Effect of pH, water percentage and surfactant percentage on stability of water in diesel emulsion

M A Alsaadi1,2, H Sh Majdi3, Q F Alsalhy4, W A Yehye1, Q Marwan1, B O Betar1, K M Omar2

1 Nanotechnology & Catalysis Research Centre (NANOCAT), IPS Building, University of Malaya, 50603, Kuala Lumpur, Malaysia.
2 National Chair of Materials Sciences and Metallurgy, University of Nizwa, Sultanate of Oman, Nizwa, Oman.
3 Al-Mustaqbal University College, Babylon, Iraq
4 Membrane Technology Research Unit, Chemical Engineering Department, University of Technology, Alsinaa Street No. 52, B. O. 35010, Baghdad, Iraq.
mdsd68j@gmail.com

Abstract. Water-in-diesel system is one of the most conceptual promising proposed solutions to overcome nitrogen oxide and smoke emission which environmental harmfully produced from using conventional fuel systems. Stability of water-in-diesel emulsion (WIDE) is a major issue in applying this system. In this research, stability of WIDE was investigated by using two surfactants, namely, Span 20 and Tween 85. Two stages of experimental investigation were conducted. The first stage was a screening to select the proper surfactant and mixing time to obtain the best emulsification. Span 20 was found to give higher stability as compared to that of tween 85. In addition, WIDE showed higher stability when the mixing time was thirty minutes. The second stage, response surface method (RSM) with central composite design (CCD) were applied for modelling and optimization of WIDE mixing conditions. Three parameters (water/diesel percentage, surfactant percentage and pH value) were studied in this technique to obtain the optimum stability. ANOVA analysis showed that the model was significant and the water percentage of 5% and surfactant percentage of 1% showed the highest emulsion stability. pH affected on WIDE system under mild acidic and alkali conditions. The results showed that the pH plays an important role for the stability of WIDE.

1. Introduction
Combustion of diesel results in many pollutants release to air, such as CO, CO2, PM, SOx, NOx, unburned HC, and black smoke [1-2]. These pollutants are harmful to human health and the environment. A recent report for (European Environment Agency, 2016) showed that the emissions of NOx in the year 2014 were reached up to 39% from road transport, 7% from non-road transport, and 7% from industrial processes. Diesel machines such as vehicles and electricity generation plants had a major contribution in NOx emission among these three categories [3].

There are many ways to minimize the type and the amount of the released pollutants. One of these solutions is the use of oil mixed with water to form an emulsion. Through the use of water emulsified diesel, the water vapour lowers the combustion temperature, which led to the reduction of NOx and PM emissions [4]. During combustion, micro-explosions of water particles play a major role in combustion efficiency. The micro-explosion will lead to particles atomization and then, less fuel consumption with cleaner emissions. Generally, the emulsion oil consists of a specific amount of water, diesel, surfactant, and sometimes antioxidant. The stability of any emulsion oil can be
determined according to the amounts of these constituents, besides, the surfactant type, mixing speed and its duration, emulsion temperature, and diesel viscosity also affect the stability of the emulsion.

The surfactant (also called emulsification agent or emulsifier) is used to increase the system stability through reducing the interfacial surface tension between the water and the diesel particles [5]. Some of the common surfactants are: butylated hydroxytoluene (BHT), 2-ethylhexyl nitrate (EHN), N, N'-diphenyl-1, 4-phenylenediamine (DPPD), N-phenyl-1, sorbitan monooleate, sorbitol sesquioleate (SSO), polysorbate 20 (tween 20), 4-phenylenediamine (NPPD) [6-8]. The surfactant burns in the engine with the diesel emulsion. Although the range of the surfactant in the emulsion is small (0.5-5% (v/v)), it should be burned without emissions of PM or soot, NOx or SOx [6-8].

Generally, there are two emulsion phases: water in diesel (W/O) and diesel in water (O/W). The water in diesel is better than diesel in water due to the micro-explosions of the water drops. According to the special distribution of the water and diesel, the emulsion can be classified as two or three phases emulsion. The three emulsion phases of water-diesel-water is called W/O/W, and the diesel-water-diesel emulsion called O/W/O.

Several studies reported using different types of surfactants and different water ratios in order to obtain a stable water in diesel emulsion [9]. A system consisted of mixed surfactant (span 80 and tween 85) were used with isopar fluid and water to investigate acrylamide as a surface-active agent between water and the isopar fluid. Tween 85 also used in different concentrations to investigate the stability/water solubility of a system consisted of oil, water, and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) [10]. Span 20 was investigated by many studies [11-17]. Several surfactants investigated, i.e. Span 20, Span 60, Span 80, Span 85, Tween 20, Tween 60, and Tween 80 on the emulsion stability. Results showed that the most effective mixture was for span 80 and tween 80 at total dosage of 5% concentration and 10% water content [18]. Moreover, some studies suggested that combination of two or more surfactants results in more stabilization affect for water in diesel emulsion [19].

Detailed investigation of water in diesel emulsion is still limited in literature, especially the effect of several parameters, such as pH, temperature and others. Thus, this study reports the impact of some parameters on stability of WIDE by following three stages of experimental investigation. The first stage was a screening to select the proper surfactant and mixing time to obtain the best emulsification. The second stage, response surface method (RSM) with central composite design (CCD) were applied for modelling and optimization of WIDE mixing conditions. The third stage was to investigate for the first time pH effect on WIDE system under mild acidic and alkaline conditions.

2. Experimental

2.1. Materials
Commercial diesel was collected directly from Shell gas station (Kuala Lumpur) and kept in glass containers. Sorbitan monolaurate (Span® 20) and Polyoxyethylene sorbitan Trioleate (Tween® 85) were obtained from Sigma-Aldrich, used without further treatment, and kept inside fridge.

| Test                              | Unit       | Method  | Results |
|----------------------------------|------------|---------|---------|
| Density at 15 ºC                 | Kg/L       | D 4052-96 | 0.8     |
| Colour                           | -          | D 1300-98 | 2.0     |
| Kinematic Viscosity at 40 ºC     | cSt        | D 445-97 | 4.0     |
| Distillation Recovered at 90%    | ºC         | D 86-00a | 365.7   |
| Total Acid Number                | mgKOH/g    | D 974-97 | 0.1     |
| Water by Distillation            | vol %      | D 95-99  | < 0.05  |

2.2. Surfactant screening
Two surfactants were selected and tested to stabilize WIDE, namely, polyoxyethylene sorbitan trioleate (tween 85) and sorbitan monolaurate (span 20). To select the highest surfactant stability, the commercial diesel, were tested using tween 85 and span 20 at low percentages (1% w/w), moderate percentages (3% w/w), and high percentages (5% w/w). Water percentages in the emulsion was fixed at 17.5% (w/w) [20]. The emulsion stability was experimented visually and counted from the blending time until the water is separating from the diesel.

2.3. Effect of mixing time on emulsion stability
To select the best mixing time for the most stable WIDE, the emulsion agitation was conducted using laboratory tube immersion blenders at 3000 rpm. Mixing time is an important process condition which can affect the stability of emulsion [20]. Five samples were prepared using commercial diesel with 30% (w/w) water and 5% (w/w) span 20 at total sample weight of 20 g. The samples were mixed at different durations of 1, 5, 10, 30, and 60 min.

2.4. Optimization of pH, water, and surfactant percentages
The effect of water percentage surfactant percentage and pH value on water in diesel emulsion were studied using a response surface method (RSM) with central composite design (CCD) by using Design-Expert software (StatEase, v10). A total of 17 runs (with 3 centre points) were performed as shown in Table 2, and the selection of optimum results was done according to ANOVA analysis. The pH of water was controlled by balancing HCl and NaOH solutions using pH meter (EUTECH, pH 2700). The variable input parameters were water (% w/w) of 5%–30%, surfactant (% w/w) of 1%–5% and pH value of 5.5-7.5. The emulsion stability was experimented visually. The emulsion agitation was conducted using laboratory tube immersion blenders at 3000 rpm.

Table 2. Experimental design for optimization of pH, water and surfactant percentages

| Run | Factor 1 | Factor 2 | Factor 3 |
|-----|----------|----------|----------|
|     | A: water (% w/w) | B: surfactant (% w/w) | C: pH value |
| 1   | 30.00    | 3.00     | 6.50     |
| 2   | 5.00     | 5.00     | 5.50     |
| 3   | 30.00    | 5.00     | 7.50     |
| 4   | 30.00    | 1.00     | 5.50     |
| 5   | 5.00     | 1.00     | 7.50     |
| 6   | 5.00     | 5.00     | 7.50     |
| 7   | 17.50    | 3.00     | 6.50     |
| 8   | 17.50    | 3.00     | 7.50     |
| 9   | 17.50    | 3.00     | 6.50     |
| 10  | 30.00    | 5.00     | 5.50     |
| 11  | 17.50    | 3.00     | 5.50     |
| 12  | 17.50    | 5.00     | 6.50     |
| 13  | 17.50    | 3.00     | 7.50     |
| 14  | 5.00     | 1.00     | 6.50     |
| 15  | 17.50    | 3.00     | 6.50     |
| 16  | 30.00    | 1.00     | 7.50     |
| 17  | 5.00     | 3.00     | 6.50     |

3. Results and discussion
The first stage screening experiments were conducted in order to compare the stability behaviour of two different WIDE systems. First step in this stage was using Span 20 and tween 85 to select the surfactant that gives higher stability upon mixing with water and diesel. Figure 1 displayed the efficient of Span 20 and Tween 85 on conventional diesel emulsion. It was found that the highest stability for conventional diesel was 100 hr at 1% (w/w) of span 20, while the highest stability for tween 85 was 28 hr at 5% (w/w). Comparing the efficiency of tween 85 with the control sample
(without any surfactant), the stabilities with tween 85 was slightly higher than the control stability (18 hr).

These results were convincing and came in agreement with the general concept which was the basis of selection rule for the proposed surfactants and also many published research [21] confirmed the same phenomena. This phenomenon could be attributed to the force balance exerted on surfactant molecule by the molecule of water and oil in contradiction directions. This force balance is expressed by HLB (Hydrophile-Lipophile Balance). HLB is an empirical expression for the relationship of the hydrophilic and hydrophobic groups of a surfactant. Span 20 and tween 85 have HLB values of 8.6 and 11.0, respectively. The higher the HLB value, the more water-soluble the surfactant. Based on that, Span 20 was selected for further optimization work.

It was reported that the radii of the droplets in the emulsion decreased with increasing stirring speed and emulsifying time. The emulsifier becomes more effective with increased mixing time [21]. If the mixing time is too long the effectiveness of emulsifier will be decreased because the intense stirring will cause the emulsifier to drop out from the oil-water interface. Figure 2 shows the effect of mixing time on water in diesel emulsion. It was noticed the emulsion stability increased as mixing time increased from 1 to 30 min. Furthermore, the more the mixing time the less the emulsion stability, with concerning of other system components. Results showed that mixing time for 30 min gave the highest stability as compared to that of other mixing durations, as shown in Figure 2. Mixing time of 30 min was selected and applied for all experiments.

**Figure 1.** Efficient of Span 20 and Tween 85 on commercial diesel emulsion.
After selecting the surfactant and fixing the mixing time as concluded from the first stage, the second stage was optimization and modelling for the effective parameters on WIDE stability to generate fundamental knowledge about qualitative and quantitative standardizing for the process. Not only the direct effect of individual parameters but the interactive effect of three parameters namely water percentage, surfactant percentage and pH value on WIDE system stability were studied using a response surface method (RSM). Central composite design (CCD) was adopted for modelling of the date set suggested by using Design-Expert software (StatEase, v10). The obtained results for conventional diesel stabilities were listed in Table 3.

![Figure 2. Emulsion stability under mixing time of: (a) 1 min, (b) 5 min, (c) 10 min, (d) 30 min, and (e) 60 min.](image)

**Table 3.** Experimental design results for three factors ratios optimization

| Run | Factor 1  | Factor 2  | Factor 3 | Response stability (hr) |
|-----|-----------|-----------|----------|-------------------------|
| 1   | 30.00     | 3.00      | 6.50     | 70                      |
| 2   | 5.00      | 5.00      | 5.50     | 134                     |
| 3   | 30.00     | 5.00      | 7.50     | 4                       |
| 4   | 30.00     | 1.00      | 5.50     | 3                       |
| 5   | 5.00      | 1.00      | 7.50     | 200                     |
| 6   | 5.00      | 5.00      | 7.50     | 120                     |
| 7   | 17.50     | 3.00      | 6.50     | 72                      |
| 8   | 17.50     | 3.00      | 7.50     | 78                      |
| 9   | 17.50     | 3.00      | 6.50     | 72                      |
| 10  | 30.00     | 5.00      | 5.50     | 24                      |
| 11  | 17.50     | 3.00      | 5.50     | 65                      |
| 12  | 17.50     | 5.00      | 6.50     | 70                      |
| 13  | 17.50     | 3.00      | 7.50     | 24                      |
| 14  | 5.00      | 1.00      | 6.50     | 140                     |
| 15  | 17.50     | 3.00      | 6.50     | 72                      |
| 16  | 30.00     | 1.00      | 7.50     | 5                       |
| 17  | 5.00      | 3.00      | 6.50     | 140                     |

ANOVA showed that the model was significant where the p-value (Prob > F) was 0.0288 i.e. less
than 0.05 and that value indicates the significance of the model. $R^2$ value was 0.9604 which is in reasonable agreement with Adj $R^2$ of 0.8417, as listed in Table 4 ANOVA for Response Surface Reduced Cubic Model. Adequate Precision measures the signal to noise ratio, which was 9.647 of the model. A ratio greater than 4 is desirable. The ratio of 9.647 indicates an adequate signal. This model can be used to navigate the design space.

### Table 4. ANOVA for Response Surface Reduced Cubic Model

| Source      | Sum of Squares | df | Mean Square | F Value | p-value | Prob > F | results  |
|-------------|----------------|----|-------------|---------|---------|----------|----------|
| Model       | 195.63         | 12 | 16.30       | 8.09    | 0.0288  | significant |
| A-water     | 5.89           | 1  | 5.89        | 2.92    | 0.1626  |          |          |
| B-surfactant| 1.816E-003     | 1  | 1.816E-003  | 9.010E-004 | 0.9775 |          |          |
| C-pH        | 0.75           | 1  | 0.75        | 0.37    | 0.5750  |          |          |
| AB          | 2.21           | 1  | 2.21        | 1.09    | 0.3544  |          |          |
| AC          | 1.03           | 1  | 1.03        | 0.51    | 0.5136  |          |          |
| BC          | 2.34           | 1  | 2.34        | 1.16    | 0.3419  |          |          |
| A\(^2\)     | 2.68           | 1  | 2.68        | 1.33    | 0.3132  |          |          |
| B\(^2\)     | 1.05           | 1  | 1.05        | 0.52    | 0.5106  |          |          |
| C\(^2\)     | 5.38           | 1  | 5.38        | 2.67    | 0.1776  |          |          |
| A\(^2\)C    | 0.36           | 1  | 0.36        | 0.18    | 0.6928  |          |          |
| AB\(^2\)    | 0.024          | 1  | 0.024       | 0.012   | 0.9185  |          |          |
| AC\(^2\)    | 1.65           | 1  | 1.65        | 0.82    | 0.4173  |          |          |
| Residual    | 8.06           | 4  | 2.02        |         |         |          |          |

The final model of stability time prediction is presented in eq.1 in terms of coded factors.

$$\text{Sqrt(Stability} + 2.00) = +8.90 - 1.72 \times A - 0.021 \times B - 0.53 \times C + 0.74 \times A \times B - 0.51 \times A \times C - 0.76 \times B \times C + 1.09 \times A^2 - 0.83 \times B^2 - 1.46 \times C^2 + 0.48 \times A^2 \times C - 0.28 \times A \times B^2 - 2.53 \times A \times C^2 \quad (1)$$

Wherein A is water percentage, B is surfactant percentage and C is pH value.

Figure 3 shows 3D Contour Plot for Conventional Diesel Optimization between A and B factor and the stability as a response. It can be seen that the stability was increased with the decrease of water and surfactant in the emulsion, and vice versa.
Figure 3. 3D contour plot for conventional diesel optimization between A and B factor and the stability as a response.

The stability of WIDE increased with the increase of the pH value, as shown in Figure 4 and Figure 5. This could be attributed to the effect of proton concentration in water drops on the hydrophilic OH moiety in the surfactant molecule. It is also expected in acidic condition to create a kind of electronegativity disturbance among the interacted molecule in the system. This finding has been reported previously in WIDE system research and may open a wide door for further investigations in both emulsification and separation processes as well. Eventually, controlling of pH could be the key factor in obtaining higher stable emulsion.
Figure 4. 3D contour plot for conventional diesel optimization between A and C factor and the stability as a response.

Figure 5. 3D contour plot for conventional diesel optimization between B and C factor and the stability as a response.
After obtaining the significant imperial –statistical model, it became possible to optimize the conditions which enable to design the desired combination of WIDE mixing system. From engineering point of view, restrictions most be considered to select the best solution of the interacted multifunctional parameters which affect the process. In our case we firstly stated the desired main target is to obtain the maximum possible stability. Secondly is to minimize the percentage of surfactant for economic and environmental reasons. Thirdly, Water percentage should be moderated to avoid thermodynamically efficiency failures and engine corrosion. And finally pH must be also a concern in terms of keeping nonabrasive conditions by selection of in-range restriction.

Eventually, based on the explained criteria, the optimum solutions for water and span 20 in the conventional diesel emulsion were listed in Table 5. According to solution no. 1, seven samples were prepared at 5% (w/w) water and 1% (w/w) span 20 and tested under different pH values.

| No. | Water % | Surfactant % | pH  | Stability | Desirability | 
|-----|---------|--------------|-----|-----------|--------------|
| 1   | 5.00    | 1.00         | 7.50| 200       | 1.000        |
| 2   | 5.14    | 1.00         | 7.50| 197.16    | 0.996        |
| 3   | 5.00    | 1.07         | 7.50| 199.535   | 0.990        |
| 4   | 5.43    | 1.00         | 7.50| 191.457   | 0.987        |
| 5   | 5.64    | 1.00         | 7.50| 187.32    | 0.981        |

4. Conclusion
Span 20 showed higher emulsion stability as compared to that of Tween 85 when surfactant screening was conducted. The mixing time was optimized to be 30 min for all the experiments. The second stage of modelling resulted into significant model according to ANOVA study. Optimization process for the highest emulsion stability resulted into water percentage of 5% and surfactant percentage of 1%. The alkali water in the emulsion has considerable impact on the stability of conventional diesel. The stability was increased at mild alkali condition.

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