INTRODUCTION

The Release of the green house gases from the exhaust of diesel fueled vehicles has reached a noticeable level nowadays. As a result, climate change activities that embodied in the forms of heavy rains, acid rains, floods and hurricanes have been continuously threatening lives as well as properties. Hence the need for reducing green house gases and hazardous materials from diesel fueled machineries is still in demand (Bamgboye and Hansen, 2008; Mustafa canakci and Gerpen, 2001). Although diesel engines are commonly used in various applications, including agricultural, transport, industrial entities, yet they all share a common denominator which is high emission of greenhouse gases. Hence, more and more researches have been dedicated in finding a ways to abate these toxic emissions (Cheng-Yuan Lin and Shiou-An Lin, 2007). According to Energy policy Act, the order 12844 of 1992, the reduction of the use of petroleum based fuels, and the introduction of new environmental friendly fuels is highly recommended. With ever-increasing environment protection issues and stringent mandatory against greenhouse gases emission, researchers are constantly urged to look for new ways of energy sources that could cope with the legislations. Some of such alternative fuels are biodiesel, and emulsion fuel diesel (Ebna Alam fahd et al., 2013).

Emulsion fuel which is the focus of the current research is normally produced via mixing little amount of water to the commercial diesel fuel. The introduction of water to diesel fuel is believed to enhance the combustion and reduce the production of green house gases.

Very few researches have thus far conducted in the topic of emulsion fuel. Moreover, most of the researchers have focused their objectives on the burning efficiency and green house gases reduction capability. No much researches thus far investigated the changes in the properties of the emulsion fuel compared to the properties of the original commercial diesel fuel. Therefore, it is the objective of this research to investigate the changes in the physical properties (Cetane number, rheology and stability) of the diesel based emulsion fuel.

Emulsions: definition and classification

Emulsion refers to mixture of two immiscible liquids such as water and oil that are stabilized by specific surfactants (Richard F. Lee, 1999). Emulsions are categorized into either w/o when...
the oil is the continuous phase or o/w when water is a continuous phase. Technically, emulsions types are normally determined via observing the dispersability of the fresh prepared emulsion droplets when it is added to a volume of pure water in a test tube (Binks and Lumsdon, 2000). The addition of water to the diesel fuel (emulsion fuel) is believed to add value to the fuel, since water is assumed to disperse in the forms of small droplets suspended within the bulk fuel that can vaporize during combustion leading to more efficient combustion of fuel (Kadota and Yamasaki, 2002). Although stable emulsion can resist the splitting of the phases for certain period of time (shelf life), yet most of emulsions tend to separate back to their original phases gradually and slowly as time passes. The rate of separation of emulsion to its original phases with time is known as emulsion stability, a process which is normally assessed by recording the volume of phases (water or oil) separated (Sedimentation or creaming) from the emulsion as function of time (Souleyman et al., 2013).

Most emulsions are thermodynamically unstable, therefore given enough settling time, the small droplets would aggregate and form bigger ones which eventually flocculate and coalesce to larger ones (Manar el-sayed, 2012). Every coalescence process is normally a result of other main steps namely: Flocculation, film drainage, film thinning and film rupture (Abdurahman H. Nour and Rosli Mohd Yunus, 2006).

When an emulsion sample is left in shelf for certain period of time, the Attractive van der waals forces together with the gravitational forces would attract the neighboring Droplets toward one another until they attain congregated flocks (flocculation). The flocculated droplets are separated by thin film called interfacial film. The interfacial film is formed due to the balance of the attractive force driving the droplets together and hydrodynamic (resistance force) of the fluid captured in the gap. Given enough time, this fluid held in film starts to drain or flow out of the film (film drainage), if the repulsive forces are long ranged and weaker than attractive (van der waals forces) forces. After most of the fluid had drained out of the film, it would starts to shrink (film thinning). After all fluids and surfactants forced out of the film, the film shall torn and vanish away (film rupture). After film rupture, the two droplets merge together losing their identity and form one big droplet (coalescence) which is the last process, the same procedure happen to other droplets and leads them to form multiple flocks of bigger volumes. As time goes on, These cluster of flocks would coalesce to more bigger ones till their masses would exceed the gravitational forces and pull them out of the mixture as separate phase (sedimentation)(film thinning citation) (Dimiter N. Petsev, 2000)

Emulsions have the tendency to separate with time because of gravitational forces that tend to pull the heavier liquid particles downward. In the case of surfactant stabilized emulsions, when two droplets approach each other, the surfactant chains move away from the interface toward the bulk fluid leaving a gap that generates local region of almost pure continuous phase without surfactants, this makes the osmotic pressure in the fluid surrounding the particle pair exceeds that between the particles and pushes the particles to merge together (Kunio Furusawa et al., 2002). Surfactant molecules have the tendency to migrate at the interface whenever it is placed between two immiscible phases. Thus, the primary role of the surfactants is to reduce the interfacial tension between the two phases which leads to decrease on the surface mobility of the dispersed droplets leading to stable emulsions (Langevin et al., 2004). Beside the surfactants, other parameters such as mixing power (RPM) and mixing time also of paramount importance in synthesizing any experimental emulsions. To form stable water-in-oil emulsions, surfactant molecule must have larger hydrophobic regions and smaller hydrophilic regions, That is because every single water droplet needs to be encapsulated by gel like surfactant molecules that would stabilize the water droplets and hinder them from coalescence, and this would eventually leads to the increase in the viscosity and improves the stability of emulsions (Souleyman A. Issaka et al., 2013).

Regarding emulsion fuel, it improves the combustion efficiency and tremendously lower the emission of the toxic gases such as unburned HC, CO, CO2, NOx. The NOx reduction is believed to occur through the lowering of combustion temperature (Al-sabagh, 2012). Emulsion fuel is normally produced by mixing the diesel with pure water in the presence of emulsifying agent. One of the challenges facing emulsion industries is stability, since emulsion need to be assessed for shelf life compatibility before being sent to market. Generally heavy oil emulsions are categorized into four categories. Namely, stable, unstable, mesostable and entrained, each category has its own properties (Merv Fingas, 2009).

At high water content (droplet phase) stable emulsion generally can persists water resolution for at least 30 days, having viscosity of about double of the starting oil, and keeping almost 80% of the water unresolved. While unstable emulsion would not retain more than 10% water, and its viscosity is normally less than double of the starting oil. Indeed the meso-stable emulsion would lies between the aforementioned two categories. The entrained emulsion is not a true emulsion. It takes up around 45% of the water initially, then loses it gradually with time (Merv Fingas, 2009).

Emulsion stability is normally measured via the periodic monitoring and measuring the amount of clear phases separated out of the emulsion with time (Abdurahman H. Nour, 2010). The viscosity of water-in-oil emulsions are normally increased with increasing water volume fraction and decrease with increasing temperature (Abdurahman H. Nour, 2010). One important characteristics of any diesel fuel system is the cetane number. Cetane number is similar to octane number in gasoline indicates the fuel quality (Ingwald obernberger, 2004). It determines the readiness of the fuel to auto-ignite when injected into the engine, it is dependent on the composition of the fuel and affect the stability of the engine, noise level, and exhaust emissions (Ingwald obernberger, 2004). The cetane number for commercial diesel fuel is between 40 and 45 and that for biodiesel is between 45 and 67 (Klopfenstein, 1985). Adding water to fuel has the following attributes, Water vaporization maximizes the dispersibility of the fuel, water also scatter in the form of smaller droplets within the bulk fuel which in turn increases the contact surface between the fuel and air (enhance combustion), also during combustion water would form a high
pressure steam which induces micro-explosion (Enrico Carlo Fumagalli, 2013).

Water vaporization induces fuel atomization and mixing that would enhance the burning rate, reduces the amount of particulate matters (PM), and increases the likelihood of soot oxidation by the free OH radicals (Enrico Carlo Fumagalli, 2013). Also water is expected to decrease the flame temperature which reduces the temperature and pressure in the cylinder as well as NOx formation (Cherng-yuan lin and Kuo-Hua Wang, 2003).

Cetane Number

Cetane number is a very important parameter of diesel fuel, since it indicate the quality and readiness of diesel fuel to auto-ignite when injected into the engine. It is the time delay between when the fuel is first injected into the cylinder and when the ignition occurs. It is a very strong function of the composition of the fuel and can affect the engine stability and noise level (Gerhard Knothe, 2014). Although cetane number is conceptually analogous to the octane number for gasoline, yet it was reported that, compound with high octane number found to have low cetane number (Gerhard Knothe, 2014). Cetane number also used commonly as indicator for determining biodiesel fuel quality. It was reported that, the cetane number of the biodiesel fuel varies in accordance with the chemical composition of the feedstock (Gerhard Knothe, 2005). The cetane number of biodiesel was found to decreases with decreasing chain length, increased branching, and increased saturation as well as Iodine values. Higher cetane number indicates that the fuel will ignite faster than those with lower cetane values (Gerhard Knothe, 2005). Oliveira L. E and friends have investigated the effect of mixing different concentrations of biodiesel with petroleum based diesel fuel and their effect on the cetane number. However, they observed that the presence of biodiesel from Tilapia Viscera oil blended with petroleum diesel improves the cetane number (Gerhard Knothe, 2005). B. Freedman had studied the cetane number of homologous series of saturated n-alcohols in the range of C5 to C12 and C14, thus, they observed a linear increase in cetane numbers with increasing carbon numbers (Freedman and Bagby, 1990).

Yu A. Borisov and coworkers have investigated the octane number of water-in- gasoline emulsion sample. Results of the octane number measurement revealed that, as the water content of the emulsion increased, the octane number increased non-linearly. Furthermore, they found the octane number of the fuel is dependent on the octane number of the original fuel (Borisov et al., 1983). Thus far no one have studied the cetane number of the petroleum based emulsion fuels, therefore one of the objectives of this study is to investigate the cetane number of the emulsion fuel produced from mixture 20-80% water-indiesel fuel as function of time in comparison to the commercial diesel fuel.

Some literature on the previous emulsion fuels researches

One of the challenges facing the evolution of emulsion fuel is the stability. Especially at higher water contents, and that makes the emulsion fuel to poses very poor shelf life. Therefore, it is another objective of this paper to study the stability and shelf life based on several parameters including, viscosity as function of shear rate and time, water resolution as function of time, and cetane number as function of time as well. Viscosity of synthetic emulsion is mainly depends on, temperature, volume fraction of the dispersed phase, viscosity of continuous phase, shear rate, droplet sizes distribution and pressure (Rasha Mohammed Abd et al., 2014). A.I.Bamgboye and friends have developed a relation between the Fatty acid ester (biodiesel) composition and the cetane number via regression analysis methods, and came up with an equation to relate the cetane number to the weigh percentage composition of fatty acid methyl ester (biodiesel fuel). However, their results proved that, the predicted cetane number of the biodiesel agrees well with the measured cetan number values (Bamgboye and Hansen, 2008).

Cherng-yuan and friends have investigated the emulsification characteristics and fuel properties of the multiple emulsion systems (O/W/O), however they have identified the important parameters which could affect the multiple emulsion formulation. Thus, their results revealed the effect homogenizing speed which induced strong effect on the droplet sizes, and water to oil ratios which affected the viscosity (Cherng-Yuan Lin and Kuo-Hua Wang, 2004). Roy and coworkers have investigated the combustion performance and efficiency of three different diesel fuels namely, pure fossil diesel, biodiesel blended fossil diesel, and water blended (emulsion) fossil diesel. However, their results proved that water blended (emulsion) fossil diesel showed improved combustion followed by biodiesel blended fossil diesel then pure diesel (Roy J. Crookes et al., 1997) P. Schulz and colleagues have investigated the stability of emulsion fuel based on the INSEDEL method which describe the quality of emulsion based on visual observation as well as thermodynamic evaluation of the progress of the emulsion at given temperature (Schulz et al., 2004). Others have investigated the stability of nanoemulsion fuel based on droplets sizes, interfacial tension and water content, and emulsifiers’ consideration. Water content was varied as 5, 9 and 14%. Ultraturax pro 200, UAS homogenizer was used to provide the mixing energy which was 20000 rpm (Saelagh et al., 2011).

M. Ebna Alam Fahd and colleagues have conducted comparative test between base diesel fuel and 10% water mixed emulsion fuel performances on diesel engine, their results proved that 10% w/o emulsion fuel could reduce the exhaust gas temperature significantly at higher engine load as well as NOx and CO gases from the exhaust (Yang et al., 2013). M. Senthil and colleagues have investigated the use of animal fat, water and alcohol based emulsion fuel to derive diesel engine, however they reported noticeable improvement in engine performance and massive reduction in emissions (Senthil Kumar et al., 2006). Anders Andreasen and colleagues had conducted comprehensive investigations on developing water-in-diesel fuel emulsion for marine diesel engine fuel. Their objective was to reduce the emission of NOx and CO gases, and accordingly their result had showed noticeable
reduction in CO as well as NOx gases (Andres Andreasen, 2011). Others have studied the effects of the combined multiple emulsion as such w/o/w or o/w/o and NOx inhibitor agent to reduce the NOx emission from the combustion gases. Their results showed that aqueous ammonia would reduce the emulsion stability as well as kinematic viscosity and specific gravity (Cheng-Yuan Lin and Hsiu-An Lin, 2008; Cheng-Yuan Lin and Kuo-Hua Wang, 2004). Also Gonglun chen and friends have investigated the effects of different parameters on diesel emulsion stability. they reported the followings: The optimum dosage of emulsifiers is 0.5%, oil to water ratio was 50-50% respectively, stirring intensity was 250 rpm and emulsification temperature was 30°C (Gonglun chen, 2005). Similar results were reported by souleyman and colleagues who studied the stability parameter for decolorized crude oil. However, they found the optimal emulsifiers’ dosage to be 0.5%, rpm of 1600 and mixing temperature of 30°C (Souleyman A. Issaka et al., 2010).

**Methodology**

This section describes all the techniques, materials and procedures used to accomplish the objectives of the current research, thus the methodology shall be narrated in two sections namely material and methods.

**Materials**

The homogenizer type used in this study was IKA- stativ MAX. Load: 100kg SFH 150 ATEX. While the rheometer was Brookfield DV-III Ultraprogramable rheometer, S.N: RY80663. The cetane number was measured via SHATOX SX-200PORTABLE OCTANE METER. Commercial fossil based diesel fuel and surfactants were purchased from local companies.

**Methods**

Emulsion was prepared through by the agent in oil method mentioned earlier. According to this method, the emulsifying agent is first dissolved in the diesel and homogenized for 5 minutes then water was added little by little as the homogenization was going on. Homogenization was continued for total period of 2 hours. After that a sample of 1000 ml was put in i graduated cylinders for stability test, and other samples were taken for rheology measurement. The measurements were made in a daily bases for to total observation time of one month.

The stability test was performed by measuring the amount of water separated from the emulsion in a daily interval for one month.

The percentage of water or oil separated from emulsion was calculated using equation (1).

\[
V_w (%) = \frac{V_i - V_M}{V_i} \times 100 \quad \text{-------------------------------- (1)}
\]

Where:

\[ V_w (%) \]: percentage of water separation from emulsion

\[ V_i \]: Initial volume of water in the emulsion

\[ V_M \]: Measured volume of water

**RESULTS AND DISCUSSION**

Data of these experiments were collected from a series of measurement that is based on rheological properties and cetane number for a period of one month. Thereafter, the stability of the fuel emulsion was studied based on the water resolution. However the water resolution was measured in daily bases for one month. Both water precipitate and oil floating layers were read off.

**Viscosity of emulsion with aging**

In this section, the viscosity of emulsion was measured as function of the revolution (RPM) of the spindle (viscometer) for a period of one month. That is to observe the change in rheological properties with time. Figure 2 reveals data of viscosity of the emulsion fuel with respect to time, for duration of two weeks (14 days).
with the theory, which sates that shear rate have very minor effects on emulsion stability. Furthermore, the experimental results also revealed that, aging have very minor effects on emulsion viscosity. However, this is in accordance with results reported by Svetlana, who investigated the effects of aging on multiple emulsions (Aomari et al., 1998).

Similar trend was observed in Figure 4. Which shows the phenomena from day 28 to 33.

From these observation in Figures 2, 3 and 4, it is clear that aging does not affect the viscosity of the emulsion fuel within this particular period of one month. viscosity of emulsion fuel compared to original sample (diesel), and stability.

Indeed, its possible to conclude that for measuring the rheology of emulsion fuel, its advisable to set the spindle rotation beyond 100 (RPM), That is because the results of this study showed that the viscosity of the emulsion fuel had reached nearly stable plateau after the viscometer rpm reached 100 (Figures 2,3 and 4).

Figure 5 shows a rheogram of the of shear rate versus shear stress of emulsion fuel samples measured in different days. Results showed that emulsion had Newtonian behavior in the first day, and nearly newtonian afterward (day 7, 14, 21, 27, and 33), that means the rheology of the emulsion can to some extent be altered with aging, that might be due to the movement of droplets and flocks within the sample. Overall observation shows that almost all curves lead toward the origin confirming to somehow Newtonian behavior. Indeed the Newtonian behavior is obvious at low shear rate.
Figure 6 represents the effect of aging on the viscosity of the emulsion fuel as a function of shear rate. The variation in viscosity with shear rate was observed to be similar for all samples. Thus, Emulsion viscosities was observed to increase with shear rate at a low shear rate and reached their maximum values at shear rate of 41 s⁻¹. Soon after that, all viscosity curves seemed to have a constant plateau beyond shear rate 41 s⁻¹. This in a direct contrast to the previous observation given by Ong-Wook Ha and friends (Jong-Wook Ha et al., 1999), and that may be ascribed to the emulsion types.

Another important observation is that, there is a fluctuation in the values of viscosity with respect to time. For instance, the average viscosity of pure diesel fuel is 6.25 mpa.s, and the viscosity of the fresh prepared emulsion 8.1 mpa.s. This is normal since viscosity of emulsions is normally higher than that of their initial raw materials, but after one week, the average viscosity of emulsion had reduced to 5.8 mpa.s, this might be due to either the existence of biocontinuous emulsions or phase inversions. However, the trend was fluctuated slowly in the following weeks to 7.0, 7.7, 6.2 and 8.0 in days 14, 21, 27, and 33 respectively. This could be due to particles motions between the two phases while they were either sedimenting or floating.

Overall, the little variations in viscosity observed for these curves in Figure 6 proved that aging have little effects on emulsion fuel viscosity.

Stability assessment (water resolution)

Since most of emulsions are thermodynamically unstable, they all tend to resolve if sufficient time is given because of the effects of gravitational and hydrodynamic forces. Thus, emulsion stability is normally assessed via measuring the percentage of water/oil separated with time using Equation 1. Figure 7 shows the effect of aging on water/oil resolution from emulsion fuel.

![Figure 7. % of water/oil resolved from the emulsion vsus time (days)](image)

The phase resolutions were observed every day (24 hours intervals). Oil phase started resolving significantly from day 10, and progressively increased from below 1% in day 10 to 10% in day 30 and beyond. Regarding water separation, it started in day 25, and increased sharply from below 1% in day 25 to 8% in day 30 and beyond. Figure 8 shows a visual pictures of emulsion fuel samples, the left side picture is a freshly prepared emulsion in the first day, and the right side picture is the same sample after three days 3. From Figure 8 it was clear that, in the first day the sample was uniform, but separated into two distinct layers in day 3 (Figure 8).

![Figure 8. Picture of emulsion fuel sample (Day 1 and 3)](image)

Figure 9 is visualization of the emulsion after day 10. Beyond 10 days, emulsion appeared to be consisted of several regions (Layers). The upper part changed to gray and separated into two distinct layers. The uppermost layer (Layer 4) in Figure 9 claimed to be pure diesel, then followed by layer 3 which might be diesel mixed with some water drops (diesel rich emulsion).

![Figure 9. Emulsion fuel picture (Day 10)](image)

The down part also again split into two distinct layers, the down most layer (Layer 1) in Figure 9 is assumed to be a water rich emulsion and the light top layer (layer 2) is assumed to be a transition layer of sedimenting flocks. According to previous findings, the bottom layer might be a dense multiple emulsions of either (w/o/w or o/w/o) types, and sedimented surfactants particles merged together forming very stable jell like viscose liquid (Hong et al., 2003).
Beside that current authors suspected The upper layers may consist of water-in-oil microemulsions and excess oil phase, the lower layer may consists of oil-in-water microemulsion and excess water phases, while the middles layer could be a multiple emulsions and free water.

**Measured cetane number**

The effect of aging in the cetane number of the diesel emulsion fuel is reported in this part. Cetane number is of paramount importance in diesel quality, thus the variation in the cetane number of the prepared emulsion fuel in the course of time in comparison to the pure diesel fuel is investigated. Figure 10 shows the effect of aging on cetane number, it is obvious that water addition caused a major effect on the cetane number of the diesel, the values of the cetane number of the pure diesel was 56.9. While the cetane number of the emulsion fuel had an average value of 63.2.

![Figure 10. Water/oil resolution from the emulsion](image)

However, aging does not have much effects on the cetane number, sine the values kept fluctuating not too high above and below 63 until the last day of the observation. This result would emphasise the idea that fuel with high cetan number have shorter ignition delay, hence here no cetane improvers are required.

**Conclusion**

The stability and rheologival properties of the emulsion fuel was investigated in this experimental study. The 20-80% emulsion fuel was found to have viscosity range from 5.5-9 mpa.s, hence 20% water had increased the viscosity from 5.5 mpa.s in the original commercial diesel to as high 9 mpa.s in the emulsion fuel samples. Stability study showed that, there was a lesser distinct phase separation, but rather a regions of oil rich mixture at the top, and water rich mixture at the bottom. The percentage of pure water and oil separated were 7 and 10% respectively within the period of one month. Regarding Cetane number the water mixed 20-80% water-in-diesel emulsion had cetane number of 63.2, that is greater than the original commercial diesel cetane number. Since the original cetane number in the commercial diesel is 56.9. Aging shows very minor effects on the values of the cetane number, since most of the measured values were beyond 62.

Although from visual qualitative standpoint, aging have no much effect on the measured characteristic of the emulsion fuel, yet visually the fuel had shifted from pure milky white color in the beginning to multiples layers along the way and to completely gray at the end.

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**REFERENCES**

Al-sabagh, A. M. Water-in-diesel fuel nano-emulsion drop size and stability, and emission characteristics, J. of Surfac Deterg (2012); 15:139-145
Andres Andreasen, Water-in-fuel emulsion as marine engine fuel for reduced Nox and particulate emissions, Danish ministry of the environment, environmental project No. 1380 (2011)
Bamgboye A. I., A. C. Hansen, prediction of cetane number of biodiesel fuel from the fatty acid methyl ester (FAME) composition, In Agrophysics, (2008); 22:21-29.

Enrico Carlo Fumagalli. Emulsion of diesel oil and water, WO 2013098630A1

Freedman B., M. O. Bagby. Predicting cetane numbers of n-alcohol and methyl esters from their physical properties, JAOCs, (1990); 67:565-571.


Gonglun chen. An experimental study of stability of oil-water emulsion, J. of Fuel processing technology, (2005); 86:499-508


Ingwald obernberger, Gerald Thek. Physical characterization and chemical composition of densified biomass Fuels with regard to their combustion behavior, Biomass and Bioenergy, (2004); 27:653-669.


Kadota T., H. Yamasaki. Recent advances in the combustion of water fuel emulsion, progress, in energy and combustion science (2002); 28:385-404

Klopfenstein, W. E. Effect of molecular weight of fatty acid esters, on cetane number as diesel fuels JAOCs, (1985);62:1029-1031


Langevin, D., S. Poteau, I. Henaut and J. F. Argillier, crude oil emulsion properties and their application to heavy oil transportation, Journal of Oil and Gas Science and Technology, (2004); 59:511-521


Mustafa canakci, J. V. Gerpen. The performance and emision of a diesel engine fueled with biodiesel from yellow Grease and soybean oil, An ASAE meeting presentation (2001); 01:60-50.

Rasha Mohammed Abd, Abdurahman H. Nour and Ahmad Ziad Sulaiman. Experimental investigation on dynamic viscosity and rheology of water-crude oil two phases flow behaviour at different water volume fractions, American Journal of Engineering Research (2014) (AJER);3:113-120


Souleyman A. Issaka, Abdurahman H. Nour, Rosli M. Yunus, and Azhary H. Nour, Journal of Applied Science, ISSN 1812-5654


