesel. In trade terms, diesel oil mixed with biodiesel is stated in B-XX notation. For example, the B-10 shows that the fuel mixture contains 10% biodiesel volume and 90% diesel fuel volume. At present, Indonesia is the country that implements the mixing of biodiesel into diesel the highest in the world, which is 20% by volume (known as B20). The utilization of B20 has been approved by the Japanese Automobile Manufacturers Association (JAMA) has also made an open statement accepting and approving the use of B20 in tropical countries as long as the biodiesel is made from palm oil [1].

Although it is recognized as the best today, palm biodiesel has several weaknesses:

a. Cloud point is relatively high, which is around 18 °C. This makes palm biodiesel unusable at relatively high levels of blending in cold regions such as North Europe, North America, Japan, Korea, China, South Australia and New Zealand and (in Indonesia) the PT Freeport mining operations in Papua. This is a result of the fact that palm biodiesel contains many unbranched fatty acid groups (palmitate and stearic).
b. Compared to diesel fuel (B0), the oxidative stability of palm biodiesel is still much lower. The reason for this is that palm biodiesel still contains unsaturated fatty acid groups (especially polyunsaturated ones).

Soerawidjaja (2015;2017) states that the ideal biodiesel (or high-performance biodiesel) is biodiesel which has the following characteristics: (1) does not contain methyl esters from polyunsaturated fatty acids; (2) the chain of saturated fatty acids is not straight but branched methyl in the middle; and (3) preferably, containing several percent methyl esters of lauric oil (coconut, palm kernel) [2, 3].

Achievement of feature #3 can only be done by mixing a small amount of coconut biodiesel or palm kernel-core biodiesel into palm biodiesel, while feature #1 and feature #2 can only be achieved if appropriate chemical processing is done, which includes: (1) Elimination of groups polyunsaturated fatty acid groups through extraction and/or hydrogenation, and (2) Isomerization of the methyl branching of saturated fatty acid groups.

Polyunsaturated FAMEs, such as linoleic and linolenic, have low cetane rates and very low oxidative stability [4]. In addition, the presence of methyl esters of polyunsaturated fatty acids in biodiesel will have a catalytic effect significantly reducing the stability of biodiesel oxidation.

Methyl oleate has oxidation stability of about 14 hours while methyl linolenic oxidation has a stability of about 0.2 hours. If the mixing has a linear effect on the stability of oxidation, then the oxidation stability of the mixture of 88% methyl oleate - 12% methyl linolenic should be (0.88 x 14) + (0.12 x 0.2) = 12.34 hours. Figure 3 shows that the mixture has only about the same oxidation stability as methyl linolenic acid, thus showing the very poor catalytic effect of the presence of polyunsaturated FAMEs on the stability of biodiesel oxidation [5].

So to produce biodiesel with high oxidation stability, polyunsaturated FAMEs need to be removed from biodiesel. Furthermore, hydrogenation of these polyunsaturated FAMEs to at least monounsaturated FAMEs will allow it to be re-mixed into biodiesel components. The removal of polyunsaturated FAMEs can be done by extraction [6] or fractionation [7].

The purpose of this research is to determine the ratio between biodiesel feed and the amount of $AgNO_3$ used as a solvent so that polyunsaturated fatty acids can be removed entirely from feed biodiesel products and analyze the iodine number of raffinate products from the extraction process.

2. Methods

The study focused on testing the saturation FAME fractionation procedure (iodine number <30-40) and unsaturated (iodine number > 70) by extraction method using silver nitrate ($AgNO_3$) solvent [6]. The biodiesel used is obtained from domestic biodiesel producers, namely PT. Wilmar Bioenergy Indonesia. The raw material preparation stage consists of making an indicator of $MgSO_4$ desiccated, the FAME dehydration process (biodiesel), and the manufacture of $AgNO_3$ solvent reagents.

The FAME extraction step consists of the complex formation reaction phase between Ag^+ ions and the carbon double that is owned by unsaturated FAME. This reaction is estimated to reach equilibrium within 3 hours. After equilibrium is reached, the saturated fatty acid phase is separated from the aquatic phase (which contains the complex compounds produced) so that the saturated FAMEs can be separated from the unsaturated FAMEs. Then the washing and purification process is carried out for each saturated and unsaturated FAMEs that has been successfully separated.

The initial FAMEs (as received) and the saturated as well as unsaturated FAMEs that have been successfully separated were then analyzed with GC-MS to quantify their composition of the fatty acids. Their iodine numbers were also analyzed using the Wijs reagent follows the standard method of AOCS Cd 1-25. FAMEs composition analysis using GC-MS. Samples were diluted 20 times with hexane. The GC-MS used is the 2010 Shimadzu brand equipped with RTX-5 MS columns with dimensions of 30 m x 0.25 mm x 0.25 μm with AOC-20i auto-injector.

3. Results and Discussion

At the fractionation stage in connection with this series of studies, no direct oil and vegetable fats or fatty acid esters have been made thereof but using biodiesel obtained from PT Wilmar as a sample of raw material for the experiment. The GC-MS analytical results of fatty acid ester/acid compositions in feed biodiesel obtained from PT. Wilmar are presented in Table 1.

Table 1. Composition of fatty acids/esters in the original biodiesel (obtained from PT. Wilmar)

No	Fatty acid	%
1	Laurate acid (C12:0)	0.68
2	Miristate acid (C14:0)	2.15
3	Palmitate acid (C16:0)	39.17
4	Stearate acid (C18:0)	7.18
5	Oleate acid (C18:1)	42.41
6	Linoleate acid (18:2)	5.87
7	Others	2.54
	Total	100

The composition of saturated, monounsaturated, and polyunsaturated fatty acid ester metal (FAME) fractions based on GC-MS chromatogram data is presented in Table 2.

Table 2. Composition of saturated and unsaturated biodiesel in the original biodiesel

No	Biodiesel feed (FAME)	%
1	Saturated FAMEs	49.18
2	Monounsaturated FAMEs	42.41
3	Polyunsaturated FAMEs	5.87
3	Others	2.54
	Total	100

The biodiesel fractionation was carried out through a series of dehydration experiments of water molecules from the pristine biodiesel, which is carried out through the stripping of water molecules from the biodiesel sample using MgSO4 characterized in a desiccator. The process was then continued with the application of extraction treatment using silver nitrate ($AgNO_3$) as reported by Teramoto et al. (1994) [6]. Both series of experiments mentioned above, carried out on biodiesel initially which has an iodine number (AI) 57.22 gr I2/100 gr sample. The hope, with the extraction method Teramoto et al. (1994) will produce saturated biodiesel with an AI range of 30-40. From the beginning, the accent of

this research was to produce high-performance/high-performance biodiesel, which is biodiesel with low cloud point (<< 18 °C) and high oxidation stability.

The results of the test for the composition of fatty acids/esters of fatty acids contained in saturated biodiesel (extraction results) have been carried out with GC-MS instruments. The results of the composition analysis are presented in Table 3.

Table 3. Composition of fatty acids/esters in the original biodiesel and saturated FAMEs

No	Fatty Acid	%-area			
		Biodiesel feed	Saturated FAMEs		
			ratio 2:1	ratio 1:2	ratio 1:2.5
1	Laurate acid (C12:0)	0.68	1.22	0.73	0.75
2	Miristate acid (C14:0)	2.15	3.47	2.34	2.23
3	Palmitate acid (C16:0)	39.17	42.73	42.48	41.37
4	Linoleate acid (C18:2)	5.87	4.27	0	0.03
5	Oleate acid (C18:1)	42.41	38.4	44.82	41.48
6	Stearate acid (C:18:0)	7.18	6.42	7.19	7.25
7	Others	2.54	3.49	2.44	6.89
	TOTAL	100	100	100	100

The data in Table 4 shows the progress of the separation of saturated and unsaturated biodiesel by the extraction method using silver nitrate ($AgNO_3$) solvent. There is a significant increase in C16 saturated fatty acids, along with a decrease in monounsaturated fatty acids (C18: 1) in three series of extraction experiments. This phenomenon implies that the extraction process using silver nitrate solvent takes place quite well, because at a ratio of 1: 2 all polyunsaturated fatty acids can already be removed from biodiesel feed products.

Table 4. Data of iodine number and oxidation stability of each extraction product in the variation of the feed ratio to the $AgNO_3$ solvent

No	Ratio of feed to solvent	Parameter	Biodiesel feed	Saturated FAMEs	Unsaturated FAMEs
1	2 : 1	Iodine number (gr I_2/100 gr sample)	57.22	52.62	155.71
2	1 : 2	Iodine number (gr I_2/100 gr sample)		53.21	159.04
3	1 : 2.5	Iodine number (gr I_2/100 gr sample)		52.21	157.42

3.1. Optimization of biodiesel extraction through the demetalization process

Biodiesel extraction is still carried out using silver nitrate solvent, $AgNO_3$, pro analysis with variation ratio of biodiesel volume: $AgNO_3$ solution (1: 2). As explained by the ratio of biodiesel volume: $AgNO_3$ of 1: 2, has been proven to be able to separate all FAMEs polyunsaturated (aquatic phase) from saturated and monounsaturated FAMEs (biodiesel phase). Optimization of the extraction process is carried out by continuously flowing inert gas (Nitrogen) into the reactor to prevent oxidation reactions, which will reduce the oxidation stability of the extracted biodiesel phase.

The data shown in Table 5 indicate that the presence of each water and Ag on biodiesel influences the iodine value of saturated FAME. This indicates that the high iodine value in the saturated biodiesel

volume ratio experiment to $AgNO_3$ solution (1: 2) occurs due to the presence of Ag^+ and water left in the extracted biodiesel phase. Thus, efforts should be made to eliminate Ag content (demetalization) and evaluation of the washing process in the extracted biodiesel phase. Therefore, the iodine number was tested for the extraction results. Data on iodine figures of the two experiments are presented in Table 5.

Table 5. Best experiment (biodiesel volume ratio: $AgNO_3$ = 1: 2)

No	Parameter	Biodiesel feed	Saturated FAMEs	
			Without demetalization	With demetalization
1	Iodine number (gr I_2/100 gr sample)	57.22	53.21	47.38

Table 6 shows that after the demetalization process, the iodine number figures decreased by 9.84 points from biodiesel feed while the reduction in Ion Figures in the extraction experiments without demetalization is only 4.01 points from the original biodiesel.

In the second phase of the experiment, the Cloud Point and Pour Point Analyses were carried out on the extracted saturated biodiesel in the ITB laboratory. Table 6 presents the results of the analysis.

Table 6. Cloud point and pour point data

Sample	*Cloud Point* (°C)		*Pour Point* (°C)	
Biosolar	4.2	4.1	-1.0	-1.0
Biodiesel Wilmar	12.8	12.7	9.0	9.0
Saturated Biodiesel (1:2) with demetalization	13.2		9.0	

4. Conclusion

Extraction of ethyl methyl fatty acids (FAME) with $AgNO_3$ solvent with biodiesel volume ratio: $AgNO_3$ which is 1: 2 can separate all polyunsaturated FAMEs from saturated and monounsaturated FAMEs. The iodine value of saturated biodiesel demetalization products is 47.38 gr I_2/gr sample, or 9.84 points reduced from feed biodiesel going to the expected Iod number range (30-40).

5. References

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