International Journal of Engineering Research and Technology. ISSN 0974-3154, Volume 13, Number 12 (2020), pp. 5247-5251


# The Influence of Outdoor Temperature and Storage Conditions on Stability of Biodiesel and Blends: Acidity and Hygroscopycity Behavior

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**Abstract**

Different storage conditions can affect the stability of biodiesel and petrodiesel during storage. The study focused on analyzing changes in the acidity and hygroscopisity of biodiesel and blends, it compared with petrodiesel during 120 days of storage. The storage test is carried out on an outdoor fuel tank and ground fuel tank. It is concluded that the water content of biodiesel in the ground tank increasing significantly during 17 weeks of storing, from 329 ppm to 1491 ppm. In the outdoor tank, the water content of biodiesel increased from 329 ppm to 534 ppm. The acid number of biodiesel increased from 0.31 mg KOH/g to 0.36 mg KOH/g in the outdoor tank, and to 0.41 mg KOH/g for ground tank. The water content and acid number of B30 has relative increasing with petrodiesel, for the outdoor and ground tank. For biodiesel, hygroscopicity plays as main role that it is increasing water content and acid number during store on the ground tank. While store biodiesel on the outdoor tank has similar effect on acidity, but not for hygroscopicity.

**Keyword:** biodiesel blends, B30, storage test, hygroscopicity, acidity.

## I. INTRODUCTION

Biodiesel is a renewable fuel for diesel-engined vehicles consisting of methyl esters from constituent fatty acids (FAME). Generally, biodiesel is produced through the transesterification of vegetable oils, such as palm oil, soybeans, even cooking oil, as well as animal fats [1]. The composition of saturated and unsaturated fatty acids in the raw materials of biodiesel production affects the achievement of biodiesel quality. Saturated fatty acid components affect biodiesel performance at low temperatures, while unsaturated fatty acid components affect biodiesel oxidation stability. Besides, biodiesel is more polar than petrodiesel, affecting hygroscopic properties [2], [3].

The tendency of oxidized biodiesel is generally related to the presence of unsaturated fatty acid chains in ester molecules [4]. Chemically, unsaturated fatty acid components in biodiesel play a role in auto-oxidation reactions when in contact with light, heat, water, or metals. This is influenced by the process of oxidation of biodiesel, one of which takes place in double bonds in unsaturated fatty acids. The compound easily reacts with oxygen when in contact with the air [5], [6]. In contrast, components of saturated fatty acid compounds have higher oxidation stability but the poor performance at low temperatures. The oxidation process generally consists of 3 stages: initiation, termination, and propagation. At the initiation and propagation stage occurs the formation of hydroperoxide and free radicals. At the termination stage, secondary oxidation products such as aldehydes, carboxylic acid, hydrocarbons, ketones, and polymers are irreversible [7], [8]. Biodiesel oxidation stability is associated with acidity, peroxide production, and oxidation-induced organic acids that will increase kinematic viscosity and decrease the time of the induction period. Exposure to sunlight and air can accelerate biodiesel degradation [9].

One of the most important factors to maintain the quality of biodiesel is handling biodiesel at the storage conditions and time. Different storage conditions can affect the stability of biodiesel and petrodiesel during storage [7], [10], [11]. Based on the storage stability, the effect of time and storage conditions on the quality of biodiesel is important for analysis. Concerning the commercial and quality aspects of biodiesel, oxidation stability, and hygroscopic properties of biodiesel are evaluated to maintain the quality of biodiesel in the handling and storage of fuel [12]. Some changes in the physical-chemical properties of biodiesel due to inappropriate storage and affect the quality and quality of biodiesel include water content, acidic numbers, and oxidation stability [5], [13]. It should be noted that oxygen exposure, contamination from metals and other radical initiatiors, water exposure, light exposure, and heat could all contribute to degradation of fuel quality. Further research would be advantageous to determine how degradation caused by exposure to water and heat, also in the case of underground storage and limited oxidizing conditions [14], [15]. The study focused on analyzing changes in the acidity and hygroscopicity of biodiesel and blends, anf then it compared with petrodiesel during 120 days of storage. The storage test of biodiesel and petrodiesel is carried out on an outdoor fuel tank and ground fuel tank.

## II. MATERIAL AND METHOD

This research was conducted at the Research and Development Center for Oil and Gas Technology "LEMIGAS", Jakarta, Indonesia.

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The commercial biodiesel used in this work was produced from palm oil, by the transesterification process. The methyl esters composition of palm oil biodiesel was determined by gas chromatography (see Table 1). The commercial petrodiesel used in this work was high-speed diesel with cetane number 48 and sulfur content 0,10 mass %. The basic properties of petrodiesel and biodiesel were shown in Table 2.

**Table 1.** Chemical composition of palm oil biodiesel by gas chromatography

| **Methyl Ester** | **Mass Percent** |
|---|---|
| C12:0 | 0.34 ± 0.02 |
| C14:0 | 1.19 ± 0.01 |
| C16:0 | 44.51± 0.05 |
| C18:0 | 4.69 ± 0.02 |
| C18:1 | 40.15 ± 0.01 |
| C18:2 | 7.67 ± 0.04 |

**Table 2.** Basic Properties of Petrodiesel and Biodiesel

| No | Characteristics | Test Results | | Testing Methods |
|---|---|---|---|---|
| | | Petrodiesel | Biodiesel | |
| 1 | Cetane Number | 49.6 ± 0.1 | 55.8 ± 0.1 | ASTM D 613 |
| 2 | Density at $15^0$C (kg/$m^3$) | 837.3 ± 0.5 | 875.7 ± 0.3 | ASTM D 4052 |
| 3 | Viscosity at $40^0$C (cSt) | 2.84 ± 0.03 | 4.53 ± 0.04 | ASTM D 445 |
| 4 | Sulfur Content (mass %) | 0.12 ± 0.0 | 0.08 ± 0.0 | ASTM D 4294 |
| 5 | Water Content (mg/kg) | 73.88 ± 4.4 | 328.90 ± 5.1 | ASTM D 6304 |
| 6 | Total Acid Number (mg KOH/g) | 0.05 ± 0.02 | 0.30 ± 0.02 | ASTM D 664 |
| 7 | Oxidation Stability (minutes) | > 2880 | 1314 ± 2 | EN 15751 |

The storage test of biodiesel and petrodiesel is carried out on an outdoor fuel tank and ground fuel tank. Fuel is filled into each tank ± 200 liters. The fuel storage tank used in this study, designed with the main criteria: meeting safety factors, being able to withstand loads, safety against fire hazards and environmental pollution, and safe from stored products loss; tank material that is compatible with fuel, strength, and stability of construction so that it can be used for a long time. Storage tanks are also equipped with digital thermometers to measure fuel temperature and environment, nozzles, venting, and sampling points. Fuel sampling is conducted based on ASTM method D 4057, which is taken at the middle point with an interval of sampling time every 10 days for 120 days of shelf life. Water content was measured according to ASTM D 6304. The acid number was determined following ASTM D 664.

The temperature data recorded during the storage stability test were shown in Fig. 1. For each day, the highest temperature was recorded at noon and dropped to the lowest temperature at midnight. The maximum higher and lower temperature difference was 9°C, with mean was 27°C.

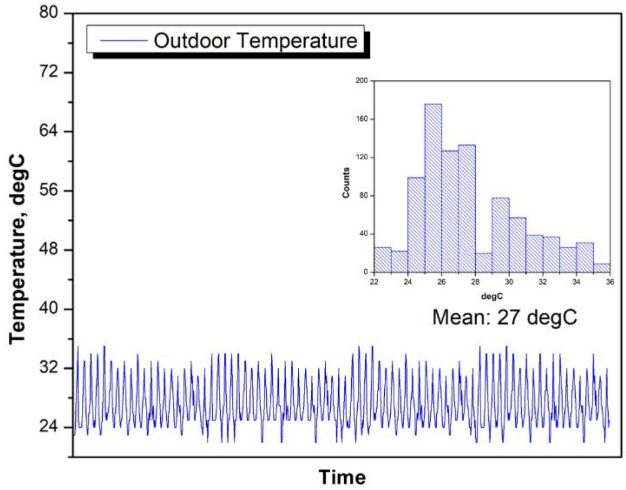


**Fig 1.** Temperature Data Record During Stability Test

## III. RESULT AND DISCUSSION

The result and discussion are divided into 3 discussions, namely acidity, water content, and the correlation of them.

- **Acidity**

Experimental results for evaluate acidity of fuel during storage stability test were fitted into the equation by the Analysis of Variance (ANOVA). The best equation that fits the results was linier in nature. The results of ANOVA for acid number of fuel on outdoor tank were shown in Table 3. The model *F-value* given by ANOVA was 30.78 for petrodiesel, 112.2 for B30, and 109.90 for biodiesel, which imply that the model is significant and has only a 0.01% chance to occur due to noise. The value of probability of error (P) is far lesser than 0.05 that the mathematical model is significant at the 5% confidence level. For experimental results from storage stability on the ground tank were shown in Table 4. The model *F-value* given by ANOVA was 30.78 for petrodiesel, 94.73 for B30, and 201.03 for biodiesel, which imply that the model is significant and has only a 0.01% chance to occur due to noise. The mathematical model is significant at the 5% confidence level since the value of probability of error (P) is far lesser than 0.05.

**Table 3.** Analysis of variance (ANOVA) results for the acid number for storage stability test on outdoor tank

| Fuel | *F-value* | *P* | Adj. $R^2$ | Equation |
|---|---|---|---|---|
| Petrodiesel | 30.78 | 0.00017 | 0.7128 | $y = 0.044 + 0.001x$ |
| B30 | 112.2 | <0.0001 | 0.9026 | $y = 0.315 + 0.0029x$ |
| Biodiesel | 109.90 | <0.0001 | 0.9007 | $y = 0.142 + 0.0019x$ |

**Table 4.** Analysis of variance (ANOVA) results for the acid number for storage stability test on ground tank

| Fuel | *F-value* | *P* | Adj. $R^2$ | Equation |
|---|---|---|---|---|
| Petrodiesel | 30.78 | 0.00017 | 0.7968 | $y = 0.042 + 0.002x$ |
| B30 | 94.73 | <0.0001 | 0.8865 | $y = 0.1342 + 0.0032x$ |
| Biodiesel | 201.03 | <0.0001 | 0.9434 | $y = 0.3217 + 0.0052x$ |

Furthermore, Fig. 2 and 3 showed the result of acidity during storage stability tests. The acid number of biodiesel on the ground tank showed an unstable and significant increase than on the outdoor tank. The acid number of biodiesel increased from 0.31 mg KOH/g to 0.36 mg KOH/g in the outdoor tank. In ground tank, the acid number of biodiesel was increasing to 0.41 mg KOH/g. The acid number of petrodiesel showed different results than biodiesel. In the outdoor and ground tank, the acid number of petrodiesel was stable at 0.05-0.07 mg KOH/g during 17 weeks test. For B30, biodiesel content to 30%, give the more effect to increasing acid number of B30, when storing at ground tank than outdoor tank. This value corresponds to the hygroscopicity of biodiesel while storing in ground tank also plays a role to increasing acidity than oxidize.

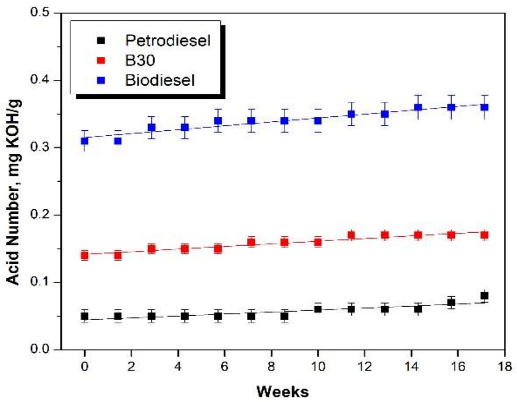


**Fig 2.** Acid number of test fuels during storage stability on outdoor tank

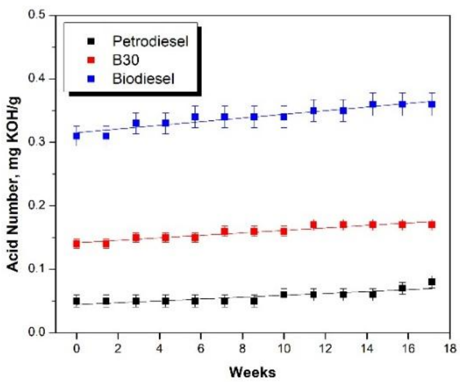


**Fig 3.** Acid number of test fuels during storage stability on ground tank

- **Water Content**

Experimental results for evaluate acidity of fuel during storage stability yest were fitted into the equation by the Analysis of Variance (ANOVA). The best equation that fits the results was linier in nature. The results of ANOVA for acid number of fuel on outdoor tank were shown in Table. The model *F-value* given by ANOVA was 263.96 for petrodiesel, 56.48 for B30, and 880.63 for biodiesel, which imply that the model is significant and has only a 0.01% chance to occur due to noise. The value of probability of error (P) is far lesser than 0.05 that the mathematical model is significant at the 5% confidence level. For experimental results from storage stability on the ground tank were shown in Table. The model *F-value* given by ANOVA was 479.14 for petrodiesel, 190.01 for B30, and 763.17 for biodiesel, which imply that the model is significant and has only a 0.01% chance to occur due to noise. The mathematical model is significant at the 5% confidence level since the value of probability of error (P) is far lesser than 0.05.

**Table 5.** Analysis of variance (ANOVA) results for the water content for storage stability test on outdoor tank

| Fuel | *F-value* | *P* | Adj. $R^2$ | Equation |
|---|---|---|---|---|
| Petrodiesel | 263.96 | <0.0001 | 0.9564 | $y = 97.89 + 6.12x$ |
| B30 | 56.48 | <0.0001 | 0.8224 | $y = 252.55 + 6.65x$ |
| Biodiesel | 880.63 | <0.0001 | 0.9865 | $y = 318.17 + 13.32x$ |

**Table 6.** Analysis of variance (ANOVA) results for the water content for storage stability test on ground tank

| Fuel | *F-value* | *P* | Adj. $R^2$ | Equation |
|---|---|---|---|---|
| Petrodiesel | 479.14 | <0.0001 | 0.9755 | $y = 89.78 + 7.85x$ |
| B30 | 190.01 | <0.0001 | 0.9403 | $y = 244.49 + 10.02x$ |
| Biodiesel | 763.17 | <0.0001 | 0.9845 | $y = 216.36 + 73.64x$ |

Fig. 4 and 5 shows water content results on the D 6304 test for each petrodiesel, B30, and biodiesel for which this parameter was measured. The water content of biodiesel on the ground tank showed an unstable and significant increase. The results showed, the water content of biodiesel in the ground tank increasing significantly during 17 weeks of storing, from 329 ppm to 1491 ppm. In the outdoor tank, the water content of biodiesel increased from 329 ppm to 534 ppm. This results showed that hygroscopisity of biodiesel has significant effect, while storing on the ground tank. The average of increasing water content of biodiesel every 4 weeks was 51 ppm on outdoor tanks and 290 ppm on the ground tanks. The water content of petrodiesel showed different results than biodiesel. In the outdoor and ground tank, the water content of petrodiesel was 74 ppm to 200 ppm during 17 weeks test. It was observed from Fig. 4 and

Fig. 5 that the water content of B30 has relative increasing with petrodiesel, for the outdoor and ground tank.

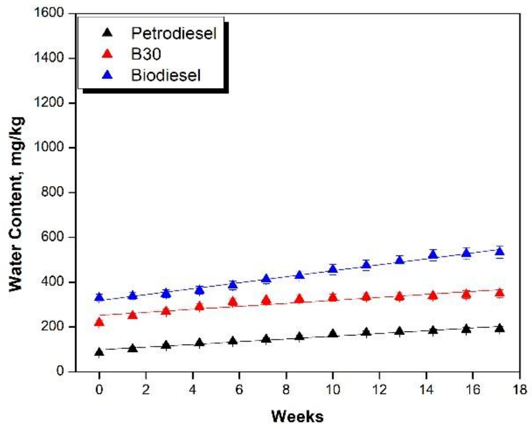


**Fig 4.** Water content of test fuels during storage stability on outdoor tank

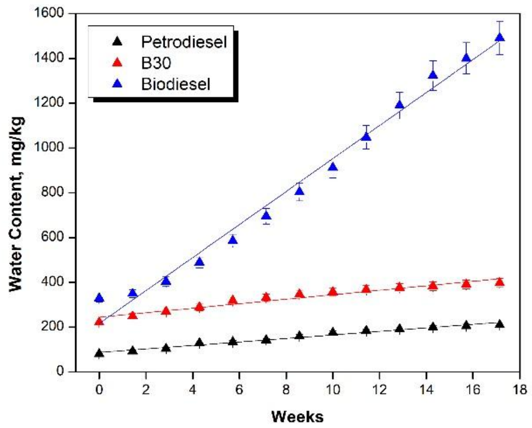


**Fig 5.** Water content of test fuels during storage stability on ground tank

- **Correlation of Acid Number and Water Content**

The issue of acidity is different because negative differences have been notices only with respect to temperature, contact time, and elevated moisture content. Storage stability test results for biodiesel and blends, comparing to petrodiesel indicate that hygroscopicity and acidity of biodiesel plays main role due to change the quality during storing [16]–[18]. Furthermore, the relationship between acidity as acid number and hygroscopicity as water content of biodiesel is given in Fig. 6. The experimental results for this correlation were fitted into the polynomial fits. The best fitted polynomial model, in terms of coded factors are represented by Eq. (1) with $R^2 = 0.9646$:

$$y = 1.3895 - 8.66x + 13.80x^2 \quad (1)$$

where $y$ represent water content and $x$ represents acid number. This property is important to maintenance biodiesel blends quality during storage.

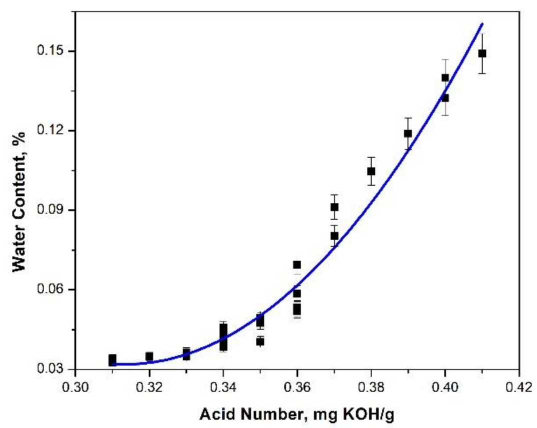


**Fig 6.** Correlation of acidity and hygroscopicity of biodiesel

The soluble water content of biodiesel and blends depens strongly on the temperature and blend ratio. Another experimental showed biodeisel absorbed (1500 to 1980) mg kg-1 of water at temperatures of (283 to 323) K, which was 10 to 15 times higher than that of petrodiesel in the same temperature range [19]. This showed that unique polar chemical structure of carboxyl groups in biodiesel methyl ester. At constant temperature biodiesel have the maximum saturated water content was 1840 mg kg-1. The result from fits analysis showed an increases of water content correlate with increases of acid number, it could be acidity and hygroscopisity, two important properties due to store biodiesel and blends [20], [21].

## IV. CONCLUSION

In this work, the effect of outdoor temperature and storage conditions for biodiesel and blends, comparing to petrodiesel was conducted. It is concluded that the water content of biodiesel in the ground tank increasing significantly during 17 weeks of storing, from 329 ppm to 1491 ppm. In the outdoor tank, the water content of biodiesel increased from 329 ppm to 534 ppm. The acid number of biodiesel on the ground tank showed an unstable and significant increase than on the outdoor tank. The acid number of biodiesel increased from 0.31 mg KOH/g to 0.36 mg KOH/g in the outdoor tank, and to 0.41 mg KOH/g for ground tank. The water content and acid number of B30 has relative increasing with petrodiesel, for the outdoor and ground tank. However, these results are intriguing in that it is possible to store biodiesel blends B30 over the long term. For biodiesel, hygroscopicity plays as main role that it is increasing water content and acid number during store on the ground tank. While store biodiesel on the outdoor tank has similar effect on acidity, but not for hygroscopicity. In the case, store of fuels on the ground tank is limited oxidizing conditions, but have negative effect on hygroscopicity. Otherwise, store of fuels on the outdoor tank, is limited hygroscopicity and will undergo oxidize due to light and heat exposure. Regularly measuring acid number and water content during storage is recommended as monitoring program by fuel specifications.

**ACKNOWLEDGEMENT**
We are so grateful for the work of our team in Fuel Characteristics Laboratory and Performance Laboratory in Research and Development Center for Oil and Gas Technology "LEMIGAS", Jakarta, Indonesia.

**REFERENCES**

[1] S. K. Hoekman, A. Broch, C. Robbins, E. Ceniceros, and M. Natarajan, "Review of biodiesel composition, properties, and specifications," *Renew. Sustain. Energy Rev.*, vol. 16, no. 1, pp. 143–169, 2012.
[2] P. Benjumea, J. Agudelo, and A. Agudelo, "Basic properties of palm oil biodiesel-diesel blends," *Fuel*, vol. 87, no. 10–11, pp. 2069–2075, 2008.
[3] F. Bücker *et al.*, "Impact of biodiesel on biodeterioration of stored Brazilian diesel oil," *Int. Biodeterior. Biodegrad.*, vol. 65, no. 1, pp. 172–178, 2011.
[4] M. Canakci and H. Sanli, "Biodiesel production from various feedstocks and their effects on the fuel properties," *J. Ind. Microbiol. Biotechnol.*, vol. 35, no. 5, pp. 431–441, 2008.
[5] S. Jain and M. P. Sharma, "Long term storage stability of Jatropha curcas biodiesel," *Energy*, vol. 36, no. 8, pp. 5409–5415, 2011.
[6] G. Karavalakis, D. Hilari, L. Givalou, D. Karonis, and S. Stournas, "Storage stability and ageing effect of biodiesel blends treated with different antioxidants," *Energy*, vol. 36, no. 1, pp. 369–374, 2011.
[7] Z. Yaakob, B. N. Narayanan, S. Padikkaparambil, S. Unni K., and M. Akbar P., "A review on the oxidation stability of biodiesel," *Renewable and Sustainable Energy Reviews*, vol. 35. pp. 136–153, 2014.
[8] G. Dwivedi and M. P. Sharma, "Investigation of Oxidation stability of Pongamia Biodiesel and its blends with diesel," *Egypt. J. Pet.*, vol. 25, no. 1, pp. 15–20, 2016.
[9] E. Christensen and R. L. McCormick, "Long-term storage stability of biodiesel and biodiesel blends," *Fuel Process. Technol.*, vol. 128, pp. 339–348, 2014.
[10] G. Karavalakis, S. Stournas, and D. Karonis, "Evaluation of the oxidation stability of diesel/biodiesel blends," *Fuel*, vol. 89, no. 9, pp. 2483–2489, 2010.
[11] M. Farahani, D. J. Y. S. Pagé, M. P. Turingia, and B. D. Tucker, "Storage stability of biodiesel and ultralow sulfur diesel fuel blends," *J. Energy Resour. Technol. Trans. ASME*, vol. 131, no. 4, pp. 0418011–0418016, 2009.
[12] M. Meira *et al.*, "Determination of the oxidation stability of biodiesel and oils by spectrofluorimetry and multivariate calibration," *Talanta*, vol. 85, no. 1, pp. 430–434, 2011.
[13] R. O. Dunn, "Antioxidants for improving storage stability of biodiesel," *Biofuels, Bioproducts and Biorefining*, vol. 2, no. 4. pp. 304–318, 2008.
[14] T. K. Jose and K. Anand, "Effects of biodiesel composition on its long term storage stability," *Fuel*, vol. 177, pp. 190–196, 2016.
[15] A. K. Agarwal and D. Khurana, "Long-term storage oxidation stability of Karanja biodiesel with the use of antioxidants," *Fuel Process. Technol.*, vol. 106, pp. 447–452, 2013.
[16] P. Bondioli, A. Gasparoli, A. Lanzani, E. Fedeli, S. Veronese, and M. Sala, "Storage stability of biodiesel," *J. Am. Oil Chem. Soc.*, vol. 72, no. 6, pp. 699–702, 1995.
[17] M. R. Thompson, B. Mu, C. M. Ewaschuk, Y. Cai, K. J. Oxby, and J. Vlachopoulos, "Long term storage of biodiesel/petrol diesel blends in polyethylene fuel tanks," *Fuel*, vol. 108, pp. 771–779, 2013.
[18] A. Broatch, B. Tormos, P. Olmeda, and R. Novella, "Impact of biodiesel fuel on cold starting of automotive direct injection diesel engines," *Energy*, vol. 73, pp. 653–660, Aug. 2014.
[19] P. B. L. Fregolente, L. V. Fregolente, and M. R. Wolf MacIel, "Water content in biodiesel, diesel, and biodiesel-diesel blends," *J. Chem. Eng. Data*, 2012.
[20] C. Attaphong, A. Charoensaeng, N. Sorrasuchart, S. Khaodhiar, N. Arpornpong, and D. A. Sabatini, "Phase behaviors and fuel properties of palm oil-based microemulsion biofuels using sugar-based surfactants," *Conf. Proc. - 2017 17th IEEE Int. Conf. Environ. Electr. Eng. 2017 1st IEEE Ind. Commer. Power Syst. Eur. EEEIC / I CPS Eur. 2017*, no. August 2018, 2017.
[21] M. A. Wakil, M. A. Kalam, H. H. Masjuki, A. E. Atabani, and I. M. Rizwanul Fattah, "Influence of biodiesel blending on physicochemical properties and importance of mathematical model for predicting the properties of biodiesel blend," *Energy Convers. Manag.*, vol. 94, pp. 51–67, 2015.