

12-20-2020

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Yusri, Silvy; Nasikin, Mohammad; and Sutanto, Hery (2020) "Effect of Surfactant Addition on the Dispersion and Antioxidant Performance of Pyrogallol in Biodiesel," *Makara Journal of Science*: Vol. 24 : Iss. 4 , Article 6.

DOI: 10.7454/mss.v24i4.1018

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Cover Page Footnote

Authors would like to thank The Ministry of Research, Technology and Higher Education Republic of Indonesia for financial support through Penelitian Terapan Unggulan Perguruan Tinggi research grant (contract no. 2639/L4/PP/2019).

Effect of Surfactant Addition on the Dispersion and Antioxidant Performance of Pyrogallol in Biodiesel

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Received December 15, 2019 | Accepted July 13, 2020

Abstract

Biodiesel is one of the most feasible energy sources that can be used as a replacement for fossil fuel. Biodiesel has several advantages over conventional fuels because of its availability, renewability, and high combustion efficiency. However, biodiesel that contains unsaturated fatty acid methyl esters is prone to oxidation during the blending process and storage period. The complete oxidation reaction of biodiesel produces insoluble gums that could potentially plug the fuel engines. This reaction has become the main barrier for biodiesel to compete with other biofuels. Among several methods, the addition of antioxidants is the most cost-effective method to prevent the oxidation reaction in biodiesel. Pyrogallol (PY), which is one of the best antioxidant additives for biodiesel, was used in this research to evaluate its performance. However, the fact that PY is partially soluble in biodiesel is considered a problem in the application of PY as an antioxidant additive in biodiesel. In this research, three different surfactants were added to increase the dispersion and performance of PY in biodiesel. Dispersion test, acid number analysis, and iodine value analysis were performed to evaluate the effect of surfactant addition on the dispersion and antioxidant performance of PY in biodiesel. The surfactant glycerol monostearate showed the best result in increasing the dispersion of PY in biodiesel compared with sorbitan monooleate and polyglyceryl-4-isostearate (PG4IS). By contrast, the best performance of PY in preventing the oxidation of biodiesel was achieved with the addition of PG4IS.

Keywords: antioxidant, biodiesel, dispersion, pyrogallol, surfactant

Introduction

The limited reserve of fossil fuel and the environmental impacts caused by its emission have motivated scientists to develop alternative fuels. Biodiesel or fatty acid methyl ester is one of the best candidates to substitute fossil fuel in the transportation and industrial fields, which use diesel engines [1]. Biodiesel has several advantages over conventional fuels because of its renewability, low emission, and biodegradability [1,2]. Despite its advantages, biodiesel that contains unsaturated fatty acid methyl esters is prone to the oxidation reaction. The oxidation reaction in biodiesel leads to the formation of hydroperoxides and insoluble high-molecular-weight polymers [3]. Hydroperoxides from the reaction further produce insoluble gums and sediment that can plug the fuel filters and deposit on the fuel injector. Insoluble high-molecular-weight polymers as the final product of the oxidation reaction can increase the viscosity of biodiesel. The increase in the viscosity of biodiesel causes poor fuel atomization [4]. Moreover, the combustion of oxidized biodiesel leads to high emission of carcinogenic

products, such as formaldehyde, acetaldehyde, acrolein, and polycyclic aromatic hydrocarbons [5]. This reaction has become the main barrier for biodiesel to compete with other renewable fuels in the energy market.

Several methods have been used to solve the oxidation problem in biodiesel, such as the implementation of vacuum technology, low-temperature storage, enzyme deactivation, structural modification, and antioxidant addition [4,6,7]. Among these methods, the addition of a phenolic antioxidant to biodiesel is considered to be the most cost-effective method to prevent or delay the oxidation reaction in biodiesel. Pyrogallol (PY), butylated hydroxytoluene, *tert*-butylhydroquinone (TBHQ), and butylated hydroxyanisole are the most commonly used antioxidants for biodiesel [8-11]. Two types of antioxidants, namely, chain breaker (or primary antioxidants) and hydroperoxide decomposers (or secondary antioxidants), are used to prolong the shelf life of biodiesel fuels. Primary antioxidants delay or prevent oxidation by donating a hydrogen atom to free radicals, whereas secondary antioxidants decompose hydroperoxide,

which is the intermediate product of the oxidation reaction [12,13].

PY has been reported to be the most effective antioxidant for nearly all types of biodiesels [14-16]. However, PY is partially soluble in biodiesel because of its polarity [4]. The accumulation of insoluble PY in biodiesel leads to the formation of sediment, which causes engine failure. Therefore, the solubility of PY in biodiesel needs to be increased. Structural modification of PY was done by adding methyl linoleate molecules to PY molecules to increase the solubility of the synthesized product. The synthesized product has a higher solubility and antioxidant activity in biodiesel than PY [17-20]. The increase in the solubility of polar antioxidant additives can also be achieved by the addition of surfactants to the mixture of biodiesel and antioxidant. The addition of surfactants successfully increases the dispersion of TBHQ in biodiesel and its performance as an antioxidant [21].

In this research, the effect of surfactant addition on the dispersion of PY in biodiesel was observed. Three types of surfactants, namely, glycerol monostearate (GMS), sorbitan monooleate (SMO), and polyglyceryl-4-isostearate (PG4IS), were selected. The dispersion of PY in biodiesel, acid number, and iodine value were measured to evaluate the solubility and antioxidant activity of PY in biodiesel.

Materials and Methods

Materials. Biodiesel was prepared from palm cooking oil. The antioxidants used in this research were pro analysis grade PY and TBHQ from Merck TBK. The surfactants used were SMO, GMS, and PG4IS. The reagents used for the dispersion test, acid number analysis, and iodine value analysis were pro analysis grade hexane, ethanol, potassium hydroxide (KOH), chloroform, and sodium thiosulfate, phenolphthalein and starch indicators, and Wijs solution. All of the reagents were obtained from Merck TBK.

Instruments. The dispersion test was conducted using the PG Instruments Model T60 UV-Vis Spectrophotometer. The acid number and iodine value were measured using the titration method.

Sample preparation. Samples were prepared in six glass bottles at room temperature. The samples consisted of mixtures with different compositions, namely, biodiesel only, biodiesel with PY, biodiesel with TBHQ, and three samples containing a mixture of biodiesel, PY, and three different types of surfactants.

Each antioxidant at 2,000 ppm (w/v) was added to biodiesel. Meanwhile, each surfactant at 100 ppm (w/v) was added to the mixture of biodiesel and antioxidant.

The samples were stored under controlled conditions and observed weekly for 4 weeks.

Dispersion test. The dispersion test was conducted using the method adopted from Sutanto [21]. A portion of the 0.25 mL sample was taken from the same depth and distance on the sample's surface and homogenized using a vortex shaker by adding 19.75 mL hexane. The optimum wavelength of PY (280 nm) and absorbance of PY in the sample were measured using the UV-Vis spectrophotometer. The dispersion of the sample was calculated by measuring the absorbance difference of PY between week 0 and week 1. A sample that consists of biodiesel without additive was used as a blank. The dispersion test was performed in duplo or two replications.

Acid number analysis. Acid number analysis was conducted using a standard test method for the acid number of petroleum products (ASTM D6642). A portion of the 2.5 g biodiesel sample was dissolved in 100 mL ethanol in a 250 mL Erlenmeyer flask. Phenolphthalein was added to the solution as an indicator. The sample was stirred until it became homogeneous. The sample was titrated using 0.01 N KOH until the color of the solution changed from colorless to light pink. The color change indicates that KOH completely reacted with acid in the sample. A mixture of all reagents without biodiesel was prepared as the blank sample. The total volume of KOH from the titration was used to calculate the acid number of each sample. The titration was performed in duplo or two replications. The acid number (in mg KOH/g sample) was calculated using the following formula:

$$\text{acid number} = \frac{(V - V_0) \times N \text{ KOH} \times M_w \text{ KOH}}{W} \quad (1)$$

where V_0 is the volume of 0.01 N KOH used in the blank (in mL), V is the volume of 0.01 N KOH used in the sample (in mL), N is the normality of KOH, M_w is the molecular weight of KOH, and W is the weight of oil in the sample (in g).

Iodine value analysis. The iodine value of each sample was measured using the AOCS Cd 1-25 Wijs method for iodine [21]. Approximately 0.15 g of the biodiesel sample was mixed with 15 mL chloroform in a 500 mL Erlenmeyer flask. Then, 25 mL Wijs solution was added to the sample. The Erlenmeyer flask was sealed with aluminum foil and incubated in a dark environment for 1 h. After the incubation period, 20 mL potassium iodide solution and 150 mL demineralized water were added to the sample. The sample was immediately titrated using 0.1 N sodium thiosulfate until the color of the sample changed from brown to light yellow. Afterward, 2 mL starch indicator was added to the

sample and the titration was continued until the color of the sample changed from blue to colorless. A mixture of all reagents without biodiesel was prepared as the blank sample. The final volume of sodium thiosulfate in the titration was used to calculate the iodine value of each sample. The titration was performed in duplo or two replications. The iodine value (in g I₂/100 g sample) was calculated using the following formula:

$$\text{Iodine value} = \frac{(V_0 - V) \times N \text{ Na}_2\text{S}_2\text{O}_4 \times M_w \text{ Na}_2\text{S}_2\text{O}_4 \times 100}{W}$$

where V_0 is the volume of 0.1 N Na₂S₂O₄ used in the blank (in mL), V is the volume of 0.1 N Na₂S₂O₄ used in the sample (in mL), N is the normality of Na₂S₂O₄, M_w is the molecular weight of Na₂S₂O₄, and W is the weight of oil in the sample (in g).

Results and Discussion

Dispersion test. PY as a polar organic compound is partially soluble in biodiesel. PY will settle in the storage tank after a long storage period. The addition of a surfactant that has both polar and nonpolar functional groups or both hydrophilic and hydrophobic ends in one molecule could potentially increase the solubility of PY in biodiesel. The polar group of the surfactant will bind with PY, whereas the nonpolar group will bind with biodiesel.

The dispersion of PY in biodiesel was measured using the UV-Vis spectrophotometer. Spectrophotometry is one of the most effective methods to observe the dispersion of a compound in a solution or mixture [22]. The absorbance of PY in each sample was measured at the initial stage and after a storage period of 1 week. The absorbance difference shows the decrease in the dispersion of PY in biodiesel. As shown in Table 1, the highest absorbance difference of PY was observed in the sample containing biodiesel and PY only. This phenomenon confirmed that PY is not dispersed or soluble in biodiesel.

The addition of surfactants successfully increased the dispersion of PY in biodiesel. All samples containing surfactants show lower absorbance differences of PY than the sample without surfactant. The increase in the dispersion or solubility of a polar compound in a

nonpolar compound is called solubilization. The application of surfactant as a solubilizing agent is widely employed in the cosmetics field to increase the solubility of polar compounds in nonpolar solvents or vice versa [23]. Solubilization in a surfactant can only occur when the surfactant reaches its critical micelle concentration (CMC) [24]. CMC is the minimum concentration of surfactants above which micelles form. The CMC of the nonionic surfactants used in this research is approximately 10⁻⁵ to 10⁻⁴ M [25]. Each surfactant has 5.7 × 10⁻³, 4.7 × 10⁻³, and 4.2 × 10⁻³ M of GMS, SMO, and PG4IS, respectively. All surfactants used in this experiment have reached their CMC, which leads to the formation of micelles and the increase in the solubility of PY in biodiesel.

The dispersion test shows that the best dispersion of PY was achieved with the addition of GMS. The best dispersion is indicated by the lowest decrease in the absorbance of PY at 280 nm. The dispersion of PY by the surfactant was affected by the stability of the micelles formed. The expected form of micelles can be determined using the “packing parameter” concept [26-29], which can be expressed as follows:

$$P = \frac{V_0}{a_e I_0} \quad (3)$$

where V_0 is the surfactant tail volume, a_e is the equilibrium area per molecule at the aggregate interface, and I_0 is the tail length.

According to the chemical structure of the surfactants shown in Figure 1, all surfactants have hydrophobic tails with similar lengths but hydrophilic heads with different sizes. Given that the hydrophobic tails of the three surfactants are similar, the size of the hydrophilic head group determines the shape of the surfactant's micelle. The larger the size of the hydrophilic head group is, the larger the equilibrium area per molecule at the aggregate interface (a_e). PG4IS has the largest hydrophilic head group, followed by SMO and GMS. Given that the a_e value is inversely proportional to P value, the P value trend of the surfactants from highest to lowest is GMS < SMO < PG4IS. On the basis of the packing parameter concept, the shape of micelles from highest to lowest P value can be bilayer, cylindrical, and spherical. Hence, the expected shape of PG4IS, SMO, and

Table 1. Absorbance Difference of Biodiesel Samples

Sample composition	Average absorbance		
	Week 0	Week 1	Absorbance difference
Biodiesel + PY 2,000 ppm	2.4300	2.2925	0.1375
Biodiesel + PY 2,000 ppm + GMS 100 ppm	2.4150	2.4080	0.0070
Biodiesel + PY 2,000 ppm + SMO 100 ppm	2.4080	2.3215	0.0865
Biodiesel + PY 2,000 ppm + PG4IS 100 ppm	2.4820	2.3900	0.0920

GMS is spherical, cylindrical, and bilayer, respectively. PY with high polarity is dispersed better with GMS in the form of a bilayer micelle than with PG4IS in the form of a spherical micelle and SMO in the form of a cylindrical micelle. On the basis of the characteristic collision time of surfactants, the bilayer micelle is more stable than the spherical and cylindrical micelles [30].

Figure 2 illustrates the micelle structure of the surfactant SMO and PY in biodiesel. Because the solvent used in the system is nonpolar/organic, the micelles formed are reverse micelles. As shown in the figure, the hydrophilic heads face inward, the hydrophobic tails extend outward, and PY as a polar component is trapped inside the micelle.

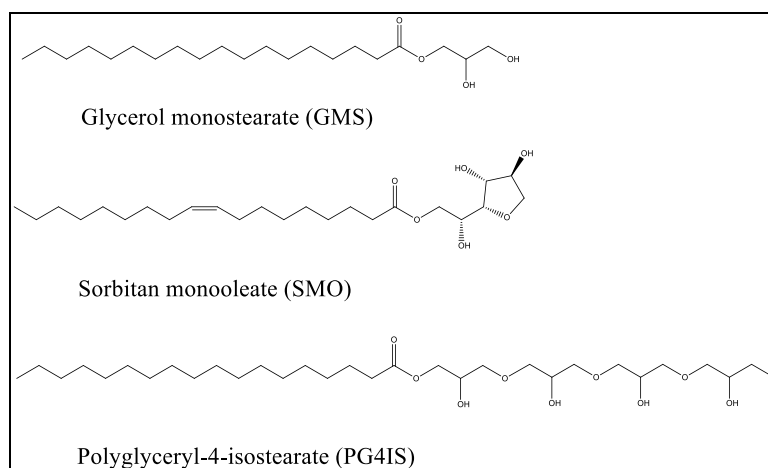


Figure 1. Chemical Structure of Surfactants

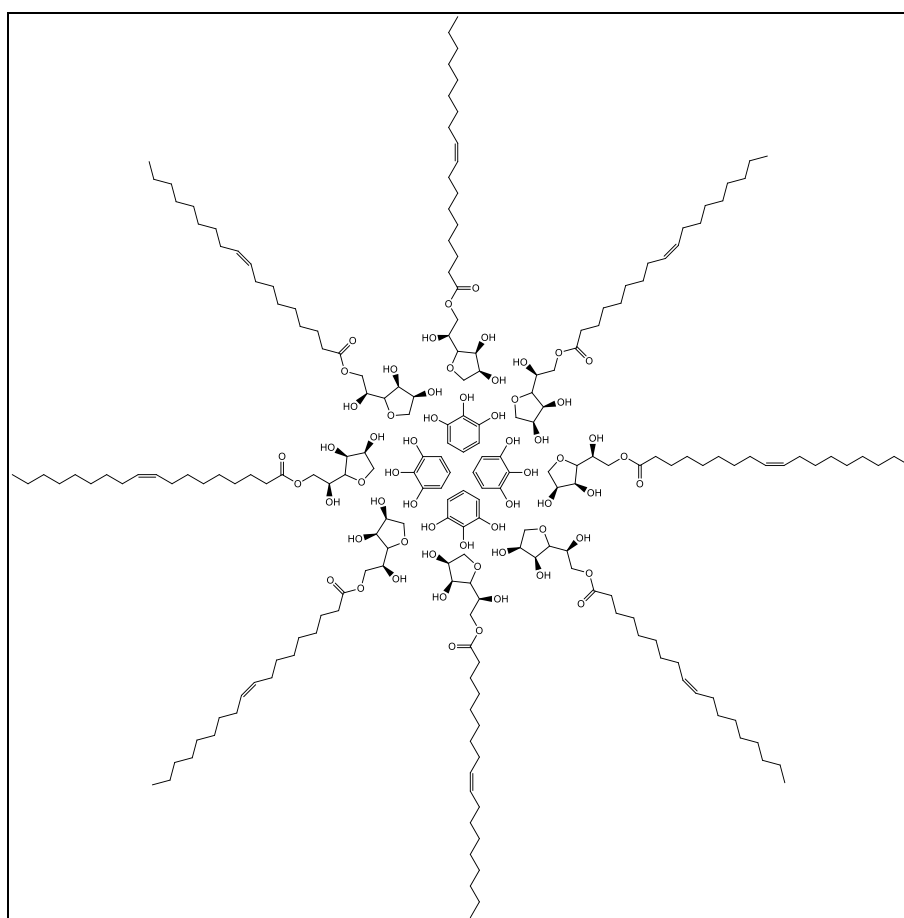


Figure 2. Illustration of the Micelle Structure of the Surfactant Sorbitan Monooleate (SMO) and Pyrogallol (PY) in Biodiesel

Acid number. The acid number is one of the most important parameters used to analyze the oxidative degradation of biodiesel. The oxidation reaction initiates the production of hydroperoxides. The next process is the decomposition of hydroperoxides into several acid products, such as carboxylic acid and aldehyde [31]. Figure 3 illustrates the formation of hydroperoxides from the oxidative degradation of the most common fatty acid in biodiesel, i.e., linoleic acid. Free radicals interact with oxygen to initiate the formation of peroxide. Then, peroxide propagates the chain reaction through the abstraction of the hydrogen atom from another molecule of linoleic acid methyl ester. This reaction produces new carbon radicals and hydroperoxide. Furthermore, hydroperoxides are decomposed to form several products, with aldehydes as the main product. Further oxidation of aldehydes leads to the formation of a large number of short-chain fatty acids [3]. Therefore, the increase in the acid number indicates the oxidation of biodiesel.

The addition of PY as an antioxidant for biodiesel was evaluated by measuring the acid number of the sample. Another phenolic antioxidant, i.e., TBHQ, was also included in the measurement as a comparison. The results of acid number analysis are shown in Figure 4. The acid number of all samples increased after a storage period of 4 weeks, which indicates the oxidation reaction. The rate of oxidation in the sample was determined by calculating the slope of the acid number enhancement. Considering the linear correlation between acid number and storage period, the higher the slope value is, the faster the oxidation reaction time. Thus, the order of acid number enhancement from highest to lowest is

biodiesel only > biodiesel with TBHQ > biodiesel with PY, with the slope of 0.8603, 0.6158, and 1.1415, respectively. The rate of oxidation in biodiesel without antioxidant additive is the highest, i.e., biodiesel oxidizes rapidly without the addition of antioxidants. By contrast, the addition of antioxidants can delay the oxidation of biodiesel, which has been proven by the low slope value of acid number enhancement. Both PY and TBHQ are classified as primary antioxidants because they interrupt the oxidation reaction by donating a hydrogen atom to free radicals.

PY exhibited a better performance as an antioxidant than TBHQ. This phenomenon can be explained by the bond dissociation enthalpy (BDE) theory. BDE is the driving force behind the hydrogen transfer from antioxidants to free radicals. The BDE value of antioxidants should be lower than that of peroxide and hydroperoxide free radicals (368–376 kJ/mol). PY and TBHQ meet the requirement to be used as antioxidants because they have low BDE values, which are 284.5 and 310.9 kJ/mol, respectively [32]. Moreover, PY, which has a lower BDE value than TBHQ, is a more effective antioxidant for biodiesel than TBHQ.

The effect of surfactant addition on the mixture of biodiesel and PY was analyzed by comparing the slope of acid number enhancement. As shown in Figure 5, the slope values of the biodiesel only, biodiesel with PY, biodiesel with PY and GMS, biodiesel with PY and SMO, and biodiesel with PY and PG4IS samples were 0.8603, 0.1415, 0.2095, 0.185, and 0.0695, respectively. Among the three surfactants, GMS showed the highest slope, followed by SMO and PG4IS. Moreover, the

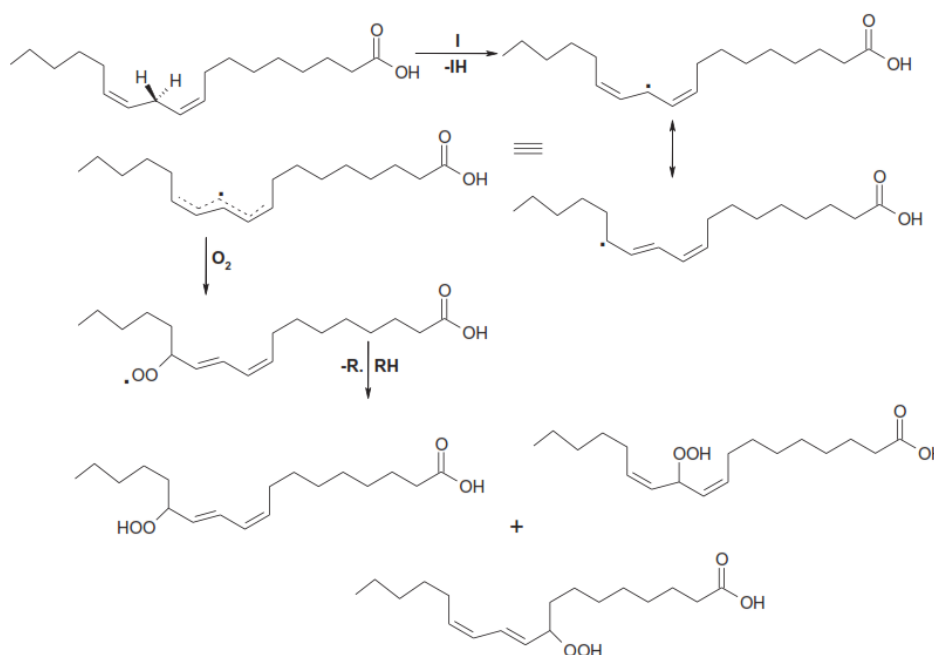


Figure 3. Formation of Hydroperoxides Through the Oxidative Degradation of Linoleic Acid (Yakoob, 2014)

addition of GMS and SMO to PY resulted in a higher slope than PY without surfactant. The presence of GMS and SMO inhibited the activity of PY as an antioxidant. By contrast, the addition of PG4IS to PY resulted in the lowest dispersion of PY, leading to the best performance in increasing the activity of PY. The trend of the dispersion of PY with the addition of surfactants was contradicted by the increase in the solubility of PY in biodiesel.

The increase in the dispersion of PY in biodiesel with the addition of the surfactants GMS and SMO causes a decrease in its activity as an antioxidant in terms of acid number. This phenomenon occurred because the oxidation reaction was initiated on the surface of biodiesel [4]. The partially soluble antioxidant, i.e., PY, is enriched at the oil-air interface. Hence, PY effectively inhibits the reaction initiated by free radicals on the surface of biodiesel. By contrast, the utilization of PY to prevent oxidation, which is caused by dissolved oxygen under the surface of biodiesel, is ineffective because of its uneven distribution in biodiesel [33]. The addition of surfactants enables the dispersion and distribution of a certain amount of PY in biodiesel. The higher the dispersion of PY is, the larger the amount of PY that will be distributed in biodiesel to prevent the oxidation reaction from occurring under the surface of biodiesel. Figures 6 and 7 illustrate the distribution of PY in biodiesel with and without the addition of surfactants. With the addition of the surfactants GMS and SMO, which results in a significant increase in the dispersion of PY in biodiesel, the amount of PY on the surface of biodiesel will be smaller than that with the addition of the surfactant PG4IS. This condition decreases the degree of protection on the surface; hence, the oxidation reaction more likely occurs. The best result was obtained with the addition of PG4IS because PY was better dispersed both on and under the surface of biodiesel than that with the addition of GMS and SMO.

PY acts as an antioxidant or free radical scavenger in biodiesel. The hydroxyl group in PY donates its hydrogen atom to free radicals to form long-lived phenoxyl radicals. The unpaired electron in phenoxyl radicals is delocalized around the aromatic structure of PY and is

stabilized by high resonance energy. The mechanism of free radical scavenging in biodiesel by PY is shown in Figure 8.

On the basis of the European biodiesel quality standard EN 14214 and United States' ASTM 6751, the acid number of biodiesel should be less than 0.5 mg KOH/g sample. The acid number of biodiesel samples with the addition of PY and surfactants still meets the standard after a storage period of 1 week. Meanwhile, the acid number of the two other samples, i.e., biodiesel only and biodiesel with the addition of PY, is greater than the standard.

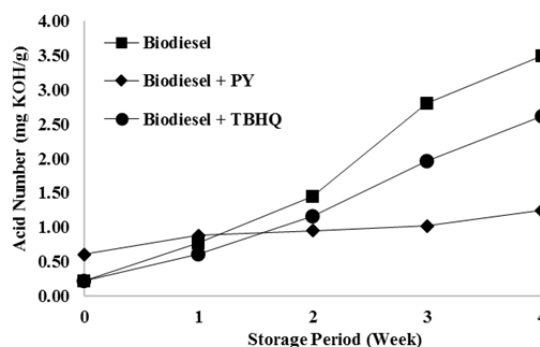


Figure 4. Acid Number of Biodiesel Samples with the Addition of Antioxidants

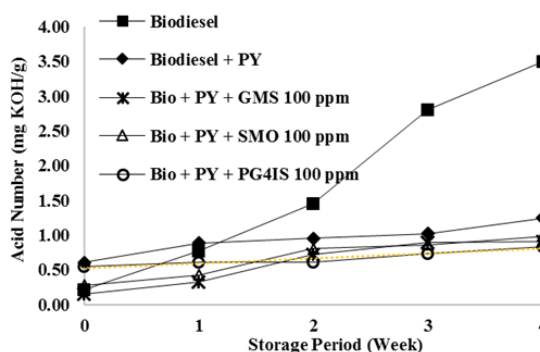


Figure 5. Acid Number of Biodiesel Samples with the Addition of PY and Surfactants

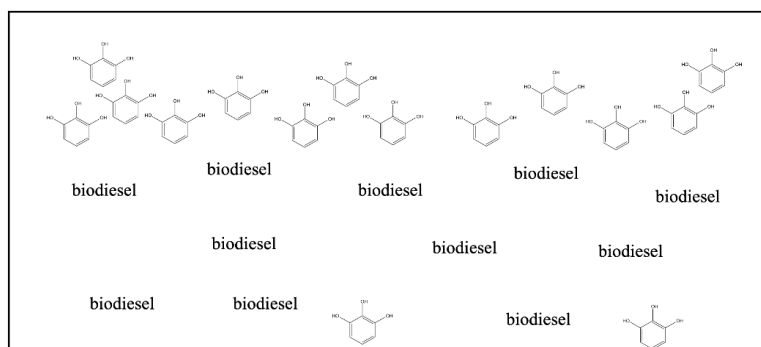


Figure 6. Distribution of PY in Biodiesel without the Addition of Surfactants

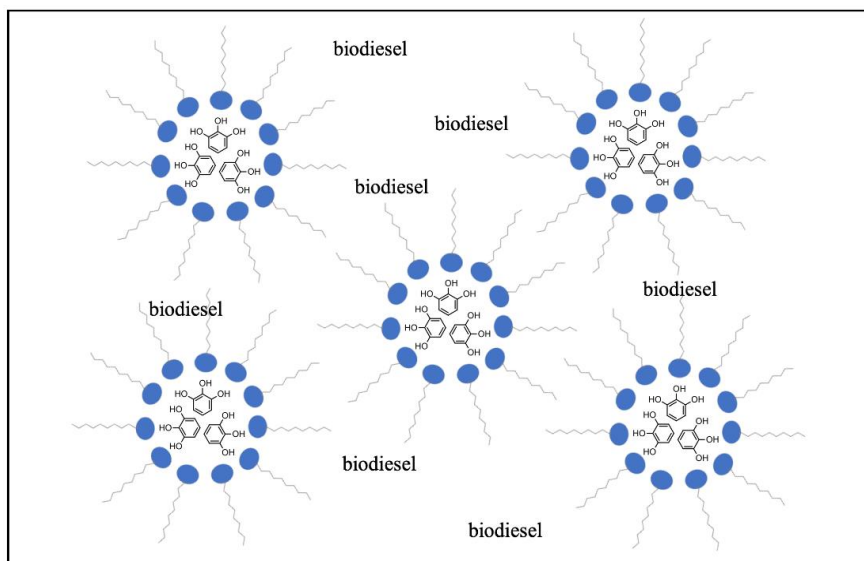


Figure 7. Distribution of PY in Biodiesel with the Addition of Surfactants

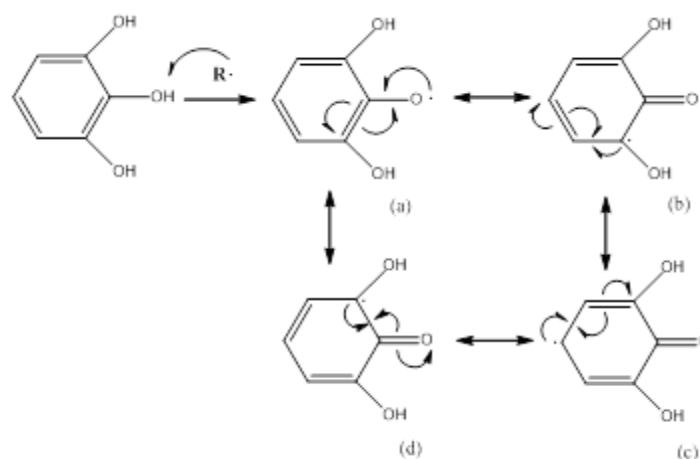


Figure 8. Free Radical Scavenging in Biodiesel by PY

Iodine value. The unsaturated fatty acid content is the main cause of the oxidative instability of biodiesel. The double bond in unsaturated fatty acid has high reactivity to oxygen and can trigger the oxidation reaction [34]. During oxidation, the number of double bonds or the degree of saturation in biodiesel will decrease over time. The degree of saturation in biodiesel can be measured by iodometric titration called the iodine value method. The iodine value is expressed as the amount of double bond in grams of iodine absorbed per 100 g oil [35].

The stability of biodiesel during oxidation could be analyzed from the decrease in the iodine value during the storage period. The iodine value of biodiesel samples was measured for 4 weeks. The results of iodine value analysis are shown in Figure 9. The regression slope of the iodine value of the biodiesel without antioxidant, biodiesel with PY, biodiesel with PY and GMS, biodiesel

with PY and SMO, and biodiesel with PY and PG4IS samples were -4.6472 , -4.0503 , -3.7357 , -3.2790 , and -2.5903 , respectively. Biodiesel without antioxidants showed the worst decrease in the iodine value, which indicates the highest degree of oxidation. The addition of PY to biodiesel successfully delayed the oxidation reaction.

The addition of surfactants to biodiesel showed a positive effect, i.e., the increase in the activity of PY as an antioxidant. All samples with the addition of surfactants have a lower iodine value slope than the sample without surfactant. The order of the effectiveness of the surfactant in delaying the oxidation reaction in biodiesel based on the iodine value change is $PG4IS > SMO > GMS$. This pattern fits the results of the stability test of biodiesel using the acid number.

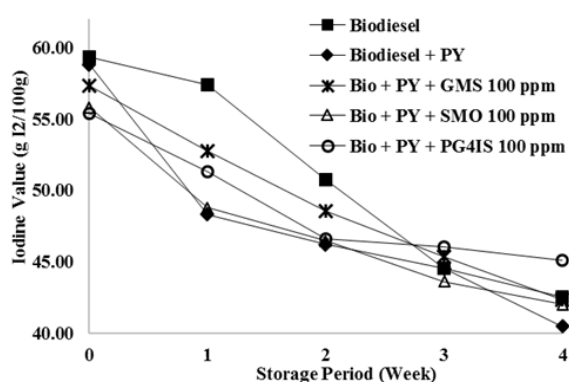


Figure 9. Iodine Value of Biodiesel Samples with the Addition of PY and Surfactants

The data from iodine value measurement confirmed that the dispersion of PY by the surfactant was inversely proportional to the increase in the activity of PY. As previously discussed in the sections pertaining to acid number, the presence of PY at the oil–air interface effectively inhibited the oxidation reaction in biodiesel. The dispersion of PY with the addition of PG4IS was lower than that of PY with the addition of the two other surfactants. The small amount of soluble PY that resulted from solubilization using PG4IS increased the instability of biodiesel, which caused by dissolved oxygen.

Conclusion

The addition of surfactants showed a positive effect, i.e., the increase in the performance of PY in preventing the oxidation of palm-oil-based biodiesel. The dispersion of PY increased with the order of PG4IS < SMO < GMS. Thus, the best antioxidant activity of PY can be achieved with the addition of the surfactant GMS.

By contrast, the increase in the dispersion of PY is inversely proportional to its antioxidant activity in terms of acid number and iodine value. The antioxidant activity of PY in biodiesel decreased with the order of PG4IS > SMO > GMS. Thus, the best surfactant that can be used to increase the activity of PY in biodiesel is PG4IS.

Acknowledgements

The authors would like to thank The Ministry of Research, Technology, and Higher Education Republic of Indonesia for financial support through Penelitian Terapan Unggulan Perguruan Tinggi research grant (contract no. 2639/L4/PP/2019).

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