*Journal of Oil Palm Research Vol. 20 December 2008 p. 571-576*

# WATER-IN-OIL EMULSION OF PALM BIODIESEL

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## ABSTRACT

*Emulsification technique is one of the most significant approaches to the reduction of pollutant emission of diesel engines. In this research, water-in-oil emulsion of palm biodiesel was prepared by mixing palm biodiesel and water in the presence of emulsifier. For experimental purposes, different types of emulsifiers were screened for their effectiveness in stabilizing the emulsion system. The results of the experiment showed that the polymeric surfactant was found to be the most suitable emulsifier for palm biodiesel emulsion. It was also found that the stability of the emulsion system was increased by increasing the mixing speed. Even though the preliminary engine test showed significant reduction of nitrogen oxides ($NO_x$) emission, data from this research also showed that the calorific value of the fuel also decreased with the increase of water content in the formulation.*

**Keywords:** biodiesel, emulsion, fuel, water-in-oil, pollutant.

**Date received:** 19 March 2008; **Sent for revision:** 13 May 2008; **Received in final form:** 13 August 2008; **Accepted:** 5 September 2008.

## INTRODUCTION

One alternative pollution measure is operating internal combustion engines on an emulsified fuel (Lin and Wang, 2003; Gunnerman, 2003). Emulsified fuels, which have been used since the 1960s, use a carbonaceous or petroleum derived fuel such as diesel, gasoline and other types of fuel which were mixed with a non-carbonaceous component like water. When the carbonaceous fuel is mixed with larger quantities of water, the emulsion is called a water-based emulsion. When water is mixed into a larger quantity of carbonaceous fuel, the emulsion formed is a fuel-based emulsion (Lin and Wang, 2004).

Many researchers who study emulsions as a form of pollution control measure found that it is more difficult to implement water-based emulsions than fuel-based emulsions. This is because internal combustion engines - which run on water-based emulsions - must be re-engineered in order to run on such type of emulsion. Since water-based emulsions are corrosive to an engine's internal components, such emulsions require agents to enhance lubricity and to operate without significant power loss. Therefore, engines have to be modified to handle the large quantity of water present in the emulsion (Gunnerman, 2003).

Oil-based emulsion fuels, on the other hand, generally do not require any substantial modification of the engine (Gunnerman, 2003; Hori *et al*., 2002). This is because they are not considered to be more corrosive on engine parts or system than regular fuel. Furthermore, due to the presence of water during the combustion process, the resulting combustion emissions from emulsion fuels contain lesser amounts of harmful pollutants. Although emulsion fuel has been used to reduce engine emission (Lin and Wang 2004; Torres and Zamora, 2002), most previous relevant applications were restricted to emulsion-based petroleum diesel (Lin and Wang, 2004). Therefore, the objective of this work is to develop palm biodiesel emulsion system.

## MATERIALS AND METHODS

### Materials

Palm biodiesel was prepared using the Malaysian Palm Oil Board (MPOB) pilot plant. Typical compositions are 45% of $C_{16}$ methyl esters, 5% of $C_{18}$ methyl esters, 39% of $C_{18:1}$ methyl esters and 10% of $C_{18:2}$ methyl esters (Choo *et al*., 1995). Tween 60 (polyoxyethylene sorbitan monostearate, W60), Tween 80 (polyoxyethylene sorbitan monooleate,

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W80), Span 20 (sorbitan monolaurate, O20) and Span 60 (sorbitan monostearate, O60) were purchased from the Malaysian Oleochemical Company. Polymeric hydroxystearic acid (DHSA) surfactants (P1, P2, P3) were prepared in our laboratory by reacting DHSA or DHSA-estolide with polyhydric alcohol.

### Emulsification Process

Emulsions were prepared by mixing the palm biodiesel, water and emulsifier - using a homogenizer (Model Ultra Turax T25, Ika Labortechnik). This palm biodiesel which contained emulsifier was pre-heated at 50°C. A required amount of water was then added into the oil phase and this mixture was mixed for 5 min at the adjusted speed of 200 to 1300 rpm.

### Measuring the Stability of the Emulsions

The prepared emulsions under different conditions were tested for their stability by transferring each type of emulsion into a 25 ml graduated test tube. The degree of separation was observed everyday for seven days. Any formation of different layers such as water layer, sediment layer, emulsion layer and oil layer were recorded. The volumetric proportion of each layer was defined as the volume ratio of each layer to the total emulsion in the test tube. The emulsion stability was then defined as the volume ratio of the emulsion layer to the total volume in the test tube.

The dynamic viscosity of the freshly prepared emulsions was determined by a Brookfield viscometer (Model LVT). Each emulsion sample was transferred to a double jacketed glass cell which was connected to a thermostatic circulating water bath. The thermostat was adjusted at the measuring temperatures. The spindle type and the rotational speed were selected according to the viscosity of the emulsion.

### Determination of Pour Point

The pour point of the emulsions was determined by an automatic Pour Point Analyser (model ISL-CPP97-2); in accordance to the ASTM D-97 standard method.

### Determination of Energy Content

Gross energy content, or heat of combustion of all fuels, was determined according to ASTM method D240-92. A LECO AC 350 automatic oxygen bomb calorimeter (LECO Corporation, Michigan, USA) was used.

### Determination of Exhaust Gas Emission

A horizontal, four stroke, four-cylinder Isuzu 4FB1 diesel engine was used in the experiments without any modification. The engine specifications were: type, Isuzu 4FB1, 4-cylinder, 4-stroke, indirect injection; cooling, water; swept vol/stroke (litre), 1.817; bore (mm), 84; stroke (mm), 82; compression ratio, 20; nominal power output (kW) at revolutions/min, 39 at 5000. A variable speed range from 1500 to 3500 rpm with 50% throttle setting was selected for all tests. A Bosh gas analyser (model ETT 008.36) was used to measure HC and CO emissions. A Bacharach (model CA300NSX) analyser (Standard version, k-type probe) was used to measure $NO_x$ concentration.

## RESULTS AND DISCUSSION

In consistence with the objective of this research, various factors that may affect emulsion stability were analysed. Factors which were taken into consideration were: emulsifier used, water content, mixing speed, mixing time and surfactant concentration.

### Screening of Emulsifier

Seven potential emulsifiers were evaluated for the production of water-in-oil emulsion of palm biodiesel. Based from the observation, PEG dipolyhydroxystearate, P3, was the most suitable emulsifier to stabilize the palm biodiesel water-in-oil (W/O) emulsion system (*Figure 1*). Therefore, P3 was selected as the emulsifier for further research.

### Effects of Water Content on the Stability of the Emulsion

The effects of water content of the emulsion on its stability, pour point and viscosity were also investigated. From *Table 1*, it is clear that the stability of the emulsion remained unchanged after being stored for seven days - at room temperature (RT) – for the system contained 2%-5% water. However, for

**TABLE 1. STABILITY AND POUR POINT OF THE EMULSION WHICH CONTAIN DIFFERENT AMOUNT OF WATER CONTENT AFTER SEVEN DAY STORAGE AT ROOM TEMPERATURE**

| Water content (%) | Emulsion stability (%) | Pour point (°C) |
|---|---|---|
| 2 | 100 | 6 |
| 5 | 100 | 12 |
| 7 | 96 | 12 |
| 10 | 90 | 14 |
| 20 | 83 | 14 |

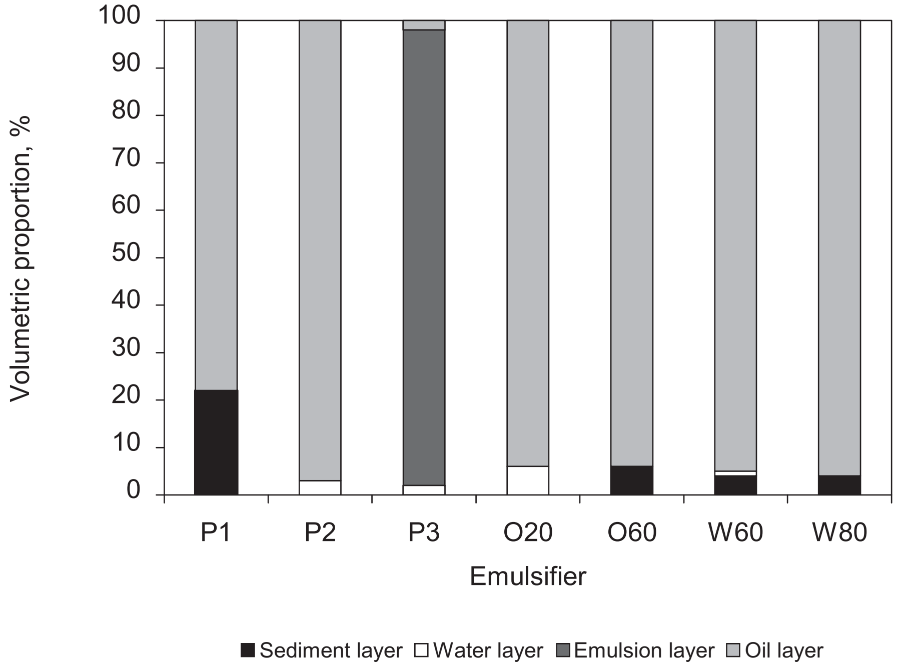

*Figure 1. Volumetric proportion of the emulsified fuel using different types of emulsifiers after seven days storage at room temperature. O20=Span 20, O60= Span 60, W60= Tween 60, W80=Tween 80, P1;P2;P3=surfactant produced from hydroxystearic acid.*

other systems which have more than 7% water, some oil separation did take place and the level of sediment layer increased. These results were expected because according to Nehal, as the volume of the dispersed phase increases, the rate of coalescence increases - owing to the increased entropy for effective collisions between the dispersed droplets (Nehal *et al*., 1999). The pour point of the emulsion also increased as the water content increased and this was due to the increase in viscosity.

### Effects of Surfactant Concentration on the Stability of the Emulsion

Based from the findings of this research, economically, it would be more profitable to decrease – as much as possible - the surfactant concentration required to stabilize the emulsion system. In this study, the surfactant concentration varied between 0.1% to 2.0%. The emulsion stability, as a function of different surfactant concentrations, was determined after a seven-day storage at RT. It was found that the emulsion stability increased as the surfactant concentration increased. A higher emulsion stability was also observed for the surfactant concentration ranging from 1.0% to 2.0% at mixing speed of 500 rpm (*Figure 2*). This result was due to the increased number of surfactant molecules absorbed at the oil-water interface at higher surfactant concentration. Below this level of concentration, the emulsion stability would then decrease. However, it was possible to increase the stability of the emulsion system containing 0.5% surfactant by increasing the mixing speed from 500 rpm to 1300 rpm.

Similar trend was reported by Ahmad *et al.* (1999) in their research on the formation of fluid heavy oil-in-water emulsions for pipeline transportation. In their analysis, Ahmad found that the stability of the emulsion increased because the increase in mixing speed results in the decrease of the droplet size of the oil/water dispersed phase (Rosen, 1989).

### Exhaust Gas Emission of the Emulsion Fuel

To learn about the effects of emulsified fuel on carbon monoxide (CO) concentration, the exhaust gas emission of petroleum diesel, palm biodiesel and emulsified palm biodiesel, at variable engine speed, were evaluated. The gathered data showed that emulsified fuel did not show significant effects on CO concentration because a naturally aspirated or turbo-charged diesel engine uses more oxygen (excessive air) to burn the fuel. Since the operating conditions were exclusively lean, with an air/fuel ratio of around 1.8 X stoichiometric, the CO concentration value for all fuels were low; even less than 0.1% as shown in *Figure 3*. A slight increase in hydrocarbons (HCs) emission was observed for emulsified fuel, but this emission was still lower than petroleum diesel (*Figure 4*).The emissions of $NO_x$ from emulsified fuel were lower than petroleum diesel and neat palm biodiesel (*Figure 5*). This was due to the fact that emulsified fuel produced lower heat release rate at premix combustion phase; which is at the peak of combustion temperature, and this

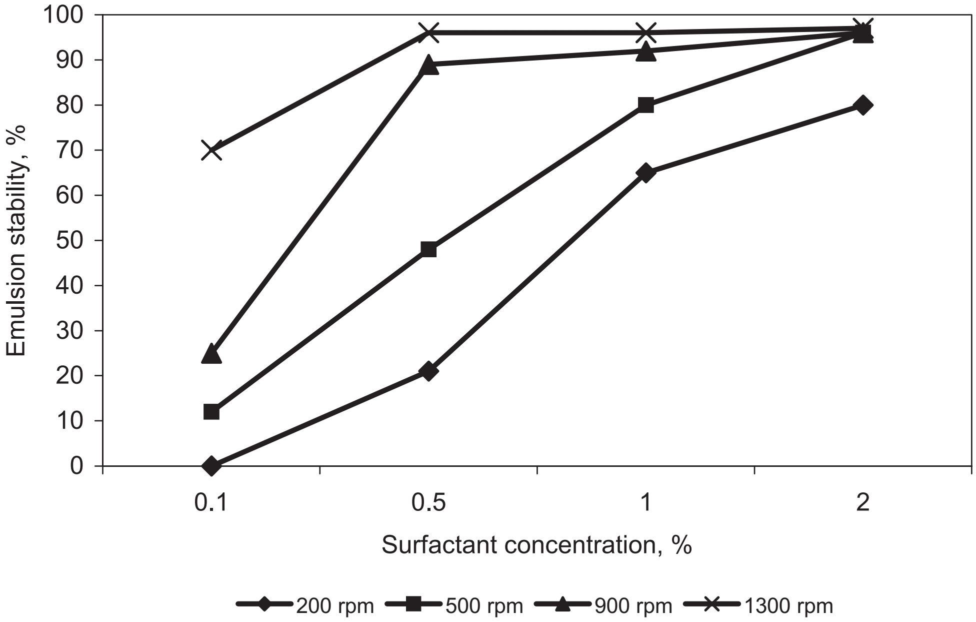

*Figure 2. Effects of surfactant concentration and mixing speed on the stability of the emulsion system after seven days storage.*

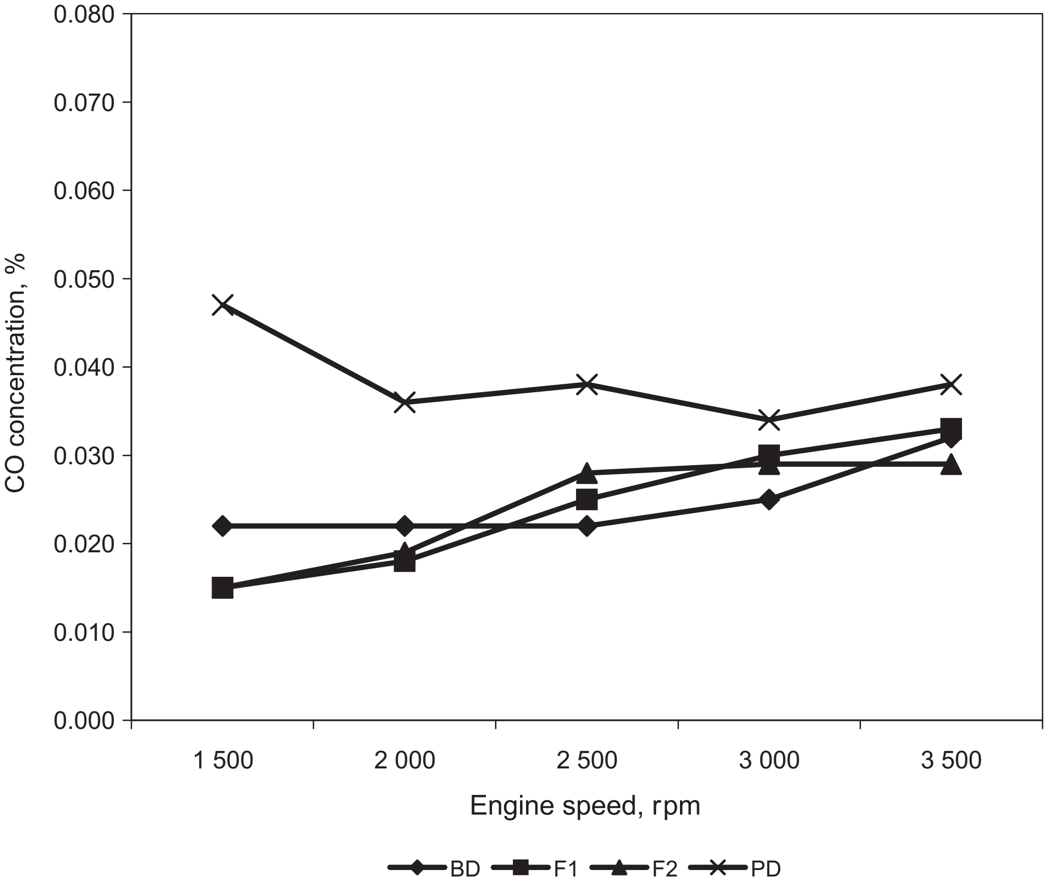

*Figure 3. CO emission of palm biodiesel, emulsified palm biodiesel and petroleum diesel* vs. *engine speed. BD=palm biodiesel, F1=emulsified palm biodiesel containing 5% water, F2=emulsified palm biodiesel containing 15% water, PD=petroleum diesel.*

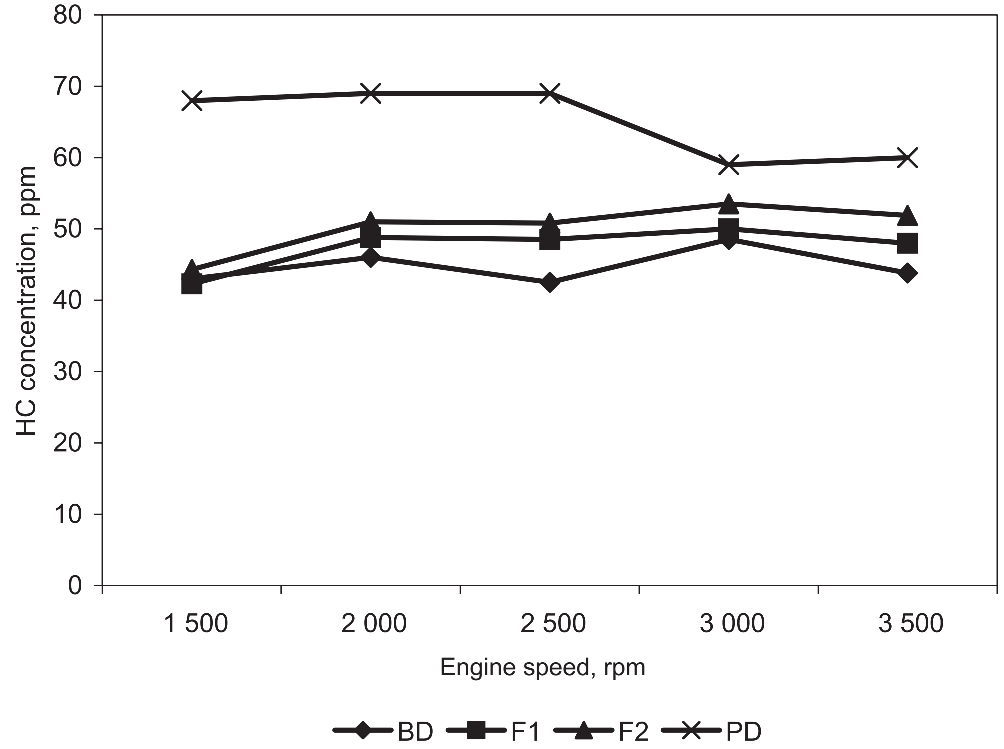

*Figure 4. Hydrocarbons emission of palm biodiesel, emulsified palm biodiesel and petroleum diesel* vs. *engine speed. BD=palm biodiesel, F1=emulsified palm biodiesel containing 5% water, F2=emulsified palm biodiesel containing 15% water, PD=petroleum diesel*

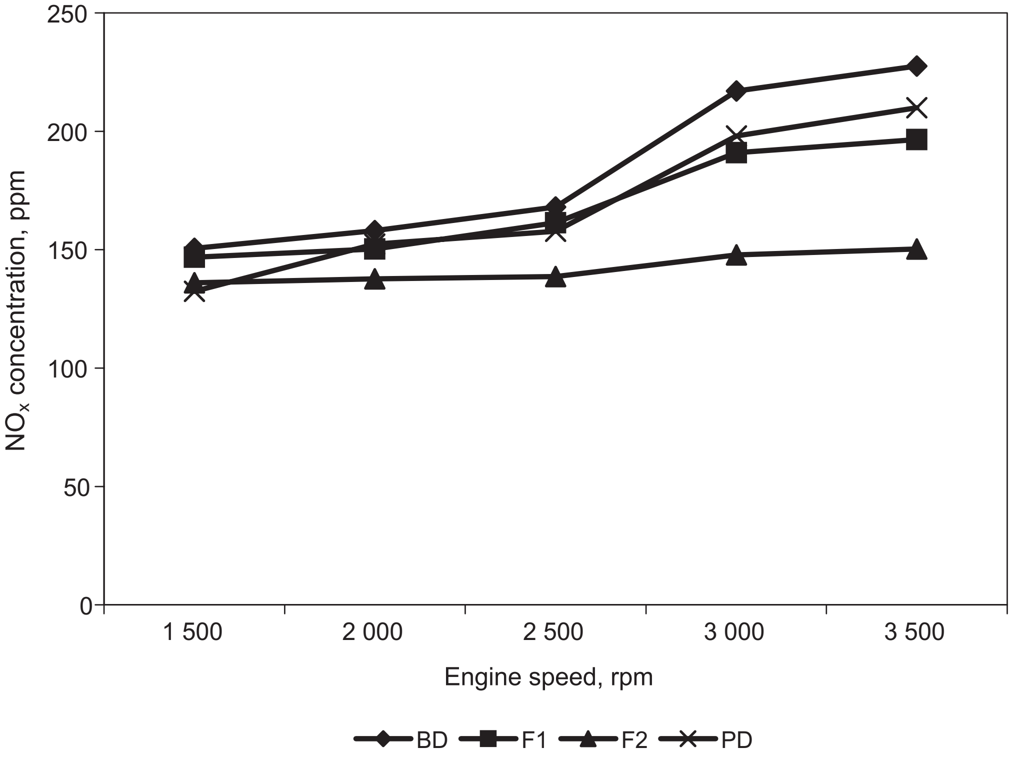

*Figure 5. NO$_x$ emission of palm biodiesel, emulsified palm biodiesel and petroleum diesel* vs. *engine speed. BD=palm biodiesel, F1=emulsified palm biodiesel containing 5% water, F2=emulsified palm biodiesel containing 15% water, PD=petroleum diesel.*

hence reduces $NO_x$ emission. Although emulsified fuel could reduce $NO_x$ emission, the viscosity of the fuel was slightly higher. The collected data also demonstrated that the viscosity increased by 1.2 times and 1.4 times respectively after 5% and 15% water was added to the emulsion system. The higher viscosity is primarily due to the larger number of water droplets dispersed in the emulsion system. It was reported that high viscosity fuel may cause injector coking and ring sticking in both direct-injection and indirect-injection diesel. In addition, the calorific values of the emulsified fuel were 0.43% and 5.46% lower, respectively than that of palm biodiesel (*Table 2*).

TABLE 2. PROPERTIES OF EMULSIFIED FUEL AND PALM BIODIESEL

| | **Palm biodiesel** | **F1** | **F2** |
|---|---|---|---|
| Viscosity, cP@25°C | 6.55 | 8.10 | 9.37 |
| Density, kg litre$^{-1}$ | 0.8722 | 0.8752 | 0.8880 |
| Energy content, J g$^{-1}$ | 39 539 | 39 370 | 37 378 |
| Pour point, °C | 12.0 | 12.0 | 14.0 |
| Flash point, °C | 175 | ND | ND |

Notes: F1= Emulsified palm biodiesel containing 5% water.
F2= Emulsified palm biodiesel containing 15% water.
ND = Not determined.

## CONCLUSION

Polymeric surfactant could be used as an emulsifier for the production of W/O emulsion of palm biodiesel. Compared to regular palm biodiesel, the emulsion had lower $NO_x$ emission, but slightly higher CO and HC emissions. Also, the density and viscosity of the emulsified fuel were higher than neat palm biodiesel.

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