



Original Article

## Biodiesel as a lubricity additive for ultra low sulfur diesel

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### Abstract

With the worldwide trend to reduce emission from diesel engines, ultra low sulfur diesel has been introduced with the sulfur concentration of less than 10 ppm. Unfortunately, the desulfurization process inevitably reduces the lubricity of diesel fuel significantly. Alternatively, biodiesel, with almost zero sulfur content, has been added to enhance lubricity in an ultra low sulfur diesel. This work has evaluated the effectiveness of the biodiesel amount, sourced from palm and jatropha oil, and origin in ultra low sulfur diesel locally available in the market. Wear scar from a high-frequency reciprocating rig is benchmarked to the standard value (460  $\mu\text{m}$ ) of diesel fuel lubricity. It was found that very small amount (less than 1%) of biodiesel from either source significantly improves the lubricity in ultra low sulfur diesel, and the biodiesel from jatropha oil is a superior lubricity enhancer.

**Keywords:** ultra low sulfur diesel (ULSD), lubricity, HFRR, biodiesel, palm oil, jatropha oil

### 1. Introduction

In general, fuel viscosity is an indicator for a fuel to provide wear protection, but this is not the case anymore for the ultra low sulfur diesel (ULSD), since it was reported that ULSD with high viscosity could cause severe adhesive wear or scuffing in rotary distributor pumps (Anastopoulos *et al.*, 2002). Diesel lubricity comes naturally from occurring polar compounds, which form a protective layer on the metal surface. Heterocyclic aromatics and nitrogen/oxygen compounds (rather than sulfur) were identified most important for lubricity (Wei and Spikes, 1986). The mechanisms for lubrication vary with test methods and operating conditions. For instance, monolayers of the additive, usually carboxylic acids or methyl esters, form on the surface; thus preventing contact between the two metal surfaces and reducing the

wear. Under other conditions, the formation of organometallic polymers from carboxylic acids on metallic surfaces has been observed. The desulfurization process, e.g. hydrotreating, inevitably destroys some of this natural lubricant. Oxygen containing compounds (especially with phenolic-type or carboxylic acid groups), such as fatty acids, can adsorb or react on rubbing surfaces to reduce adhesion between contacting asperities. In fact, it was found half a century ago that the addition of a small amount of fatty acid to a non-polar mineral oil or to a pure hydrocarbon can result in a considerable reduction in the friction and wear (Bowden and Tabor, 1950).

### 2. Experimental Procedure

Even though there are many prior works on various additives for ULSD especially in EU, USA, and Japan owing to low sulfur regulation of <50 ppm, not much has been done in Thailand due to the current sulfur regulation of <350 ppm. However, it was recently announced by Department of

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Energy Business (DoEB) that for the diesel specification a new target of <50 ppm would be set by January 1, 2012 (DoEB, 2007). To the best of the authors' knowledge on the investigation of Thai low sulfur diesel, there was only one prior work several years ago. Specially processed diesel with sulfur content of 140 ppm was blended with 1% of biodiesel from coconut, palm, and stearin oils, and their lubricity properties were investigated via HFRR (Bunyakiat *et al.*, 2003). An improvement of 25-40% was found with the additives having wear scar within the diesel standard for all three cases. However, the previous study (Bunyakiat *et al.*, 2003)

only used the diesel with sulfur content not classified as ULSD (<10 ppm) and did not investigate on the tribological behavior in details.

In the present study, ULSD with sulfur of 6 ppm was specially requested from one of the oil refineries in Thailand, since ULSD is not yet commercially available, and blended with biodiesel from palm and jatropha oil at various amounts. Both palm and jatropha biodiesel samples were synthesized locally with their properties according to Thai FAME biodiesel standard (DoEB, 2007). The lubricity of diesel is typically measured via a high-frequency reciprocating rig apparatus according to diesel standard shown in Figure 1(a), where the ball specimen is rubbed against the plate in the reciprocating fashion, both submerged in the diesel fuel as shown in Figure 1(b). The testing parameters and conditions are conformed to CEC-F-06-A-96 standard (CEC, 1996), as shown in Table 1. After 75 minutes, the ball and plate are separated and cleaned. The ball is inspected under the optical microscope for the wear scar measurement in two perpendicular directions. Since the wear scar is very sensitive to the ambient conditions (e.g. temperature and humidity), the CEC-F-06-A-96 standard recommends the reported value of wear scar at standard vapor pressure of 1.4 kPa (WS1.4) instead. During the reciprocating motion, three parameters, oil bath temperature, coefficient of friction, and %film formation, were continuously monitored, as shown in Figure 1(c). The average values were then reported for each test.

### 3. Results and Discussion

Since the fraction of biodiesel as an additive in ULSD for the present study is only up to 2% (100% is used as reference), there is a negligible effect from biodiesel onto the density and viscosity of the ULSD with additive, which is thus not shown here. Furthermore, the current diesel standard allows biodiesel blend of 1.5-2% (v/v) without any modification to the diesel specification. Figure 2 and 3 show the results for ULSD with 0, 0.25, 0.5, 1, 2, and 100% of

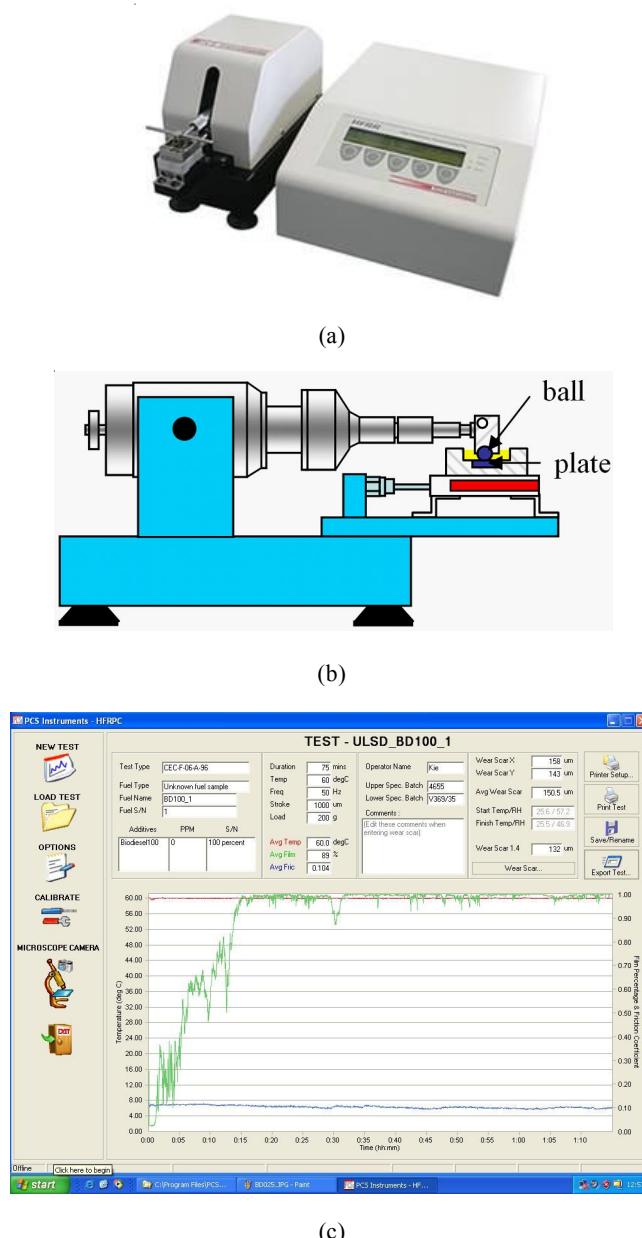


Figure 1. (a) High frequency reciprocating rig (HFRR) apparatus with (b) the schematic drawing and (c) the software to monitor the results such as coefficient of friction (COF) and %film formation.

Table 1. Summary of HFRR test conditions (CEC, 1996)

Fluid vol (ml)	2.0±0.20
Fluid temp (°C)	60±2
Bath surface area (cm <sup>2</sup> )	6.0±1.0
Stroke length (mm)	1.0±0.02
Frequency (Hz)	50±1
Applied load (g)	200±1
Test duration (min)	75±0.1
Specimen steel	AISI E-52100
Ball diameter (mm)	6.00
Surface finish (ball)	<0.05 µm R <sub>a</sub>
Hardness (ball)	58-66 Rockwell C
Surface finish (plate)	<0.02 µm R <sub>a</sub>
Hardness (plate)	190-210 HV 30
Ambient conditions	See Chart

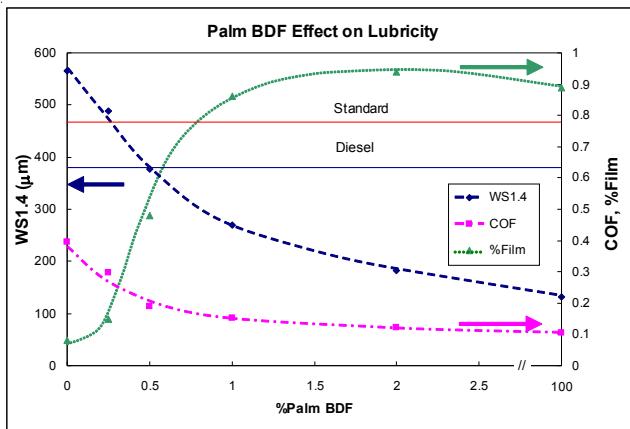


Figure 2. Effect of %Palm BDF additive in ULSD on WS1.4, COF, and %film.

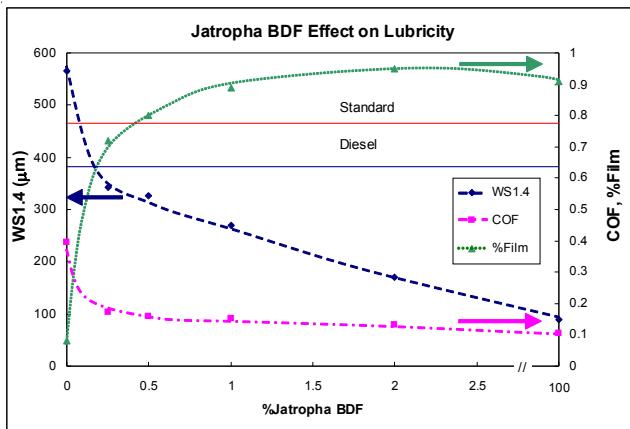


Figure 3. Effect of %jatropha BDF additive in ULSD on WS1.4, COF, and %film.

biodiesel from palm and jatropha oils, respectively, superimposed with the values for Thai commercial diesel and diesel standard of 460 µm (DoEB, 2007). The average values of COF and %film are based on 4,500 data points taken every second during the 75 min testing time. Both figures clearly show that with a small amount of additive into ULSD, WS1.4 is well within the lubricity standard for diesel fuel. The dependencies of WS1.4 and COF on %BDF additive are similar. Adding a small %BDF additive, up to 2%, promotes a significant drop with slight decrease afterwards. These decreases are confirmed by the increase in %film, as shown in Figure 2 and 3. The results are consistent with what has been reported in the literature (Wei and Spikes, 1986; Anastopoulos *et al.*, 2002).

Comparing the results from Figure 2 and 3, it can be implied that the decreases of wear scar are not only affected by %BDF but also by the source of biodiesel. In Figure 3 it can be seen that with only 0.25% jatropha BDF additive the WS1.4 was reduced to be lower than the standard value of 460 µm and at this point, 0.72 %film was reported. In order to achieve the same %film, adding around 0.75% palm BDF or 3 times of jatropha BDF is required. Hence, BDF made from

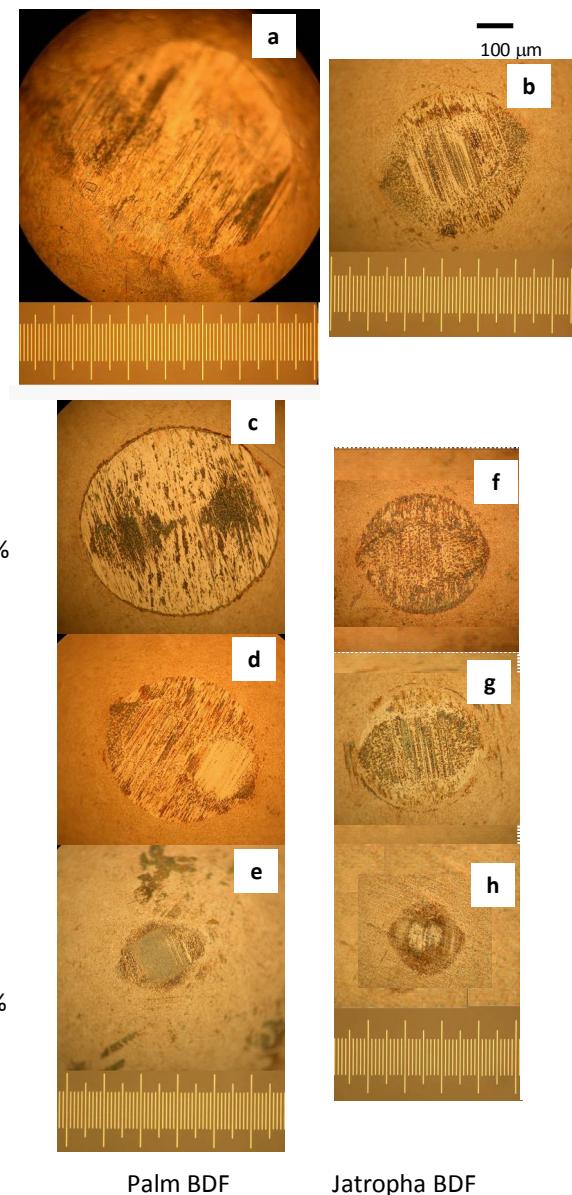


Figure 4. Wear scars on ball from HFRR tests with (a) ULSD, (b) commercial diesel, (c) ULSD+0.25% palm BDF, (d) ULSD+0.5% palm BDF, (e) 100% palm BDF, (f) ULSD+0.25% jatropha BDF, (g) ULSD+0.5% jatropha BDF, and (h) 100% jatropha BDF.

jatropha oil shows superior lubricity property than that from palm oil. This is due to the longer carbon chains of the fatty acid in jatropha oil (linoleic acid, C18:2) as opposed to palm oil (palmitic acid, C16:0). It was shown that the effect of carbon chain length on the lubricity was stronger than the saturation of the carbon bonds (Anastopoulos *et al.*, 2005).

Wear scar characteristics were examined on both the ball and the plate. However, since the results from both show the similar tendencies, only the wear scars on the ball specimens are presented here for the cases of Thai commercial diesel, ULSD, ULSD+0.25% BDF, ULSD+0.5% BDF, and 100%

BDF. The micron marker is superimposed with the special resolution of 10  $\mu\text{m}$  for the smallest division.

As expected, the wear scars for ULSD are most severe with a decrease of the wear scars when adding more %BDF. ULSD+0.5% palm BDF is similar to commercial diesel while ULSD+0.25% jatropha BDF shows less wear. The least wear occurred when 100% BDF from both palm and jatropha were examined.

#### 4. Conclusions

The effects of biodiesel from palm and jatropha oils on improving the lubricity properties of ultra-low sulfur diesel were investigated via the high-frequency reciprocating rig technique, with the following findings:

1. The lubricity of ultra low sulfur diesel (6 ppm) does not meet the diesel standard of 460  $\mu\text{m}$  WS1.4.

2. The lubricity property of biodiesel used as an ultra low sulfur diesel additive is varied dependent on the source and amount of the biodiesel.

3. Biodiesel can be used as a lubricity additive to ultra low sulfur diesel with as little as 0.25-0.5% blends.

4. Biodiesel improves the lubricity property by film formation preventing mechanical contact between the two metal parts.

5. Jatropha biodiesel is a superior lubricity additive than the palm biodiesel due to the longer carbon chains of the fatty acid in jatropha oil as opposed to palm oil.

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