Water content in biodiesel for diesel fuel blends: measurement using centrifuge and coulometric titration method

L Aisyah1*, S A Bethari1, C S Wibowo1, N Hermawan1, D U Alwi1, D Rulianto1, R Anggarani1
Fuel and Lubricant Research Group, R&D Center for Oil and Gas Technology
“LEMIGAS”, Jakarta, Indonesia

*Corresponding author: laisya@gmail.com, sylviayubethari@gmail.com

Abstract. Biodiesel nowadays is being used as a blend with diesel fuel to promote the renewable fuels. One of the critical parameters of biodiesel is water content, both free and soluble water is covered. Water presence in biodiesel is limited by the specification to prevent fouling in storage and handling facilities and to avoid trouble in fuel system of engine. Currently in Indonesia, the measurement of water in biodiesel use the centrifuge method that measure both of water and sediment content. Refer to diesel fuel specification, water content is measured separately from sediment content. In order to prepare higher biodiesel percentage in diesel blends (up to 30%) as the Government of Indonesia planning in 2020, water content measurement in biodiesel need more accurate method. In this study, we present the measurement of water content in 20 biodiesel samples using 2 methods: the centrifuge and coulometric titration method. The result show that all biodiesel samples having different water content vary from 173.36 ppm to 968.12 ppm, while all water and sediment content from 20 biodiesel samples are mostly nil, only 1 sample has 0.05 vol % water and sediment.

Keywords: water content, biodiesel, centrifuge, coulometric, titration method

1. Introduction
Water content in biodiesel is mainly originated from the production process that include washing of the transesterification products. Generally biodiesel purification use 2 methods; wet washing and dry washing [1]. Wet washing use water to separate impurities, whether dry washing use adsorbent compounds such as magnesium silicate and silica gel. Wet washing is more common in biodiesel plant than dry washing. After the removal of impurities, water then should be separated from final biodiesel using distillation process. Advance separation method such as reactive distillation column is introduced [2], however the conventional distillation unit still being used in most plants.

To guarantee the biodiesel quality, a specification should be regulated by the government. In Indonesia, the biodiesel specification is set by Directorate General of New and Renewable Energy and Energy Conservation [3] that rules the parameters and limited values, and also the test methods. One of the critical parameter of biodiesel is water content. The presence of water affects the spray and combustion characteristics in diesel engine [4] and plays significant role on the deterioration of diesel-biodiesel blends caused by microbial growth [5]. Biodiesel naturally has hygroscopic characteristic that tend to adsorb humidity from the surrounding ambient. A study by Lapuerta et al [6] proved that
presence of water in the air affects wear scar through increasing water content in the fuel, and that biodiesel is more hydroscopic than paraffinic and aromatic fuels.

Currently water content in biodiesel is measured along with the sediment content, as called water and sediment content. In national standard for biodiesel stated in SNI 7182:2015, the test method for measuring water and sediment content is refer to ASTM D1796 “Standard Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)” [7]. The specification limits the value of water and sediment content to maximum 0.05% volume. Internationally, biodiesel specification intended for diesel blends follows the Biodiesel Guidelines published by Worlwide Fuel Charter Committee [8]. This WWFC specify the limit of water at maximum 500 mg/kg using test method of EN 12937 Karl Fischer coulometric titration, they also limit the water and sediment content to maximum 0.05% volume using test method ASTM D2709 [9] by centrifuge method. On the same sub section with water and sediment content, WWFC also limits the Total Contamination at maximum 24 mg/kg using test method of ASTM D 2276 “Standard test method for particulate contaminant in aviation fuel by line sampling”.

The plan of the government to increase biodiesel percentage in diesel fuel blends up to 30% in 2020 [10] needs tighter support from biodiesel quality. Some parameters that needs to be tighten are water content, monoglyceride content, pour point, cloud point, and cold filter plugging point [11]. The measurement of these parameters becomes necessary to give high accuracy in order to get real value of the measured samples.

This paper presents a work performed at Fuel and Aviation Laboratory of LEMIGAS on the measurement of water content in 20 biodiesel samples collected from 20 biorefineries. The measurement was done using 2 methods, the centrifuge method refer to ASTM D2709 that produce both of water and sediment content, and the Karl Fischer coulometric titration method refer to ASTM D6304 that generate only water content. By presenting these results, we aim to emphasize the necessity of measuring water content accurately and being separated from other parameter such sediment content.

2. Materials and Methods

2.1. Materials

All the experiments were performed employing 20 Biodiesel samples of typical commercial Indonesian biodiesel obtained from various biodiesel company. Karl Fischer Reagent: Aquamax KF Reagent A, Aquamax KF Reagent Cathode and Aquamax KF Reagent Oil (GRScientific) were used for Karl Fischer analyses.

2.2. Methods

2.2.1. Karl Fischer Measurement. To evaluate the water content present in biodiesel samples the volumetric Karl Fischer technique was used according to ASTM D6304. The equipment used was an Aquamax KF Coulometric from GRScientific.

2.2.2. Water and Sediment Measurement. To evaluate water and sediment content in biodiesel samples centrifuge technique was used according to ASTM D2709. The equipment used was a S.D.M. Apparecchi Scientific srl. unipersonale.

3. Results and Discussion

Water determinations in biodiesel were first performed setting standard parameters. Water content in biodiesel (fuel) is water that is dissolved and not dissolved in fuel. Insoluble water (free water) in the fuel can be separated by precipitation and then drainage. The presence of water will cause lower heating
value, foaming and corrosion [12]. Volatile substances dissolved in water, can be measured as water. When the temperature is cold, water can crystallize which cause fuel line clogging. Water content result of 20 biodiesel samples is shown in Table 1. From the test result, all biodiesel samples having different water content vary from 173.36 ppm to 968.12 ppm.

| Samples | Water (mg/kg) |
|---------|---------------|
| 1       | 293.33        |
| 2       | 549.68        |
| 3       | 338.90        |
| 4       | 333.57        |
| 5       | 326.58        |
| 6       | 430.30        |
| 7       | 730.74        |
| 8       | 301.83        |
| 9       | 887.74        |
| 10      | 808.79        |
| 11      | 225.73        |
| 12      | 470.62        |
| 13      | 398.35        |
| 14      | 968.12        |
| 15      | 509.62        |
| 16      | 186.75        |
| 17      | 205.38        |
| 18      | 720.77        |
| 19      | 194.15        |
| 20      | 173.36        |

Measurement of water content in biodiesel by Karl Fischer coulometric titration method as shown in Table 1 is considered as highly accurate technique employed for moisture determination in non-aqueous solvent [13]. The ability of this coulometric titration to measure water content as low as hundred mg/kg makes this method as the most accurate method for low water level determination [14]. By showing certain value measured in mg/kg unit, it would be our advantages to know that our biodiesel is good enough to enter the fuel system and the combustion chamber without causing any defects.

Water and sediment contents were measured by centrifugation method. Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of the fuel-handling facilities and to give trouble in the fuel system of a burner or engine. An accumulation of sediment in storage tanks and on filter screens can obstruct the flow of oil from the tank to the combustor. Water in middle distillate fuels can cause corrosion of tanks and equipment, and if detergent is present, the water can cause emulsions or a hazy appearance. Water is necessary to support microbiological growth at fuel water-interfaces in fuel systems [9]. Water and sediment content result of 20 biodiesel samples is shown in Table 2.
From the test results, all water and sediment content from 20 biodiesel samples are mostly nil, only 1 sample has 0.05 vol % water and sediment.

Table 2. Results of water and sediment measurement using ASTM D2709 method

| Samples | Water and Sediment (vol %) |
|---------|---------------------------|
| 1       | 0                         |
| 2       | 0                         |
| 3       | 0                         |
| 4       | 0                         |
| 5       | 0                         |
| 6       | 0                         |
| 7       | 0                         |
| 8       | 0                         |
| 9       | 0.05                      |
| 10      | 0                         |
| 11      | 0                         |
| 12      | 0                         |
| 13      | 0                         |
| 14      | 0                         |
| 15      | 0                         |
| 16      | 0                         |
| 17      | 0                         |
| 18      | 0                         |
| 19      | 0                         |
| 20      | 0                         |

Currently, biodiesel specification in Indonesia only regulate water and sediment content (ASTM D2709). Measurement of water content as water and sediment content (ASTM D2709) only to found out free water in biodiesel while measurement of water content based on ASTM D6304 is to determine total water in biodiesel. Therefore, it is important to add water content parameter based on ASTM D6304 to biodiesel specification because it determines different purpose in analysis. By comparing Table 1 and Table 2, we may understand that using coulometric titration method, amount of water can be presented accurately into unit of mg/kg and it would be necessary to measure water content separately to support better biodiesel quality.

4. Conclusions

Water content determination in biodiesel is needed to be performed separately from sediment measurement. The coulometric titration method generates accurate water content value, while centrifuge method provides good prediction on the amount of water together with sediment content.
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