Comparison of Synthetic and Plant Extract Antioxidant Additives on Biodiesel Stability

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Abstract. Oxidation stability is a critical parameter on biodiesel quality. Relates to The Indonesian Government policy to increase the percentage of biodiesel in diesel fuel blends, it is necessary to improve biodiesel quality so the diesel blends can meet the specification. This research focus on the effects of antioxidant additive to biodiesel quality, especially on oxidation stability characteristics, represented by Acid value, kinematic viscosity and induction period. Three additives used on this study were synthetic antioxidant additives tert-Butylhydroquinone (TBHQ), Propyl Gallate (PG) and a natural based antioxidant from Mango leaves extract prepared at LEMIGAS laboratory. Palm Oil based biodiesel is added with these three additives. A sample which is biodiesel without any additive was used for reference. All samples stored at an open glass tin for 12 weeks period. The Acid value, kinematic viscosity and induction period were measured for each 2 weeks. The result shows that additive TBHQ gives better performance in terms of Acid value, where sample containing TBHQ increase only 2.86% compare to PG and mango leaves extract that increase 11.43% and 22.22% respectively during 12 weeks storage. In terms of kinematic viscosity, these three additives shows similar result where the increasing of viscosity isn’t significant during test period. From the oxidation stability which is measured by induction period, PG additive show the lowest decreasing with only 1.96% lower from its initial value compare to TBHQ and mango leaves extract which decrease 5.03% and 18.76% respectively. From the result we conclude that the synthetic additives give better performance on biodiesel oxidation stability that the natural based additive.

Keywords: antioxidant additives, induction period, Acid value, oxidation stability

1. Introduction

Biodiesel used in most countries are produced mainly from plant oils using transesterification pathway. The main component is alkyl esters in saturated and unsaturated form. Transesterification does not alter the fatty acid composition of the feedstock. Fatty acids in biodiesel feedstock and some will still exist after the transesterification are consist of saturated and unsaturated chain. Ramos et.al [1] stated clearly that the number of poly-unsaturated chain in biodiesel relate directly to the decreasing of oxidation stability. The number of unsaturated fatty acids will depends on the feedstock used. In the case of Indonesia, since we use mostly palm oil is a benefit for us because palm oil rich in esters of saturated fatty acid and low in unsaturated fatty acid. The oxidation process is the main reason on the degradation
of biodiesel quality. Oxidation process caused by 2 mechanism; (1) high temperature (usually above 250-300 °C), and (2) the presence of oxidator (mostly oxygen from air, or dissolved oxygen) [2]. Another experiments done by Yang et.al [3] investigate the factors in the storage that affects biodiesel stability such as solvents, metals, and antioxidant additives and conclude that the solvents did not contribute on the change of Induction Period (IP). Copper and lead showed strong catalytic effect on decreasing of oxidation stability, but not for steel and aluminium alloy. The addition of pyrogallol and TBHQ as antioxidant additive showed the strongest enhancement on the IP.

The effects of antioxidant additives in increasing the oxidation stability is widely recognized. The most investigative oxidation process is autoxidation, which comprise three stage; initiation, termination and propagation. In the steps of initiation and propagation, where antioxidant may interfere, free radicals and hydroperoxides, primary oxidation products are formed. In the termination step, the aldehydes, carboxylic acids, hydrocarbon, ketones, and polymers that so called secondary oxidation products are formed. At this point, the process is completely irreversible [4]. One of the most efficient methods on delaying the oxidation of biodiesel is the use of antioxidant additives. Commercial antioxidant additives are widely available, with most of them are primarily used in food industries. Sterically hindered phenols and secondary aromatic amines are considered primary antioxidants that inhibit the oxidation via chain termination reaction. They contain one or more highly labile hydrogen (OH or NH group) that can be removed by a peroxy radical more easily than one’s from fatty oil esters. The resulting antioxidant radical (phenolic or aminic) is very stable and leads to stable molecules without removing a proton from the fatty acid chain [5].

As in Indonesia, since 2016 the Government already apply the mandatory policy to blend diesel fuel with 20% biodiesel. The biodiesel used for blends are mostly come from palm oil. Some references state that synthetics antioxidant additives has proven effects on various biodiesel, such as Pyrogallol improves The stability of Pongamia biodiesel [6], TBHQ expand the storage period for Callophyllum inophyllum biodiesel [7], and the capability of TBHQ and BHT to prevent corrosion affected by copper and Steel carbon immersed in soybean biodiesel [8]. The antioxidant activities is affected by climate of the Environment. In tropical areas as in Indonesia, many studies performed to know the antioxidant Activities of some commercial additives. Anggaraini [9] stated that TBHQ as the most effective effect as antioxidant than BHT. Fathurrahman [10] investigate 5 plant leaves extract on its antioxidant effect, including Mangifera indica leaves.

In this paper, antioxidant additive TBHQ (Tert-Butyl Hidroquinon) and Propyl Gallate (PG) are selected among other synthetic additives and the extract of Mango leaves (Mangifera indica) is prepared as natural based additive. The extraction of Mangifera indica leaves were done at LEMIGAS laboratory. Biodiesel used is from palm oil produced by biodiesel plant operated in Gresik, East Java.

2. Materials and Methods

2.1 Material

Biodiesel used in this study is produced by biodiesel plant in East Java. Synthetic antioxidant TBHQ and PG are bought from commercially packed additive. Extract of Mangifera indica leaves was prepared using ethanol solvent. The apparatus used are magnetic stirrer, soxhlet extractors, and dryers.

2.2 Methods

2.2.1 Preparation

Biodiesel from commercial producer is measured refer to biodiesel standard specification SNI 7182:2015. The leaves of Mangifera indica were washed and dried at room temperature before processed in simplicia powder with mesh 60. The simplicia then being extracted with ethanol to get the phenolic substance. The additive TBHQ and PG then weighed into certain amounts to get the concentration of 0.05% weight blended to biodiesel. The extract of mango leaves were added to biodiesel in concentration of 0.1% weight.

2.2.2 Stability Test Experiment
Biodiesel divided into 4 glass bottle by 1000 ml each then added by additive TBHQ, PG and mango leaves extract, whether 1 bottle remain free from additive to be used as reference. All samples are stirred using magnetic stirrer for 30 minutes. The samples then stored at storage room for 12 weeks. An oxidation stability testing were performed using induction period of Rancimat method (EN 15751), where measurement of Acid value was using titration method (ASTM D664) and the kinematic viscosity was performed using ASTM D 445.

3. Results and Discussion

3.1 Biodiesel Properties

Biodiesel used in this study is tested for its quality refer to SNI 7182:2015. The result show conformity to SNI 7182:2015 as listed in Table 1.

| No. | Properties                              | Unit      | Test Result | Limit Min. | Limit Max. | Test Method  |
|-----|-----------------------------------------|-----------|-------------|------------|------------|--------------|
| 1.  | Cetane number                           |           | 59          | 51         | -          | ASTM D 613   |
| 2.  | Density @40°C                           | kg/m³     | 857         | 850        | 890        | ASTM D 4052  |
| 3.  | Viscosity @40°C                         | mm²/s     | 4.37        | 2.3        | 6.0        | ASTM D 445   |
| 4.  | Sulfur content                          | mg/kg     | 1.19        | -          | 50         | ASTM D 4294  |
| 5.  | Distillation @90% rec                   | °C        | 348.5       | -          | 360        | ASTM D 1160  |
| 6.  | Flash Point                             | °C        | 172         | 100        | -          | ASTM D 93    |
| 7.  | Cloud Point                             | °C        | 15.0        | -          | 18         | ASTM D 2500  |
| 8.  | Carbon residu at sample; or             | % m/m     | nil         | -          | 0.05       | ASTM D 4530  |
|     | At 10% distillation residue             |           | -          | 0.3        |            | ASTM D 189   |
| 9.  | Water and sediment                      | % vol     | nil         | -          | 0.05       | ASTM D 2709  |
| 10. | Phosphor                                | mg/kg     | 0.013       | -          | 10         | AOCs Ca 12-55 |
| 11. | Copper strip corrosion (3 hours, 50°C)  | Merit     | 1a          | -          | class 1    | ASTM D 130   |
| 12. | Sulfated ash                            | % mass    | 0           | -          | 0.02       | ASTM D 874   |
|     | AOCs Cd 3d-63                           |           | -          | 0.02       |            | AOCs Cd 12-56 |
| 13. | Acid value                              | mg KOH/g  | 0.3         | -          | 0.5        | ASTM D 664   |
|     | AOCs Ca 14-56                           |           | -          | 0.02       |            | AOCs Ca 14-56 |
| 14. | Free Glycerol                           | % mass    | 0,016       | -          | 0.02       | ASTM D 6584  |
|     | AOCs Ca 14-56                           |           | -          | 0.24       |            | AOCs Ca 14-56 |
| 15. | Total Glycerol                          | % mass    | 0,10        | -          | 0.24       | ASTM D 6584  |
|     | AOCs Ca 14-56                           |           | -          | 0.24       |            | AOCs Ca 14-56 |
| 16. | Methyl ester content                    | % mass    | 98.77       | -          | 96.5       | SNI 7182:2012 |
| 17. | Iodium content                          | % mass    | 44.37       | -          | 115        | AOCs Cd 1-25  |
Monoglyceride content % mass 0.43 - 0.8 Titration (SNI 1782:2015)

Oxidation stability
Induction period (Rancimat); Minute 1157 480 - EN 15751

3.2 Antioxidant Additives Effect to Stability of Biodiesel
Oxidation stability measurement in the study is performed using Rancimat method, where kinematic viscosity and acid value are measured as an indication of oxidation products. Measurement was conducted every 2 weeks. The mango leaves extract was prepared by drying the leaves. The dried leaves then processed into simplicia powder with water content less than 10%. This level is limited because microorganism can grow on simpisia with water content higher than 10% and affect the enzymatic reaction which cause the decomposition and degradation of bioactives component and secondary metabolites in simpisia [11]. The simpicia then dissolved into ethanol in order to get the phenolic substance. The extract-ethanol solution then concentrated using rotatory evaporator that kept under temperature of 50 °C until the water content is minimized.

3.2.1 Oxidation Stability
Oxidation stability properties is also critical in biodiesel quality. Oxidation stability relates with decomposition degree of oil and fat. Unsaturated fatty acid can react with oxygen at its double bond to form peroxide. Refer to SNI 7182;2015, Indonesia limit the oxidation stability for biodiesel at minimum 480 minutes using the Rancimat method (EN 15751).

Figure 1 show the induction period change over storage time between biodiesel without additives (reference) and biodiesel added with additives. The reference has induction period of 1069 minutes at week 1, and after 12 weeks the induction period decrease to 788 minute or 26.29%. The most stable sample is the biodiesel added with Propyl Gallate where after 12 weeks storage the induction period decrease to 1050 minute or 1.96%. The TBHQ additive also show good stability, it can keep the stability of the sample to decrease only 5.03%. The mango leaves extract produce lower stability where the induction period decrease to 875 minute or decrease 18.76%.

Figure 1. Effect of additives on Induction period change over storage time of biodiesel
Generally antioxidant additives can be divided into 2 groups, the primary antioxidants and secondary antioxidants. Primary antioxidants are substances that role as free radical acceptors so it can inhibit the
mechanism of free radical formation in oxidation process. Meanwhile, the secondary antioxidants has the role of decomposing the hydroperoxide to form non-radical substances. The synthetic additive has good effects on oxidation stability because it has phenol function. This phenol increase the reactivity of the antioxidant on inhibit the oxidation process. The natural based additives processed from mango leaves also contain phenol substance but the extraction process needed to be improved.

3.2.2 Acid value
Acid value is a critical parameter regarding the stability of biodiesel. Acidity of biodiesel increase because of the accumulation of short chain acid as the result of oxidation which decompose peroxide and hydroperoxide compounds. The increasing of acid value alto caused by the formation of free fatty acid during oxidation as a products of double bond oxidation from unsaturated fatty acid. The function of antioxidant additive on prevent the increasing of acid value start from inhibition of peroxide formation by H atom (proton) so the formed lipid radicals can be stabilized. In term of biodiesel blend application in Diesel engine, the acid in biodiesel can cause a damage on the engine.

![Figure 2. Effect of additives on Acid value change over storage time of biodiesel](image)

Acid value show the amount of mineral acid and free fatty acid contained in biodiesel. Acid value expressed as miligram KOH/gram biodiesel, with the limit value is maximum 0.5 mg KOH/gr biodiesel. During the storage, hydrolytic reaction happens on the ester bond so the acid value increase. On Figure 2, we can observe that first measurement on week 1 the reference biodiesel has the acid value of 0.35 mg KOH/g. After 12 weeks, the acid value of the reference increase to 0.48 mg KOH/g, or increase 37.14%. The addition of TBHQ has the best effectivity to inhibit the increasing of acid value, with the increasement 2.86% after 12 weeks storage, compare to Propyl Gallate which increase the Acid value of biodiesel to 11.43% after 12 weeks. This finding is in line with Anggraini [9] that conclude the effectivity of TBHQ is better than other synthetics additives.

3.2.3 Kinematic viscosity
Kinematic viscosity is used as the indicator of the oxidation products in the biodiesel. The oxidation products include acids, which can change the consistency of the biodiesel. From figure 3 we can observe that kinematic viscosity of all samples show only slight changes compare to initial value. It means that the oxidation process that may happened did not affect the kinematic viscosity significantly.
4. Conclusion

Synthetic antioxidant additive TBHQ and Propyl Gallate gives better effect on the oxidation stability of biodiesel than the natural based additive from mango leaves. The synthetic additives provide more stable biodiesel, which only decrease of the induction period in 1.96% for Propyl Gallate and 5.03% for TBHQ, compare to mango leaves extract that decrease the induction period to 18.76%. The acid value increase of sample with synthetic additives also lower than the natural based additive, where the acid value increase in sample with TBHQ and Propyl Gallate is 2.86% and 11.43% respectively, compare to mango leaves extract that increase 22.22%. The kinematic viscosity of all samples shows similar result, no significant change detected during test period. The natural based additive from mango leaves extract still has lower effectivity as antioxidant, it is recommended to perform further research on the extraction techniques so the targeted substances that has high antioxidant activities can be purified effectively.

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References
[1] Ramos, M J., et al. 2009. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresource technology. 100(1): p. 261-268.
[2] Lapuerta, M., et al. 2012. Effect of the test temperature and anti-oxidant addition on the oxidation stability of commercial biodiesel fuels. Fuel. 93: p. 391-396.
[3] Yang, Z., et al.. 2013. Factors affecting oxidation stability of commercially available biodiesel products. Fuel processing technology, 106: p. 366-375.
[4] Medeiros, M.L., et al. 2014. Efficient Antioxidant Formulations for Use in Biodiesel. Energy & Fuels, 28(2): p. 1074-1080.
[5] Serrano, M., et al. 2013. Oxidation stability of biodiesel from different feedstocks: influence of commercial additives and purification step. Fuel. 113: p. 50-58.
[6] Dwivedi, G., Sharma, M.P. 2016. Investigation of Oxidation stability of Pongamia Biodiesel and its blends with diesel. Egyptian Journal of Petroleum. 25 : p. 15-20.
[7] Shameer, P.M., Ramesh, K. 2017. FTIR Evaluation on the fuel stability of callophyllum inophyllum biodiesel; Influence of Tert Butyl Hydroquinone (TBHQ) antioxidant. Journal of Mechanical Science and Technology. 31 : p. 3611-3617.
[8] Aquino, I.P., Celiberto, B., Alves, T.P., Aoki, I.V., Torres, R. 2015. Influence of the synthetic
antioxidants, BHT and TBHQ, on Soybean biodiesel corrosiveness and degradation. *Proceeding of 2015 AIChE Annual Meeting.*

[9] Anggraini, Arum. 2007. Pengaruh Jenis dan Konsentrasi Antioksidan terhadap Ketahanan Oksidasi Biodiesel dari Jarak Pagar. *Thesis.* Bogor (ID): Departemen Kimia, Fakultas Matematika dan Ilmu Pengetahuan Alam, Institut Pertanian Bogor.

[10] Fathurrahman, Nur Allif. 2016. Inhibisi Ekstrak Air Lima Tanaman Obat terhadap Glikasi Protein secara in vitro dan Potensinya sebagai Antipenuaan. *Thesis.* Bogor (ID): Departemen Kimia, Fakultas Matematika dan Ilmu Pengetahuan Alam, Institut Pertanian Bogor.

[11] Gordon, M.H. 1990. The mechanism of antioxidants action in vitro. B.J.F. Hudson, editor. *Food Antioxidants. Elsevier Applied Science,* London.