ABSTRACT

The use of biodiesel is still experiencing problems due to large amount of water content which produce from the transesterification process, making it has unstable oxidizing properties. The large amount of water content in biodiesel causes the emergence of microorganisms which becoming sludge in the engine room, and can clog the fuel filter. In this study, we propose the application of oxygenate bio-additives to minimize water and particulate content by using turpentine essential oils, clove terpenes, rhodinol, camphor oil, and synthetic additive 2EHN. Based on the study’s results, the water content of biodiesel B35 with the AC bio-additive mixture experienced the highest decrease in water content, which was 18% or 287.2 ppm and performs well in reducing particulate levels of 4, 6, and 14 microns. The completely randomized design (CRD) test results for non-factorial moisture content on days 0, 3, 5, 7, and 14 and particulate matter 4, 6, and 14 microns showed no significant difference because each P value was obtained greater than α (0.05).

1. INTRODUCTION

Along with the development of transportation equipment (especially diesel-engined vehicles), the quality of fuel is also growing. The diesel engine is a machine that is widely used as a driving force for power plants, agricultural machinery, and transportation. The operation of diesel-powered engines has an environmental impact because it produces toxic exhaust gases such as Hydrocarbons (HC), Carbon Monoxide (CO), and Nitrogen Oxide (NOx), as well as particulates. Diesel engines in the combustion process use diesel fuel produced from petroleum from a distillery called B0. The availability of fossil fuels is dwindling, in the last 10 years Indonesia has experienced a decrease in the amount of oil production from 346 million barrels in 2009 to 283 million barrels in 2018. Therefore,
there is a need for alternative fuel solutions to replace diesel fuel. One of them is the
use of biodiesel in accordance with the Minister of Energy and Mineral Resources
Regulation No. 12/2015 30% biodiesel utilization by 2050 (ESDM, 2015; Sivaganesan et
al. 2017; Sekretariat Jendral Dewan Energi Nasional 2019; Martin et al. 2020). The
Indonesian government has acted even faster by implementing B35 since February
2023.

On the other hand, the use of biodiesel can reduce combustion heat, reduce
injector performance, and clog fuel filters due to the appearance of microorganisms
which can become sludge in the engine compartment due to the large amount of
water in biodiesel. The presence of water content is inseparable from the hygroscopic
nature of biodiesel because there is still glycerol in biodiesel from the
transesterification process. Glycerol contains OH which is able to bind water. According
to (Suleman et al., 2019), the formation of water can be overcome by using methanol,
and methanol is a type of oxygenate. The oxygenate content is a group of compounds
consisting of several oxygen atoms that can improve fuel in engines. Essential oils have
a class of oxygenic compounds that can replace methanol so that they can be used to
reduce water content, and can even increase the cetane number (cetane).

Bioadditives derived from plants that have essential oils can be used as mixed fuel
in biodiesel fuel. Essential oils have properties that are similar to or close to fuel oil
because they are volatile, have a low specific gravity, and are composed of certain
organic hydrocarbon compounds, and have a chemical structure in the oxygenate
component that can increase the heating value thereby perfecting the combustion
process. The structure and chemical composition of essential oils can improve the
combustion properties of fuel and clean the dirt that has accumulated in the
combustion chamber. This happens because essential oils have cyclic bonds, double
bonds, and hydrocarbon bonds and contain oxygenates (Haryono et al. 2019; Utomo,

There are several essential oils that can be used as a mixture of biodiesel fuel,
including turpentine oil which has an oxygenate compound group of 45% -77%. This oil
has the potential to be used because it easily mixes with biodiesel, therefore it can be
used as a mixture for diesel fuel because it can reduce particulates (Ansari et al. 2022;
Ankney et al. 2022; dan Yadav et al. 2022). In addition, there is clove terpene with an
oxygenate compound group of 84.31% and a rhodinol fraction derived from citronella
oil with 33.31% of an oxygenate compound group which can reduce particulates (Kaur
et al. 2019; Kaur et al. 2021; Purnama et al. 2021). Camphor oil is also potential
because it has an oxygenate compound group of 51.27%. One of the artificial additives
that can be used is 2-Ethylhexyl nitrate which can reduce fuel consumption, increase
cetane values, and can reduce particulates (Nasikin et al. 2002; Srivastava & Hancsok
2014; Bhandari et al. 2022).

Research conducted by Halimi et al. (2020), Prahmana et al. (2020), and Purnama et
al. (2021) regarding bioadditives from essential oils in fuel including kesambi oil as a
bioadditive which can save 20% of fuel, clove and citronella oil as bioadditives in diesel
engines can reduce particulates by 16%, while citronella compounds can reduce 28% of
particulates. Research on the use of bioadditives made from essential oils of lemon oil
by Permanasari et al. (2021) able to reduce the use of diesel fuel. Throughout the
author’s investigation, there is no information about bioadditive research with a
mixture of turpentine oil, clove terpene, rhodinol, and camphor, as well as the
synthetic additive 2-Ethylhexyl nitrate for biodiesel B35. Therefore, this study aims to
determine the performance of essential oil bioadditives in a mixture of essential oils of
turpentine, clove terpene, rhodinol, and camphor as well as artificial additives
(synthetic) of 2EHN (2-Ethylhexyl nitrate) on decreasing water content and decreasing particulate matter.

2. MATERIALS AND METHODS

The research was conducted from July to December 2022, at the Surfactant and Bioenergy Research Center (SBRC), Bogor, and S.O.S. PT Trakindo Utama, Tangerang.

2.1. Research Materials and Stages

The research was conducted using bioadditives made from essential oils of terpentine, clove terpene, rhodinol, and camphor oil, as well as synthetic additive 2-Ethylhexyl Nitrate. Each essential oil and synthetic additive was formulated, after which 0.1% v/v bioadditive was added to each biodiesel sample except for blank. Mixing bioadditives functions as an additional ingredient in biodiesel. The biodiesel used is B35 resulting from mixing B100 biodiesel with B30 biodiesel fuel with 0.15% water added. This stage was then carried out by testing the water content on day 0 on all samples (12 samples). The next step was observing the water content test (days 0, 3, 5, 7, and 14th day), and particulate tests on 12 samples that were placed in glass bottles with tightly closed conditions with the aim of knowing which treatment could show better performance. good for reducing water content and reducing particulates.

2.2. Analysis Techniques

This research was conducted using the American Standard Testing and Materials (ASTM), namely the analysis of water content tests on biodiesel samples using Karl Fischer ASTM D1744, while the particulate reduction test using ASTM D7596. The data obtained were then analyzed using a non-factorial completely randomized design with RStudio.

3. RESULTS AND DISCUSSION

3.1. Water Content

The water content in biodiesel is a matter of concern to biodiesel users because it can clog the filter thereby disrupting the flow of fuel to the engine so that it can cause the vehicle to die suddenly, it can even damage the engine if biodiesel is deposited for a long time, so it is necessary to add bioadditives in biodiesel fuel to reduce its water content. Table 1 shows the effect of adding essential oil additives on the development of biodiesel water content during storage up to 14 days.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Water content (ppm) ASTM D1744</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day 0</td>
</tr>
<tr>
<td>Blank</td>
<td>334.0b</td>
</tr>
<tr>
<td>A</td>
<td>331.3b</td>
</tr>
<tr>
<td>AC</td>
<td>352.2a</td>
</tr>
<tr>
<td>AE</td>
<td>337.3ab</td>
</tr>
</tbody>
</table>

Note: Numbers followed by same lowercases in the same column are not significant at $\alpha=0.05$.

The results of the research on the moisture content test on day 0 (Figure 1, left) obtained 331.3 ppm in biodiesel B35 mixed with bioadditive A with the smallest
average value of water content compared to biodiesel B35 mixed with other bioadditives and biodiesel B35 without mixing bioadditives (blank), while biodiesel B35 with a mixture of AC bioadditives obtained the greatest value from an average water content value of 352.2 ppm compared to biodiesel B35 without a mixture of bioadditives, and biodiesel B35 with a mixture of bioadditives A, and biodiesel B35 with a mixture of AE bioadditives. The water content in the B35 biodiesel used as a sample still meets the water content standards issued by the regulations for the maximum limit of water content in biodiesel contained in the Decree of the Director General of Oil and Gas No. 195.K/EK.05/DJE/2022 (ESDM, 2022), the maximum limit for the maximum water content of biodiesel B35 is 340 mg/kg (ppm). Based on non-factorial CRD analysis of water content on day 0 there was no significant difference because the P value was obtained 0.0741 > α (0.05).

Figure 1. The average value of the water content of biodiesel B35 observed on day 0 (left) and day 3 (right).

The results of non-factorial CRD analysis for water content on day 3 showed no significant difference because the P value was 0.429 > α (0.05). The results of the research on the 3rd day of observation of the sample experienced a decrease in water content (Figure 1, right), the sample of biodiesel B35 without a mixture of bioadditives experienced a decrease in water content to 313.2 ppm on an average water content value or decreased by 6% when compared to the results of the water content on day 0, the sample of biodiesel B35 without the addition of bioadditives was the sample that had the highest water content on day 3 when compared to the sample of biodiesel B35 which was given the addition of bioadditives. The decrease in water content shows that the biodiesel sample has been given additives by stakeholders with the aim of reducing the water content in biodiesel, but according to Indrarto et al. (2018), the biodiesel obtained is of low quality. Laboratory tests on biodiesel samples showed that there was still a lot of water content in the biodiesel mixture. In addition to its easily oxidized nature which can absorb water (hygroscopic), it causes the formation of bacteria or acids in the storage tank. Poor handling of distribution, storage of biodiesel in dirty tanks and leaky storage drums. So for biodiesel consumers this is not profitable, because biodiesel can become sludge in the tank within 6 months. Therefore it is necessary to add bioaddictive materials to reduce water content.

Samples on biodiesel with a mixture of bioadditive A experienced a decrease in water content from an average water content value of 331.3 ppm (day 0) to an average water content value of 292 ppm on day 3 or experienced a decrease in water content of 12%, because biodiesel B35 with the addition of bioadditive A contained 45% - 77% of the oxygenate compound group in turpentine essential oil, rhodinol fraction derived from citronella oil amounted to 33.31% of the oxygenate compound group, and clove
terpen contained 84.31% oxygenate compound group.

Biosolar B35 with a mixture of AC bioadditives experienced the highest decrease in water content, which was 18% or there was a decrease in the average water content value of 287.2 ppm when compared to day 0 of 352.2 ppm, the average value of the water content that was sampled with the highest water content on day 0 when compared to other biodiesel samples. There was a decrease in the highest water content due to the addition of camphor oil which has an oxygenate compound group of 51.27% so that it has a significant effect when compared to the biodiesel B35 sample in the treatment given a mixture of bioadditives A and AE.

The AE bioadditive as a mixture of B35 biodiesel obtained the lowest average water content value of 285.8 ppm on the 3rd day of observation when compared to other bioadditives and there was a 15% decrease in water content when compared to the water content on day 0. water because the 2EHN additive can increase the octane value, the increase in octane is one of the characteristics of the oxygenate compound group. The presence of an oxygenate group of compounds means that a reaction occurs between the carboxylic acid and the alcohol resulting in the formation of an ester.

A significant decrease in water content in biodiesel B35 added with essential oil bioadditives on day 3 when compared to biodiesel B35 without the addition of bioadditives was due to the addition of oxygenate compound groups to biodiesel B35 which added bioadditives A, AC, and AE.

Increasing the class of oxygenate compounds in biodiesel when administering bioadditives made from essential oils can increase the alcohol in biodiesel, because essential oils contain oxygenate compounds in the form of alcohol. The presence of alcohol makes a reaction on the fatty acid to form a methyl ester and suppresses the carboxyl group. The increase in methyl esters due to the addition of alcohol from essential oils can reduce the water content because water can dissolve in alcohol, which levels increase. Increasing the alcohol used can suppress the acid to be low. The process of decreasing water content can be seen in Figure 2.

![Figure 2. Bioadditive process for reducing water content in biodiesel](image-url)

According to Zalifiatri et al. (2019), a decrease in acid levels occurs when fatty acids react with triglycerides in alcohol to form methyl esters, because triglycerides react well to metal methoxide in alcohol so that methyl esters increase when the alcohol is
added. The greater the addition of alcohol, the methoxide ions become more reactants as a substitute for carboxylate ions. The methoxide ion is a strong nucleophile formed by the reaction of an alcohol with a base catalyst. These ions can easily exchange carbonyl groups in fatty acids.

The results of the water content test on the 5th day of observation (Figure 3, left), samples of biodiesel B35 without the addition of bioadditives and treatment of biodiesel B35 with the addition of bioadditives experienced an increase in water content, the highest increase in water content occurred in biodiesel B35 with the addition of bioadditives AE treatment with an increase rate of 14%, biodiesel B35 without the addition of bioadditives increased water content more slowly so that it only experienced an increase in water content of 3%, while biodiesel B35 with the addition of bioadditive A increased the rate of increase in water content by 8%, and biodiesel B35 with the addition of bioadditive AC increased 12% at the rate of increase in water content. The increase in water content is caused because biodiesel has unstable oxidizing properties, oxidation is a problem for biodiesel fuel because in the process of mixing diesel fuel with biodiesel it produces water content. According to Indrarto et al. (2018), the process of making biodiesel by transesterification produces an oxygen content of 11% which results in oxidation instability. The oxygenate compound group can reduce the water content, but cannot stabilize the biodiesel properties, namely oxidation. Based on non-factorial CRD analysis of water content on day 5 there was no significant difference because the P value was obtained 0.0616 > α (0.05).

![Figure 3. The average water content of biodiesel B35 on day 5 (left), day 7 (center), and day 14 (right)](image)

The results of the non-factorial CRD test for water content on the 7th day showed no significant difference because the P value was 0.0762 > α (0.05). Testing the water content of biodiesel B35 on the 7th day of observation (Figure 3, center) experienced a decrease in the water content again, the decrease that occurred experienced a significant decrease in water content in all samples of biodiesel B35. The decrease in water content at a high rate occurred in the biodiesel B35 sample with the addition of bioadditive A of 20% or to 251.8 ppm at the average moisture content value when compared to the average water content value on day 5 of 316.4 ppm, the sample biodiesel B35 with the addition of AC bioadditives experienced a low water content decrease with an average water content value of 279.5 ppm or 14% of the comparison of the average water content value on day 5, which was 326.3 ppm. Biodiesel B35 without the addition of bioadditives and biodiesel B35 with the addition of the bioadditive AE experienced the same decrease in water content, which was 19%, a
difference of 1% when compared to biodiesel B35 with the addition of bioadditive A.

The occurrence of a significant decrease in water content on the 7th day (Figure 3, center) indicated that biodiesel B35 with the addition of bio-additive ingredients of essential oils had a good time to evaporate water completely and the peak of the methyl ester reaction suppressed the carboxyl group, before the hydrolysis reaction occurred and the fatty acid content increased which caused the content of the water got high the next day.

Based on the results of the non-factorial CRD test for water content on day 14 (Figure 3, right) there was no significant difference because the P value was obtained 0.0793 > α (0.05). The results of the test for the water content of the B35 biodiesel samples for all treatments on the 14th day (Figure 6) experienced an increase in water content, the rate of increase in the water content of the B35 biodiesel samples with the addition of bioadditive A was faster when compared to other B35 biodiesel samples because the increase was 25% when compared with the average value of water content on the 7th day of observation with the same sample, followed by the B35 biodiesel sample without the addition of bioadditives, the rate of increase in water content was high, which was 24%, although it differed only 1% lower when compared to the B35 biodiesel sample with the addition bioadditive A. The B35 biodiesel sample with the addition of the AE bioadditive had a lower increase rate of 20%, 4%-5% lower when compared to the B35 biodiesel sample without the addition of the bioadditive and the B35 biodiesel sample with the addition of the bioadditive A. Biosolar B35 with the addition of the AC bioadditive the lowest rate of increase in water content was 11% when compared to other samples, the low rate of increase in water content was due to the use of camphor oil which had 51.27% oxygenate compound class as an additional bioadditive, more content of oxygenate compound groups when compared to the sample Another B35 biodiesel causes a methyl ester reaction to suppress the carboxyl group to inhibit the hydrolysis reaction rate and inhibit the increase in fatty acids.

The increase in water content in all samples from day 7 to day 14 was caused by the properties of biodiesel besides being oxidizing, it also has hygroscopic properties which can absorb water from humidity during storage. Therefore, the storage area must be closed and tightly closed immediately, because open storage for a long time can increase the water content higher because biodiesel is exposed to air for a long time. The results of the average moisture content of all samples from day 0 to day 14 can be seen in Figure 4.

Figure 4. The average water content of biodiesel B35 observed from day 0 to day 14

3.2. Particulate Content
Particulates cause air pollutants produced from burning diesel fuel from diesel-engined vehicles, exposure to particulates has a negative effect on human health which can
cause respiratory infections, asthma, lung cancer, stroke, and even cause heart disease. This problem has a bad impact on diesel vehicles because it can be the main cause of air pollution due to the large number of particulates that are spread in the air due to the exhaust of diesel engines, so it is necessary to do handlers to suppress or reduce the particulate content produced by diesel engines. The use of essential oil bioadditives in biodiesel fuel can reduce particulate content because it has a class of oxygenate compounds (Pepiot-desjardins et al. 2008; Hounslow et al. 2018; Li et al. 2018; Salvador 2018; Zhang et al. 2020; Sedghi et al. 2022).

Table 2 shows the mean particulate content in biosolar influenced by additive addition. The results of the 4-micron particulate test of biodiesel B35 with the addition of bioadditive AC were lower when compared to the sample of biodiesel B35 without the addition of bioadditive, the addition of bioadditive A, and the addition of AE bioadditive with respective percentage values of 17%, 24%, and 13%. While the B35 bioadditive AE sample was lower by 4% and 13% when compared to the B35 biodiesel sample without the addition of bioadditive, and the addition of bioadditive A and the results of the non-factorial CRD test obtained P value 0.091 > α (0.05), so no real difference.

Based on non-factorial CRD analysis of 6 micron particulates, there was no significant difference because the P value was 0.0699 > α (0.05). The 6 micron particulate test on biodiesel B35 with the addition of bioadditive AC obtained an average particulate test value of 1236.7 (count/mL), 8%, 14%, and 25% lower when compared to the biodiesel B35 sample without the addition of bioadditives, the addition of bioadditive A, and addition of AE bioadditives.

Table 2. The average results of the particulate content (count/mL) according to particle size

<table>
<thead>
<tr>
<th>Treatment</th>
<th>4 µ</th>
<th>6 µ</th>
<th>14 µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanko</td>
<td>12164.7ab</td>
<td>1340.3a</td>
<td>81.7a</td>
</tr>
<tr>
<td>A</td>
<td>13318.3a</td>
<td>1439.3a</td>
<td>89.3a</td>
</tr>
<tr>
<td>AC</td>
<td>10089.7b</td>
<td>1236.7a</td>
<td>79a</td>
</tr>
<tr>
<td>AE</td>
<td>11637ab</td>
<td>1657.7a</td>
<td>131a</td>
</tr>
</tbody>
</table>

Note: Numbers followed by same lowercases in the same column are not significant at a = 0.05.

The results of the 14 micron particulate test on biodiesel B35 with the addition of bioadditive AC produced the smallest particulate content compared to other treatments, because the percentage values were 3%, 12%, and 40% lower when compared to the biodiesel B35 sample without the addition of bioadditives, the addition of bioadditive A, and the addition of AE bioadditives. The results of the non-factorial CRD test for 14 micron particulate matter showed no significant difference because the P value was 0.268 > α (0.05).

Therefore, the addition of camphor oil performs well to reduce particulate levels, because camphor has an oxygenate compound group of 51.27%. In accordance with Sedghi et al. (2022), oxygenate additives can properly reduce particulate levels. The addition of 2EHN performs well to reduce particulate levels at 4 micron in size, because it is smaller than biodiesel B35 with blank treatment and the addition of bioadditive A. Biosolar B35 with the addition of bioadditive A results in higher particulate levels than biodiesel B35 without the addition of bioadditives and biodiesel with the addition of AC bioadditive, and A.E. The value of particulate matter for biodiesel B35 with the addition of bioadditive A was higher than that of other samples, presumably because the sample collection or sample site for the particulate test was contaminated with
other compounds, because biodiesel with the addition of bioadditives should have a lower particulate value than blank biodiesel.

4. CONCLUSION

Based on non-factorial CRD analysis of water content tests on days 0, 3, 5, 7, and 14 there was no significant difference because each P value was obtained greater than $\alpha$ (0.05). The results of the water content test until the 7th day decreased the water content, while on the 14th day there was an increase in the water content in all B35 biodiesel samples where the B35 blank reached a moisture content exceeding the set standard. This means that blank B35 biodiesel cannot be stored for more than 14 days. The results of the non-factorial CRD test for particulates 4, 6, and 14 microns showed no significant difference because each P value was obtained greater than $\alpha$ (0.05). Biosolar B35 with the addition of AC bioadditive added with camphor oil performed well to reduce particulate levels of 4 microns, 6 microns and 14 microns. Biosolar B35 with the addition of the bioadditive AE performed well to reduce particulate levels at 4 microns in size when compared to biodiesel B35 with the blank treatment and the addition of bioadditive A.

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