The Influence of Essential Oil Addition to Oxidative Stability of Palm Oil Biodiesel

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Abstract. Palm oil biodiesel is a methyl ester of fatty acid which potentially facing oxidative rancidity during storage due to both internal or external factors, resulting in an increase of free fatty acid and peroxide compounds. This study aimed to determine the effect of essential oils addition as biodiesel antioxidants. The essential oils used were cloves leaves oil, patchouli oil and citronella oil with concentrations of 0.25% and 0.5%v/v. Oxidative stability was observed at storage temperature of 27°C and 60°C. The best treatment was chosen based on the highest CPI (Composite Performance Index) value, obtained from 0.5% clove oil addition at storage temperature of 27°C. The CPI value was 339.75, acid number 0.68 mg KOH/g, peroxide number 17.54 mg O2/100 g, kinematic viscosity 4.48 cSt and rancimat test 12.91 hours.

1. Introduction
Increasing energy demand, decreasing crude oil production and the occurrence of increasingly dangerous air pollution, encourage energy diversification efforts. Some alternative energy come from renewable resources (bioenergy), such as biodiesel, bioethanol and biogas. Indonesia is very potential to develop biodiesel, considering Indonesia is known as the second largest producer of crude palm oil (CPO) in the world. Biodiesel is derived from the reaction of plant oil (triglycerides) with an alcohol using an alkaline catalyst at a certain temperature and composition, resulting in two substances called alkyl ester (methyl ester or biodiesel) and glycerol. Biodiesel was developed in 1890 by the inventor of Rudolph Diesel, the diesel engine being the engine of choice for power, reliability and high fuel economy worldwide. Biodiesel is the name of a fuel-based ester (fatty ester).

Fatty acids are generally more reactive to oxygen by increasing the number of double bonds in the molecular chain. Therefore, the higher the number of fatty acids binding together in an oil, the higher the occurrence of oxidation process, which in the oxidation process will produce a variety of substances, one of which is a free fatty acid whose existence is very detrimental to the quality of oil [1].

Antioxidant addition is need to prevent oxidation reactions in biodiesel that can reduce the quality of oil and damage the diesel engine. The most widely used antioxidant substances today are Butylated Hydroxy Toluene (BHT) and Butylated Hydroxy Anisole (BHA). However, those antioxidants is chemically synthetic, therefore it is necessary to find alternative antioxidant substances which are
natural. Essential oil is volatile oil extracted from plants which rich in terpenes, aromatics, and other miscellaneous compounds.

Essential oils contain compounds that function as antioxidants that have anti-radical properties. Essential oils consisting of fatty acids such as palmitic acid, ethyl palmitate, and ethyl stearate and carboxylic acid derivatives such as methyl hexadecanoate, ethyl octate and 14, 16 dienoic, methyl nonadeca 15, 17 are considered possible as proton donors to DPPH so that nonradical DPPH is formed who have the ability as antioxidants. Antioxidant activity against essential oil components is influenced by the compound structure [2]. In general essential oils have lower antioxidants compared to commercial antioxidants [3].

Ester compounds in essential oils are known to have antioxidant properties, so research is needed to try the use of essential oils as an antioxidant agent in biodiesel oil. This study aims to identify the ability of citronella oil, clove oil and patchouli oil as palmoil biodiesel antioxidants.

2. Methodology

2.1 Materials

The materials used in the study were pure biodiesel from palm oil (olein), essential oils of clove, patchouli and citronella. For the acid value test, 95% ethanol, PP indicator, and KOH 0.1 N. The test of peroxide value using glacial acetic acid, chloroform, saturated KI, 1% starch indicator and Na$_2$S$_2$O$_3$. Analytical instrument was spectrophotometer and rancimat equipped with 743 Rancimat 1.0 Personal Computer Program at Laboratory of Fuel Technology Center and Design Engineering (BPPT)

2.2 Method

Essential oils were added to the biodiesel in concentration of 0.25 and 0.5% (v/v). Biodiesel was then poured in a clear glass bottle with fabric stopper, and stored in a temperature of 27 °C and 60 °C. The selected container is a clear bottle, so that the light can interact with biodiesel and the stopper was made from fabric and not to be airtight so that oxygen was easily contact with biodiesel. With the presence of light and oxygen is a factor that accelerates the oxidation is not hindered, so the activity of the three essential oils as an antioxidant can be tested for its ability in inhibiting the oxidation process. The effects of antioxidative activity was evaluated in different concentration and temperature by measuring peroxide value, acid value, viscosity, and oxidative stability by DPPH and rancimat.

Antioxidant activity was determined by DPPH method (1,1-diphenyl-2-picrilhydrazil). Each sample was dissolved in methanol and prepared in concentrations of 50, 100, 150, 200, and 250 mg/L. The sample was then piped 1 ml with a micro pipette, then 1 ml of 0.1 mM DPPH solution in methanol was added. The solution mixture was homogenized and the absorption was measured by a UV-Vis spectrophotometer at a maximum wavelength of DPPH of 517 nm [4]. The test was conducted three times for each concentration of sample solution. The standard solutions were ascorbic acid with concentrations of 2, 4, 6, 8, and 10 μg/ml. Antioxidant activity was determined by the amount of DPPH radical uptake resistance by calculating the percentage of DPPH uptake inhibition, which was by the formula as follows. IC$_{50}$ value calculated based on concentration and inhibition percentage using linear regresson.

\[
\%\text{Inhibition} = \frac{\text{absorbance blank} - \text{absorbance sample}}{\text{absorbance blank}} \times 100\%
\]

Data analysis used was the CPI (Comparative Performance Index) decision-making method, which can determine the appraisal or ranking of various alternatives (i) based on several criteria
especially the criteria / different parameters of data trends. Results are determined from the highest rating ratings of the calculations. The formula used in CPI techniques can be seen as follows:

\[
\begin{align*}
A_{ij} & = X_{ij} \times 100 / X_{ij} \times 100 \\
A_{i(j+1,j)} & = X_{ij} / X_{ij} \times 100 \\
I_{ij} & = A_{ij} \times P_j \\
I_j & = \sum_{j=1}^{n} I_j
\end{align*}
\]

With:
- \( A_{ij} \) = alternative value in j criteria
- \( X_{ij} \) = alternative value in j first minimum criteria
- \( A_{i(j+1,j)} \) = alternative value in i+1 in j first criteria
- \( X_{i(j+1,j)} \) = alternative value in i+1 in j first criteria
- \( P_j \) = weight in j criteria
- \( I_{ij} \) = alternative index in i
- \( i \) = 1, 2, 3, …, n
- \( j \) = 1, 2, 3, …, m

3. Result
Oxidation process take place when there is a contact between oxygen in the air with oil or fat. The easiest way to know that there has been oxidation reaction in oil or fat is by the smell of rancid. Oxidation usually begins with the formation of peroxides and hydroperoxides. The next level is the decomposition of fatty acids accompanied by the conversion of hydroperoxides into aldehydes and ketones and free acids. Rancidity is formed by aldehydes rather than by peroxides, so peroxide value (PV) increases only as an indicator.

Compared to petroleum, biodiesel has lower oxidation stability. As an automotive fuel, biodiesel should meet EN 14214 standard on oxidation stability. Damage to oils and fats due to oxidation is classified into two, namely auto oxidation and thermal oxidation. Auto-oxidation occurs when fats or oils are exposed to air at room temperature, and the oxidation process occurs slowly so that the peroxide will accumulate in the oil and fat. Thermal oxidation is a phenomenon where the rate of oxidation reaction increases due to high temperatures. The products were hydrogen peroxide, carbonyl component such as aldehyde and polymer, so its viscosity increases.

**Peroxide Value**
The highest peroxide value of biodiesel was obtained by addition of citronella oil with concentration of 0.25% and heated at 60 °C. The properties of vegetable oils in general contain unsaturated fatty acids that will easily oxidize and cause a rapid increase of peroxide numbers. Clove oil at 0.5% concentration has the lowest peroxide number of 17.5 meq peroxide/kg biodiesel. Clove oil was more effective inhibiting oxidation reaction.

Peroxide value may be used as indicators of oxidative damage occurring in oils, fats, or oil-containing materials. The higher the peroxide value, indicating that oils have lower oxidative resistance, and will cause rancidity. Before the addition of essential oils, the peroxide value of biodiesel at room temperature was 18.87 meq/kg and after added with various essential oils at room temperature, the peroxide value continued to increase. The rate of increase varied depending on the effectiveness of each type of antioxidant.
It can be seen from Figure 1 that biodiesel without the addition of antioxidants (control) heated at 60 °C has increased the highest peroxide value compared to biodiesel with the addition of antioxidants at room temperature in general. This suggests that the oxidation process in biodiesel is accelerated through heating. Heat is one of the external factors that result in oxidative damage. The oxidation reaction is caused by the presence of unsaturated fatty acids which oxidized to form peroxide compounds [5]. The unsaturated lipid oxidation mechanism begins with the initiation stage. Lipids which contact with heat, light, metal ions or oxygen will form free radicals (R*). This reaction occurs in the methylene group adjacent to the double bond -C = C- (Buck, 1991). Peroxide radicals can impact to undamaged oils rich in double bonds (-C = C-) producing more peroxides.

**Acid Value**

The analysis of acid value is important because it indicates acid concentration which quite dangerous due to corrosion on the engine. Biodiesel without the addition of antioxidants can cause an increase in acid value quickly.
From the Figure 2, biodiesel at room temperature without the addition of antioxidants has an acid value of 0.57 mg KOH/g, while biodiesel heated at 60 °C has an acid value of 0.64 mg KOH/g. The increase of acid value due to the formation of free acids during oxidation of double bond of unsaturated fatty acids [6]. Biodiesel with 0.25% citronella oil at room temperature has the lowest acid value. Acid yields in nearly all treatments in biodiesel (except 0.5% clove at 60 °C) have met SNI 04-7182-2006 with acid values <0.80 mg KOH/g [7][8]. Biodiesel with 0.5% clove at 60 °C has the highest acid value due to the oxidation of unsaturated fatty acids from biodiesel and phenolic alcohol eugenol from clove to form aldehyde and carboxylic acid compounds [5].

DPPH Test

Table 1. Results of DPPH test

| Sample     | IC50 (ppm) |
|------------|------------|
| Clove oil  | 1515.83    |
| Patchouly oil | 96.74    |
| Citronella oil | 286.42  |

The value of IC50 (Inhibition Concentration 50) is the concentration of antioxidant (μg/mL) which is able to absorb 50% free radical compared to control through a linear equation. The value of IC50 is obtained from the intersection of the line between inhibition and concentration axis, then put into the equation y = a + bx, with y = 50 and the value of x denotes the value of IC50, a denotes the intercept value, and b denotes the slope value. The extract was declared active as an antioxidant when the IC50 value was less than 200 μg/mL [4]. Patchouli oil can be expressed as an active antioxidant. However, when DPPH test was conducted, the sample and test solution were not mixed homogeneously, so the value read in spectrophotometer were fluctuated.

The oxidation inhibition reaction of fat by the phenolic group antioxidants takes place by donating H atoms on lipid radicals. The ability of antioxidants in inhibiting oxidation is due to the presence of an alkyl group in the ortho meta position, and those which can increase the electron density of the hydroxyl group through the inductive effect, which will decrease the O-H bond energy, and the H atom will be easily released to be deposited on lipid radicals. A lipid radical that receives an H atom donor will not react with oxygen because it is stable so it can prevent peroxide formation.

The antioxidant potential of free radical trapping can be determined by using DPPH (1,1-diphenyl-2-picrylhydrazyl) methods that is a stable radical in methanol solution and capable of receiving an electron or a hydrogen radical. The DDPH method is a simple, fast, sensitive method of measuring antioxidants, less amount of sample and does not require many solvents as other tests (xanthine-xanthine oxidase, thiocyanate method). DPPH, when reacted with a substance which can donate hydrogen (antioxidant), is reduced to 1,1-diphenyl-2-picrylhydrazine which is characterized by the loss of violet color changed become pale yellow from the remaining picryl.

Rancimat Analysis

Vegetable oils and fatty-acid methyl esters (FAME) or so-called biodiesel have a relatively short storage time this is because the oil can be oxidized slowly by oxygen in the atmosphere. Oxidation products from biodiesel fuels or biodiesel blends will produce rancid fuel which damage the diesel engines. Oxidation stability is one of the important quality standards to be monitored in both the biodiesel production process and its storage (EN 14112).

Oxidation stability analysis of palm oil biodiesel (olein) and after addition of essential oils conducted by modified Rancimat method. Rancimat testing determine the end point limit as a minimum limit of fuel resistance to oxidation. The Rancimat method is also commonly called the Automated Swift Test
or Accelerated Oxidation Test where the Rancimat method is used instead of the previously very troublesome testing methods of Active Oxygen Method (AOM). The resulting induction time indicates the character of the fuel resistance to oxidation. The term induction time is more commonly termed as Oil Stability Index (OSI).

**Rancimat Test**

![Rancimat Test](image)

**Figure 3.** Rancimat test of biodiesel with the addition of essential oils

Oxidation stability by Rancimat test was set at minimum of 6 hours according to Biodiesel Quality Standard (SNI 04-7182: 2015) [7]. The highest value was obtained by induction time of 12.91 hours from the mixture of biodiesel with cloves at a temperature of 27 °C with a concentration of 0.50% while the lowest value was obtained with 1.77 hours of mixture of biodiesel and citronella at 60 °C.

The mixture of biodiesel and essential oils with a temperature treatment of 27 °C had higher oxidation stability compared to 60 °C. The mean value of the result from the 27 °C temperature treatment was 9.83 hours while the mean temperature of 60 °C was 5.14 hours. However, in a sample using cloves at 60 °C and 0.5% concentration had good results with a value of 9.55 hours.

The mixture of biodiesel with cloves has better results compared to patchouli and citronella. The mixture of biodiesel and citronella only has one sample above the limit with a concentration of 0.25% at 27 °C. For the mixture of biodiesel and patchouli oil have value above the limit at temperature of 27 °C for two different concentration, while for cloves, all above the limit except 0.25% at 60 °C. It can be concluded that temperature was more influenced to the oxidative stability than essential oil concentration.

**Viscosity**

![Viscosity](image)
Figure 4. Viscosity of biodiesel with the addition of essential oils
At storage, biodiesel tends to be susceptible to oxidation process and hydrolysis due to the presence of unsaturated fatty acids or methyl esters. The oxidation process take place when there is contact with light and oxygen. Rancid odor produced from the formation of peroxides and labile hydroperoxides, then causing the increase of viscosity value.

Based on data obtained from viscosity analysis and compared with Biodiesel Quality Standard (SNI 04-7182: 2015), viscosity of almost all biodiesel added with essential oil were slightly increased [7].

The initial viscosity of biodiesel was 4.35 cSt which was in the range of specified standard (1.9 – 6.0 cSt). High viscosity of fuel can make difficulties in fuel injection into combustion chamber, resulting in poor atomization of fuel which correlates directly with combustion quality, engine power, and exhaust emissions. If the viscosity is too low there will be a lot of maintenance and repair of the injection line.

CPI Analysis
The best treatment for the essential oil as antioxidant determined by the Composite Performance Index (CPI) which ranked the various alternatives (i) based on criterion (j). Alternatives here were acid number, peroxide number and Rancimat test result with 12 criteria of mixing treatment of biodiesel and atsiri. The results of CPI analysis can be seen in the following table.

| No | Sample          | Acid  | Peroxide | Rancimat | Acid  | Peroxide | Rancimat | Alternative | Rating |
|----|-----------------|-------|----------|----------|-------|----------|----------|-------------|--------|
| 1  | Citronella 27°C/0.25% | 0.36  | 38.22    | 8.62     | 30.00 | 13.77    | 194.80   | 238.57      | 6      |
| 2  | Citronella 27°C/0.50% | 0.46  | 25.85    | 5.86     | 23.48 | 20.36    | 132.43   | 176.26      | 8      |
| 3  | Patchouly 27°C/0.25% | 0.61  | 29.36    | 10.35    | 17.70 | 17.92    | 233.90   | 269.53      | 3      |
| 4  | Patchouly 27°C/0.50% | 0.61  | 21.90    | 10.08    | 17.70 | 24.03    | 227.80   | 269.53      | 4      |
| 5  | Clove 27°C/0.25%  | 0.53  | 27.65    | 10.63    | 20.38 | 19.03    | 240.23   | 279.63      | 2      |
| 6  | Clove 27°C/0.50%  | 0.68  | 17.54    | 12.91    | 15.88 | 30.00    | 291.75   | 337.63      | 1      |
| 7  | Citronella 60°C/0.25%| 0.64  | 52.54    | 2.87     | 16.88 | 10.02    | 64.86    | 91.75       | 11     |
| 8  | Citronella 60°C/0.50%| 0.68  | 46.80    | 1.77     | 15.88 | 11.24    | 40.00    | 67.13       | 12     |
| 9  | Patchouly 60°C/0.25%| 0.64  | 44.33    | 5        | 16.88 | 11.87    | 112.99   | 141.74      | 9      |
| 10 | Patchouly 60°C/0.50%| 0.71  | 44.59    | 4.88     | 15.21 | 11.80    | 110.28   | 137.29      | 10     |
| 11 | Clove 60°C/0.25%  | 0.78  | 43.66    | 7.83     | 13.85 | 12.05    | 176.95   | 202.85      | 7      |
| 12 | Clove 60°C/0.50%  | 0.89  | 37.12    | 9.55     | 12.13 | 14.18    | 215.82   | 242.13      | 5      |

Trend Parameter - - +
Criteria weight 0.3 0.3 0.4

Trend on Composite Performance Index (CPI) was identified as positive (the higher the better) and negative (the lower the better). For positive trend, the minimum value on each criterion is transformed to 100, while the other value is transformed proportionately higher. For negative trend, the minimum value on each criterion is transformed to 100, while the other value is proportionally lowered. Acid number has negative trend, the greater value mean that biodiesel mixture was increasingly oxidized, as well as peroxide value. From the result of CPI analysis, it was found that the best treatment was obtained from mixing of biodiesel oil with cloves at 0.5% concentration, with storage temperature 27 °C and the lowest rank was obtained by citronella oil with 0.5% concentration at storage temperature 60 °C.
4. Conclusions
Essential oils can be used as antioxidants in biodiesel but not all type was good for biodiesel blends. The best antioxidant for biodiesel was cloves with 0.50% concentration and storage temperature of 27 °C. This result was obtained from CPI analysis with an alternative value of 337.63. Temperature was the parameter that more influenced on the storage of biodiesel, while essential oils concentration was not very influential. There is a potency to use essential oils as antioxidant in biodiesel, but other types of essential oil should be discovered and also different parameters, such as temperature, concentration, and engine fuel test.

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