Determining Water Content of Non-Surfactant Emulsion Fuel Using Bomb-Calorimeter

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Abstract. Non-surfactant Water-in-Diesel emulsion fuel (NWD) has short stability period and tend to separate immediately into water and diesel. NWD needs to be supplied into the diesel engine or combustor as soon as it was formed. Since the combustion and emission performance are closely related to the water content of an emulsion fuel, the immediate water content of NWD needs to be more closely inspected. The ASTM D95 standard provides a method to determine the water content of an NWD, but this method takes a long time to perform (up to 2 hours) and arduous. This paper describes the estimation of water content in a non-surfactant emulsion fuel by bomb-calorimetry, which can deliver quicker results than ASTM distillation. Experiments were performed with samples of emulsion fuel using and void of surfactant. The samples were first homogenized using an ultrasonic bath before they were sent to a bomb-calorimeter. The higher heating value of the emulsion was estimated using the weighted average since the components were deemed to be non-reactive. The bomb-calorimetric results of the non-surfactant emulsion fuel showed a close proximation, while the emulsion fuel with surfactant delivered less conclusive results. It was concluded from this study that an estimation of water content in NWD could be performed using bomb-calorimetry eight times faster than using the ASTM D95 standard with a deviation of maximum 3%.

1. Introduction
Interest in the research of diesel emulsion fuel as an alternative fuel is gaining a lot of recent interests. Water-in-diesel emulsion fuel (WD) is proven to reduce the emission of nitrogen oxides (NOx), black smoke and particulate matter (PM) simultaneously, while also improves the combustion efficiency. Moreover, WD can be used in a regular diesel engine without major modification [1,2].

WD is defined as an immiscible blend of dispersed water droplets as an internal phase in diesel as the continuous phase [3]. A surfactant in low concentrations is added to prolong emulsion’s stability and lower the energy requirement [4], which is often supplied by mechanical agitation [5]. The emulsion fuel is produced in an external facility before storage in the fuel tank. After its stability period expires, WD ultimately breaks down into its separate phases, which can cause problems for the engine.
To address the storage issues, researchers devised a solution by producing emulsion on demand in the absence of any surfactant. The resulting fuel was designated as non-surfactant water-in-diesel emulsion fuel (NWD). NWD is thus a variation of WD which does not require the presence of a surfactant yet possesses the same benefits in fuel economy and emissions. Various studies in standard emulsion fuel with surfactant (WD) showed a strong correlation between the emulsion’s water content and the combustion and emission performances. Cottel patented a device based on ultrasonic mixing in 2008, which mixed water and diesel in-line using an ultrasonic transducer [6]. In 2015 at the VSE Lab in MJIIT-UTM Malaysia, Muhsin developed a system called the RTES (Real-Time non-surfactant Emulsion Fuel Supply System). This system produces NWD by combining an ultrasonic transducer with a high shear mixer and was proven to be able to feed a 5 kW stationary engine [7,8] and a light-duty lorry [9].

NWD was observed to deliver comparable combustion and emission performance as WD. While standard diesel emulsion fuel which uses a surfactant (WD) has fixed water content, NWD’s water content varies during engine operation. Due to the absence of surfactant, NWD tends to break down into diesel and water immediately [10]. Therefore, NWD has to be prepared as close as possible to the fuel injection system. Unlike the fixed nature of the water content in WD, the immediate water content of NWD varies during the engine operation. The variations were mostly caused by product recycle in the preparation device and the return lines in the diesel fuel system [8,9,11].

The characterization of the emulsion water content that enters the engine was mostly done by averaging the consumed water and fuel after a certain duration of engine use. The actual water content that enters the combustion chamber can vary. If the actual water content can be characterized, a more precise behaviour of the engine combustion and emission performance can also be more accurately identified.

The ASTM D95, as schematized in Figure 1 (A), provides a test method for water in petroleum products and bituminous materials by distillation [12]. The water fraction of NWD was the difference between the sample weight before (A2), and after it was completely distilled (A4). In separate work, this method was utilized to inspect the water content of steam generated NWD [13]. The procedure was arduous since it involved an accurate weighing of samples. Moreover, complete distillation (A3) consumed a long time since the heat flux must be kept low to prevent bubble explosions in the sample. The procedure took around 2 hours to complete. Because a lot of samples are required to obtain a representative correlation between NWD’s water content and the engine performances, this method was not practical. Therefore, this work introduced a simpler and quicker method to obtain the water content of a non-surfactant emulsion fuel.
Figure 1. ASTM D95 vs Bomb calorimetry to inspect sample's water content

2. Methodology
The method introduced in this work is schematized in Figure 1 (B). Sample preparation (B1) was performed by putting an approximately 10 g D2M as base fuel in a 25 ml reaction tube. The weight was then registered and water or SPAN80 was added where applicable according to the typical composition in Table 2. One sample was prepared to produce WD with 5% water and 2% SPAN80 (E5). Four NWD samples were prepared without surfactant with respectively 3, 5, 8 and 10% water (NWD3, NWD5, NWD8 and NWD10).

Ultrasonication was proven in various works to create homogenous emulsion fuel [14-16]. Hence, in this work, the samples were homogenized using an ultrasonic bath for 5 minutes (B2). After the homogenization, samples were extracted from the middle of the vial with a syringe into the bomb calorimeter’s crucible (B3) to obtain a representative result. Then, the weight of the sample was taken (B4) before it was sent to a CAL2K ECO bomb calorimeter (B5) to get the higher heating value (HHV) per the ASTM standard D-2015 [17]. The procedure was performed in quadruplicate for reproducibility.

The HHV of a non-reacting mixture could be estimated with the weighted average method. Each component was assumed to contribute to the mix’s HHV according to the percentage of its weight [18]. The estimation can be presented as follows:

\[
HHV_f = \frac{HHV_a \cdot m_a + HHV_b \cdot m_b}{m_{\text{tot}}}
\]  

(1)

Since water is not combustible, it was assumed that its HHV\(_b\) was 0 MJ/kg.
The water content \( f_{mw} \) could then be derived from Equation 1 that the drop in HHV (HHV\(_{\text{drop}}\)) was equal to \( f_{mw} \) and is given by Equation 2.

\[
\text{HHV}_{\text{drop}} = f_{mw} = \frac{\text{HHV}_a - \text{HHV}_f}{CV_f} \tag{2}
\]

Where HHV and m indicated each component’s HHV and weight where applicable.

Malaysian Euro 2 standard diesel (D2M) was used as base fuel (Table 1), and tap water was used as the water source to create NWD samples. Where applicable, Sigma Aldrich sorbitan monooleate (SPAN80) was selected as the surfactant. Seven kinds of fuel were investigated for this study. D2M was tested as the baseline, followed by D2M mixed with 2% SPAN80.

**Table 1.** Malaysian Euro 2 diesel specifications.

| Properties                        | Unit   | Value  |
|-----------------------------------|--------|--------|
| Higher Heating Value              | MJ/kg  | 45.28  |
| Cloud Point                       | °C     | 18     |
| Density @15°C                     | kg/L   | 0.8538 |
| Total Sulphur                     | mass % | 0.28   |
| Viscosity                         | cSt    | 7.6 @20°C |
|                                  |        | 5.1 @40°C |
|                                  |        | 4.0 @60°C |
| Distillation Temperature, 90% recovery | °C | 367.9   |
| Flashpoint                        | °C     | 93.0   |
| Pour Point                        | °C     | 12     |
| Cetane Number                     |        | 54.6   |
| Carbon                            | wt %   | 84.1   |
| Hydrogen                          | wt %   | 12.8   |
| Sulphur                           | wt %   | 0.2    |
| Nitrogen                          | wt %   | < 0.1  |
| Oxygen                            | wt %   | 3.9    |
| Dielectric constant               |        | 2.1    |

**Table 2.** Typical composition of emulsion samples.

| Fuel designation | D2M | Water | SPAN80 | Total |
|------------------|-----|-------|--------|-------|
| D2M              | 100 | 0     | 0      | 100   |
| E5               | 93  | 5     | 2      | 100   |
| NWD3             | 97  | 3     | 0      | 100   |
| NWD5             | 95  | 5     | 0      | 100   |
| NWD8             | 92  | 8     | 0      | 100   |
| NWD10            | 90  | 10    | 0      | 100   |

3. **Result and discussions**

Including the ultrasonication, sampling, weighting and bomb-calorimetry, the procedure took approximately 15 minutes per sample compared to 2 hours for the ASTM procedure. The ultrasonic bath produced a homogenous sample. Table 3 displays the HHVs of the various samples.
Table 3. Bomb calorimetry results of various samples.

| Sample          | HHV (MJ/kg) | Average HHV (MJ/kg) |
|-----------------|-------------|---------------------|
|                 | 1           | 2                   | 3           | 4           |               |
| D2M             | 46.7481     | 46.0832             | 46.3462     | 46.4026     | 46.4783       |
| SPAN80          | DNF         | DNF                 | DNF         | DNF         | 0             |
| D2M + 2% SPAN80 | 44.6486     | 45.1422             | 45.4635     | 45.9661     | 45.3051       |
| E5              | 44.7385     | 44.0296             | 45.4784     | 44.0189     | 44.5663       |
| NWD3            | 44.2731     | 45.5703             | 45.4589     | 44.9478     | 45.0625       |
| NWD5            | 44.6295     | 43.4379             | 44.194      | 44.1619     | 44.0833       |
| NWD8            | 43.2876     | 42.5807             | 42.3343     | 42.4038     | 42.6516       |
| NWD10           | 41.7174     | 41.2341             | 41.8703     | 42.8336     | 41.9139       |

The average in the data in Table 3 is plotted in Figure, where it can be observed that D2M produced the highest HHV of 46.4783 MJ/kg. It was obvious that the emulsions (E5, and NWD3 through NWD8) had lower HHV than D2M, because of the water content. The weighted average method described in Equation 1 and 2 implicitly lead to a lower HHV since water has zero heating value.

When a sample of SPAN80 was put into the bomb calorimeter, the result was ‘did not fire’, which means the sample failed to fire. SPAN80’s HHV was then assumed as zero (0 MJ/kg). This would suggest that the HHV will also be reduced according to the SPAN80’s content. Both water and SPAN80 fraction were further denoted as sink fraction \( x_{\text{sink}} \), which means that water content and SPAN80 caused the HHV of the fuel to drop.

The drop in HHV from neat D2M was calculated using Equation 2 and is tabulated in Table 4. The deviation \( \Delta_x \) is defined as the increment or decrement of the drop in HHV (HHV\text{drop}) against the sink fraction \( x_{\text{sink}} \), and can be described as:

\[
\Delta_x = \frac{\text{HHV}_{\text{drop}} - x_{\text{sink}}}{x_{\text{sink}}} \times 100
\]

Table 4 shows the drops in HHV for NWD specimens (NWD3 through NWD10). The HHV\text{drop} were in close estimation to the water content, and they deviated at a maximum of 3% (with NWD5). On the other hand, where SPAN80 as surfactant was present, the correlation between HHV\text{drop} and \( x_{\text{sink}} \) was less evident. Although the percentage of SPAN80 was only 2%, the HHV drop of the mixture of D2M and SPAN80 was higher by 0.52%. This translates to a large deviation of 26%.
| Sample             | Surfactant (%) | Water content (%) | HHV drop (%) | Δx (%) |
|--------------------|----------------|-------------------|--------------|--------|
| D2M                | 0              | -                 | 0            | -      |
| SPAN80             | 100            | -                 | 0            | -      |
| D2M + 2% SPAN80    | 2              | -                 | 2.52         | +26.0  |
| E5                 | 2              | 5                 | 4.11         | -17.8  |
| NWD3               | 0              | 3                 | 3.05         | +1.7   |
| NWD5               | 0              | 5                 | 5.15         | +3.0   |
| NWD8               | 0              | 8                 | 8.23         | +2.9   |
| NWD10              | 0              | 10                | 9.82         | -1.8   |

Moreover, E5, which also contained 2% SPAN80 and 5% water only showed a drop of 4.11%, a deviation of 17.8%. The role of SPAN80 to the HHV of fuel was thus unclear. When water was absent the deviation Δx was in positive territory while in E5 where water is present, Δx was contrastingly in the negative territory.

Figure 3. The calorific value of fuel samples

The results of bomb calorimetry showed a good correlation between water content $x_{sink}$ and HHV drop for NWDs. Where SPAN80 was present, the correlation in HHV drop and $x_{sink}$ was less conclusive.

Figure 4. The calorific drop of each fuel compared to Malaysian Euro 2 diesel (D2M)
4. Conclusion
The method of water content determination was borne out of the needs of a quick and practical method to approximate it. ASTM D95 provides the best analytical method. However, the ASTM D95 was not practical since the inspection could span almost 2 hours. The bomb calorimetry suits the requirement better since it can deliver close approximation to the actual water content within only 15 minutes. The correlation of the drop in the higher heating value (HHV drop) and the water content in a non-surfactant emulsion fuel (NWD) are within maximum 3% deviation. When surfactant is present, the correlation showed less conclusive results with up to 26% deviation. Across the operating water content range used in the field of NWD, which is between 5 and 20%, this method can provide a practical solution for estimating the immediate water content during a combustion test.

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