Physicochemical and FTIR Study of Diesel-Hydrogen Peroxide Fuel Blend

Muhammad Saad Khan¹, Iqbal Ahmed²,³, Bhajan Lal¹, Al-Amin Idris¹, Muhammad H. Albeirutty², Muhammad Ayoub¹, Suriati binti Sufian¹

¹Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Tronoh, Perak, Malaysia.
²Center of Excellence in Desalination Technology, King Abdulaziz University, P.O. Box 80200, Jeddah 21589, Saudi Arabia.
³Faculty of Engineering - Department of Mechanical Engineering, King Abdulaziz University, P.O. Box 80200, Jeddah 21589, Saudi Arabia.

*Corresponding author. Tel.: +0-060-17-9486804; E-mail address: khansaad@gmail.com; bhajan.lal@utp.edu.my

Abstract. Physicochemical properties of combustion fuels play a key role in determining the qualitative and quantitative characteristics, reliability and health effects associated with emissions. This paper reports the preparation of polysaccharide (PS) based emulsifier for stable blending of petroleum diesel-hydrogen peroxide (H₂O₂) and investigated the influence of H₂O₂ as diesel fuel blends on the physicochemical properties and characteristics. The quantity of PS-emulsifier was kept at 5 volume % (vol. %) and the volume ratio of H₂O₂ were varied 5-15 vol. % to reference diesel (RD), respectively. The blended diesel/H₂O₂ fuel were prepared under inert oxygen (O₂) gas closed heating system; afterthought, physiochemical properties of diesel/H₂O₂ blend were evaluated at standard ASTM D-975 testing method. The kinetic properties show the interaction of RD and H₂O₂ blend at presence of PS emulsifier which exhibit the phenomenon to diminish the interfacial tension among the two different phases to form a homogenized stable solution. Results revealed that H₂O₂ is capable of enhancing the diesel fuel properties and showed that the addition of H₂O₂ in a diesel fuel blend are lied within the ranges of standard ASTM D-975. Due to further oxygen atom present in H₂O₂, it can facilitate the combustion process which ultimately effect on exhaust emission.

Keywords: ASTM test, diesel, FTIR, H₂O₂, physicochemical properties and PS emulsifier

1. Introduction
After the foremost breakthrough invention in 19th century by Rudolf Diesel made an invention in the field of internal-combustion engines (ICE). Ever since this invention, petro- diesels have been a vital fuel in energy generation and power of engineering equipment all around the world [1]. Diesel derived engines were turned out to be extremely productive in terms of supplying the required energy levels for their utilization use at very low working (operational) and maintenance costs when contrasted to
other power generation machines. In reality the flow has dramatically switching from a gasoline
driven world economy towards the diesel based world economy. Generally, petroleum derived diesel
includes around 75% of saturated hydrocarbons (primarily paraffin’s including n, iso, and
cycloparaffins), along with 25% aromatic constituents (including alkylbenzenes and naphthalenes).
The approximate range of hydrocarbon in diesel fuel are from C_{10}H_{20} to C_{15}H_{28} with average chemical
formula of common diesel fuel is C_{12}H_{23}, [2].

However, crude diesel fuel produces major hazard of a variety of types of air pollutant emission
with adverse environmental impact especially on the urban air quality in the form of harmful oxides of
nitrogen (NOx), carbon monoxide (CO), Particulate matter (PM), and other carcinogenic compounds
[3]. Even though ULSD (blended diesel) diesel engine exhaust produces crowd of destructive
materials including airborne carbon soot, PM, polycyclic aromatic hydrocarbons, toxic metals, carbon
dioxide (CO\_2), CO, NOx which persuade ozone formation along with volatile organic compounds
includes acroleine and formaldehyde [4]. Concerns over the availability, price and carbon emissions
from petroleum sources are among major concerns which provide motivation for the research on
alternative sources, especially for automobiles fuels [5].

Various types of fuels had investigated in recent years for improving the quality and performance
of diesel fuel. Principally for the decrease of released pollutants; researchers have engrossed their
importance on the fuel modification techniques. For instance, the use of alternative fuels; frequently in
fumigated form or gaseous fuels of renewable nature that are considered as environmentally friendly
in nature [6]–[11] or oxygenated compounds as fuels, that display the capability to diminish hazardous
pollutants, specially particulate emissions [12]–[17]. Lot of attention has given on alternative fuel with
superior physiochemical properties for protecting environmental and enhancing the fuel efficiency aspect,
especially alcoholic fuels. In alcohols, principal attention has given to ethanol fuel because of
its admirable properties [18]–[24]. Methanol (M100) had looked into as an alternative diesel fuel for
used in heavy-duty vehicles [25]–[28]. Blends of methanol and ethanol used in gasoline, with a focus
on blends contained 85% alcohol (M85 and E85) [29] were evaluated as alternative light-duty vehicle
fuels. To attain substantial reductions in emissions, it is believed that, reformulation of diesel fuel
properties has play a very significant role. The reformulation of diesel fuels embrace; lowering of the
aromatic and sulfur contents, or addition of the potential oxygen carriers within the fuel. It has been
revealed that, numerous oxygenates are quite effective in dropping particulate emissions from diesel
engines sources. For that reason, considerable research has attentive on selection of oxygenative fuel
additives including alcohols, ethers and esters.

Hydrogen peroxide (H\_2O\_2) is light blue liquid, somewhat more viscous than water, which seems
colorless in dilute aqueous solution. It’s weak acid which possess strong oxidizing and bleaching
properties. Recently few of the researches explore the oxidative nature of H\_2O\_2 as oxidizer which
could provide additional oxygen during fuel combustion process in the internal combustion (IC)
engines. H\_2O\_2 also possesses higher cetane value (125) as reported by Ashok and Saravanan [16],
[30]. This agreement has also proven by the recent study fr om Yusuf et al.,[17] in their thermal
evaluation of diesel-H\_2O\_2 fuel blend.

Chemical Equation
H\_2O\_2 spontaneously decomposes (disproportionate) exothermically into oxygen and water:
H\_2O\_2 \rightarrow \frac{1}{2} O\_2 + H\_2O (steam) + heat

(1)

This is thermodynamically favorable process has a \(\Delta G^o\) of \(-119.2\) kJ/mol\(^{-1}\) with \(\Delta H^o\) of \(-98.2\)
kJ/mol\(^{-1}\) along with \(\Delta S\) value of 70.5 J/mol\(^{-1}\)K\(^{-1}\). The rate of H\_2O\_2 decomposition are depends upon
certain things which includes temperature, concentration of the H\_2O\_2, pH and along with presence of
stabilizers and impurities.

H\_2O\_2 decomposes in presence of catalyst at ordinary temperature produce water in the form of
steam and gives free half mole of oxygen with enormous amount of heat that could enhance the
efficiency of the diesel engine. This excess oxygen will also decrease the emission of carbon
monoxide (CO) because it converts CO into carbon dioxide (CO\_2). For Diesel, Equation becomes:
\[ 2\text{C}_{12}\text{H}_{26} + 37\text{O}_2 \rightarrow 24\text{CO}_2 + 26\text{H}_2\text{O} \text{(steam)} + \text{heat} \] (2)

This reaction requires an air fuel ratio of 20:1. It means for every mole of diesel requires 20 moles of air. Appropriate air fuel ratio and composition of \( \text{H}_2\text{O}_2 \), would increase the lean operation limit, improve the lean burn ability and will decrease the exhaust emission of compression ignition engine. Thus, based on above hypothesis in this project, introduction of \( \text{H}_2\text{O}_2 \) as blend for diesel were carried out experimentally. Various compositions of \( \text{H}_2\text{O}_2 \) were tested in order to enhance the properties of diesel, starting from lean crude diesel until obtaining optimum condition. Polysaccharide based emulsifier reduces the surface tension between the diesel and \( \text{H}_2\text{O}_2 \) and stabilizes the blend for the longer period.

2. **Experimental Design & Set-Up**

2.1. **Material**
Reference diesel fuel (commercial diesel) was obtained from PETRONAS Sdn Bhd and Table 1 shows the physical properties of commercial diesel fuel that was used in this study. Commercial grade \( \text{H}_2\text{O}_2 \) (30%) was obtained from Chemical Company of Malaysia Berhad (CCM). Commercial grade acetone (98.8%) was purchased from university registered supplier. Polysaccharide (PS) bio-polymer (contain hydrophilic and lipophilic properties) were purchased from Merck. Laboratory characterization equipment have utilized to complete characterization for the physical and chemical properties of each material (except PS) at room temperature (25±1°C); and the comparisons were made with their corresponding literature values. The comparisons results are summarized in Table 1. Prior to the measurements, all liquids were partially degassed under vacuum before experiments. Then, the densities of each material and blend fuels all the mass measurements were performed by using an electrical balance (Dhona 200 D, India) accurate to 0.0001mg. All apparent masses were corrected for buoyancy. The densities of each liquid (RD, \( \text{H}_2\text{O}_2 \), and acetone) were measured with a bi-capillary pycnometer which gave an accuracy of 5 parts in 105.

2.2. **Preparation of emulsifier and diesel/\( \text{H}_2\text{O}_2 \) fuel blend using closed heating technique**
The emulsifier was prepared beforehand mixing of reference diesel (RD) and \( \text{H}_2\text{O}_2 \) diesel fuel blend which briefly described in our earlier work [17].

2.3. **Properties of Diesel Fuel Blends**
Laboratory experiments were performed to more completely describe the physical and chemical properties of stable diesel/\( \text{H}_2\text{O}_2 \) blend emulsion in presence of PS emulsifier. ASTM D-975 testing method was adopted using diesel test standard to determine the following properties; density (ASTM D-1298), viscosity and kinematic viscosity (ASTM D-445) and FTIR characterization. Table 1; describe the literature and experimental values of components of the fuel in accordance with ASTM D-975 diesel fuel testing method.

3. **Results and Discussion**

3.1. **Influence of \( \text{H}_2\text{O}_2 \) on density of the fuel blend**
The density of diesel fuel varies between 0.81 and 0.89 g/cm\(^3\). In this work, the densities of prepared blend fuel were laid between these values. Since, density was much easier to model over wide temperature ranges for most liquids including fuels. PS emulsifier possess the lowermost density of 0.6123g/cm\(^3\) amid the different component, while \( \text{H}_2\text{O}_2 \) density is 1.130 g/cm\(^3\) which having a higher value than pure diesel fuel (see Table 1). The density of the RD and each diesel/\( \text{H}_2\text{O}_2 \) fuel blends at different temperatures shown in Figure 1. It can be observed that as the vol. % of \( \text{H}_2\text{O}_2 \) in the diesel fuel blends was increases, the density also increases. However, the density difference of each blend
was about 0.89-1.3% higher than RD. Yet, the difference of each fuel blend density was lying within the ASTM D-1298 standard and the difference of blend diesel was not too high as what we expect due to higher water concentration in H\textsubscript{2}O\textsubscript{2}, which was almost 1.3 times higher than RD. Consequently, the density of the higher concentration of H\textsubscript{2}O\textsubscript{2} in diesel blend increases a bit higher particularly at 13 vol.%–15 vol.% of H\textsubscript{2}O\textsubscript{2}. However, for the concentration of 5 vol.% to 8 vol.%. Results from Figure 1 shown that the density decreased less as compared to higher concentration of H\textsubscript{2}O\textsubscript{2} in diesel.

The obtained results suggested that the presence of PS based emulsifier addition had the important impact on diesel blend density and stability due to its hydrophilic and hydrophobic balance which is significantly participate to diminish the interfacial tension among polar and non-polar to formulate homogenized solution. Nevertheless higher density of diesel/H\textsubscript{2}O\textsubscript{2} fuel blend proven as a good agreement of higher cetane number several researchers were also reported same tendency [5], [31]. Figure 1 were also established that the density of the fuel blends dependent on temperature variations. With temperature increase, the densities of the fuel blends decreasing. Similar results were seen for conventional diesel and neat biodiesel [32].

### 3.2 Properties of Diesel Fuel Blends

Usually, the viscosity of diesel fuel usually varies 2-5 cP. In this experimental work, the viscosities of blend fuel have laid well between these values. The value of viscosity of R.D is 4 cP. PS Emulsifiers possess the maximum kinematic viscosity value of 17 cP among the individual components [5]. H\textsubscript{2}O\textsubscript{2} having a viscosity value of 1.2 cP, which was minimum value of all the constituents of the blend fuel. The experimental values of viscosities of R.D and diesel fuel blends at various temperatures presented in Figure 2.

**Table 1: Comparison of physical properties between experimental and literature of each materials used in this study**

| Physical Properties | PETRONAS Diesel (R.D) | H\textsubscript{2}O\textsubscript{2} (30% conc.) | Acetone | PETRONAS Diesel (30% conc.) | H\textsubscript{2}O\textsubscript{2} | Acetone |
|--------------------|-----------------------|----------------------|---------|--------------------------|-----------------|---------|
| Chemical Formula   | C\textsubscript{12}H\textsubscript{25} | H\textsubscript{2}O\textsubscript{2} | C\textsubscript{6}H\textsubscript{6}O | – | – | – |
| Density (kg/m\textsuperscript{3}) | 827.98±0.2 | 1128.87±0.2 | 790.95±0.2 | 830 | 1130 | 791 |
| API gravity | 37.257 | – | – | 0.83 | 1.113 | 0.791 |
| Viscosity (centipoises) at 27°C | 3.78±0.2 | 1.223±0.2 | 0.313±0.2 | 3.9 | 1.245 | 0.322 |
| pH | 4.000 | 3.20 | 7.2 | – | 3.22 | 5-6 |
| Boiling Point (°C) | 287±0.5 | 148±0.5 | 56.5±0.5 | 180-330 | 150.2 | 56-57 |
| Flash Point (°C) | 88 | – | -17.5±0.5 | 52-96 | – | -17 |
| Fire point (°C) | 97.5 | – | -13.015 | 68-116 | - | -12 |
| Cetane Number | 49±0.5 | 120±0.5 | 7±0.5 | 50 | >125 | – |
| Refractive Index at 22°C | 1.476 | 1.348 | - | 1.4798 | 1.355 | 1.358 |
| Surface tension (cm\textsuperscript{3}/dynes) at 22°C | 23.810 | 73.897 | 26.062 | 23.721 | 74.218 | 25.23 |
| Self-ignition Temperature (°C) | – | – | – | 200-420 | 160 | 465 |
| Stoichiometric air/fuel ratio (wt. /wt.) | – | – | – | 14.6 | 11.1 | – |
| Lower heating value (MJ/kg) | 44 | 33.9 | 29.9±0.5 | – | – | 30.86 |
| Specific heat capacity (J/kg°C) | 1851.22±0.5 | 2335±0.5 | 2089±0.5 | 1850 | 2019 | 2175 |
The effects of temperature on diesel/H$_2$O$_2$ density were presented over the temperature range of 15°C to 60°C. The viscosity of each fuel blends are reduces with increased the amount of H$_2$O$_2$ in the blend due to higher contents of water of H$_2$O$_2$ along with lesser viscosity. However, all the viscosities of the fuel blends showed very close values to each other, similar trend also observed at various temperature levels. Hypothetically, the viscosity of the blends fuel approach to be decreased, in comparison with the diesel fuels as the H$_2$O$_2$ concentration increases in the fuel blend [5], [33], [34].

3.3. Influence of H$_2$O$_2$ on density of the fuel blend
Kinematic viscosities are a very important role for determination of kinetic properties of the blend like excess energy of activation and excess viscosities of fuel blend [17]. Usually, the kinematic viscosity of diesel fuel usually varies 2-6 cSt (mm$^2$/s). In this work, the kinematic viscosities of blend fuel have laid well between these values. The value of kinematic viscosity of RD is 5.5 cSt at ambient temperature. PS emulsifier possess the maximum kinematic viscosity value of 17 mm$^2$/s among the individual components while, H$_2$O$_2$ having a kinematic viscosity value of 1.10 mm$^2$/s, which was minimum value of all the constituents of the blend. The experimental values of kinematic viscosities of RD and fuel blends have presented in Figure 3. Results revealed that, as the quantity of H$_2$O$_2$ in the blends upsurges, oxygen contents improved due to the peroxiding nature of H$_2$O$_2$, although viscosity, density and high heat value was decreased slightly. Generally, it already known that higher density and lower viscosity leads to higher flow, thus, these results suggested that the lower viscosity of diesel/H$_2$O$_2$ blend fuel could succeed to lower fuel injection with an early ignition time. Moreover, the drop of viscosity of each stable blend as compared to RD and lower concentration of H$_2$O$_2$ in fuel blends observed due to the higher molar ratio of peroxiding group. It also suggested that the 70% water content of H$_2$O$_2$ were formed water droplet inside the diesel and these droplet were mixed well due to PS emulsifier, thus the viscosity of blend fuels were lower than RD. In addition, all the diesel-H$_2$O$_2$ blends possess densities and viscosities data which are quite acceptable for the standard limit for diesel fuels. These results indicate the same trend as those of prior efforts [5], [15], [35]. Additionally, the effects of temperature on diesel/H$_2$O$_2$ density were displayed in Figure 2, over the temperature range of 15 °C to 60 °C. The kinematic viscosity of each fuel blends are decreases with increased the amount of H$_2$O$_2$ in the blend due to higher contents of water of H$_2$O$_2$ value 1.110 (Pa.s). However, the kinematic viscosities of the blends showed very close values to each other. Similar trend were also
observed at various temperature level. Hypothetically, the viscosity of the blends approach to be decreased those of the diesel fuels as the H$_2$O$_2$ concentration increases in the fuel blend.

3.4. Influence of H$_2$O$_2$ on density of the fuel blend

The significance of absorption phenomenon on the radiation scattering of the fuel droplets in diesel devices is among an interesting fuel research area. This phenomenon indirectly affects fuel evaporation and heating capabilities, which directly affect the auto-ignition of fuel vapors. Fourier Transform Infrared (FTIR) Spectroscopic analyses were conducted to determine the presence of H$_2$O$_2$ in all fuel blends. Following Figure reflects the trend of RD compare with various percentages of H$_2$O$_2$ in diesel fuel blend such 0 vol.% H$_2$O$_2$, 5 vol.% H$_2$O$_2$, 10 vol.% H$_2$O$_2$, and 15 vol.% H$_2$O$_2$, respectively and combined results presented in Figure 4. From Figure 4 it was observed that the infrared rays reflected greater peaks level when increases the amount of H$_2$O$_2$ due to strong electronegativity of H$_2$O$_2$ [4]. The experimental data of density and viscosity were showing a good agreement to explain the greater peaks levels of diesel blend fuels. In addition, H$_2$O$_2$ showed a definite trend in peak like in 1st region around 3850-3700 wavelength, where addition of H$_2$O$_2$ enhances the peak concentration due to higher OH molecules presents in the H$_2$O$_2$. In 2nd region that ranges between 2900-2750 which has shown a increments in peaks as 15 % H$_2$O$_2$ have a very clear indication of peak shown the functional group of Saturated aliphatic (alkanes/alkyl) group frequencies which are the essential constituents of diesel fuel. 3rd region has belongs to a functional group of frequencies for thiols or thio-substituted molecules which have a range between 2650-2500; mainly due to an occurrence of inorganic mixtures in the shape of amino and ammonium based compounds or salts of carboxylic acids in the form of Polysaccride [33], [34]. These peaks verify the presence of the emulsifier. However, FTIR result also proved that the H$_2$O$_2$ present in the diesel fuel blend causes the enhancement of the OH and oxygen contents for the diesel fuel blend; other regions also strongly indicate presence of H$_2$O$_2$ significantly enhances the peaks of hydrocarbons.

![Figure 2: Viscosity (cP) of H$_2$O$_2$ vol. vol. %, in diesel blend at various temperatures](image-url)
Figure 3: Kinematic viscosity (cSt) of various vol. % of H$_2$O$_2$ in diesel blend at different temperatures

Figure 4: Comparative FTIR Spectrums of diesel and blend fuel

4. Conclusion

In this experimental study, influence of the addition of H$_2$O$_2$ with diesel fuel has been carried out using various compositions of diesel fuel blend. The results of physicochemical characterizations found in accordance with ASTM D-975 which showed that addition of H$_2$O$_2$ in a blended form lied within the ranges of standard diesel fuel (compared RD fuel). Fourier Transform and Infra-Red (FTIR) results were also illustrated the spectroscopic presence of H$_2$O$_2$, which proved the enhancement of the hydrogen and oxygen contents in diesel fuel blend.

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