# Physical-Chemical Properties of Water-in-Diesel Fuel Emulsions

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**Abstract:** The addition of water dispersed phase into the diesel continuous phase will lead to the formation of water-in-diesel (W/D) emulsion, which significantly reduces the pollution level of $NO_x$ and particulate matters in the diesel engines. Small amount, 0.2% by volume, of surfactant material was necessary in the preparation of a stable W/D emulsion. The study of the physical and chemical properties of stable W/D emulsions is important to understand the flow behavior characteristics of these emulsions. Pure diesel fuel and three samples of W/D emulsions (10%, 20% and 30% by volume water) were examined in this study. The following properties are measured according to the corresponding ASTM standards for the pure diesel and its emulsions with 10%, 20% and 30% water: heating value, pour point, flash point, distillation data, density, viscosity, calculated cetane index, total acid number, and sulfur content. The addition of water in the emulsion caused a drop in the calorific value, final boiling point, cetane index, total acid number, and sulfur content. Increasing the water also increased the pour point, flash point, and density.

**Keywords:** Water-in-diesel emulsion, viscosity, shear rate, shear stress.

## 1. INTRODUCTION

Owing to high thermal performance and fuel consumption economy, diesel- engines have several important applications in our modern technologies. Diesel engines are widely utilized as a source of power for many industrial and civilian activities. Some of these applications are power plants, hospitals, marine-, land-, and rail-transportations. But, the diesel engines emissions usually cause a serious negative effects on the air quality. The diesel engines exhaust contains nitrogen oxides, particulate matters, black smoke, carbon mono-oxide, and carbon-dioxide. The results of these materials in our environment will lead to serious damage to the atmosphere such as destruction of the ozone layer, acid rains, and green-house effects [1]. Due to the recent environmental policies, the decrease of the negative effects of diesel engines gas emissions is important. For example, the emission of particulate matters and $NO_x$ usually lead to serious problems in the large city environments where traffic congestion is very heavy. Many researchers have reported that the water addition into the diesel fuel to produce water-in-diesel fuel emulsion (may reach 50% water in the emulsion) significantly reduces the pollution level of particulate matters and $NO_x$ [2-4]. Nicholls *et al*. [2] reported a decrease of 90% in the nitric oxide when they introduced 25% - 100% water (compared to fuel consumption) in the intake system of the engine. Lestz *et al.* [3], injected high amount of water in a diesel engine (3 times the fuel consumption) and found the NOx has been reduced. Andrews *et al*. [4], added 20% water to diesel fuel to form emulsified fuel and found a reduction in the NOx gases.

The addition of water in a dispersed droplets phase into a continuous diesel fuel phase will result to the formation of water-in-diesel emulsion (W/D emulsion). In general, there are several important industrial and environmental applications for water-in-oil emulsions. Some examples are: oil spill [5] and transportation of heavy crude oil with water emulsion through pipeline [6]. Some other examples that involve stable emulsions are food industries (e.g. mayonnaise), pharmaceutical industries (e.g. drug emulsions) and cosmetics industries (e.g. skin lotion). In the preparation of W/D emulsion, the addition of surface active agent is very necessary to stabilize the W/D emulsion. There are two roles for the effect of the surface active agent within the W/D emulsion. The first role for the surface active material is to decrease the interfacial tension between the water phase and the diesel fuel phase in order to help the formation of W/D emulsion. The second role is to stabilize the water droplets phase within the diesel fuel phase to prevent the coalescence of the water phase [7]. Surface active material accumulates at the interfacial film between the water droplets phase and the diesel fuel continuous phase to stabilize the water droplets phase and consequently stabilize the emulsion. If the concentration of emulsified agent

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materials is reasonably high, the merging of water droplets will be prevented [8-9].

Muzio *et al*. [10] reported that the formation of $NO_x$ is due to the presence of nitrogen within the diesel fuel, excess oxygen, and high temperature of the combustion gas. On the other hand, if water is added into the diesel fuel in the form of W/D emulsion, the W/D emulsion fuel produces less $NO_x$ emission than the non emulsion diesel fuel. According to Lin *et al*. [11] the W/D emulsion with 20% water reduced $NO_x$ emission by 56.8%. During the combustion process of W/D emulsion, the W/D emulsion is sprayed into numerous liquid droplets through a nozzle. Due to the water boiling point is less than that of diesel fuel, the water enveloped layer explodes through the outer oil layer. As a result of micro-explosion behavior, the atomized emulsion drops are further atomized into much finer droplets. This mechanism of micro-explosion leads to a stronger mixing and a faster rate of reaction between the atomized fuel droplets and the surrounding air [11]. Therefore, a higher extent of combustion is completed. In addition the emission of $NO_x$, particulate matters, and smoke are significantly reduced [12-17]. Rheological studies have not been comprehensively developed for any stabilized W/D emulsions in the past. It is commonly agreed that in the formulation and specification of emulsions fuels, rheology is extremely important. Almost no work has been found that completely characterizes the rheological behavior at different water content and temperatures.

Therefore, the objective of the current study is to investigate the physical and chemical properties of the water-in-diesel stabilized emulsions with different concentrations of water addition over the range of 0 to 30% in 10% increments.

## 2. EXPERIMENTAL WORK

### 2.1. Emulsions Preparation

Diesel fuel from ADNOC-United Arab Emirates was used in the preparation of stable W/D emulsion and consequently in the investigation of the prepared samples. Table **1** shows the physical properties of the employed regular diesel fuel. The used diesel fuel had an elemental composition by weight of 87.2% carbon, 12.8% hydrogen and 0.0225% sulphur, and an aromatic content of 29.3% (13% monoaromatics, 13.3% diaromatics and 3% polyaromatics).

In general, Water-in-oil emulsion can be prepared by mixing the two immiscible fluids in the presence of a surface active material. The mixing system produces very small water droplets phase dispersed within the oil continuous phase. The emulsifying agent added to the mixture reduces the interfacial tension between the water and the oil, which is necessary to form the emulsion and to stabilize the water droplets phase within the continuous oil phase. Stable water-in-diesel emulsion was prepared by gradual addition of certain amount of water into the diesel fuel phase that contains 0.2% by volume of surfactant agent while a high speed mixer was in rotation. A non-ionic surfactant, Triton

**Table 1: Basic Properties of No.2 Diesel Fuel**

| Properties | Units | ASTM standard | Diesel fuel No. 2 |
|---|---|---|---|
| Density at 25°C | $Kg/m^3$ | D7042 | 833 |
| Mass high heating value | MJ/kg | D129 | 51.76 |
| Cloud point | °C | D2500 | 8 |
| Kinematic viscosity at 40°C | $mm^2/s$ | D7042 | 4.16 |
| Initial boiling point | °C | D86 | 181.7 |
| Temperature at 50% recovered | °C | D86 | 290.3 |
| Final boiling point | °C | D86 | 356.8 |
| Calculated cetane index | - | D4737 or D976 | 55/56 |
| Total acid number | mL KOH/mg | D664 | 0.056 |
| Ash content | wt% | D482 | 0.003 |
| Sulfur content | wt% | X-Ray | 0.0483 |
| Conradson carbon residue | g | D189 | 0.134 |

X-100 (from BDH Middle East L.L.C.–United Arab Emirates), was used as an emulsifying agent. Three samples of W/D emulsions were prepared using 10%, 20% and 30% by volume water. Different mixing speeds for different mixing times were examined to prepare stable W/D emulsions. The prepared samples of emulsion were placed into graduated glass cone-containers to check the stability of the sample. The main criterion for the stable emulsion is the presence of only one phase. If more than one layer is found, it must be considered as unstable emulsion. It is necessary to find the experimental conditions required to maintain the W/D emulsion in stable status for a reasonable period of time to cover the different stages of the experimental measurements. Experimentally, it has been found that 5000 rpm for six minutes of mixing time was sufficient to prepare stable W/D emulsions. All the experimental measurements were carried out at room temperature of 25$^{o}$C. The temperature was controlled through a thermostate circulating bath.

### 2.2. Experimental Procedure

All the presented data in the present work have been measured experimentally in the laboratory using standard equipment following the corresponding standard methods. For the data to be compared to other data in literature, they need to be taken according to similar standard method.

The following are the standard methods used for each property presented.

All properties are measured according the standard methods seen in Table **1**. Density was determined using calibrated glass API gravity hydrometers. A mineral oil bath with a temperature control precision of ±0.02$^{o}$C was used for measuring density at different temperatures, from 15 to 100$^{o}$C. High or gross heating value was determined using an automated bomb calorimeter. All fuels tested were distilled following the standard procedure. The temperature values measured were normalized to standard atmospheric pressure by means of the Sidney–Young correlation, as recommended by the standard method. The calculated cetane index for the fuels tested was determined as a function of their densities and distillation curve data using the empirical correlations recommended by the standard procedure.

Maximum experimental errors in measuring all presented quantities with the instrument name are summarized in Table **2** for the physical and chemical properties respectively. Maximum percentage error of 0.5% is found in measuring the total acid number.

## 3. RESULTS AND DISCUSSION

Successful commercialization and market acceptance of water/diesel emulsion requires stringent quality assurance standards. By means of the diesel fuel standards, the straightforward determination of some properties can be performed. Properties of water /diesel emulsion are presented here as a function of the water blending ratio.

Table **1** illustrates the physical and chemical properties of the used diesel fuel. The most critical property of the fuel (or its emulsion with water) is its kinematic viscosity, due to the nature of diesel injection

**Table 2: Maximum Error (or Maximum Percentage Error) for the Measured Quantities and the Name of Equipment**

| Properties | Maximum Error | Equipment Name |
|---|---|---|
| Density at 25 $^{o}$C | 0.0005 g/cm³ from 0.65 to 1.5 g/cm³ | Anton paar-SVM 300 |
| Mass high heating value | benzoic acid should not exceed 0.3% | Parr plain calorimeter |
| Cloud point | +/- 1 C | Stan-hope seta |
| Kinematic viscosity at 40 $^{o}$C | 0.002 mm$^{2}$/s | Anton paar-SVM 300 |
| Initial boiling point | 0.1 C | ISL distillation |
| Temperature at 50% recovered | 0.1 C | ISL distillation |
| Final boiling point | 0.1 C | ISL distillation |
| Calculated cetane index | N/A | Theoretical calculation |
| Total acid number | 0.5 % | Automatic titration |
| Sulfur content | 0.001 % | Tanaka-x-ray-Japan |
| Flash point | 0.1 C | Stan hope seta |

process in diesel engines. This requires low kinematic viscosity and also it affects the atomization and other physical and chemical pre-combustion steps. The high viscosity is not acceptable for diesel engine injection and combustion. It has recently been found that the high viscosity of biodiesel fuel may be reduced by either heating it or adding very low viscosity fluid like di-ethyl ether (Selim, 2009 [18]).

### 3.1. Heating Value

Low heating values (LHV) were calculated from the measured high heating values (HHV), taking into account the elemental composition of the pure fuels and the enthalpy of vaporization of water. As can be seen in Figure **1**, the LHV of water / diesel emulsion decreases in direct proportion to the water content as the diesel oil has a higher heating value than any water/diesel emulsion tested. Diesel fuel has a heating value of about 51.76 MJ/kg compared to about 45 MJ/kg at 10% water, 38.4 MJ/kg at 20% water and 36 MJ/kg for 30% water. The heating value in addition to ensuring a complete combustion of the fuel it ensures that the power output of the diesel engine will not decrease in case of using the emulsion. There should not be any need to change the injection equipment of the engine if an emulsion with comparable heating value has been used.

### 3.2. Cloud Point and Pour Point

Figure **2** shows the effect of water content in the emulsion on the pour point (TCP) from pure diesel (0% water) to 30% water. It may be observed that the pour point for the blends increased when increasing the percentage amount of water in the emulsion. For pure diesel, the pour point is -4°C compared to 0°C for 30% water emulsion. A Similar trend may be expected for the cloud point of water in diesel emulsion. It may be emphasized here that these properties are for pure water in diesel emulsion without adding any other additives to change properties. As with the diesel fuel case, additives to reduce cloud and pour points may be used also with emulsion if it is used in low temperatures environment.

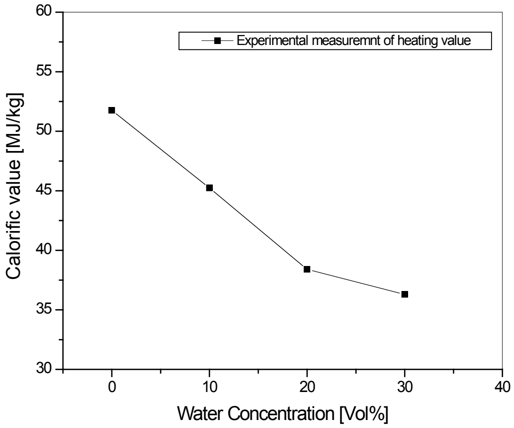

**Figure 1:** Effect of water addition on the diesel heating value.

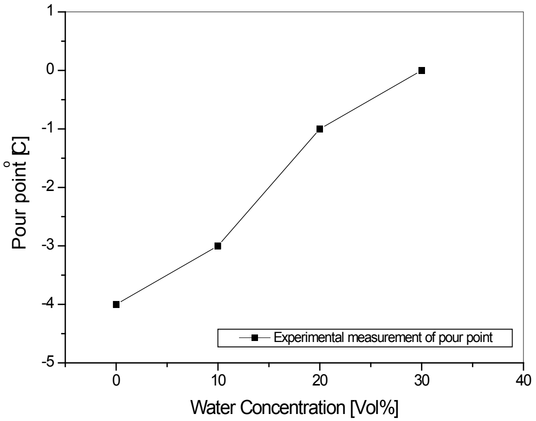

**Figure 2:** Effect of water addition on the diesel pour point.

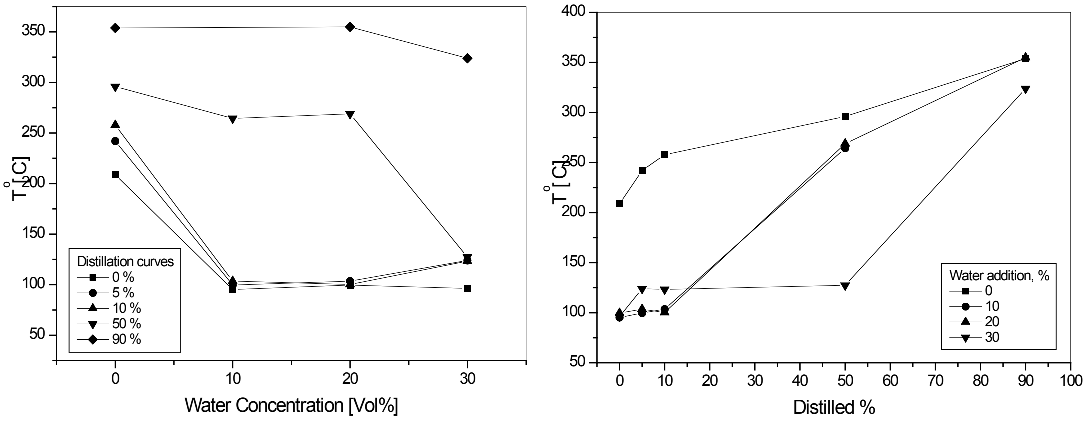

**Figure 3:** (**a**) Effect of water addition on the distillation curves. (**b**) distillation curves for the diesel blends.

### 3.3. Distillation Curve Points

Figures **3a** and **3b** show the distillation curves for pure diesel fuel and for water / diesel emulsions. As can be seen in Figure **3a** that, the curves are almost the same for 0% and 20%water, where at near total evaporation (at 90%) the temperature drops from 353°C to 323.9°C. Figure **3b** shows the effect of water content on the distillation temperatures corresponding to representative distilled percentages: 0%, 5%, 10%, 50% and 90%. Three temperatures are designated as T10, T50 and T90, and the maximum values for these are commonly specified in engine fuel quality standards. For initial distillation temperatures, the water / diesel emulsion exhibits lower values (easier to boil). Initial distillation temperature for pure diesel fuel is 208.7°C, where it is 95.2°C for 10% water, 99.6°C for 20% water and 96.2°C for 30% water. This means that water / diesel emulsions at any water ratio would be easier to evaporate than diesel fuel and this may reduce the ignition delay time when fuel is injected inside the combustion chamber–if other factors are ignored. Liquid emulsified fuel injected would need less time to evaporate, mix and react with air.

### 3.4. Viscosity and Density

Figure **4** shows the effect of water addition on the viscosity of the diesel fuel. Figure **4** shows a higher viscosity with water concentration of 30% than the pure diesel, which indicates a more viscous emulsion is formed at all temperatures. The kinematic viscosity of pure diesel drops from 6.94 at 20°C to 2.06 CSt at 80°C, whereas for 30% water, it drops from 71.57 to 20.86 CSt. This increase in viscosity of emulsions can be attributed to the droplet-droplet interaction that will cause a higher viscosity. The viscosity of an emulsified system depends upon the viscosity of the dispersed phase, the viscosity of the continuous phase, and the volume fraction of each phase. When the dispersed phase is generated within the continuous phase, the flow field becomes distorted and therefore the energy dissipation is increased. This behavior leads to an increase in viscosity.

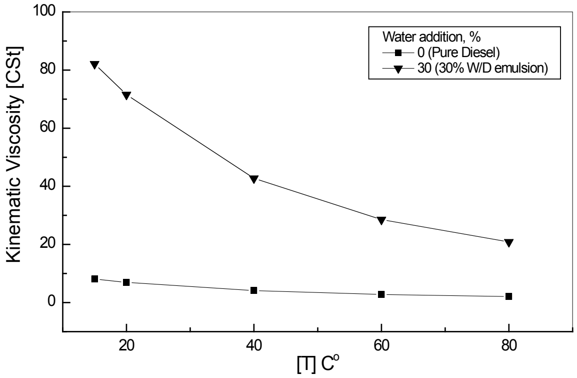

**Figure 4:** Kinematic viscosity behaviour of diesel and 30% W/D emulsion.

The effect of increasing temperature is an important technique that can be utilized to lower the viscosity of a given fuel and its emulsions and, therefore, enhance their flowability. As can be concluded from the Figure, temperature has a strong effect on the fuels viscosity and their viscous behavior. The effect of temperature on the viscosity of the tested fluids can be referred to the negative influence of the applied heat on the structure of the heavier components in the diesel fuel and on the interactions of the water droplets within the fuel continuous phase.

The variation in emulsion density with water content is shown in Figure **5**. As may be seen, and as the water has higher density than diesel, the emulsion density is directly increasing in proportional to water content and decreases steadily with temperature. As expected, increasing the temperature decreases the density of all water emulsions in diesel.

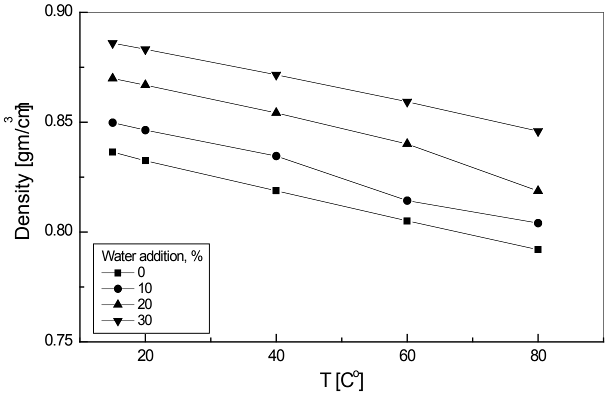

**Figure 5:** Effect of temperature on the density behavior of different W/D emulsions.

### 3.5. Calculated Cetane Index

The cetane number is a basic property of diesel fuels that indicates ignition characteristics. This parameter can be measured in a specially designed test engine (ASTM D613) or in a constant volume combustion apparatus (ASTM D6890). However, these tests are awkward and expensive. For this reason there have been many attempts to develop methods to estimate the cetane number of a fuel. In order to differentiate predicted from measured values, the former is called calculated cetane index (CCI), and the latter cetane number. The CCI can be determined using empirical correlations in accordance with the

ASTM D976 and D4737. Using ASTM D976, this parameter is obtained as a function of fuel density at 15°C and the T50 distillation curve point. ASTM D4737 additionally takes into account T10 and T90 values. Distillation curve points were taken according to the measured values and the values of density at 15°C.

The general trend for the calculated cetane index is to decrease with adding more water to the water / diesel emulsion, as may be seen in Figure **6**. The calculated cetane index dropped from 57 for pure diesel to around 50 for 30% water emulsion.

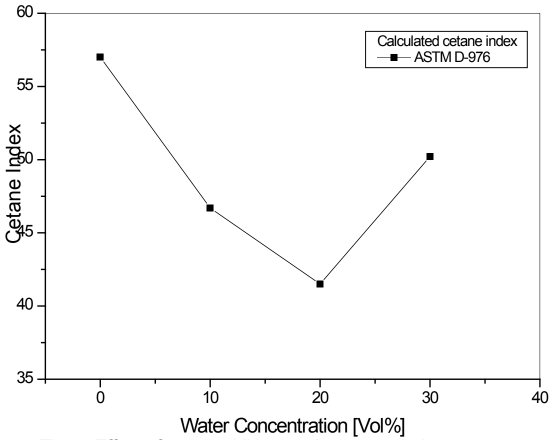

**Figure 6:** Effect of water addition on the cetane index.

The cetane index may still be within the acceptable range especially if compared to some other fuels e.g. biofuels, it would be more favorable. Higher cetane number ensures easy combustion (less time to evaporate, mix and react with air) and this ensures complete, knock-free and smooth combustion within the time available for engine cycle. This short ignition duration also ensures reduced engine combustion pressure rise rate and associated less noise.

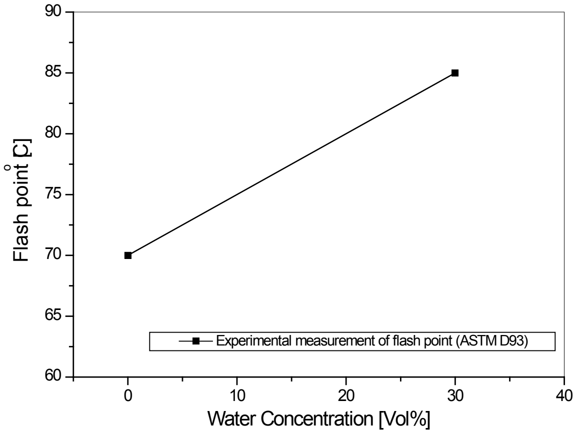

**Figure 7:** Effect of water on the diesel flash point.

### 3.6. Flash Point

The flash point for the water / diesel emulsion may be found in Figure **7**. The flash point of a volatile liquid is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Measuring a liquid's flash point requires an ignition source. At the flash point, the vapor may cease to burn when the source of ignition is removed. The flash point is often used as a descriptive characteristic of liquid fuel, and it is also used to help characterize the fire hazards of liquids.

"Flash point" refers to both flammable liquids and combustible liquids. There are various standards for defining each term. There are two basic types of flash point measurement: open cup and closed cup, and the closed cup is used in these experiments. From Figure **7**, it is evident that the flash point temperature for water / diesel emulsion is higher than that for pure diesel. This gives more safety to the water / diesel for storage and during transportation. If the temperature of liquid increases, it will be far away from accident-ignition. For pure diesel fuel the flash point is 70°C compared to 85°C for 30% water / diesel emulsion.

### 3.7. Total Acid Number

As mentioned above and compared to other alternative fuels like biodiesels, the total acid number should to be lower than 0.50 mg KOH/ml. This is since the Free Fatty Acids produced from biodiesel combustion may corrode automotive parts and these limits protect vehicle engines and fuel tanks. It may be seen from Figure **8** that for water / diesel emulsion, the acid number decreases for all water / diesel emulsions used. For pure diesel fuel, the total acid number is about 0.68 mg KOH/ml, where it is dropped to about 0.25 for 30% water. As far as this property is concerned, those emulsions may be used easily with no need to add any other additives to the emulsion.

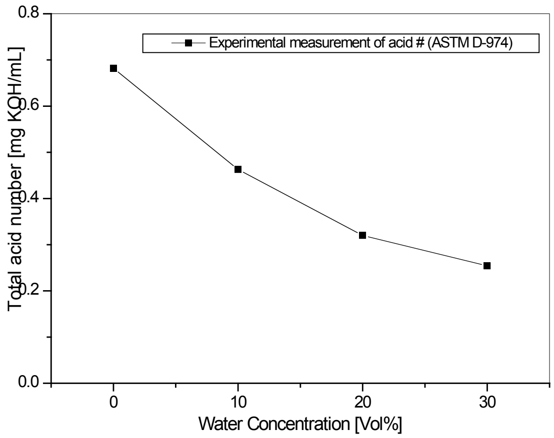

**Figure 8:** Effect of water addition on the diesel acid number.

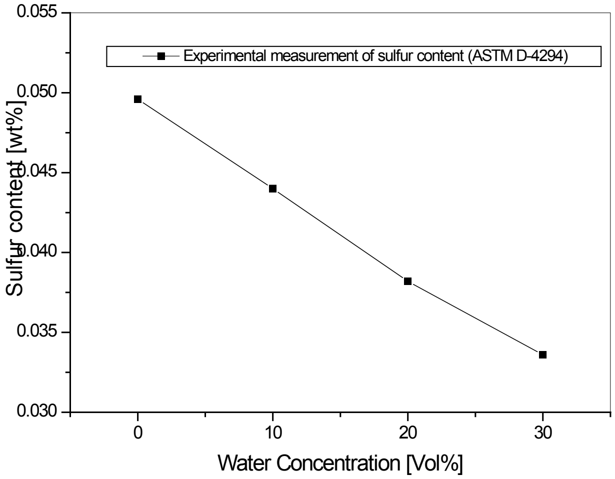

**Figure 9:** Effect of water addition on the diesel sulfur content.

### 3.8. Sulfur Content

To assist diesel engine manufacturers in meeting mandated limits for particulate matter in diesel engine exhaust, sulfur content is limited by law to 0.05% for diesel fuel used in on-road applications. This property is very important to diesel engine as it ensures that the sulfuric acid produced during the combustion process is kept to minimum amount to reduce the corrosion of engine components as well as to reduce the exhaust of sulfur compounds in exhaust gases. It may be seen from Figure **9**, that it is advantageous to use more water in the water / diesel emulsion. This will reduce the sulfur content percentage in the fuel as seen in the Figure. The sulfur mass content percentage dropped from 0.0496% for pure diesel to 0.0336% for 30% water emulsion.

## CONCLUSIONS

- Basic properties of water / diesel emulsified fuel were measured according to ASTM standards for different water contents of 10%, 20% and 30% as compared to pure diesel fuel.
- The water / diesel emulsions have some disadvantageous properties compared to diesel, e.g. viscosity, density, calculated Cetane index, and heating value. However, it has many other advantageous properties, e.g. initial and final boiling points, flash point, total acid number and sulfur contents.
- The disadvantageous properties for the water / diesel emulsion may be improved by further investigation on the emulsion producing process and to optimize the process to control the properties of the emulsion produced, and / or adding some chemical additives to the emulsion.

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