Synthesis of pyrogallol derivative as antioxidant additive for biodiesel using methyl linoleate from sunflower oil

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Abstract. Biodiesel is a renewable plant-based fuel as an alternative to fossil fuels containing fatty acid methyl esters. However, biodiesel has the disadvantage of oxidation instability because of the double bonds in the constituent fatty acid structures. One of the most effective antioxidant for biodiesel is pyrogallol. Unfortunately, pyrogallol has a low solubility in biodiesel. Subsequent research was developed by synthesizing pyrogallol derivative through the reaction between pyrogallol and a pure methyl linoleate using 2,2-diphenyl-1-picrylhydrazyl or DPPH as a catalyst. The results showed that the pyrogallol derivative formed was more soluble in biodiesel. However, the use of pure methyl linoleate is not economical because it has a high selling price. In this research, sunflower oil biodiesel with 54.13 % methyl linoleate which has been tested by GCMS will be used to synthesize pyrogallol derivative with a ratio of 10 mL biodiesel, 5 mL DPPH, and 5 mL pyrogallol. FTIR shows a shifting peak at 1240 cm⁻¹ which shows the formation of pyrogallol derivative. LCMS-MS indicates a possible molecular weight at 634 m/z consisting of methyl linoleate and dimer pyrogallol. UV-Vis of the derivatives in biodiesel shows that the derivative is more soluble in biodiesel in comparison with the solubility of pure pyrogallol.

1. Introduction

Biodiesel or Fatty Acid Methyl Ester (FAME) is a renewable plant-based fuel as an alternative to fossil fuels containing fatty acid methyl esters and also has many advantages. However, biodiesel has the disadvantage of oxidation instability [1]. This is caused by the presence of double bonds in the structure of its fatty acid constituents so that biodiesel is easily degraded by air, especially oxygen to form short-chain carboxylic acids, alcohols, ketones, and aldehydes [2]. In addition, storage conditions such as exposure to light and temperature, storage container materials, and the presence of impurity metals also include determinants of the level of oxidation of biodiesel [3].

Various studies have been carried out to improve the oxidation stability of biodiesel through the addition of antioxidant additives such as Propyl Gallate, Butylated Hydroxytoluene, Butylated Hydroxyanisole, Pyrogallol, and tert-Butylhydroquinone. Pyrogallol is the most effective antioxidant additive among other antioxidant additives to prevent oxidation that occurs in [4]. However, pyrogallol has the disadvantage of low solubility and stability against biodiesel [5]. This is because pyrogallol and biodiesel have different polarities so that they do not dissolve and cannot be distributed well [6].
Meanwhile, research shows that the combining reaction between phenolic compounds and alkyl molecules can increase the solubility and stability of oxidation by the addition of DPPH [7]. The research was then developed by synthesizing pyrogallol derivative compounds with pure methyl linoleate with DPPH catalyst and proven to increase the solubility of biodiesel [8].

In this research, methyl linoleate was obtained from sunflower biodiesel which will be reacted with pyrogallol using DPPH catalyst as a radical compound. Methyl linoleate from sunflower oil is used to replace pure methyl linoleate which is quite expensive. FTIR and LCMS were then tested to find the presence of pyrogallol derivative. UV-Vis was also tested to determine the solubility of pyrogallol derivative in palm biodiesel during a week of storage.

2. Methodology

2.1. Materials and Equipment
FAME was made through a transesterification reaction between 200 mL of sunflower oil that has been pre-heated (70 °C, 500 RPM) with a solution of KOH (molar ratio sunflower oil: methanol = 1: 6 with 1 wt% of oil mass). Sunflower oil was obtained from commercially market. Methanol, potassium hydroxide, pyrogallol and n-hexane were obtained from MERCK. 2,2-diphenyl-1-picrylhydrazyl (DPPH) was obtained from SIGMA-ALDRICH. Ethyl acetate and palm biodiesel were obtained from commercially market. Equipment were a centrifuge, Fourier Transform Infrared Spectroscopy (FTIR) Thermo Scientific™ FT-IR Spectrometer Nicolet iS5, iD5 ATR Accessory, Liquid Chromatography Tandem- Mass Spectrometry (LC-MS/MS) with MassLynx software and solvent: methanol:water (80:20) and a UV-VIS Spectrophotometer.

2.2. Synthesis Reaction
Synthesis reaction was prepared by mixing biodiesel and DPPH solution (0.1 mg DPPH / mL methanol) in a three-neck flask with nitrogen flow and rotation speed at 350 RPM. The color purple turned into a yellowish color which then was mixed with a solution of pyrogallol (1 mmol pyrogallol in 5 mL ethyl acetate). The reaction lasts for 15 min until the solution turns to yellow.

2.3. Examination of Pyrogallol Derivative Presence
Centrifugation was used to determine the homogeneity of the solution. Centrifugation was conducted for 15 min at 3500 rpm. FTIR and LC-MS/MS were used to see a shifting peak in C-O bonding, to determine a molecular weight and the possibility of pyrogallol derivative.

2.4. Solubility Test
The solubility of pyrogallol derivative in biodiesel was determined using a UV-vis spectrophotometer. The solubility of the pyrogallol derivative was then compared to the solubility of pure pyrogallol. Solubility of pyrogallol derivative in biodiesel was detected from the 360 nm wave number, while the solubility of pyrogallol in biodiesel was detected from the 343 nm wave number. Solubility test was carried out for 1 week with concentrations of 1000 and 2000 ppm for pyrogallol derivative. Meanwhile, the concentration of pyrogallol in biodiesel was 500 ppm. 0.25 mL sample was first dissolved in 19.75 mL n-hexane and stirred at 150 rpm at room temperature for 15 min.

3. Results and Discussion

3.1. GC-MS Sunflower Biodiesel
Gas chromatography-mass spectrometry (GC–MS) is an ideal technique for qualitative and quantitative determination of volatile and semi- volatile organic compounds in a wide variety of samples. GC can separate many volatile and semi- volatile compounds, but does not always selectively detect them whereas MS can selectively detect many compounds but cannot always separate them [9]. Table 1 shows the GC-MS results from sunflower biodiesel.
Table 1. Composition of methyl ester in sunflower biodiesel.

| Methyl Ester       | Retention Time (minute) | % Area |
|--------------------|-------------------------|--------|
| Methyl palmitate (C16:0) | 30.13                   | 8.33   |
| Methyl linoleate (C18:2)  | 35.07                   | 54.13  |
| Methyl oleate (C18:1)   | 35.29                   | 27.22  |
| Methyl stearate (C18:0)  | 36.01                   | 5.91   |
| Others               |                         | 4.41   |

From GC-MS results, the largest composition of sunflower biodiesel was methyl linoleate with 54.13 % area. This is consistent with the literature indicating that the largest content of biodiesel sunflower oil is methyl linoleate [10].

3.2. Synthesis Reaction
Table 2 shows the ratio variation between sunflower biodiesel, DPPH solution, and pyrogallol solution. Ratio 2:1:1 (Sunflower biodiesel: DPPH Solution: PY Solution) was the best variation because precipitates were not founded. Also, during the centrifugation test, the solution was homogeneous. This is consistent with previous research which uses a 1:1 volume ratio (pure methyl linoleate: PY solution) [8]. However, the amount of methyl linoleate which contained in biodiesel was 54.13 % so the most appropriate ratio between methyl linoleate and pyrogallol was 2:1.

Table 2. Effect of reactant composition to physical appearance of product.

| Sample | Sunflower Biodiesel Volume (mL) | DPPH Solution Volume (mL) | PY Solution Volume (mL) | Precipitate |
|--------|---------------------------------|---------------------------|------------------------|-------------|
| 1      | 5                               | 5                         | 5                      | Yes         |
| 2      | 5                               | 10                        | 5                      | Yes         |
| 3      | 5                               | 15                        | 5                      | Yes         |
| 4      | 10                              | 5                         | 5                      | No          |
| 5      | 15                              | 5                         | 5                      | Yes         |
| 6      | 10                              | 10                        | 5                      | Yes         |

3.3. Fourier Transform Infrared Spectroscopy (FTIR) Result
FTIR is a powerful tool for identifying different types of chemical bonds present in a molecule by producing an infrared absorption spectrum. Molecular bonds will vibrate at various frequencies depending on the type of bonds and element present [11]. Figure 1 shows the shift in wavenumbers between sunflower biodiesel and biodiesel pyrogallol derivative, as seen from 1243.46 cm\(^{-1}\) to 1240.35 cm\(^{-1}\). In this wavenumber, there is a C-O stretching (strong) bond which allows a shift in the wavenumber due to the reaction between methyl linoleate and pyrogallol. C atom of methyl linoleate will bind O atom of pyrogallol as the reaction mechanism described in Sutanto et al. research [8].
3.4. Liquid Chromatography Tandem-Mass Spectrometry (LC-MS/MS) Result

LCMS is a sensitive and specific analysis technique that can determine the identity and concentration of compounds in a sample at low concentrations [12]. Sample separation was conducted by the chromatography method with an Ultra High-Performance Liquid Chromatography (UPLC) system. Figure 2 shows the UPLC results for the pyrogallol derivative. Many peaks indicate that methyl linoleate was not pure.

LC-MS/MS use the C18 column as the stationary phase. Longer retention time indicates a longer component interacts with non-polar columns. So, the longer the retention time is, the more non-polar the compound is. Figure 3 with a retention time of 16.3 min found compounds with a molecular weight of 634 with a total area of 10.05 %.
Figure 3. Predicted molecular structure of pyrogallol derivative.

The possibility of this compound is methyl linoleate which binds with dimer pyrogallol (as shown in Figure 3). It is known that the molecular mass of methyl linoleate is 295 g / mol and that retention time can be seen at 14.94 min. Pyrogallol then forms a dimer pyrogallol because when pyrogallol oxidizes it can form poly-pyrogallol [13]. In this research, the molecular weight of pyrogallol is 167. LCMS tests show that most polar compounds have 167 molecular weights. Methyl linoleate will then bind dimer pyrogallol to form a pyrogallol derivative with a molecular weight of 634 at 16.31 min retention time (as shown in Figure 4).

Figure 4. Liquid Chromatography Tandem- Mass Spectrometry (LC-MS/MS) mass spectra of pyrogallol derivative with 16.3 min retention time.

Yield produced in this research is smaller than yield in previous studies [8]. One of the causes is in previous research, methyl linoleate used was pure methyl linoleate while in this research using biodiesel which has 54.13 % methyl linoleate. So, there is a possibility that methyl linoleate could react with other compounds.

3.5. Solubility Test

Biodiesel-Pyrogallol (B-PY), Biodiesel-Pyrogallol Derivative 1000 ppm (B-PD1), and Biodiesel-Pyrogallol Derivative 2000 ppm (B-PD2) were tested in the solubility test. If the solubility difference between week 1 and week 2 is close to 0, then the antioxidant has the best solubility. Table 3 presents the summary results of the solubility test.
Table 3. Solubility test results.

| Sample | Week 0  | Week 1  | Δ Absorbance |
|--------|---------|---------|--------------|
| B-PY   | 0.0559  | 0.0183  | 0.0376       |
| B-PD 1 | 0.0556  | 0.0261  | 0.0295       |
| B-PD2  | 0.0505  | 0.0197  | 0.0308       |

Table 3 shows that pyrogallol derivative antioxidants at 1000 ppm and 2000 ppm have better solubility than the solubility of pyrogallol in biodiesel.

4. Conclusion

Pyrogallol derivative was obtained from the synthesis of biodiesel which contains 54.13 % methyl linoleate and pyrogallol. Pyrogallol derivative produced may have a methyl linoleate structure that binds dimer pyrogallol. Pyrogallol derivatives have better solubility than pure pyrogallol in biodiesel.

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