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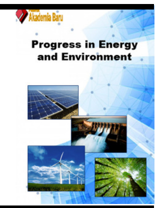

Water-in-Diesel Nano-Emulsion: A Preliminary Study on Its Formation and Short Term Physical Stability

Research Article

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ABSTRACT

Water-in-diesel nano-emulsions were developed using blended nonionic surfactants i.e. Span 20 and Tween 80 in this study. With optimal HLB number (i.e. 11.16), emulsions with varying water wt% (2 wt% - 8 wt% of water, at 6 wt% surfactant) and varying surfactants wt% (2 wt% - 8 wt%, at 5 wt% water) were particularly studied for their characteristic size. From the results obtained, droplet size increases with the increase of water wt%, but generally decrease with increase of surfactant wt%. Water content ranging from 2 wt% to 5 wt% were prepared for short term physical stability study. Generally, no phase separation was observed. Neither significant increase nor decrease in term of droplets size was recorded for emulsions prepared at 2 wt% and 3 wt% of water, after 15 days of storage at room condition

Keywords:
Water-in-diesel, Nano-emulsions, Hydrophilic Lipophilic Balance (HLB), Physical Stability Study

1. Introduction

Diesel is one of the major fuel and it is widely used in industries and transport nowadays. Nevertheless, it is also the main contributor to air pollution, such as nitrogen oxides [1] and etc. Due to high demand, diesel fuel with higher efficiency and lesser pollution is always anticipated. One governing factor controlling the formation of nitrogen oxide is the combustion temperature, i.e. the higher the combustion temperature, the larger amount of nitrogen oxide being produced. Due to high heat capacity of water, combustion temperature would be reduced with introduction of water into diesel engine. This can be done via intake manifold fumigation or direct water injection. However, long time of direct contact between diesel engine and water stand a high risk to cause oil contamination and wear formation, resulted in increase of hydrocarbon and carbon monoxide in emission. To accommodate these disadvantages, some modification is usually required on the diesel engine [2].

Water-in-diesel nano-emulsions can be a potential solution, which require no specific modification on the combustion engine. Water-in-diesel nano-emulsions are generally defined as mixture of diesel and water which contains dispersed phase no larger than 500 nm [3]. It improves the occurrence of

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micro-explosion that produce smaller diesel droplets, better spray dispersion, and less soot particles formed during burning of diesel [1].

Nano-emulsion is thermodynamically unstable but kinetically stable and transparent to naked eye. It is unique compared to other emulsion system that is usually milky or translucent, as they are smaller in characteristic size and relatively stable against sedimentation, flocculation, dilution and temperature changes [4]. Among all unstable phenomenon, most of them involve the formation of larger particles by consuming smaller particles. Coalescence and flocculation can be reduced by steric stabilization, however, Ostwald ripening which grow larger particles by consuming smaller particles is very challenging [4]. As compared to many existing approaches, ultrasonic emulsification provides nano-emulsions in a more controllable droplets size distribution with lesser energy consumption, potentially suggests a better way to produce kinetic stable nano-emulsion formulation [5].

In the current work, transparent water-in-diesel nano-emulsion were obtained using blended surfactants subjected to ultrasonic cavitation. The influence of water content and surfactant content on diesel emulsion droplet characteristic size were investigated. Also, a short-term physical stability study over 15 days at room condition was conducted.

2. Methodology

2.1 *Materials*

The automotive diesel was obtained from PETRON (Malaysia). The physical properties of the diesel used are summarized in Table 1. Surfactants i.e. Span 20 (Sorbitan Monolaurate) and Tween 80 (PEG-20 Sorbitan Monooleate) were purchased from Sigma-Aldrich (M) Sdn. Bhd. Distilled water was used across all experiments.

Table 1 Physical properties of Petron's diesel

Characteristic	Description
Concentration	Greaterthan 99%
Physical State	Liquid
Color	Pale Yellow
Relative density (15˚C)	0.84
Flash point	Greaterthan 62˚C
Auto-ignition point	Greaterthan 250 ˚C

2.2 *Formation of Nano-emulsions*

The formation of water-in-diesel nano-emulsions involved two steps. Firstly, water was added into mixture of Span 20 and Tween 80 (Optimal HLB for surfactant mixture = 11.16, which had been identified in an earlier study and not included in this paper), followed by addition of diesel. The amount of each components was recorded throughout sample preparation. The second step involved emulsification of prepared sample using ultrasonic bath. During emulsification, water bath temperature was maintained at 40˚C. Emulsification time was fixed at 5 minutes. The frequency of ultrasound is 53 kHz. To study the impact of surfactant wt% on droplet size, nano-emulsions with varying surfactant wt% (2 wt% to 8 wt%) were prepared while maintaining the water wt% at 5 wt%. Whereas, for the study of water wt% impact on droplet size, samples were prepared with varying water wt% (2% to 8%) and surfactant wt% was fixed at 6 %.

2.3 *Physical Stability Study*

Nano-emulsion with different water wt% (i.e. 2 wt%, 3 wt%, 4 wt% and 5 wt%) were prepared, while for blended surfactant the wt% was fixed at 6 wt%. 15 days of storage at room condition was set as study period.

2.4 *Droplets Size Measurement*

The droplet size of the water-in-diesel nano-emulsion was measured using dynamic light scattering (Zeta-sizer, Nano-series, Malvern, UK) at 25˚C. Equilibration time for measurement is 60 seconds and number of measurement is set at 3.

3. Results and Discussions

3.1 *Effect of Surfactant (wt%)*

Surfactants were added to reduce interfacial tension between diesel-droplet phase and water-continuous phase. As a result, Laplace pressure decreased and smaller droplets were produced [3]. **Fig. 1** showed the relationship between surfactant wt% (2 wt% to 8 wt%) and droplet size when water wt% was fixed at 5 wt%. Blended surfactants consisted of Span 20 and Tween 80 was mixed beforehand to obtain optimal HLB which is 11.16 in this study.

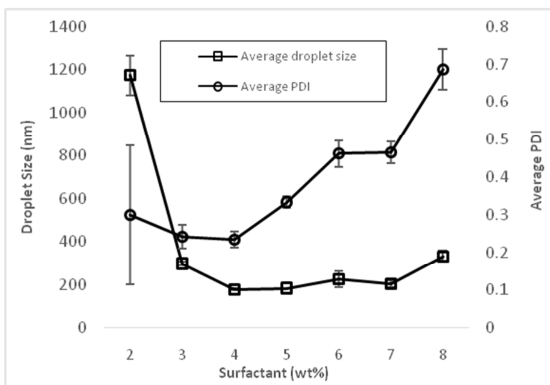

Fig 1. Droplet size and PDI of water-in-diesel nano-emulsions as a function of surfactant weight percentage (wt%)

At low surfactant wt%, the emulsions formed in micro scale and fast phase separation was observed. PolyDispersity Index (PDI) obtained with high standard deviation indicated the formation of highly inhomogeneous droplets due to insufficient surfactant. A milestone was recorded when surfactant wt% went beyond 3 wt%. Droplets size dramatically decreased and water-in-diesel nano-emulsions were formed. Droplets with the lowest droplet size were obtained when surfactant wt% further increased to 4 wt%. As an evidence for the formation of well distributed nano-emulsion, PDI with the lowest value was also observed at this point. The droplets size was therefore remained stable ranging from approximately 250 nm to 350 nm when surfactant wt% further increased to 8 wt%. The sample turned translucent when surfactant wt% was adjusted from 7 wt% to 8 wt%. The droplet size increased from 202.83 nm to 331.57 nm, and a significant increase was observed from PDI measurement. This might be a cause of surfactant overdosing in the construction of nano-emulsions. At this critical concentration, the addition of surfactant would not be able to reduce droplet surface tension, but stacking on the diesel-water interface to form bigger droplets. Due to the highly unstable surfactant stacking on droplets surface, emulsion stability deteriorated and rapid coalescence would happen.

Generally, surfactant is vital for the formation of nano-emulsions. However, when the maximum number of nano-emulsions was achieved, droplets size increase with increase of surfactant addition, and eventually pushing the unstable emulsion system to collapse.

3.2 *Effect of Water (wt%)*

Water-in-diesel nano-emulsion has potential to substitute the current diesel formulation due to its ability to reduce smoke formation and nitrogen oxide emission without engine modification. This can be achieved by the addition of well distributed water droplets in diesel continuous phase.

Water droplets reduce combustion temperature hence reduce the formation of nitrogen oxide. Furthermore, liquid water evaporated during combustion ignite micro-explosion which further enhance diesel engine performance. It is crucial to determine the water content. The relationship between droplet size and water content can be visualized in **Fig. 2**. Basically, the nano-emulsion with lower water wt% would suggest droplet in smaller size. Among all the samples, nano-emulsion with 8 wt% water exhibited the largest droplet size, which is 355.03 nm. However, PDI of nano-emulsions obtained from this trial did not show consistent trending.

Fig. 3 combine the plotting of average droplet size of nano-emulsion against water content obtained using mixture of Span 80 and Tween 80 in different HLB. In general, all the 3 samples exhibited similar trending which the droplet size increases with the increase of water content. This is especially obvious when water wt% range from 4% to 6%. A significant increase was observed when water wt% increased from 3% to 5%, at HLB of 10.72, while a relatively gentler increment was recorded for HLB of 8.58 and 9.65, respectively. From **Fig. 3**, it seems HLB of 9.65 produced the smallest diesel droplets in water, and having much better tolerance to carry more water without upset the emulsion system.

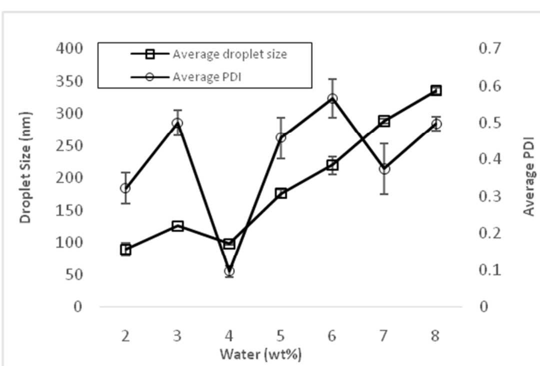

Fig 2. Droplet size of nano-emulsions as a function of water percentage (wt%). Surfactant wt% was fixed at 6 wt%

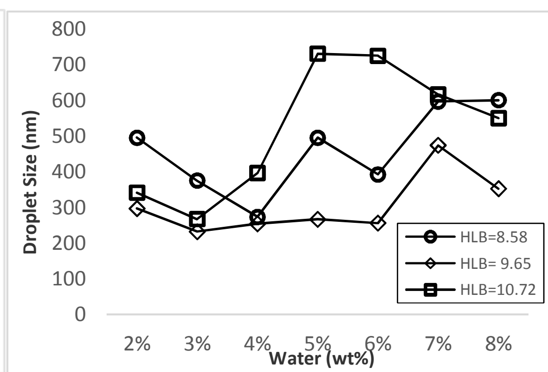

Fig 3. Droplet size of nano-emulsions as a function of water percentage (wt%). Surfactant HLB of the samples were fixed at 8.58, 9.65 and 10.72 respectively

3.3 *Stability Study*

Fig. 4 showed the nano-emulsions prepared for stability study. As seen, water-in-diesel nano-emulsions with 2 wt% of water is having the most transparent appearance. There was no change in size after 15 days of storage, it basically does not change much from its outside appearance.

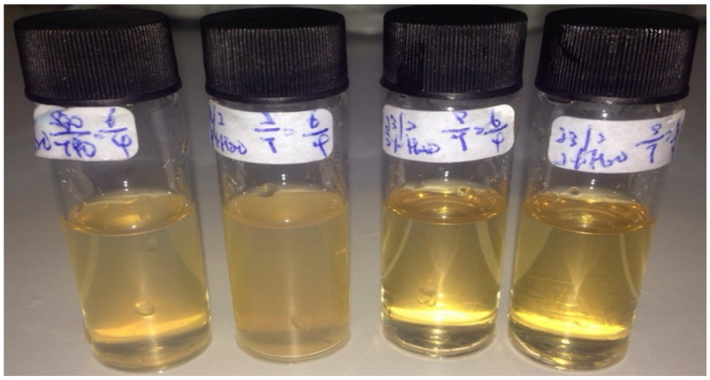

Fig 4. Water-in-diesel nano-emulsion at varying water wt%, i.e. 5 wt%, 4 wt%, 3 wt% and 2 wt% from the left

Fig. 5 shows a slight decrease for nano-emulsions prepared with 5 wt% water. Same observation was received for PDI measurement throughout 15 days of storage. **Fig. 6** shows nano-emulsions prepared with 4 wt% water. Except for the 1st day, the droplet radius and PDI remained almost unchanged throughout the study. In **Fig. 7**, though droplet size fluctuated since the 1st day, the droplet radius variation within small range between 39 nm to 41 nm. No significant droplet size reduction was observed, indicating that the sample was remained stable until the end of the study period. Fig. 8 shows the stability study of the nano-emulsion prepared with 2 wt% water. Among all, this is the most transparent sample with the lowest average droplets size, which remains at value no higher than 30 nm until the 15th day.

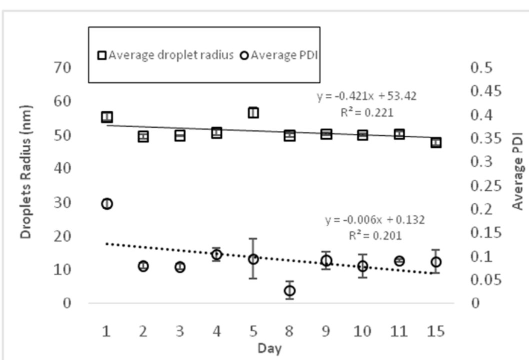

Fig 5. Stability of nano-emulsions with 5 wt% water (S20/T80=6/4, HLB = 11.16)

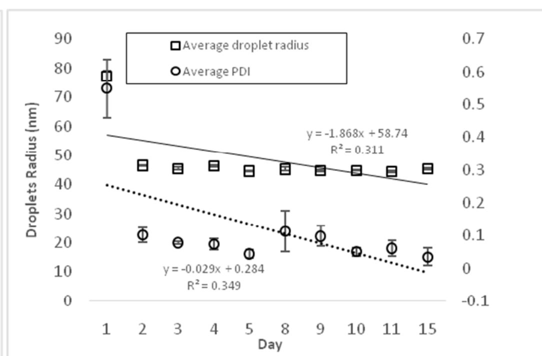

Fig 6. Stability of nano-emulsions with 4 wt% water (S20/T80=6/4, HLB = 11.16)

Fig. 9 is the Dynamic Light Scattering (DLS) measurement using Malvern zetesizer for water-in-diesel nanoemulsion throughout 10 days of storage. As compared to other formulation, this sample contribute a more significant trending in the reduction of droplets size. For stability study, it can be concluded that nano-emulsions containing higher water wt% would most likely contribute larger droplets size and lower stability during storage (Fig 10). Anyway, low PDI was obtained for all sample, good stability was confirmed after 15 days of study. It shows good evidence that blended surfactants are good candidate for water-in-diesel nano-emulsion formulation [6].

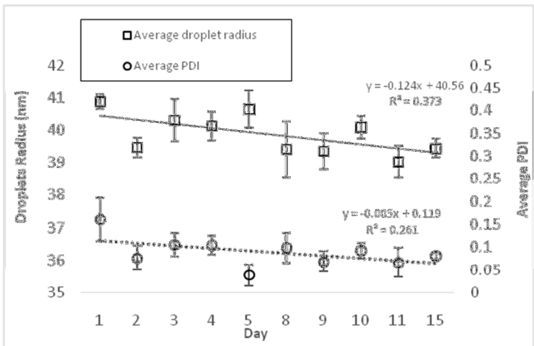

Fig 7. Stability of nano-emulsions with 3 wt% water (S20/T80=6/4, HLB = 11.16)

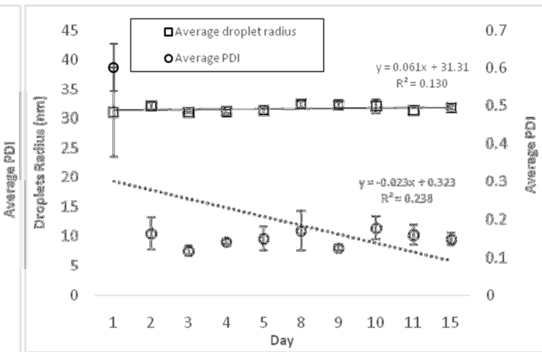

Fig 8. Stability of nano-emulsions with 2 wt% water (S20/T80=6/4, HLB = 11.16)

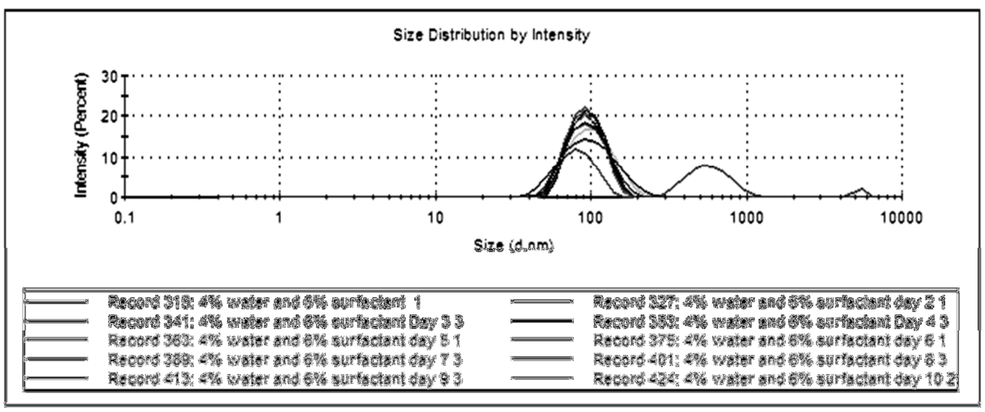

Fig 9. Dynamic Light Scattering (DLS) measurement for water-in-diesel nanoemulsion with 4 wt% water, throughout 10 days of storage

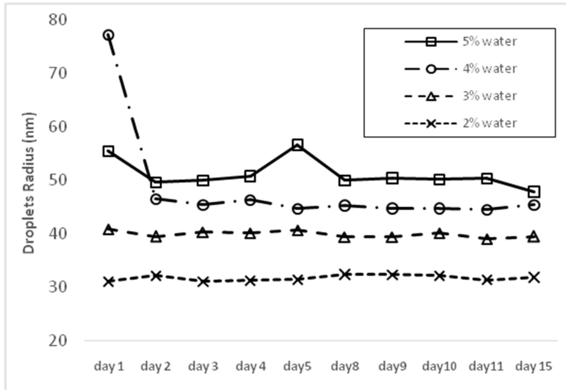

Fig 10. Stability of nano-emulsion with varying water content (S20/T80=6/4, HLB = 11.16).

4. Conclusion

Transparent water-in-diesel nano-emulsion had been successfully prepared using blended surfactants made of Span 20 and Tween 80. It had been proven that blended surfactant with HLB of 11.16 is the optimum to provide smallest possible droplets side, lowest possible PDI and the best physical stability. The increase of the surfactant wt% resulted in the formation of nano-emulsions, yet, suggesting bigger droplets once the maximum number of nanoemulsions was reached. The study also indicated that the droplet size of nano-emulsion increased with increase of water wt%. Short term stability study had been successfully conducted. Throughout 15 days of storage, water-in-diesel nano-emulsions with varying water content (2 wt% to 5 wt%) retain their good stability and no phase separation was observed. Among all, the droplet size of nano-emulsion with 2 wt% water and 6 wt% blended surfactants remained at 31.055 nm ± 4.23 % throughout the study.

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References

[1] Ali, M.A.A. and Kulchistskiy, A.R. "Influence of the structure of water in fuel nanoemulsion on diesel engine." *Fuel* 116 (2014): 703-708.
[2] Ahmad, M.I., Hirofumi, N., Hasannuddin, A.K. and Wira, J. "An overview of utilizing water in diesel nano-emulsion fuel nn diesel engine and its potential research study." *Journal of the Energy Institutue* 87 (2014): 273-288.
[3] Tharwat, T., Izquierdo, P., Esquena, J. and Solans, C. "Formation and stability of nano-emulsions." *Advance in Colloid and Interface Science* 108 (2004): 303-318.
[4] Nicolas, A., Jean-Pierre, B. and Patrick, S. "Design and production of nanoparticles formulated from nano-emulsion templates - A review." *Journal of Controlled Release* 128 (2008): 185-199.
[5] Noor Eldin, M.R., Sabrnal, H., EI-Hamouly, Mohamed, H.M., Marwa, R.M. and Ahmad, M.R. "Water in diesel fuel nano-emulsions: preparation, stability and physical properties." *Egyptian Journal of Petroleum* 22 (2013): 517-530.
[6] Noor El-Din, M.R., El-Gamal, I.M., El-Hamouly, S.H., Mohamed, H.M., Mishrif, M.R. and Ahmad, M.R. "Rheological behaviour of water-in-diesel fuel nano-emulsions stabilized by mixed surfactants." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 436 (2013): 318-324.