IOP Conf. Series: Materials Science and Engineering **316** (2018) 012019 doi:10.1088/1757-899X/316/1/012019

Reaction product of pyrogallol with methyl linoleate and its antioxidant potential for biodiesel

H Sutanto[1] , L Ainny[1], Lukman[1], B H Susanto[1], and M Nasikin[1]

[1]Chemical Engineering, Department of Chemical Engineering, Universitas Indonesia, Depok 16424, Indonesia

bambanghs@che.ui.ac.id

Abstract. The demand of biodiesel as an alternative fuel is increasing due to fossil fuel depletion. Biodiesel is a renewable diesel fuel in the form of fatty acid methyl ester or FAME as a result of an esterification of plant oils in a presence of catalyst. Compared to the conventional diesel fuel, biodiesel is more biodegradable, has higher lubricity, and lower toxic emissions. However, the high content of unsaturated fatty acid leads to a problem that biodiesel is prone to oxidation during storage period. This oxidation instability causes degradation of fuel quality and will affect engine performance. Pyrogallol and other phenolic derivatives have been used as the antioxidant additives to prevent biodiesel oxidation. As reported in many researches, pyrogallol is one of the best phenolic antioxidant. However, its low solubility in biodiesel needs an attention. Several reports indicate the increasing solubility of pyrogallol using molecule modification with the addition of alkyl groups to its benzene ring via electrophilic substitution. This paper discusses the idea about modification of pyrogallol molecule and methyl linoleate using 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical in order to increase its solubility in biodiesel while keeping its antioxidant property. Three responses were analyzed to examine the antioxidant activity: iodine value, viscosity, and color intensity. The result shown that the addition of 0.1% reaction product exhibit antioxidant activity in biodiesel.

1. Introduction

Biodiesel or fatty acid methyl ester (FAME) is a renewable alternative fuel produced from plants to overcome fossil fuel depletion problem. It has been implemented and used globally for diesel vehicles. Biodiesel production and demand increases over time due to people's awareness regarding fossil fuel crisis and environmental issue. However, biodiesel has several weaknesses in which many researchers are interested in increasing its quality.

Other Biodiesel which contains mixture of FAME molecules is highly unstable; both thermal and oxidative instability. Molecule deterioration occurs when biodiesel is exposed to air, light, high storage temperature, as well as high humidity. The unsaturated fatty acid methyl ester contents are responsible for this weakness due to their high oxidation risk. The oxidized FAME will have higher viscosity, moreover it is highly possible to produce solid precipitates which would blockage the machines' filter or nozzle. This oxidative instability of biodiesel also causes its shorter shelf life compared to the conventional fuels. In the oxidized biodiesel, the acid value increases as the increasing rate of

[1] To whom any correspondence should be addressed.

decomposition of peroxide compound as the result of oil oxidation. This will cause disadvantage as well due to the corrosive effect to the engine materials which are made of metals.

Palm oils is the main source of fatty acid in the biodiesels production. This type of biodiesel has the unsaturated carbon chain length between 16 to 20 carbon number [1]. The longer the carbon chain, the more unstable the fatty acid molecules [2]. To increase the stability of palm oils' biodiesel, antioxidant as radical scavenging agent additives are required to prevent the oxidation to the oil components.

One of the commonly used antioxidant additive is pyrogallol (PY). Pyrogallol or 1,2,3-trihydroxybenzene is a three hydroxyl substituted benzene ring molecule [3], it is belong to phenolic group. Just like other phenolic compounds, pyrogallol has an antioxidant property. In the presence of radical species, the hydroxyl hydrogen of phenols will be abstracted by the free radical during the propagation phase [4]. The next propagation step will be stopped by radical phenol by delocalizing the radical electron into several available positions. This mechanism will protect the phenoxy radical to do another unwanted radical attack or further oxidations. Pyrogallol is the most effective antioxidant for biodiesel compared to the others [5]. However, the utilization of pyrogallol still have some weaknesses. It prevents the oxidation for only on the first six hours [6]. On the other hand, pyrogallol has a solubility problem when it is mixed with oil solution like biodiesel due to the polarity difference which causes the uneven additive distribution in the mixture [7]. Pyrogallol molecule modification is necessary to adjust its polarity thus the oil dispersion increased in order to increase the antioxidant activity.

Modification of phenolic compounds has been an interesting research topic. The objective is to increase solubility of phenol as antioxidant in oils especially in biodiesel. Based on previous works, pyrogallol is one of the best phenolic antioxidant, thus it is important to develop a new synthesized molecule with pyrogallol molecule basis by connecting it with a nonpolar molecule. The idea is to combine pyrogallol which is polar with a molecule of fatty acid methyl ester as the nonpolar part. Pyrogallol as a member of benzene group is a stable molecule but in the other hand it is a highly risking molecules to be attacked by radical species. Ester groups, amine, benzylic, and heteroatomic molecules are prone to oxidation by radical [8]. [9] did the analysis of radical reaction of pyrogallol using 2,2-diphenyl-1-picrylhydrazyl or DPPH. The result shows the products was the oxidative coupling product, dimer of pyrogallol. DPPH also can be used in oil solution, usually for antioxidant analysis of unsaturated fatty acid but using different solvent [10]. This new molecule can be synthesized by using several methods. One of the possible method is by using radical mechanism. The expected product is a result of oxidative coupling between two different molecules: pyrogallol and FAME. To represent FAME, methyl linoleate is suitable. It is a polyunsaturated fatty acid omega-6 with two double bonds at C-9 and C-12 which means it has a methylene hydrogen at interrupted position at C-11. This hydrogen is susceptible for radical attack. Methyl linoleate as a derivative of linoleic acid represents vegetable oil can be radicalized using DPPH [10]. The radical methyl linoleate and radical pyrogallol are expected to undergo oxidative coupling termination. This new molecule is expected to have a high solubility in oil without decreasing the antioxidant activity of pyrogallol.

2. Materials and methods

Methyl linoleate and pyrogallol were reacted based on stoichiometric calculation. Combination of [9] and [10] experiments using ethyl acetate solvent. Pyrogallol (p.a.) obtained from MERCK (CAS number: 87-66-1). DPPH or 2,2-diphenyl-1-picrylhydrazyl obtained from SIGMA-ALDRICH (CAS number: 1898-66-4). Methyl linoleate obtained from Santacruz. The solvents methanol and ethyl acetate as well as the silica TLC plate were obtained from MERCK. Wijs solution for iodine value obtained form MERCK. Viscometer canon feske pipe. Thin layer chromatography was used for the qualitative analysis of the desired product. The Rf values will be evaluated compared to the original reactants which are pyrogallol and methyl linoleate. The product mixture then mixed with biodiesel with different concentrations in order to examine its antioxidant property. Blank sample was biodiesel without any

antioxidant addition. All samples were left open in the room atmosphere (light, air, pressure and temperature).

2.1. Synthesis reaction preparation

Synthesis reaction was prepared by mixing pyrogallol and methyl linoleate in DPPH solution. Pyrogallol solution was prepared by mixing 0.03mg solid pyrogallol with 2ml methanol. DPPH solution was a mixture of 0.07mg DPPH dissolved in 2 ml ethyl acetate producing a dark violet solution. While DPPH solution was constantly stirred, 2.5ml methyl linoleate was dropped slowly using burette into the DPPH solution to ensure all methyl linoleate were completely radicalized. The violet color of DPPH solution was gradually turned lighter as a mark of the radical production progress. After all methyl linoleate addition was finished, pyrogallol solution was added slowly. The solutions' color turned from light violet into yellowish color, and after 3 hours, it turned into darker yellow or brownish.

2.2. Application to biodiesel

The reaction mixture was added to biodiesel with different concentration (w/v): 0.05%, 0.07%, and 0.1%, while blank sample was without any addition of reaction mixture or 0.00%. The mixture as well as the blank were kept in a transparent glass bottles and left exposed to air and light with open cap to accelerate the oxidation reaction. As the responses, the measurement of iodine value, viscosity, and color intensity was determined weekly up to 4 weeks.

2.3. Iodine value determiation

Iodine value was determined using Wijs method.

2.4. Viscosity test

Viscosity test was performed by using viscometer at 40^{o}C. Standard: ASTM D445-11a.

2.5. Color intensity test

Color intensity test was performed by using visible light region graduated color intensity of the electromagnetic spectrum.

3. Results and discussion

3.1. TLC analysis

The synthesis reaction mixture was spotted on TLC plate compared with the pure pyrogallol and methyl linoleate. The calculated Rf shown on the reaction mixture spot were 0.31 (a), 0.62 (c) and 0.84 (b) as can be seen on figure 1. Spot (a) 0.31 is equal to the Rf of pyrogallol, and (b) 0.84 is equal to the Rf of methyl linoleate. It shows that some numbers of unreacted reactants are still remain on the solution. From this result, it is qualitatively concluded that aside of the remaining unreacted pyrogallol and methyl linoleate, the new product was formed indicated by the new spot with Rf 0.62 (c). This new modification products is proposed to be the oxidative coupling product between pyrogallol and methyl linoleate. The new product is the result of termination step of both pyrogallol and methyl linoleate radical which were initially produced by using DPPH.

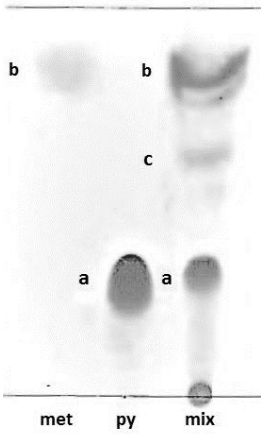

Figure 1. Thin layer chromatography result

3.2. Iodine value

Iodine value result can be seen in figure 2. Iodine value is a quantitative determination of oils' quality. The lower the iodine value means the higher the oxidation due to the decreasing of double bond number. When an unsaturated fatty acid is oxidized, one of the double bond will be transformed into single bond because of the formation of peroxide group. It is shown that the iodine value of the biodiesel sample were decreased over time for all concentrations. Compare to the 0.05 and 0.07, the lowest iodine value decreasing or ΔI was with 0.1% antioxidant, which was the most concentrated one. This result showing that the addition of antioxidant helps to prevent oxidation as also reported by [2] and [11].

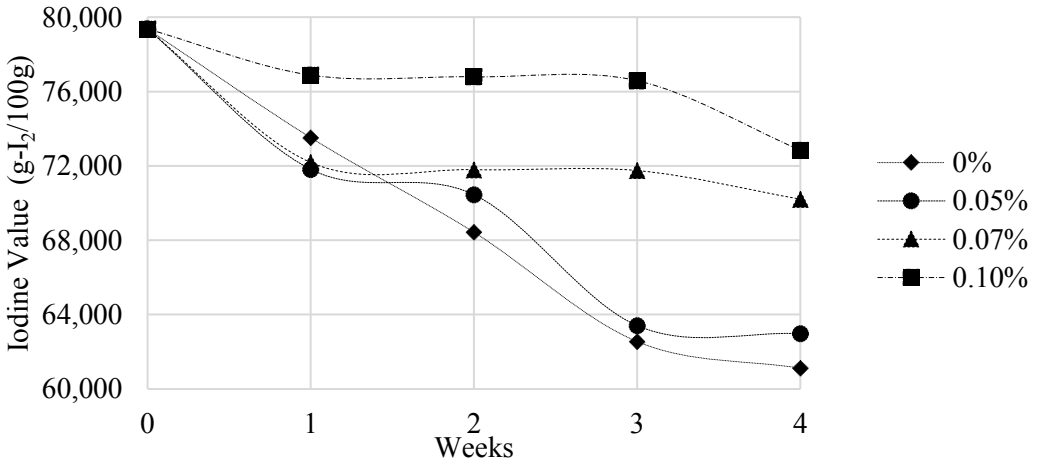

Figure 2. Iodine value

3.3. Viscosity value

Viscosity test result is shown in figure 3. Viscosity is commonly used as the marker of oils' oxidation process. The oxidized oil may transform into different types of molecule or the structure change occurrence. After the addition of 0.1% antioxidant, the viscosity value jump was lower than the blank. It is showing that the reaction product mixture kept the viscosity low, it is concluded that the antioxidant is effective in preventing oxidation. Formation of heavier yet bigger molecule such as oil polymers are responsible for the viscosity value increasing. The increasing viscosity as a marker of oils' oxidation also reported by [2], [11], and [6].

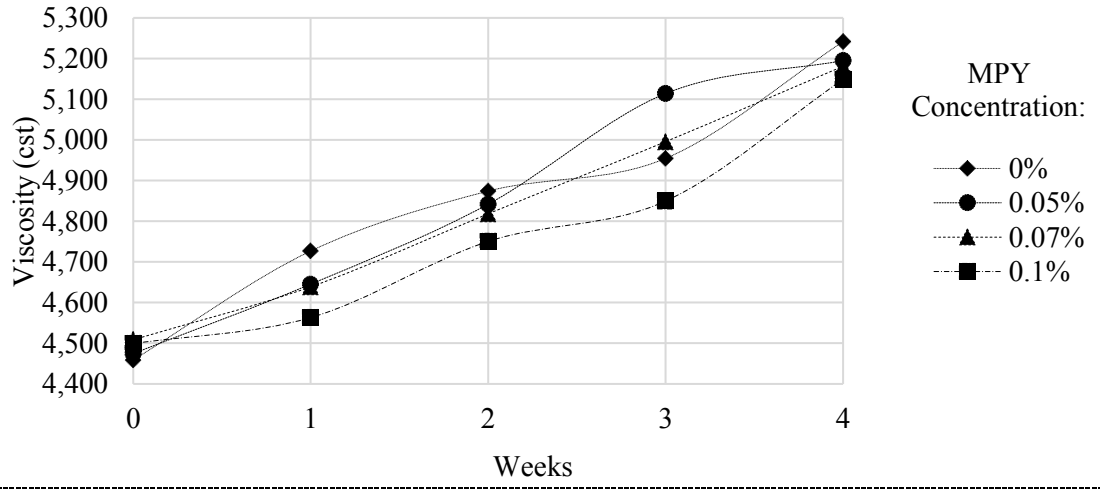

Figure 3. Viscosity value

3.4. Color intensity

Visually the color of all samples were different over time and also different on every sample. For the quantitative analysis, the color intensity was measured by measuring its optimum wavelength shifts. Within 4 weeks, the color intensity were decreased. The highest color intensity drop was the blank sample. The lowest color drop was the 0.1%. It shown on figure 4 that the higher the antioxidant concentration, the better the activity in retaining the biodiesel color. Color intensity decreasing indicates the quality degradation of the oil. The more oxidized molecule means the lighter the color due to the structural change to the FAME molecules. From this response, it is concluded that 0.1% addition of reaction mixture might act as antioxidant preventing structure deterioration from oxidation. It is proposed that glycerol molecule is responsible for the samples' color change. At high temperature or during oxidation, glycerol would cause the oils' color degradation as stated also by [12], [13], and [14].

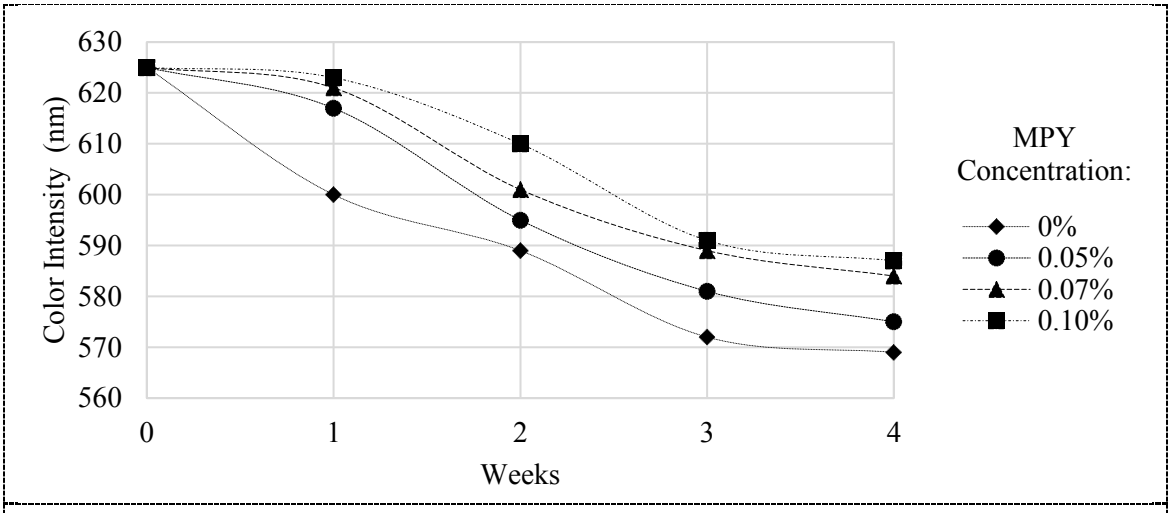

Figure 4. Color intensity.

4. Conclusion

The pyrogallol derivative molecule was synthesized using DPPH radical by adding methyl linoleate molecule via coupling oxidation mechanism. The product mixture showing antioxidant potential to be used to prevent oxidation in biodiesel. The antioxidant analysis using 3 different responses: iodine value, viscosity, and color intensity resulting the active radical scavenging effect by the addition of reaction product mixture. The best result shown by the 0.1% addition of product in biodiesel with the duration of 4 weeks.

5. References

[1] Darnoko, D, T, H, & P, G 2001 *Warta PKKS* p 17-27.
[2] Pullen, J, & Saeed, K 2012 *Renewable and Sustainable Energy* **16** p 5924-5950.
[3] XiCan Li 2012 *J. Agric. Food Chem* (america: American Chemical Society) **60** p 6418−6424.
[4] Rapopport. Zvi 2003 *Chemistry of Phenol, John Wiley & Sons*, Ltd ISBN: 0-471-49737-1.
[5] Supriyono, Sulistyo, H, Almeida, M F, & Dias, J M 2015 *Food Processing Technology* **132** p 133-138.
[6] Sorate, K A, & Bhale, P V 2015 *Renewable and Sustainable Energy Reviews* **41** p 777-798.
[7] Wilson, C P, & Houston, T 1995 United States Patent No. 2,052,858.
[8] Daley, R F, & Daley, S J 2005 *Organic Chemistry* p 530-567.
[9] Zhu, N, Wang, M, Wei, G J, Lin, J K, Yang, C S, & Ho, C T 2001 *Food Chemistry* **73** p 345-349.
[10] Prevc, T, Segatin, N, Ulrih, P N, & Cigic, B 2013 *Talanta* **109** p 13-19.
[11] Saluja, R K, Kumar, V, & Sham, R 2016 *Renewable and Sustainable Energy Reviews* **62** p 866-881.
[12] Banga, Sangita and Varshney, Pradeep K 2012 *Journal of Scientific & Industrial Research* **69** p 575-579.
[13] Keshvari, Mahtab, Asgary, Sedigheh, Jafarian-dehkordi, Abbas, Najafi, Somayeh, Ghoreyshi-Yazdi, Seyed Mojtaba 2013 *ARYA Atheroscler* **9** p 280-286.
[14] Kenreck, Gleen 2007 *Biodiesel Magazine*.

Acknowledgementt

This research was funded by Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa (PITTA UI) Universitas Indonesia 2017).