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A CASE STUDY ON PREPARATION, STABILITY AND PHYSICAL PROPERTIES OF WATER IN DIESEL EMULSION

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ABSTRACT

Water in diesel emulsion is often considered as an alternative fuel for IC engines in order to achieve fuel economy and pollution reduction through microexplosion phenomenon. Physical properties of the emulsion play a significant role in achieving the phenomenon of microexplosion. In this work, water in diesel emulsions was prepared containing 9%, 12%, 15% and 18% water. The emulsions were stabilized by mixing two different nonionic surfactants to get HLB values of 4.97 and 6.31. It was observed that the effect of hydrophilic and lipophilic balance value, amount of water and surfactant dosage has an impact on the stability and other characteristics of water in diesel emulsion. Surface tension of WiDE stabilized with 15% surfactant dosage was found to be increasing with increase in water content. Density of emulsions was increased with increase in water. Almost 50% reduction in sulphur was observed with WiDE compared to diesel. Stability of the emulsion was found to be increased with increase in surfactant concentration. Emulsion droplets stabilized with 15% and 18% water content with proportionate surfactant dosage was recorded lower Sauter mean diameter compared to WiDE with 9% and 12% water proportion.

Keywords: diesel emulsion, WiDE, microexplosion, properties of water.

1. INTRODUCTION

Emission regulations continue to get more stringent, exacerbating the need to find a solution for the emission of gaseous pollutant and particulate matter from diesel engines. With the increase of awareness in saving the environment, concerns have raised as diesel engines has been regarded as a major air pollution source [1]. Primary pollutants emitted from diesel engines are particulate matters (PM), black smoke, nitrogen oxides (NOx), sulfur oxides (SOx), unburned hydrocarbon (HC), carbon monoxide (CO), and carbon dioxide (CO_2) [2]. Water in diesel emulsion contributes to a better alternative fuel to reduce pollutant due to the secondary atomization of the diesel fuel droplets during combustion which is known as micro-explosion. It is significant to know the variables that affect the stability of the emulsified fuel and also the parameters that influence the development of micro-explosion.

An emulsion is a mixture of two or more liquids immiscible in nature, one present as dispersed phase usually water and other is oil or diesel as an continuous phase [3]. Emulsifiers or surfactants are the surface active agents used to provide the bonding between the water and oil. The presence of surfactant will reduce the interfacial tension between the diesel and water [4]. The surfactants possess a polar, or hydrophilic head and a nonpolar, or hydrophobic tail [5]. Emulsifiers used for the emulsification are selected based on their hydrophilic lipophilic balance (HLB). Nadeem *et al.*[6] states that lower HLB are suitable for producing stable emulsions. More stable emulsions are feasible by mixing two different surfactants rather than using a single surfactant [7]. Moreover, microexplosion is the key factor for reducing the main exhaust pollutants like PM and NO_X. Morozumi *et al.*, [8] in his microexplosion studies with water-n-hexadecane emulsion claimed that the mixing of two surfactants resulted in lower microexplosion temperature when compared to single emulsifier emulsion, Califano *et al.*, [9] reports that the parameters influencing emulsion stability have effect also on their tendency of microexplosion also.

The aim of the present work is to prepare emulsions with different percent of water stabilized by a surfactant mixture of surfactants with two different HLB values. Stability of the emulsion were visually observed. The effects of the HLB values, water content and droplet diameter on the emulsion stability were studied. In addition surface tension, density and viscosity of the prepared emulsion were also investigated.

2. EMULSION PREPARATIONS

The emulsions were prepared by mixing the surfactant with distilled water first before adding the mixture to the base fuel of Malaysian commercial diesel, which contains 95% diesel and 5% palm oil methyl ester. The commercial surfactants, Span 80 of Merck KGaA, Germany and Tween 85 of Acros Organics Belgium with HLB values of 4.3 and 11 respectively were used as received. The two surfactants were mixed in proportions of 70:30 which resulted in an HLB value of 6.31 and 90:10 to get an HLB value of 4.97. Huo *et al.* [10] and C.Y.Lin *et al.* [2] reported that the preferred HLB for

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stable emulsion is in the range of 5-8. The combined HLB values were obtained by the following equation.

% A= 100 x (x- HLBB)/ (HLBA- HLBB)

Where

HLBA = HLB of the 1st surfactant

HLBB = HLB of the 2nd surfactant

x = Targeted HLB value

% A = Amount of Surfactant A required

% B = Amount of Surfactant B required

The WiDE preparation matrix was selected such that different HLB values, water content, different stability period and water droplet size and distributions were achieved. All the emulsions were prepared by using an overhead stirrer fitted with customised blades rotating at 1500 rpm for 15minutes. According to Gonglum *et al.*, [11] if the mixing time is too long, efficacy of the surfactant or emulsifier will reduce by dropping out from the oil-water interface, hence the mixing duration was limited to 15minutes for all the emulsions prepared. A total number of 24 samples were prepared. The emulsions produced can be divided into two groups i.e. each group contains 12 WiDE samples. Whereas the group-1 (WiDE-1 to WiDE-12) was prepared using a surfactant mixture with HLB value equal to 4.97 as shown in table-1 and the group-2 (WiDE-13 to WiDE-24) was using a surfactant mixture with HLB value equal to 6.31 and the same protocol of mixing was followed for group-2 emulsions also. Each group of emulsion has different percentage of water and surfactant as mentioned in Table-1. For each sample, 100ml of emulsion was prepared in a clear glass bottle and the samples were then kept at room temperature to observe settling period of two weeks.

Table-1. Preparation Matrix of Group-1 WiDE.

HLB value and volume of surfactant	Sample ID	Amount of H_2O (mL)	Volume in mL	
			Diesel	Surfactant
HLB: 4.97 (5% from H_2O)	WiDE-1	9	90.55	0.45
	WiDE-2	12	87.40	0.60
	WiDE-3	15	84.25	0.75
	WiDE-4	18	81.10	0.90
HLB: 4.97 (10% from H_2O)	WiDE-5	9	90.10	0.9
	WiDE-6	12	86.80	1.2
	WiDE-7	15	83.50	1.5
	WiDE-8	18	80.20	1.8
HLB: 4.97 (15% from H_2O)	WiDE-9	9	89.65	1.35
	WiDE-10	12	86.20	1.80
	WiDE-11	15	82.75	2.25
	WiDE-12	18	79.30	2.70

3. RESULTS AND DISCUSSIONS

3.1 Stability of WiDE

The stability of WiDE samples were observed for two weeks at room temperature. WiDE-1 to WiDE-6 from group-1 emulsion samples were found to be unstable while WiDE-7 to WiDE-12 were stable for the observation period. In group-2 emulsions except WiDE-13 and14 all other samples were found to be stable. Clear water layer can be seen for samples 1 to 4 as shown in Figure-1. Coalescence of water droplets lead to phase separation within observation period.

Figure-1. Unstable WiDE 1-4 showing water layer separation.

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Few samples of stable emulsions are depicted in Figure-2. WiDE prepared with surfactant mixture of HLB value 6.31 were found to be more stable beyond the observation period than those with HLB value of 4.97. The SMD of unstable WiDE in group-1 were above 6µm.

Figure-2. Stable WiDE samples 21-24 .

It can be concluded that droplet diameter was the influencing parameter for unstable emulsion in case of WiDE with an HLB of 4.97, Whereas for emulsions with HLB of 6.31 the dominant factor could be the surfactant rather than the SMD, since the stable emulsions in group-2 were with the SMD range of 2.84 µm to 7.88 µm. Irrespective of water content it is found that stability of the emulsions increases with increasing surfactant dosage which is in agreement with the findings of Noor El-Din *et al.* [12]. Also, for the emulsions investigated higher HLB values gives better stability.

3.2 Water droplet size and distribution

The dispersed water droplets size and distribution were examined using Olympus BX51 microscope with 500X magnification and the images were captured using Moticam-5MP digital camera. Motic image plus 2.0 software was used to measure the diameter of water droplets. Water droplet distribution for selected WiDE samples is shown in Figure-3. The size of the measured droplets are expressed in terms of Sauter Mean Diameter (D_{32})

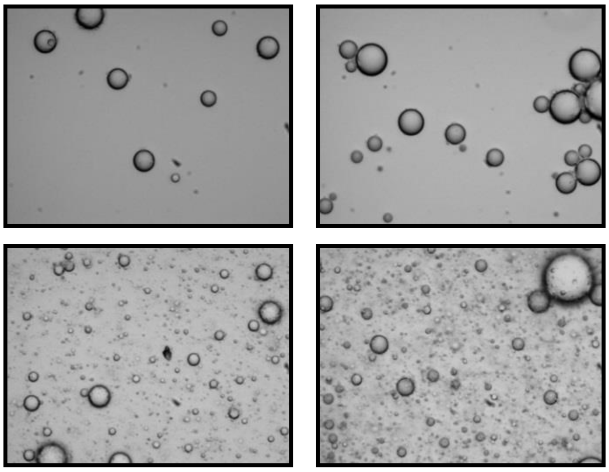

Figure-3. Water droplets distribution of unstable WiDE-2, 14, stable WiDE 12 and 24 at a magnification of 500X.

$D_{32}= \sum n_i D_i^3 / \sum n_i D_i^2$

Where D_i is the diameter of the droplet and n_i is the total number of droplets having same diameter. For the three selected surfactant dosages, wide range of dispersed water droplet diameter was witnessed for both group-1 and 2 WiDE with 9% and 12% water as shown in Figure-4.

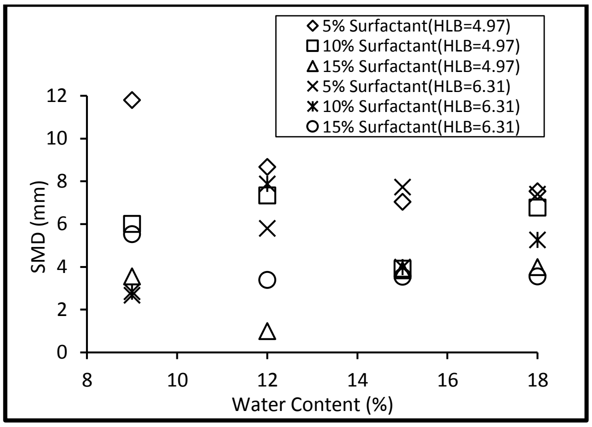

Figure-4. Sauter mean diameter of group-1 and group-2 emulsions.

But with increase in the water content with proportionate surfactant dosage i.e. for WiDE with 15% and 18% water content of both the group emulsions the difference in the SMD was found to be minimum as shown. For the emulsions studied, it is evident from these observations that there is a significant influence of both water content and surfactant dosage on maintaining the consistency of dispersed water droplet diameter in the emulsion which is fairly in agreement with Yoshio Morozumi *et al*. [8] reported that the droplet diameter are slightly influenced by the surfactant content. Likewise, the surfactants used in the emulsion should have no impact on the physiochemical properties of the fuel. Surfactants should easily burn with no soot and free of sulfur and nitrogen [13]. Table-2 shows the sulfur content of WiDE which was obtained using X-ray fluorescent test. The presence of water in WIDE reduced the sulfur content. The sulfur content for the base fuel was around 500ppm but in case of emulsions it was almost 50% lesser. This result is due to sulfur will react with oxygen from the water to form sulfur dioxide (SO2) or sulfur trioxide (SO_3).

Table-2. Sulfur content of emulsified fuel.

Sample ID	Sulfur Content (ppm)
WiDE-11	215.9
WiDE-12	204.2
WiDE-23	235.7
WiDE-24	223.0

The trend shows that more water will result in less sulfur content. It can be seen when compared samples WiDE-11 vs WiDE-12 and WiDE-23 vs WiDE-24. In addition, the reaction of sulfur and oxygen also will produce sulfate which is one of the element in particulate matter formed. Thus, reduced sulfur content in the emulsified fuel will reduce particulate matter formed.

3.3 Density and viscosity of WiDE

According to the France WiDE fuel regulations and the CWA15145 requirements and test methods, the density of the samples at 15 °C must comply with these standards. The density of the samples was measured using the KEM DA-645 density meter, which is capable of measuring density with a temperature range of 0 °C up to 90°C. The kinematic viscosity of the WiDE was measured at 40°C using DHR-1 hybrid rheometer. According to the CWA 15145 standard regulations the acceptable range for density is 828-880 kg/m^3.

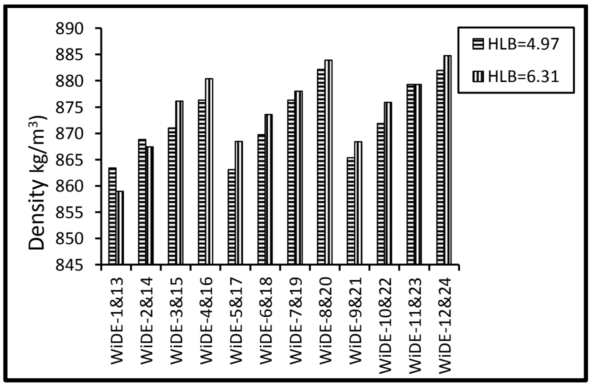

Figure-5. Density of WiDE.

Except for the WiDE-8, WiDE-12, WiDE-16, WiDE-20 and WiDE-24, the density of remaining samples were found to be within the range. The results from this experiment are shown in Figures 5 and 6. The density of all the WiDE samples increases with increase in water content. But, it can be observed from the density values of group-1 and group-2 emulsions as shown in Figure 5, WiDE with HLB value of 6.31 has higher density except for two samples with 9% and 12% water stabilized with 5% surfactant dosage. The increase in density is very small and in the range of 0.22 to 0.455%.

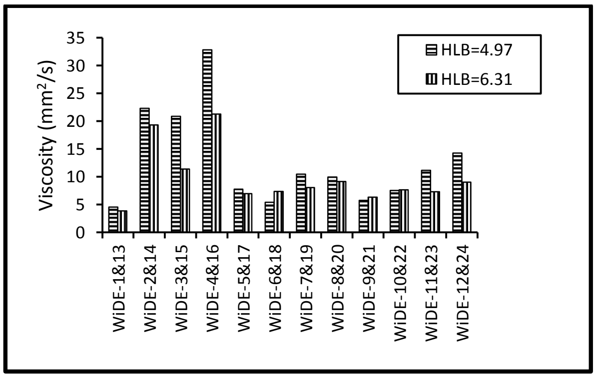

Figure-6. Viscosity of WiDE.

Hence surfactant content has insignificant influence on emulsions density. The viscosity of WiDE samples is depicted in Figure-6. No trend was observed in case of viscosity, in general viscosity of WiDE increases with increase in water content is due to the dispersion of water droplets but there was a reduction in the rate of increase of viscosity with an increase in surfactant dosage. As per the requirements and testing standard, the permitted viscosity @ 40 °C of the emulsion should be in the range of 2-5.50 mm^2/sec, but in the present study most of the WiDE samples were found to be out of the range (i.e.) except WiDE-1, WiDE-6 and WiDE-13 rest of the samples does not meet the standard.

3.4 Surface tension of WiDE

The surface tension was measured by the pendant drop method. The shape of the WiDE droplets were evaluated using software SCA-20, and measurements were recorded at 20 °C.

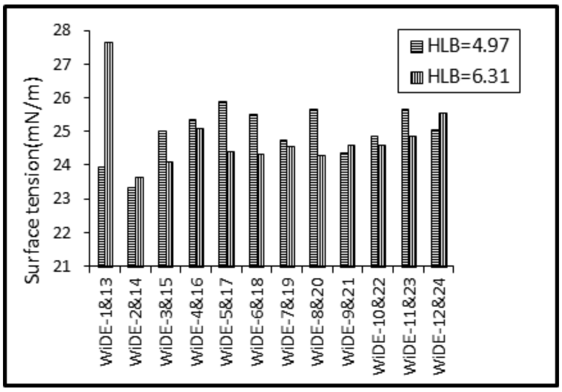

Figure-7. Surface tension of WiDE.

The variations in the surface tension of both group-1 and group-2 emulsions were found to be minimum as shown in Figure-7. In case of WiDE stabilized 10% surfactant with an HLB value of 6.31 was maintained almost constant surface tension irrespective of the variations in the water content. WiDE from both groups with 15% surfactant dosage were found to be increasing with increase in the water content. As shown in Figure-7, surface tension of the WiDE with HLB=4.97 was found to be minimum In case of WiDE stabilized 10% surfactant with an HLB value of 6.31 was maintained almost constant surface tension irrespective of the variations in the water content. Whereas WiDE from both group with 15% surfactant dosage were found to be increasing with increase in the water content. Surface tension of the WiDE with HLB=4.97 was found to be higher, except three samples.

CONCLUSIONS

Stable water in diesel emulsions was prepared with three different surfactant dosage and two different HLB values. The studied WiDE samples were prepared with 9%, 12%, 15% and 18% of water content. The stability of the emulsions was found to be increased with increase in surfactant dosage. Also higher HLB value was found to produce more stable emulsions for longer shelf life. For the emulsions studied the Sauter mean diameter of water droplets were significantly influenced by the water content and surfactant concentration. Sulfur content of WiDE was reduced with increase with water content. The surfactant dosage has less influence on density and viscosity of WiDE. WiDE produced with HLB of 4.97 has higher surface tension compared to HLB value of 6.31.

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REFERENCES

[1] O. Badrana, S. Emeishb, M. Abu-Zaidc, T. Abu-Rahmaa, M. Al-Hasana and M. Al-Ragheba. 2011. Int. J Therm Environ Eng. 3, 1-7.

[2] C.-Y. Lin and K.-H. Wang. 2003. Fuel. 82, 1367-1375.

[3] M. Fingas and B. Fieldhouse. 2004. Journal of hazardous materials. 107, 37-50.

[4] C.-Y. Lin and K.-H. Wang. 2004. Fuel. 83, 537-545.

[5] J. Jiao and D. J. Burgess. 2003. Aaps Pharmsci. 5, 62-73.

[6] M. Nadeem, C. Rangkuti, K. Anuar, M. Haq, I. Tan, and S. Shah. 2006. Fuel. 85, 2111-2119.

[7] S. Sajjadi. 2006. Chemical engineering science. 61, 3009-3017.

[8] Y. Morozumi and Y. Saito. 2010. Energy and Fuels. 24, 1854-1859.

[9] V. Califano, R. Calabria, and P. Massoli. 2014. Fuel. 117, 87-94.

[10] M. Huo, S. Lin, H. Liu, and F.L. Chia-fon, Fuel 123, 218-229 (2014)

[11] G. Chen and D. Tao. 2005. Fuel processing technology. 86(5): 499-508.

[12] M. Noor El-Din, S. H. El-Hamouly, H. Mohamed, M. R. Mishrif and A. M. Ragab. 2013. Egyptian Journal of Petroleum. 22, 517-530.

[13] Y. Zeng and C.-F. Lee. 2006. Proceedings of the 31st International Symposium on Combustion. 31, 2185–2193.