

MOISTURE ABSORPTION IN BIODIESEL AND ITS PETRO-DIESEL BLENDS

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ABSTRACT. Biodiesel has the characteristic of absorbing more moisture than petroleum diesel. High moisture content in biodiesel can cause problems such as water accumulation and microbial growth in fuel handling, storage, and transportation equipment. Currently, there is a lack of information on moisture absorbance in biodiesel and biodiesel/diesel blends. Experiments were conducted to determine the water absorbance in biodiesel of different feedstocks (three vegetable oils and two primary alcohols) at three temperatures. The effects of temperature and blending levels were explored through a central composite experimental design. Dynamic moisture absorption was studied at three constant relative humidities. Petroleum diesel was used as a reference. It was found that there were no significant differences in moisture absorbance among the biodiesel samples of different origins at given temperatures. Saturation moisture in biodiesel ranged from 0.10 to 0.17%wt in the temperature range of 4 °C to 35 °C, which was 15 to 25 times higher than that of diesel. Results also showed that in biodiesel/diesel blends, both temperature and level of blending affected the moisture absorbance. Moisture content of the blends was not a simple addition of the two moisture contents of biodiesel and petro-diesel. Blending created a mixture that had a lower capacity for moisture absorption.

Keywords. Biodiesel, Moisture content, Biodiesel blends.

Biodiesel, due to the nature of its chemical structure, has the characteristics of absorbing more moisture than petroleum diesel. The maximum amount of allowable water content in biodiesel as specified in ASTM standard D6751 is 0.050%vol (ASTM Standards, 2003). High moisture content in biodiesel may cause problems in handling, transportation, and storage (Van Gerpen, 2005); it is often caused by improper treatment after processing (Van Gerpen et al., 2005) or by the absorption of atmospheric moisture during storage. Condensation and precipitation may occur if the moisture content in biodiesel is beyond its saturation point as its storage temperature decreases. Microbial growth, which further leads to fuel filter plugging, and corrosion of storage containers and engine fuel systems are examples of the consequences of high fuel moisture content (Van Gerpen, 2005). As part of a study on biodiesel contamination, Van Gerpen et al. (1997) investigated water contamination by examining water solubility in soybean-based biodiesel and its B20 blends, but no other aspects were studied. Moisture absorption can be a problem in biodiesel storage for biodiesel producers, distributors, and consumers, and must be avoided or minimized. More appropriate

designs for respiration devices on above-ground storage tanks should be considered to avoid moisture absorption. Underground tanks are a better choice for biodiesel storage because they maintain a relatively constant temperature that eliminates the temperature effect on moisture absorption, although moisture absorption through respiration may still occur. Biodiesel should be dry (<0.050%vol water) when it leaves the production facility and kept dry during storage to ensure trouble-free utilization. The objective of this study was to explore the water absorbency and moisture saturation levels of different biodiesel and biodiesel/diesel fuel blends.

MATERIALS AND METHODS

FEEDSTOCKS

Three crude vegetable oils (high oleic soybean, canola, and yellow mustard) were used as the feedstocks for biodiesel preparation. These oils were obtained from the oil seed processing plant at the Department of Biological and Agricultural Engineering of the University of Idaho using a CeCoCo Hander oil seed screw press. After extraction, the oils were allowed to settle for two weeks. No further processing was performed before they were converted to biodiesel. The canola and mustard seeds were grown on the University farm and the high oleic soybeans were from Nebraska. Fatty acid profiles of the three vegetable oils were determined using GC (Hammond, 1991) and are listed in table 1. The primary alcohols were methanol (industrial grade; Univar USA, Kirkland, Wash.) and ethanol (industrial grade, anhydrous; Aaper Alcohol, Shelbyville, Ky.). Sodium methoxide (NaOCH₃, 30%wt solution in methanol; Degussa Corporation, Germany) was used as the catalyst. Commercial number 2 petroleum diesel fuel (D2) was purchased from a local fuel distributor.

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Table 1. Fatty acid profiles of the vegetable oils used in this study.

Vegetable Oil	Fatty Acid Composition (%wt) ^[a]							Average MW ^[b] (g/mol)
	Palmitic 16:0	Steric 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3	Eicosanoic 20:1	Erucic 22:1	
Soybean	3.3±0.1	2.9±0.1	88.4±1.1	2.4 ±0.4	3.0±0.4	--	--	882.3
Mustard	3.3±0.1	1.8±0.1	23.0±2.2	22.4±0.2	10.6±0.5	13.0±0.2	25.9±1.2	928.8
Canola	4.1±0.1	2.0±0.1	56.4±0.8	20.8±0.2	8.7±0.1	3.1±0.2	5.0±0.4	889.2

[a] Data are presented in the forms of “average±standard deviation.”

[b] Calculated from the fatty acid profiles.

BIODIESEL PREPARATION

Six types of biodiesel were prepared in the Biofuels Research Laboratory at the University of Idaho from the three oils and two alcohols. The formula for biodiesel preparation was 6:1 alcohol (methanol or ethanol) to oil molar ratio and 0.5%wt NaOCH₃ of oil. For example, for every 1200 g of soybean oil, 360 g of ethanol, and 20 g of 30%wt NaOCH₃ were added. The reaction was conducted in a two-step process at 62°C. In step one, 80% of the alcohol and 90% of the catalyst solution were added to the oil and stirred for 60 min followed by a settling time of 30 min. The glycerol formed during this reaction was drained from the bottom; the unfinished product mixture was left in the reactor. In step two, the remaining 20% alcohol and 10% catalyst solution were added to the reactor and mixed for another 60 min.

Once the reaction was complete, the mixture was allowed to settle for 12 h. The crude glycerol was drained and DI-water, 75% volume of the fuel, was added and stirred to wash out any impurities. After 2 h of stirring, the water was allowed to settle; it was drained off and a second wash was applied to ensure thorough washing. The system was then allowed to settle over night to allow time for the aqueous layer to fully separate from the biodiesel before it was drained. The biodiesel layer was transferred into a beaker and heated at 120°C for 60 min to drive off any residual water and alcohol.

KARL-FISHER MEASUREMENT

Moisture contents (MC) were measured with an automatic Karl-Fisher Coulometer (model DL37, Mettler-Toledo, Columbus, Ohio). Reagents used in this measurement were purchased from Fisher Scientific (Rockwood, Tenn.). In this coulometric technique, a small sample (~200 mg) is injected and the water in the sample reacts with the iodine in the anolyte (Hydranal-Coulomat A) and sulfur dioxide in the catholyte (Aquistar-Coulomat C). A small excess of iodine appearing in the anolyte signals the end of the measurement. The result is automatically quantified and the amount of water reported in ppm.

SATURATION MOISTURE IN BIODIESEL AND ITS PETRO-DIESEL BLENDS

The equilibrium (saturation) MC of the biodiesel samples and D2 were determined at three temperatures. The samples were prepared by contacting the fuels with an excess amount of water in well-sealed containers. Samples of each fuel and equal amounts (by volume) of DI-water were mixed in 2-L flasks in triplicate. The mixtures were then briefly shaken for maximum contact between the fuel and water. They were

placed in controlled temperatures of 4°C, 21°C (ambient temperature), and 35°C for 13 days before their MC were analyzed.

MOISTURE CONTENTS OF SATURATED BIODIESEL AND SATURATED PETRO-DIESEL BLENDS

Blends were prepared by mixing the desired amounts of biodiesel and D2. Both fuels were obtained from the saturation MC experiments at three temperatures. The blends were set aside at controlled temperatures for seven days. Samples were taken from the middle of the blends for MC measurements.

The technique of Central Composite Design (CCD) was employed for the experimental design. CCD is a response surface design that can fit a full quadratic model (Myers and Montgomery, 2002; Montgomery, 2004). CCD is widely used in scientific experimental designs to obtain maximum information while minimizing the number of experiments (e.g., Acikalin et al., 2005; Ibrahim et al., 2005; Kaminari et al., 2005; Rigas et al., 2005; Senthilkumar et al., 2005). Through CCD, the effects of independent process variables can be determined and analyzed statistically.

In this study, the CCD experimental design was constructed with three factors (biodiesel type, temperature, and level of blends), three levels for each factor, and with two central points (table 2). This experimental design was used for two separate biodiesel groups, i.e., methyl esters and ethyl esters. Sixteen combinations of the three factors were set up in triplicate for a total of 48 experiments. The statistical significance level (α value) was set at 1%. Experimental results were analyzed and the effects of the parameters on MC were determined using the statistical package DOE Pro XL (Digital Computations, Denver, Colo.). DOE Pro XL is a Microsoft Excel plug-in that is capable of constructing experimental designs and performing multiple response regression modeling, multiple response optimizations, and multiple interaction plot generation.

DYNAMIC MOISTURE ABSORPTION

Samples of biodiesel and D2 from controlled MC environments were measured for dynamic moisture absorptions. Saturated chemical solutions of CaCl₂ • 6H₂O, NaON₂, and Na₂HPO₄ • 10H₂O, which give 32.3%, 66%, and 95% constant relative humidities, respectively (Perry and Green, 1997), were prepared in desiccators three days before the experiments. Biodiesel and D2 samples with pre-quantified MC were transferred into shallow, open mouth containers in the desiccators at ambient temperature (~21°C). Samples were taken for MC measurements each day for 9 days.

Table 2. Experimental design and results of saturation MC in biodiesel/diesel blends.

Run	Variable B Temp. (°C)	Variable C Blends (%vol)	Variable A Biodiesel ^[a]	Results MC (ppm) ^[b]	Variable A Biodiesel ^[a]	Results MC (ppm) ^[b]
1	4	20	SME	174±31	SEE	204±26
2	4	80	SME	711±22	SEE	739±11
3	35	20	SME	276±23	SEE	291±4
4	35	80	SME	1,162±32	SEE	1,137±26
5	4	20	MME	179±20	MME	202±18
6	4	80	MME	648±48	MEE	831±24
7	35	20	MME	296±33	MEE	292±16
8	35	80	MME	1,104±17	MEE	1,210±58
9	21	50	CME	583±7	CEE	672±26
10	21	50	CME	581±7	CEE	663±20
11	21	50	SME	600±4	SEE	597±7
12	21	50	MME	557±4	MEE	620±9
13	4	50	CME	399±2	CEE	525±5
14	35	50	CME	639±18	CEE	753±12
15	21	20	CME	260±14	CEE	305±20
16	21	80	CME	1,049±3	CEE	1,171±19

^[a] SME = soya methyl esters, MME = mustard methyl esters, CME = canola methyl esters, SEE = soya ethyl esters, MEE = mustard ethyl esters, CEE = canola ethyl esters.

^[b] Data of moisture content are presented in the forms of “average±standard deviation.”

RESULTS AND DISCUSSION

SATURATION MOISTURE IN BIODIESEL (B100)

Before the experiments started, the initial MC of biodiesel and D2 samples were measured at room temperature (~21°C) as the base. Table 3 summarizes the initial MC and the saturation MC obtained from the experiments. Averages and standard deviations were taken to quantify variations in moisture absorbance. Data analysis showed that as the temperature increased, the MC's of the six types of biodiesel and the D2 increased.

Careful observation reveals that the saturation MC's were at similar levels among the biodiesel of different origins of vegetable oils and alcohols. F-tests applied to the combined experimental data of methyl and ethyl esters showed that the differences between the saturated MC of the six types of biodiesel at the given temperatures were not statistically significant. Therefore, it is reasonable to represent the saturation MC data of biodiesel from different origins collectively (fig. 1).

The saturation MC in biodiesel ranged from 1,000 to 1,700 ppm (or 0.10% to 0.17%) as the temperature increased from 4°C to 35°C, which was 15~25 times higher than that of D2 at the same temperatures. The rate of moisture absorption was 22.2 ppm/°C for biodiesel, which is nine times higher than that of D2 (about 2.4 ppm/°C). Therefore, biodiesel, due to its unique oxygen-containing, polar chemical structure of carboxyl groups ($-\text{C}(=\text{O})-\text{O}-$), has a much stronger tendency to absorb moisture than D2.

SATURATION MOISTURE IN BIODIESEL/DIESEL BLENDS

A question raised regarding the MC in biodiesel/ diesel blends was if water precipitated when saturated biodiesel was blended with D2. To answer this question, experiments of CCD were performed to evaluate the effects of three parameters (biodiesel type, temperature, and level of blends) in two groups (methyl esters and ethyl esters). Sixteen

experiments for each group were conducted in triplicate (table 2).

The experimental data were analyzed using the DOE Pro statistical software. Multiple response regression was

Table 3. Initial and saturation moisture contents of biodiesel and diesel samples.

Biodiesel Type ^[a]	Temp. (°C)	Initial MC ^[b] (ppm)	Saturate MC ^[b] (ppm)
SME	4		914±50
	21	96±12	1,338±63
	35		1,675±20
CME	4		1,134±80
	21	72±1	1,554±109
	35		1,812±73
MME	4		1,151±88
	21	78±5	1,443±88
	35		1,666±52
SEE	4		950±74
	21	94±6	1,356±46
	35		1,629±94
CEE	4		996±36
	21	102±11	1,473±43
	35		1,717±83
MEE	4		1,034±31
	21	104±13	1,436±13
	35		1,836±56
D2	4		40±6
	21	22±1	78±16
	35		114±14

^[a] SME = soya methyl esters, MME = mustard methyl esters, CME = canola methyl esters, SEE = soya ethyl esters, MEE = mustard ethyl esters, CEE = canola ethyl esters, and D2 = petro-diesel.

^[b] Data of moisture content are presented in the forms of “average ± standard deviation.”

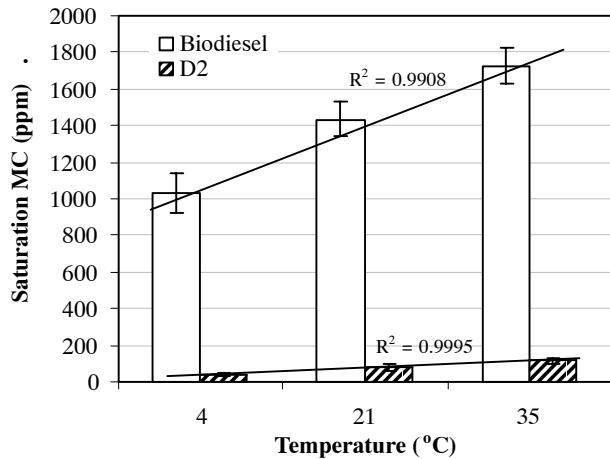


Figure 1. Saturation MC of biodiesel and diesel at three temperatures.

performed and the two- and three-way interactions of the parameters (factors) on the effects of saturation moisture absorption were analyzed. Statistical analyses on the MC data resulted in near perfect-fit multiple response regressions, indicated by the large F-value (352) at the degree of freedom (dof = 95). Probability values of far less than 0.01 indicated that the variable B (temperature) and variable C (level of blending) and their two-way interaction (B×C) were highly significant in contributing to the MC. Variable A (biodiesel type), on the other hand, was insignificant (with a high probability value of 0.7423). Biodiesel from different seed oils and alcohols as tested in this study did not significantly differ in contributing to the saturation MC in the blends. This is consistent with the conclusions made from the saturation MC of B100 biodiesel of different origins.

The relative importance and contributions of the three parameters and their interactions to the moisture absorption can be visualized from the Pareto plot of the multiple response regression models. Figure 2 shows the results of statistical analysis on the 96 measurements. All individual parameters contributed to MC positively, however, the levels of contribution differed dramatically. The contribution of variable C was 165 times higher than that of variable A, and 2.8 times higher than variable B. The two-way interaction of B×C contributed significantly to moisture absorption, about 22% that of variable C. The remaining interactions (A×B, A×C, and A×B×C), on the other hand, contributed to the MC insignificantly due to the presence of variable A. Thus, the interactions of parameter A with the other two parameters were negligible.

Figure 3 summarizes the statistical analyses of the effects of variables B and C on MC. It is evident that the MC was affected by both the temperature and level of blending independently (fig. 3a). The marginal means are the averages taken from all factors, explicitly or implicitly, that were randomized in the experiments. The combination effects, i.e., individual variables and their interactions, affected the MC at various levels. For example, at a blending level of 80%, the MC's at 4°C, 21°C, and 35°C were about 1.6 times higher with the combination effects (fig. 3b) than those of individual marginal means alone (fig. 3a). Similar conclusions were also true on the combination effects of the level

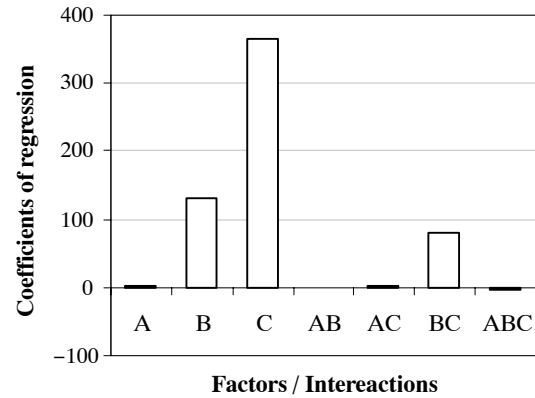


Figure 2. Relative contributions of process parameters to moisture absorption. Where Variable A = biodiesel type, Variable B = temperature, and Variable C = level of blending. AB, AC, BC, and ABC are the two-way and three-way interactions, respectively.

of blending at the given temperatures, although the effects were at a lower level.

The combination effects can also be verified by comparing the MC measurements with the predicted results using linear additions of the saturated MC of B100 biodiesel and D2 (fig. 4). It is evident that the predictions are always higher than the measured results. In other words, the MC of biodiesel/diesel blends is not a simple addition of the two MC's. Consequently, water precipitation may occur if a saturated B100 biodiesel is blended with saturated D2.

It was observed that the moisture holding capacity of the biodiesel rapidly diminished if the temperature dropped. Experiments showed that when biodiesel samples of known saturated MC obtained at 35°C were held at 4°C for 24 h, the

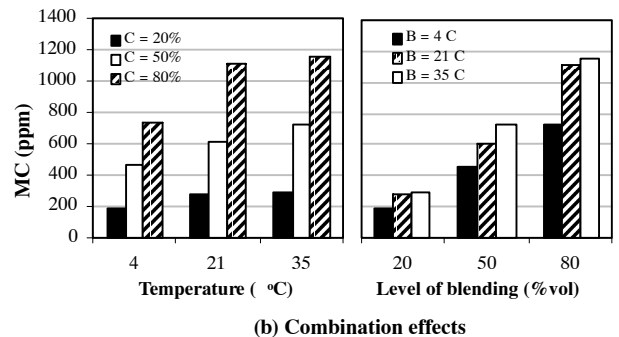
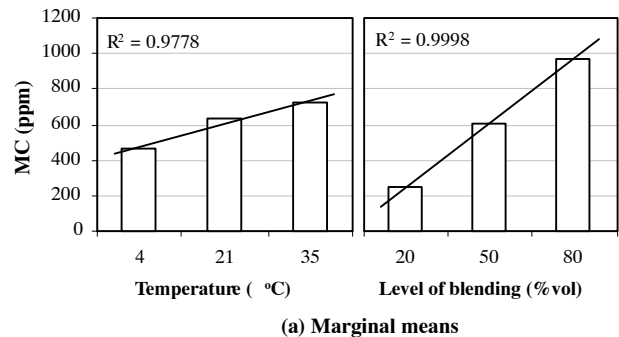


Figure 3. Statistical significance of temperature and level of blending on MC.

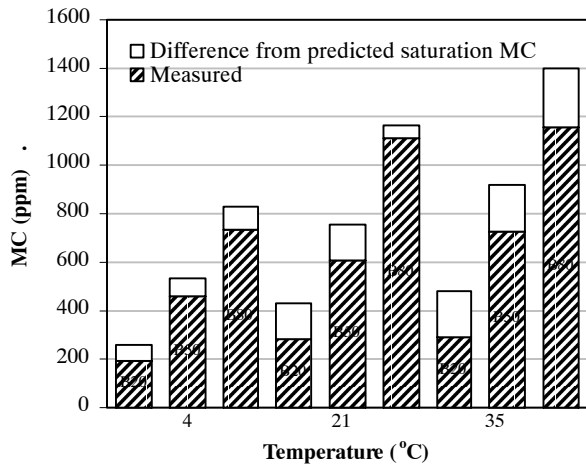


Figure 4. Comparison of the measured MC vs. predicted MC.

MC in the sample decreased to 60% of initial MC. There were no significant further MC decreases when the observation was extended to 240 h (fig. 5). The consequence of such a MC change could lead to water precipitation/accumulation at the bottom of storage vessels if the fuel temperature decreases.

DYNAMIC MOISTURE ABSORPTION

To evaluate the rate of moisture absorption from the atmosphere, biodiesel samples of different origins and D2 were put in desiccators of constant relative humidities (RH) of 32.3%, 66%, and 95% at room temperature. The moisture changes were monitored (fig. 6). Figure 6a shows the results of MC measurements in biodiesel of different origins as a function of time; fig. 6b shows the average MC of biodiesel at three constant RH conditions. It was found that the MC of the biodiesel samples rapidly increased when exposed to constant RH environments, although some differences existed between the MC of biodiesel of different origins (fig. 6a). After 24 h, the MC in the biodiesel samples reached their corresponding equilibria (i.e., approximate 400, 750, and 1200 ppm, respectively) and leveled off thereafter. This is a strong indicator that moisture absorption into biodiesel is a rapid process.

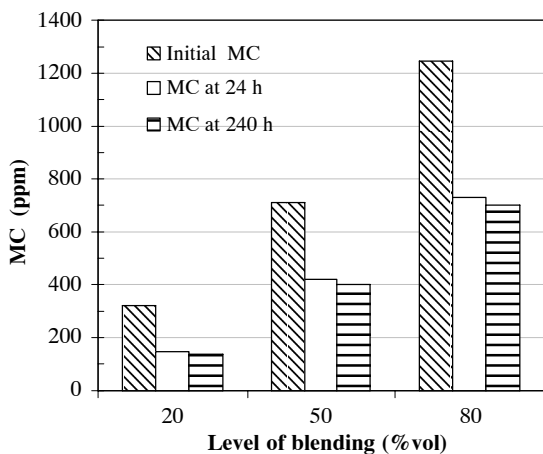
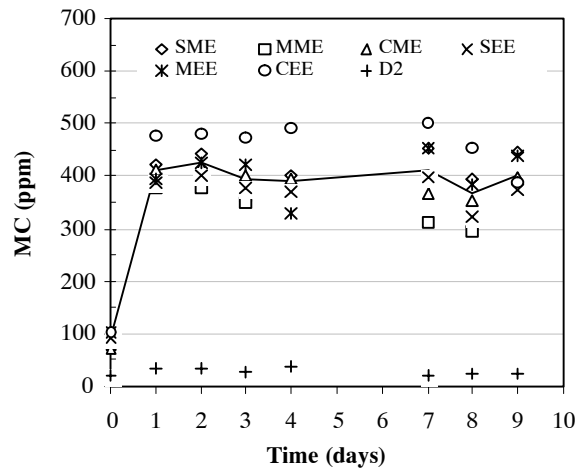
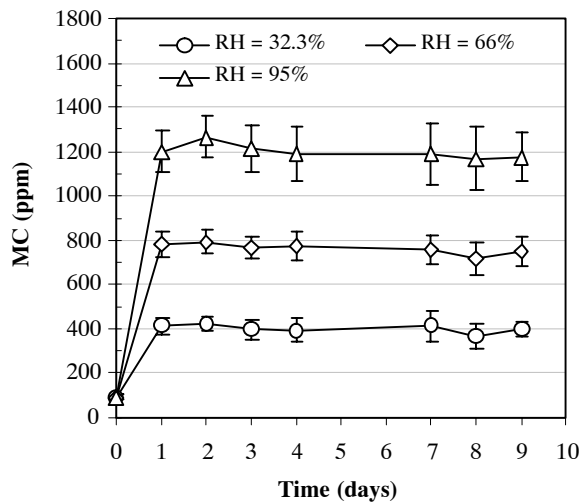


Figure 5. Change of saturation MC in biodiesel of 35°C after cooled to 4°C.



(a) MC of biodiesel vs. time at RH = 66%.



(b) Average MC of biodiesel at different RH.

Figure 6. Moisture absorption of biodiesel at constant relative humidities.

CONCLUSIONS

Experimental results have shown that there were no significant differences in moisture absorbance among the biodiesel of different origins at the given temperatures. As a clear contrast, biodiesel absorbed 1000 to 1700 ppm (0.10% to 0.17%) moisture at temperatures of 4°C to 35°C, which was 15 to 25 times higher than that of D2 in the same temperature range. Biodiesel MC had a strong relationship with its environment temperatures. As the temperature increased, MC increased at a rate of 22.2 ppm/°C which was more than 9 times higher than that of D2. This may lead to a phenomenon that stored biodiesel absorbs moisture at high temperatures which then precipitates out when the temperature drops. The process may repeat and water accumulation could occur at the bottom of storage vessels.

Results also showed that in biodiesel and D2 blends, both the temperature and the level of blending affected the moisture absorbance. The combination effects of individual parameters and their interactions affected the MC at varying levels. It was observed that the MC of blends was not a simple

addition of the MC of biodiesel and D2. Blending creates a mixture with a lower capacity for moisture absorption. Moisture absorption from the atmosphere into biodiesel was a rapid process and the MC in biodiesel reached equilibrium within 24 h under constant relative humidities.

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