Biodiesel from Various Vegetable Oils as the Lubricity Additive for Ultra Low Sulphur Diesel (ULSD)

Subongkoj Topaiboul*, Nuwong Chollacoop, and Kanit Treesuwan

Energy Research Group, National Metal and Materials Technology Centre (MTEC),
Pathumthani 12120 Thailand
Tel: 0-2564-6500 x4700, Fax: 0-2564-6403, *Email: subongkk@mtec.or.th

Abstract

With the worldwide trend to reduce emission from diesel engine, an ultra low-sulphur diesel or ULSD has been introduced with the sulphur concentration of less than 10 ppm. Unfortunately, the desulphurisation process inevitably reduces lubricity of diesel fuel significantly. Even though the current Thai regulation from the Department of Energy Business [1] still has 350ppm limit for commercial diesel, it has been recently announced the new target of 50ppm after January 1, 2012. In order to improve the lubricity of the ULSD, biodiesel, with almost zero sulphur content and excellent lubricity property, has been added. The present work aims to evaluate the effectiveness of the biodiesel amounts and types, from palm oil, jatropha, soybean, coconut and sunflower locally obtained in Thailand, in the ULSD specially processed from a Thai commercial diesel company. According to the regulation [1], a wear scar from HFRR (high-frequency reciprocating rig) apparatus is measured against the standard value (460 μm) of diesel fuel lubricity. It was found that very small amount (less than 1%) of biodiesel from all feedstock considered significantly improves the lubricity of ULSD to meet the lubricity regulation.

Keywords: Ultra low sulphur diesel (ULSD), Lubricity, Biodiesel, HFRR

1. Introduction

In diesel engine, diesel fuel is not only used as the source of energy but also lubrication of fuel injection pump. Traditionally, petroleum fuel viscosity can be used as an indicator for a fuel to provide wear protection. However, it is no longer valid with an ultra low sulphur diesel (ULSD) since ULSD with high viscosity was reported to cause severe adhesive wear or scuffing in rotary distributor pumps [2]. 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 sulphur) were identified most important for lubricity [3]. The mechanisms for lubrication vary with test methods and operating conditions. For instance, monolayer of the additive, usually carboxylic acids or methyl esters, form on the surface; thus preventing contact between the two metal surfaces and reducing wear. Under other conditions, the formation of organometallic polymers from carboxylic acids on metallic surfaces has been observed.

The desulphurisation process 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 bring about a considerable reduction in the friction and wear [4].

2. Experimental Procedure

Due to the current 350ppm limit of sulphur in Thai commercial diesel, not much work has been done in evaluating the lubricity property of Thai ULSD. To the best of authors' knowledge, there was only one prior work on the effect of blending 1% biodiesel from coconut, palm and palm stearin oils in Thai low sulphur diesel, which contains 140ppm sulphur [5]. Following the standard to determine fuel lubricity [6], improvement of 25-40% was found with the additives having wear scar within the diesel standard for all three blends. However, the sulphur content (140ppm) in the previous study [5] was not low enough to be classified as ULSD, which is usually less than 10-15ppm.

In the present study, specially processed ULSD with sulphur of 6ppm obtained from a local source in Thailand was blended with biodiesel from palm, jatropha, soybean, coconut and sunflower oils at various amounts. All biodiesel types were synthesized locally with their properties conforming to Thai biodiesel standard [1]. Following the lubricity standard [6], a high-frequency reciprocating rig (HFRR) apparatus is schematically shown in Figure 1, where the ball specimen is rubbed against the plate in the reciprocating fashion, both submerged in the testing fuel. The testing parameters and conditions are conformed to CEC-F-06-A-96 standard [6] as shown in Table 1.

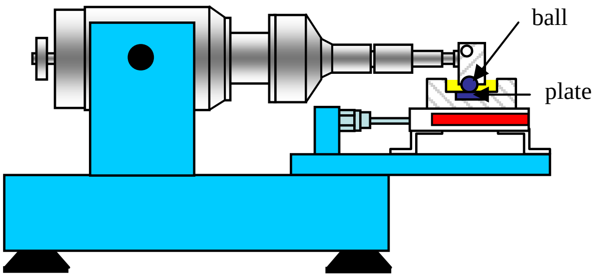


Figure 1. Schematic drawing of high-frequency reciprocating rig (HFRR) apparatus

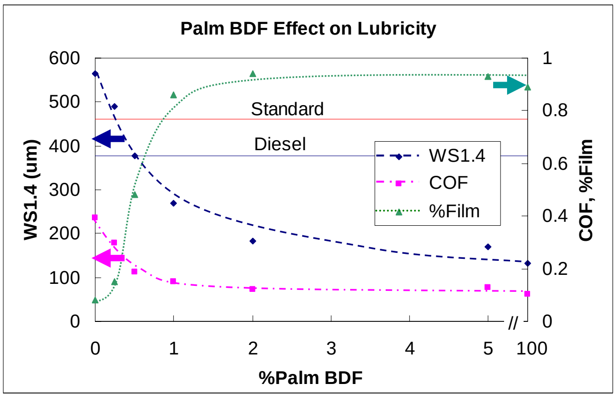
Table 1. Testing parameters and conditions [6]

Fluid volume (ml)	2.0±0.20
Fluid temp (°C)	60±2
Bath surface area (cm^2)	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_a
Hardness (ball)	58-66 Rockwell C
Surface finish (plate)	< 0.02 μm R_a
Hardness (plate)	190-210 HV 30
Ambient conditions	See Chart

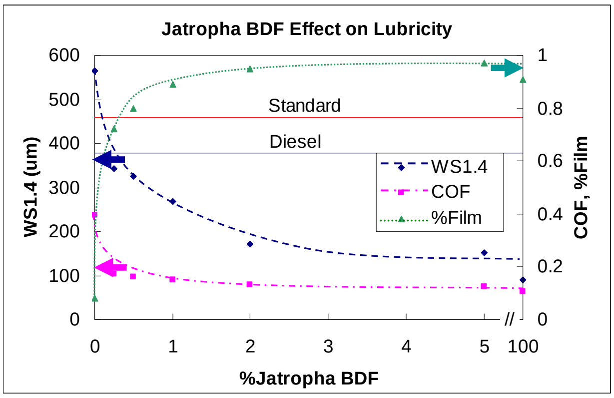
After 75 minutes, the ball and plate are separated, cleaned and examined under the optical microscope for the wear scar measurement. Since the wear scar diameter is extremely sensitive to the temperature and humidity of the testing environment [6], the measured wear scar value is then corrected with the ambient temperature and humidity, and reported as WS1.4 (wear scar at standard vapour pressure of 1.4kPa) for sensible comparison among different runs.

3. Results and Discussion

Figures 2(a)-(e) show the results for ULSD with 0, 0.25, 0.5, 1, 2, 5 and 100% (by volume) of biodiesel from palm, jatropha, soybean, coconut and sunflower oils, respectively, superimposed with the WS1.4 values for Thai commercial diesel (378 μm in this case) and diesel standard of 460 μm [1]. The coefficient of friction (COF) and amount of film formation (%film), which are averaged over 4,500 data points taken every second during the 75 min testing time, are also shown. Figures 2(a)-(e) clearly show that with only a small amount of additive, less than 1%, into ULSD, WS1.4 is well within the lubricity standard (below the Standard line). The dependencies of WS1.4 and COF on the amount of biodiesel additive are similar. Adding a small percentage of biodiesel additive, up to 2%, promotes a significant drop in both WS1.4 and COF with slightly decreasing afterwards. Hence, this implies the saturation of the BDF effect to improve lubricity in ULSD. These decreases are confirmed by the increases in film thickness (%film), as shown in Figures 2(a)-(e), for all BDF cases. The results are consistent with what has been reported in the literature [2-3].



(a)



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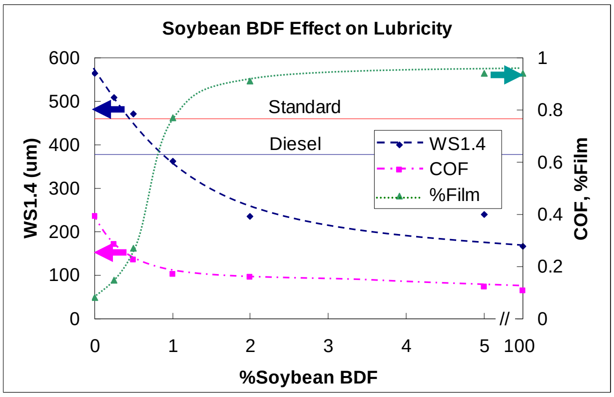
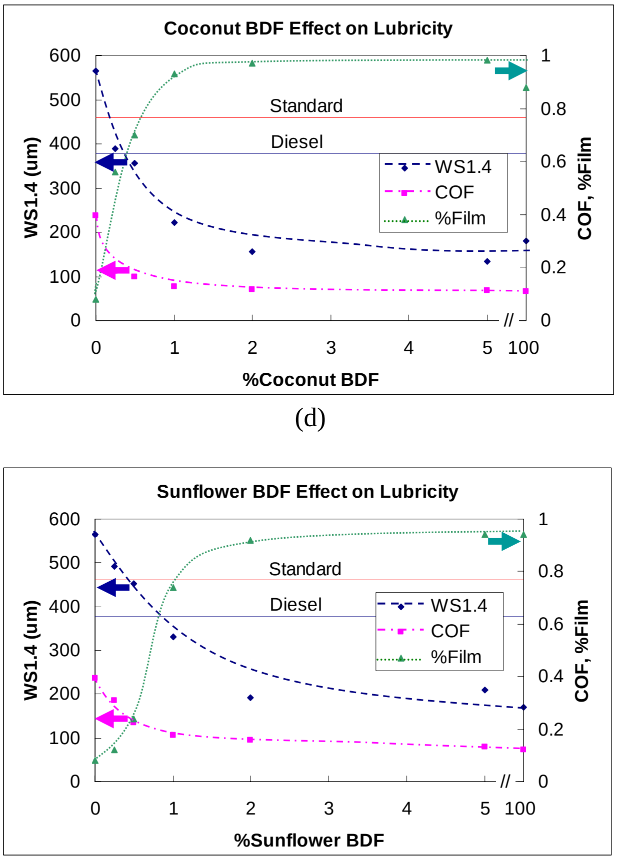


(c)



(d)

(e)

Figure 2. Effect of %BDF from (a) palm, (b) jatropha, (c) soybean, (d) coconut and (e) sunflower oils in ULSD on WS1.4, COF and %film (superimposed with WS1.4 values for a diesel standard and a commercial Thai diesel)

Comparing the results in Figures 2(a)-(e), it can be seen that the reduction of WS1.4 values measured from ULSD with various biodiesel additive are dependent on the biodiesel raw materials. Among all biodiesel types, the lubricating effect is stronger with palm, jatropha and coconut biodiesel, as shown by the smaller percentage added to meet the standard line. To achieve the WS1.4 value that is comparable to that of Thai diesel, only 0.25-0.5% is required from those, while around 1% is required in the case of sunflower and soybean. This suggests that palm, jatropha and coconut biodiesel are superior lubricity additives than soybean and sunflower biodiesel.

The balls and plates after the HFRR experiments are also investigated. Since the results from both show similar tendencies, only the balls are presented here. Figures 3(a)-(b) and Figures 4(a)-(e) present wear scars on the balls of ULSD, Thai diesel and ULSD with different biodiesel additives superimposed with a 100 µm mark. Although Figures 4(a)-(e) show the absolute wear scar sizes prior to correction with temperature and humidity of the testing environment, they clearly show the effect of biodiesel additive consistent with the WS1.4 values.

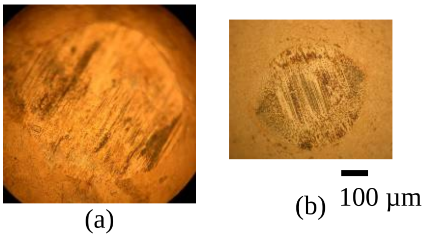


Figure 3 Wear scars on balls from HFRR tests with (a) ULSD and (b) Thai diesel

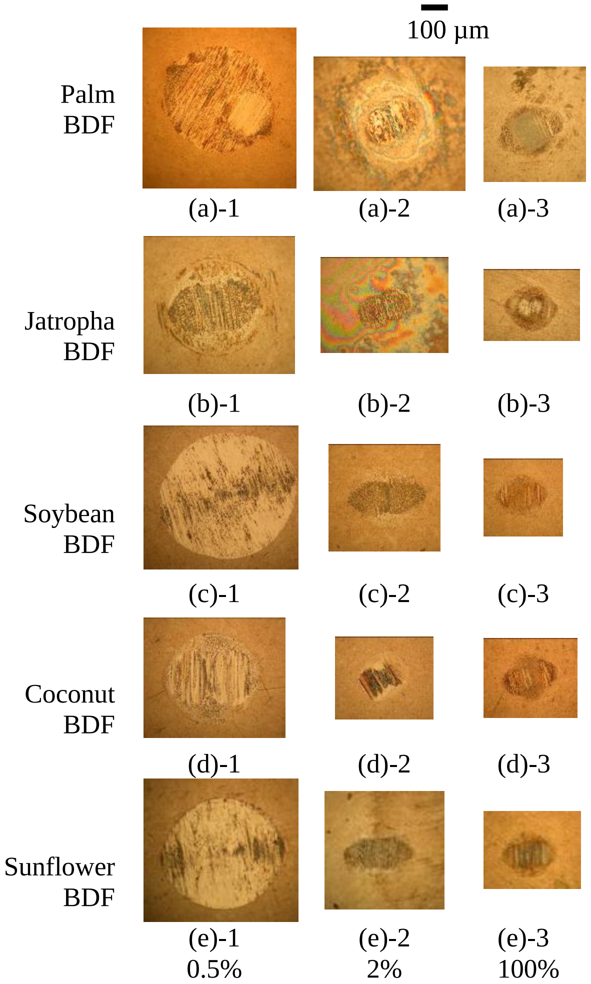


Figure 4. Wear scars on balls from HFRR tests when adding various types and amounts of biodiesel:
(a)-1 ULSD+0.5% palm BDF, (a)-2 ULSD+2% palm BDF, (a)-3 100% palm BDF;
(b)-1 ULSD+0.5% jatropha BDF, (b)-2 ULSD+2% jatropha BDF, (b)-3 100% jatropha BDF;
(c)-1 ULSD+0.5% soybean BDF, (c)-2 ULSD+2% soybean BDF, (c)-3 100% soybean BDF;
(d)-1 ULSD+0.5% coconut BDF, (d)-2 ULSD+2% coconut BDF, (d)-3 100% coconut BDF; and
(e)-1 ULSD+0.5% sunflower BDF, (e)-2 ULSD+2% sunflower BDF, (e)-3 100% sunflower BDF

As expected the wear scar of ULSD is the most severe (Figure 3a) with decreasing of the scar size when adding more percentage of biodiesel. Similar to the results in Figures 2(a)-(e), adding small amount of palm, jatropha and coconut biodiesel into ULSD promotes fuel lubricity as shown by smaller wear scars. The sizes of wear scars of all biodiesel types are not different between the 2% and 100% cases. Again, this finding confirms the saturation of biodiesel interaction.

In order to find the parameters that influence the lubrication property of biodiesel, all raw vegetable oils are analysed for their fatty acid profiles as shown in Table 2.

Table 2. Fatty acid profiles of raw vegetable oils (all values are % by weight)

Fatty acid composition (%)	Palm	Jatropha	Soybean	Coconut	Sunflower
Lauric (C12:0)	4.34	-	-	**53.73**	-
Myristic (C14:0)	2.06	-	-	**16.45**	-
Palmitic (C16:0)	**41.17**	11.3	12.10	11.10	5.08
Stearic (C18:0)	2.51	**17.0**	2.56	2.62	2.97
Oleic (C18:1)	**37.85**	12.8	**25.98**	3.82	**25.67**
Linoleic (C18:2)	11.21	**47.3**	**53.74**	2.62	**66.28**
Linolenic (C18:3)	0.58	-	5.62	-	-

The majority fatty acids of palm oil are palmitic acid (C16:0) and oleic acid (C18:1), which are saturated and unsaturated fatty acid, respectively, while around half or more of jatropha oil, soybean oil and sunflower oil are longer chain, unsaturated linoleic acid (C18:2). Different from others, coconut oil mainly contains shorter chain of saturated fatty acids, which are lauric (C12:0) and myristic acid (C12:1). From the HFRR plots in Figure 2(a)-(e) and the results in Table 2, it is shown that there is no significant correlation between the fatty acid compositions or molecular chain length and the lubricity property of biodiesel even though it was reported in many literatures that an increasing in unsaturated fatty acid could improve the lubricity [3,7,8]. These results suggest that there must be other factors influencing the lubricity more dominantly than the chain length and/or the unsaturated fatty acid.

An interesting work was done by Jianbo Hu et al [9], who tried to determine the effects of impurities in biodiesel on its lubricity. The results showed that small amount of monoglyceride, free fatty acid and diglyceride, which are considered as impurities in biodiesel according to the current standard [1], could greatly improve the biodiesel lubrication property. Furthermore, OH group such as alcohol and glycerol that may still remain in the biodiesel also help promote the lubrication in ULSD as well [8]. Hence, the effects of free fatty acid profile of the raw vegetable oil alone on the lubricity enhancing property are not conclusive. To obtain more clearly conclusions, all biodiesel should be determined for their purity in term of their compositions.

4. Conclusions

The effects of biodiesel from palm, jatropha, soybean, coconut and sunflower oils on improving the lubricity properties of ultra-low sulphur diesel (ULSD) were investigated via the high-frequency reciprocating rig (HFRR) apparatus, with the following findings.

1. The lubricity of ULSD (6ppm) does not meet the diesel standard of 460 µm WS1.4.
2. Lubricity property of biodiesel used as an ULSD additive is varied dependent on the source and amount of the biodiesel. From all five BDF sources considered here, less than 1% by volume amount effectively brings ULSD to meet diesel lubricity standard. The effect of the percentage of biodiesel becomes saturated beyond 2% addition.
3. Biodiesel improves lubricity property by film formation preventing mechanical contact between the metal ball and plate.
4. Palm, jatropha and coconut biodiesel are superior lubricity additives in ULSD than soybean and sunflower biodiesel.
5. The correlation between amounts of saturates and chain length in biodiesel compositions and the lubricity enhancer properties is not conclusive.
6. Other factors such as impurities (e.g. free fatty acid, mono- and di-glyceride) in biodiesel can affect the lubricity. So, further analysis in term of biodiesel compositions is required.

Acknowledgments

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