Comparison of pyrogallol derivative performance using methyl linoleate from sunflower oil and corn oil as biodiesel antioxidant additives

N F Ahadan\textsuperscript{1}, H Adipoetra\textsuperscript{1}, A Nuryati\textsuperscript{1}, G P Dewi\textsuperscript{1}, and M Nasikin\textsuperscript{1}

\textsuperscript{1}Chemical Engineering, Department of Chemical Engineering, Universitas Indonesia, Depok, 16424, Indonesia
mnasikin@che.ui.ac.id

Abstract. Biodiesel is an alternative fuel derived from vegetable oils. Biodiesel has the disadvantage of being easily oxidized due to unsaturated bonds. Previous studies have shown that pyrogallol and pure methyl linoleate's reaction with 2.2 diphenyl-1-picrylhydrazyl (DPPH) to form pyrogallol derivative has been proven to improve the solubility and performance of pyrogallol as an antioxidant in biodiesel. However, the use of pure methyl linoleate is not economical if applied at the industrial scale. In this research, pyrogallol derivative performance using impure methyl linoleate obtained from transesterification of sunflower oil and corn oil, which forms sunflower biodiesel and corn biodiesel, was compared. Based on GCMS, the methyl linoleate content of sunflower biodiesel was 54.13\%, and corn biodiesel was 47.27\%. FTIR showed a shift in the C-O group's peak from the base of the biodiesel spectra, which shows the formation of a pyrogallol derivative. LCMS/MS showed m/z values indicating that the compound contained methyl linoleate and pyrogallol dimer. The addition of both compounds showed a low absorbance difference value in UV-Vis, thus have better solubility in biodiesel than pure pyrogallol. The addition of both compounds showed a negative slope of iodine number and a longer induction period than palm oil biodiesel.

1. Introduction
Biodiesel or also known as fatty acid methyl ester (FAME), is an alternative fuel derived from vegetable oils that are appropriate to replace petrodiesel fuel [1]. However, biodiesel has the disadvantage of being easily oxidized due to unsaturated bonds, which can reduce biodiesel quality [2]. The unsaturated bonds in the structure of fatty acids are easily degraded by air, especially oxygen, to form other compounds such as acids, aldehydes, esters, peroxides, ketones, and alcohols [3]. The oxidation stability of biodiesel can be improved by adding antioxidants to biodiesel [4]. Based on previous studies, pyrogallol is the best antioxidant used for biodiesel [5]. However, pyrogallol has a different polarity than biodiesel, and it makes pyrogallol poorly soluble in biodiesel [6].

Sutanto et al. reacted pyrogallol with pure methyl linoleate using a 2,2-diphenyl-1-picrylhydrazyl (DPPH) to form pyrogallol derivative and has been proven to improve the solubility and performance of pyrogallol as an antioxidant in biodiesel [7]. However, the use of pure methyl linoleate is not economical. For this reason, an alternative is needed to replace pure methyl linoleate, which is an impure compound containing methyl linoleate from the fatty acid methyl ester (FAME) of sunflower oil and FAME of corn oil. This research compares the performance of pyrogallol derivative using methyl linoleate contained in the biodiesel from both oils. The reaction results in pyrogallol derivative are detected through Fourier Transform Infrared Spectroscopy (FTIR) and Liquid Chromatography-
Mass Spectrometry (LC-MS/MS). The solubility test, iodine number, and induction period (IP) were conducted to determine the performance of the two pyrogallol derivative additives in improving the oxidation stability of biodiesel.

2. Methodology

2.1 Materials and Equipment
Sunflower biodiesel was made through a transesterification reaction between 200 ml of sunflower oil that has been pre-heated (70°C, 500 RPM) and a KOH solution (molar ratio sunflower oil:methanol = 1:6 with 1 wt% of oil mass). Corn biodiesel was made through a transesterification reaction between 200 ml of corn oil that has been pre-heated (60°C, 250 RPM) and a KOH solution (molar ratio corn oil:methanol = 1:6 with 1 wt% of oil mass). Sunflower and corn oil were obtained from Mazola. Pyrogallol, methanol, potassium hydroxide (KOH), and n-hexane were obtained from MERCK. 2,2-diphenyl-1-picrylhydrazyl (DPPH) was obtained from Sigma-Aldrich, ethyl acetate was obtained from Brataco, and palm oil biodiesel was obtained from Sinarmas. Fourier Transform Infrared Spectroscopy (FTIR) Thermo Scientific™ FT-IR Spectrometer Nicolet iS5, iD5 ATR Accessory. Liquid Chromatography-Mass Spectrometry (LC-MS/MS) with MassLynx software, solvent: methanol:water (80:20). UV-Vis Spectrophotometer with a wavelength range of 190-1100 nm. Wijs solution for iodine value was obtained from MERCK. 893 Professional Biodiesel Rancimat.

2.2 Synthesis Reaction
The synthesis reaction was carried out by mixing 10 ml sunflower biodiesel and corn biodiesel with DPPH solution (1 mg of solid DPPH and 10 ml of methanol) in a 100 ml three-neck flask connected to the magnetic stirrer with nitrogen flow and rotation speed at 350 RPM. The purple color would be turned into a yellowish color, which is then mixed with a solution of pyrogallol (0.126 g solid pyrogallol and 5 ml ethyl acetate). After that, the pyrogallol solution was added and stirred continuously for 15 minutes until it turned yellow.

2.3 Antioxidant Application in Biodiesel
Antioxidants from the synthesis reaction are biodiesel-pyrogallol derivative from sunflower biodiesel (B-PD (i)) and biodiesel-pyrogallol derivative from corn biodiesel (B-PD (ii)), then added to palm oil biodiesel with different concentrations, which are 1000 ppm and 2000 ppm. In addition, palm oil biodiesel samples without antioxidants (B) and biodiesel-pyrogallol (B-PY) 500 ppm were also made.

2.4 Iodine number Test
Iodine number was measured using the wijs method. The solubility of antioxidants in biodiesel was measured using UV-Vis Spectrophotometer. The induction period was measured using the rancimat method.

3. Results and Discussion

3.1 Comparison of GCMS (Gas Chromatography-Mass Spectrometry) Result
This study used GCMS to determine the methyl linoleate content in sunflower biodiesel and corn biodiesel. The results of the GCMS analysis of the sunflower biodiesel and corn biodiesel are shown in Table 1.
Based on Table 1, sunflower biodiesel contained 54.13% methyl linoleate, and corn biodiesel contained 47.27% methyl linoleate. The difference in methyl linoleate content between the two biodiesel is caused by the difference in the content of fatty acids in oil as the primary raw material for making biodiesel. Sunflower oil contains more linoleic acid than corn oil [8].

### Table 1. Composition of Methyl Esters of Sunflower Biodiesel and Corn Biodiesel

| Methyl Ester        | Sunflower Biodiesel | Corn Biodiesel |
|---------------------|---------------------|----------------|
|                     | Retention Time      | % Area         | Retention Time | % Area |
| Methyl Palmitate    | 30.13               | 8.33           | 30.10          | 13.45  |
| (C16:0)             |                     |                |                |        |
| Methyl Linoleate    | 35.07               | 54.13          | 34.92          | 47.27  |
| (C18:2)             |                     |                |                |        |
| Methyl Oleate       | 35.29               | 27.22          | 35.18          | 33.54  |
| (C18:1)             |                     |                |                |        |
| Methyl Stearate     | 36.01               | 5.91           | 35.86          | 2.97   |
| (C18:0)             |                     |                |                |        |
| Others              | 4.41                | 2.77           |                |        |

3.2 Comparison of FTIR Result

FTIR results shown in Figures 1 and 2. In the sunflower biodiesel, there is a peak of C-O stretching (strong) bond at wavenumber 1243.46 cm\(^{-1}\), while in the corn biodiesel at wavenumber 1243.56 cm\(^{-1}\). The formation of a pyrogallol derivative caused a shift of the peak of C-O stretching (strong) bonds in the biodiesel spectrum from both oils. This shift is caused by the attachment of an oxygen atom in pyrogallol with a carbon atom in methyl linoleate to form a pyrogallol derivative according to the reaction mechanism described in Sutanto et al. research [7].

![Figure 1. FTIR Spectra of Sunflower Biodiesel and Reaction Product](image-url)
Based on the results of FTIR in Figures 1 and 2, the wavenumber obtained from the reaction of pyrogallol and sunflower biodiesel changed from 1243.46 cm\(^{-1}\) to 1240.35 cm\(^{-1}\). Meanwhile, the reaction between pyrogallol and corn biodiesel changed the wavenumber from 1243.56 cm\(^{-1}\) to 1239.53 cm\(^{-1}\).

### 3.3 Comparison of LC-MS/MS Analysis

The LC-MS/MS test is used to identify compounds found in pyrogallol derivative through chromatographic analysis. Sample separation was conducted by chromatography method with the Ultra-High-Performance Liquid Chromatography (UPLC) system with positive ionization type. LC-MS/MS used the C18 column as the stationary phase. A longer retention time indicates that a longer component interacts with non-polar columns. So, the longer the retention time, the more non-polar the compound.

#### Table 2. LC-MS/MS Results of Pyrogallol Derivative

| Pyrogallol Derivative from Sunflower Biodiesel | Pyrogallol Derivative from Corn Biodiesel |
|-----------------------------------------------|------------------------------------------|
| Retention Time (minutes) | % Area | m/z | Retention Time (minutes) | % Area | m/z |
| 7.36 | 2.31 | 167.01 | 7.43 | 17.76 | 167.01 |
| 14.94 | 1.16 | 295.26 | 13.82 | 7.77 | 625.55 |
| 16.31 | 10.05 | 634.54 | 14.37 | 10.47 | 623.54 |
| 17.36 | 2.21 | 638.57 | 15.10 | 15.12 | 625.55 |
| 17.8 | 3.35 | 638.57 | 17.40 | 23.63 | 293.25 |
| 19.51 | 3.3 | 167.01 | 19.58 | 16.32 | 167.01 |

**Figure 2.** FTIR Spectra of Corn Biodiesel and Reaction Product

[Image of FTIR Spectra]
Table 2 shows the results of LC-MS/MS. Based on LC-MS/MS results, pyrogallol derivatives from sunflower biodiesel were found at a retention time of 16.31 minutes with an area percentage of 10.05% and an m/z value of 634.54. Meanwhile, pyrogallol derivatives from corn biodiesel were found at a retention time of 14.37 minutes with an area percentage of 10.47% and an m/z value of 623.54. The type of ionization used in this LC-MS/MS test is positive ionization (M-H)+, so that in the calculation of molecular weight, a hydrogen atom is reduced by one from the m/z value. Therefore, the molecular weight of pyrogallol derivative from sunflower biodiesel and corn biodiesel is 633.54 g/mol and 622.54 g/mol.

The possibility of this compound is methyl linoleate, which is bound with a pyrogallol dimer. Pyrogallol can be dimerized through the coupling reaction using DPPH radicals [9]. In this research, the m/z value of pyrogallol is 167.01 because the LC-MS/MS test showed that the m/z value of 167.01 is the most polar compound based on retention time. Meanwhile, the m/z value of methyl linoleate in sunflower biodiesel is 295.26, and the m/z value of methyl linoleate in corn biodiesel is 293.25. Methyl linoleate then binds to the pyrogallol dimer to form a pyrogallol derivative. Pyrogallol derivative from sunflower biodiesel is more non-polar than pyrogallol derivative from corn biodiesel because it has a longer retention time based on LC-MS/MS test.

3.4 Comparison of Iodine Number Test
The iodine number indicates the alkyl ester's unsaturation, which estimates biodiesel oxidation's susceptibility and is expressed in the number of unsaturated bonds in the biodiesel fatty acid mixture. The higher iodine number indicates more unsaturated bonds in the sample [10]. Biodiesel (B), Biodiesel-Pyrogallol Derivative from sunflower biodiesel (B-PD (i)) 1000 and 2000 ppm, and Biodiesel-Pyrogallol Derivative from corn biodiesel (B-PD (ii)) 1000 and 2000 ppm will be tested in the iodine number test for 18 days duration of storage.

![Figure 3. Iodine Number vs. Storage Duration](image-url)

The results of the iodine number can be seen in Figure 3. The iodine number of all of the samples were decreased during the storage period. The addition of pyrogallol derivative in biodiesel can inhibit the decrease in iodine number and have a sloping slope compared to palm oil biodiesel.
3.5 Comparison of Solubility Test
The solubility test was carried out using the UV-Vis spectrophotometer test method. The test was carried out within two weeks of storage to determine the ability of antioxidant dispersion in biodiesel. The smaller difference in absorbance value indicates that antioxidants have a better solubility. Biodiesel-Pyrogallol (B-PY) 500 ppm, Biodiesel-Pyrogallol Derivative from sunflower biodiesel (B-PD (i)) 1000 and 2000 ppm, and Biodiesel-Pyrogallol Derivative from corn biodiesel (B-PD (ii)) 1000 and 2000 ppm will be tested in the solubility test.

| Sample          | Week 1 | Week 2 | Δ Absorbance |
|-----------------|--------|--------|--------------|
| (B-PY) 500 ppm  | 0.0559 | 0.0183 | 0.0376       |
| (B-PD (i)) 1000 ppm | 0.0556 | 0.0261 | 0.0295       |
| (B-PD (i)) 2000 ppm | 0.0505 | 0.0197 | 0.0308       |
| (B-PD (ii)) 1000 ppm | 0.0706 | 0.0471 | 0.0235       |
| (B-PD (ii)) 2000 ppm | 0.0531 | 0.0351 | 0.018        |

Based on Table 3, the difference in biodiesel's absorbance value with all pyrogallol derivatives after one week of storage showed a smaller change in absorbance value than biodiesel with pure pyrogallol (0.0376). These results indicate that pyrogallol derivatives are more soluble in biodiesel than pure pyrogallol.

3.6 Comparison of Induction Period Test (Rancimat Test)
Biodiesel, Biodiesel-Pyrogallol Derivative from sunflower biodiesel (B-PD (i)) 1000 and 2000 ppm, and Biodiesel-Pyrogallol Derivative from corn biodiesel (B-PD (ii)) 1000 and 2000 ppm will be tested in the rancimat test (induction period). Biodiesel with higher oxidation stability will have a longer induction period [11]. Table 4 is a summary of the results of the induction period test.

| Sample          | Induction Period (Hours) |
|-----------------|--------------------------|
| Biodiesel       | 2.03                     |
| (B-PD (i)) 1000 ppm | 2.26                    |
| (B-PD (i)) 2000 ppm | 2.75                    |
| (B-PD (ii)) 1000 ppm | 2.28                    |
| (B-PD (ii)) 2000 ppm | 2.39                    |

The results of the induction period test are shown in Table 4. All four biodiesel samples with pyrogallol derivative have a higher induction period than biodiesel (2.03 hours). The addition of 2000 ppm pyrogallol derivative from sunflower biodiesel increased the induction period by 0.72 hours. Meanwhile, the addition of 2000 ppm pyrogallol derivative from corn biodiesel increased the induction period by 0.36 hours. The pyrogallol derivative's polarity can cause a difference in the induction period between the two pyrogallol derivatives. Pyrogallol derivative from sunflower biodiesel is more non-polar than pyrogallol derivative from corn biodiesel based on the retention time from LC-MS/MS, which indicates that pyrogallol derivative from sunflower biodiesel is more soluble in biodiesel and increases the induction period longer than pyrogallol derivative from corn biodiesel.
4. Conclusion
The reaction of sunflower biodiesel with 54.13% methyl linoleate and pyrogallol using DPPH radical produced pyrogallol derivative compounds with an m/z value of 634.54 at a retention time of 16.31 minutes and an area percentage of 10.05%. Meanwhile, the reaction using corn biodiesel with 47.27% methyl linoleate produced pyrogallol derivative compounds with an m/z value of 623.54 at a retention time of 14.37 minutes and an area percentage of 10.47%. The addition of pyrogallol derivative to biodiesel can inhibit the decrease in iodine number and have better solubility than pure pyrogallol in biodiesel. The addition of 2000 ppm pyrogallol derivative from sunflower biodiesel increased the induction period by 0.72 hours. Meanwhile, the addition of 2000 ppm pyrogallol derivative from corn biodiesel increased the induction period by 0.36 hours. Pyrogallol derivative from sunflower biodiesel is more non-polar than pyrogallol derivative from corn biodiesel and increases the induction period longer than pyrogallol derivative from corn biodiesel.

Acknowledgments
This research was funded by Hibah PUTI UI 2020.

References
[1] Knothe G 2007 Some aspects of biodiesel oxidative stability Fuel Processing Technology 88 669-677
[2] Obadiah A, Kannan R, Ramasubbu A and Kumar S 2012 Studies on the effect of antioxidants on the long-term storage and oxidation stability of Pongamia pinnata (L) pierre biodiesel Fuel Processing Technology 99 56-63
[3] Xin J, Imahara H and Saka S 2009 Kinetics on the oxidation of biodiesel stabilized with antioxidant Fuel 88 282-286.
[4] Pullen J and Saeed K 2012 An Overview of Biodiesel Oxidation Stability Renewable and Sustainable Energy 16 5924-5950
[5] Sorate K A and Bhale P V 2015 Biodiesel properties and automotive system compatibility issues Renewable and Sustainable Energy Reviews 41 777-798
[6] Varatharajan K and Pushparani D S 2018 Screening of antioxidant additives for biodiesel fuels Renewable and Sustainable Energy Reviews 82 2017-2028
[7] Sutanto H, Susanto B and Nasikin M 2019 Solubility and antioxidant potential of a pyrogallol derivative for biodiesel additive Molecules 24
[8] Hookman S K, Broch A, Robbins C, Ceniceros E and Natarajan M 2012 Review of biodiesel composition, properties, and specifications Renewable and Sustainable Energy Reviews 16 143-169
[9] Cynthia, Florence I, Sutanto H and Akhmad D 2018 Antibacterial and Antioxidant Activities of Pyrogallol and Synthetic Pyrogallol Dimer Research Journal of Chemistry and Environment 22 39-48
[10] Soares S, Lima M J and Rocha F 2017 A spot test for iodine value determination in biodiesel based on digital images exploiting a smartphone Microchemical Journal 133 195-199
[11] Agarwal A K and Khurana D 2013 Long-term storage oxidation stability of Karanja biodiesel with the use of antioxidants Fuel Processing Technology 106 447-452