BIODIESEL AS A LUBRICITY ADDITIVE FOR DIESEL FUEL

by

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ABSTRACT

Sulfur in diesel fuel will influence particulate matter emission either in exhaust gas flow or in atmosphere. The other effect of sulfur it can cause corrosion and engine wear. Further, sulfur also can influence on catalytic system in exhaust pipe. Due to this reason sulfur level in diesel fuel should be set as lower as possible. The process can be used to reduce sulfur level is desulfurization process (hydrotreatment). At the hydrotreatment to desulfurize diesel fuel, lubricity can decrease, it is cause by reduction of fuel components which have good natural lubricity.

Lubricity, is very relevant to the satisfactory operation of diesel fuel engines which relay on the fuel to lubricate many of the moving and rubbing metal parts of the fuel injection equipment. Some injection equipment may be at risk if operated on fuels of low lubricity.

Biodiesel as results of transesterification has a good lubricity, the test results of adding biodiesel into a lower lubricity of diesel fuel indicate that biodiesel can be used to increase diesel fuel lubricity.

Key words: biodiesel, additive, diesel fuel, lubricity, wear scar diameter (WSD)

I. INTRODUCTION

Diesel fuel are complex mixture of hydrocarbon molecules derived from crude oil by distillation, generally boiling within the temperature range of 150 to 380^{o}C. Diesel fuel product quality is determined in diesel fuel specification. At present, sulfur is set lower than before and lubricity also included in diesel fuel specification.

Sulfur in diesel fuel will influence particulate matter emission either in exhaust gas flow or in atmosphere. The other effect of sulfur it can cause corrosion and engine wear. Further, sulfur also can influence on catalytic system in exhaust pipe. Due to this reason sulfur level in diesel fuel should be set as lower as possible. The process can be used to reduce sulfur level is desulfurization process (hydrotreatment) . At the hydrotreatment to desulfurize diesel fuel, lubricity can decrease, it is caused by reduction of fuel components which have good natural lubricity.

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II. METODOLOGY

Approaching the problem by literature study of diesel fuel and biodiesel, analysis the lubricity and characteristics of diesel fuel, biodiesel and their mixture samples. Evaluate the results of analysis.

III. DIESEL FUEL

A. *Conventional Diesel Fuel*

Diesel fuel are mixtures of hydrocarbon molecules drive from crude oil by distillation, generally

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boiling within the temperature range of 150 to 380°C. They are normally blended from several refinery streams, mostly coming from the primary distillation unit, but in a conversion refinery, components from other units are often used to increase diesel fuel production.

An ideal diesel fuel is one which flows easily at all temperatures, is clean and free from foreign contaminants and separated wax, ignites readily and burn quietly, cleanly and economically.

From the viewpoint of the diesel manufacturer, one of the most important fuel properties is density, which related to heating value of the fuel, and thus the energy available to generate power. However, before the fuel can be used in the engine, it has to be drawn from the tank, pass through the filters and delivered at at a low pressure to the injection pump, where a small volume will be metered precisely, compressed and injected as finely atomized spray which will ignite and burn in the combustion chamber. To pass through the vehicle fuel system, and also satisfy the performance and reliability need of the user, involves many other fuel characteristics including cold flow, viscosity, ignition quality, volatility, deposit forming tendency, cleanliness, corrosivity and lubricity.

Lubricity sometimes referred to as film strength, is the ability of a liquid to lubricate. This is very relevant to the satisfactory operation of diesel engines which relay on the fuel to lubricate many of the moving and rubbing metal parts of the fuel pump injection. It is very important because fuel injection pump is not provided by external lubrication system. Figure 1 shown an inline fuel injection pump with governor mechanism. Its moving and rubbing metal parts is lubricated by fuel which is injected into diesel engine.

Indonesian high speed diesel fuel specifications is given in Table 1. There are two kind of high speed diesel fuel, namely Diesel Fuel 48 which have mini-

Table 1
High speed diesel fuel specification

Characteristics	Unit	Diesel Fuel 48	Diesel Fuel 51	Test Method
Cetane Number, min		48	51	D 613
Cetane Index, min		45	48	D 4737
Density at 15°C	kg/m^3	815 – 870	820 – 860	D 1298/D 4052
Viscosity at 40°C	Mm^2/s	2.0 – 5.0	2.0 – 4.5	D 445
Sulfur Content, max	% m/m	0.35	0.05	D 2622
Distillation:				D 86
T90, max	°C	-	340	
T95, max	°C	370	360	
End Point, max	°C	-	370	
Flash Point, min	°C	60	55	D 93
Pour Point, max	°C	18	18	D 97
Carbon Residue, max	% m/m	0.30	0.10	D 4530
Water Content, max	mg/kg	500	500	D 1744
Oxidation Stability, max	g/m^3	-	25	D 2274
FAME Content*), max	% v/v	10	10	
Copper Strip Corrosion, max	Merit	Class 1	Class 1	D 130
Ash Content, max	% m/m	0.01	0.01	D 482
Sediment Content, max	% m/m	-	0.01	D 473
Strong Acid Number, max	mg KOH/g	0	0	D 664
Total Acid Number, max	mg KOH/g	0.6	0.3	D 664
Lubricity (HFRR scar dia @ 60°C),max	τm µm	-	460	D 6079
Particulate, max	mg/L	-	10	D 2276

mum cetane number is 48 and Diesel Fuel 51 which have minimum cetane number is 51. Cetane numbers level of both fuels show that Diesel Fuel 51 has better ignition quality than Diesel Fuel 48. Density for diesel Fuel 48 is set from 815 to 870 and for diesel Fuel 51 from 820 to 860. Viscosity of Diesel Fuel 48 is set from 2.0 to 5.0 and for Diesel Fuel 51 from 2.0 to 4.5. Lubricity for Diesel Fuel 48 is not specified and for Diesel Fuel 51 lubricity is set at maximum 460 μm.

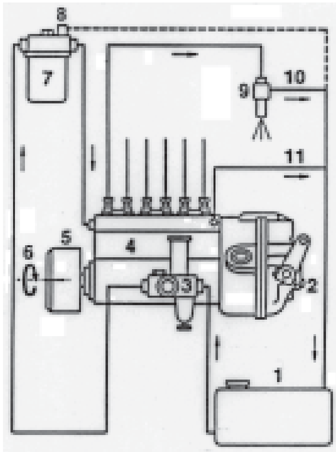

Figure 1
Inline fuel injection pump with governor mechanism[5)]

B. *Biodiesel*

Biodiesel is a diesel replacement fuel that is manufactured from vegetable oils, recycle cooking oils or animal fats. Research shows that vegetable oils used in diesel engines, can caused long term engine deposits, ring sticking, lube oil gelling, and other maintenance problems and can reduce engine life. These problems are caused mostly by greater viscosity of vegetable oils compared to that of diesel fuel for which the engines and injectors were designed. To avoid viscosity related problems, vegetable oils or animal fats are converted into biodiesel. Through the process of converting vegetable oil to biodisel its viscosity reduced to values similar to conventional diesel fuel.

The biodiesel manufacturing process converts oils into chemicals called long chain mono alkyl ester or biodiesel. These chemicals are also referred to as fatty acid methyl ester (FAME). In the manufacturing process, vegetable oils are reacted with a short chain of alcohol (usually methanol) in the presence of catalyst (usually sodium or potassium hydroxide) to form biodiesel and glycerin. Glycerin is a sugar, and is a by-product of biodiesel process.

Biodiesel specification is shown on Table 2. This specification is intended to ensure that the manufacturer produced a high quality of biodiesel to be used as a diesel fuel. Any biodiesel used in Indonesia should meet Biodiesel Specification (B100) SNI 04-7182-2006. The intent of several quality requirement in the specification is described below:

- **Viscosity** is related to the fuel injection. Lower viscosity fuels can cause loss of power by injection pump and injector leakage. Higher viscosity fuels cause poor fuel combustion that leads to deposits formation as well as higher in cylinder penetration of the fuel spray which can result in elevated engine oil dilution with fuel. Biodiesel viscosity is 2.3 – 6.0 cSt at 40^{o}C, the lower value is meet with high speed diesel fuel specification, but the higher value is slightly higher than high speed diesel fuel specification.

- **Cetane number** is required for good engine performance. Conventional diesel engine must have a cetane number of at least 40 in the United States[3)]. Higher cetane numbers help ensure good cold start properties and minimize the formation of white smoke. Biodiesel cetane numbers is set at least 51, this level is met by cetane numbers of high speed diesel fuel specification.

- **Flash point** is required for fire safety. Biodiesel flash point is much higher than high speed diesel fuel (100^{o}C compared to 60^{o}C) to ensure that the manufacturer has removed excess methanol used in manufacturing process. Residual methanol in the fuel is a safety issue because even very small amounts reduced the flash point, can also affect fuel pumps, seals and elastomers, and can result in poor combustion properties.

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Table 2
Biodiesel methyl alkyl specification (B100) SNI 04-7182-2006

No.	Parameter	Unit	Value	Test Method
1.	Density at 40 ^oC	kg/m^3	850 - 890	ASTM D 1298
2.	Kinematics Viscosity at 40 ^oC	mm^2/s (cSt)	2.3 - 6.0	ASTM D 445
3.	Cetane Number		min 51	ASTM D 613
4.	Flash Point (Close Cup)	^oC	min. 100	ASTM D 93
5.	Cloud Point	^oC	max 18	ASTM D 2500
6.	Copper Strip Corrosion (3h/at 50^oC)	No. ASTM	max No. 3	ASTM D 130
7.	Carbon Residue; - at original sample - at 10% vol bottom	% m/m	max 0.05 max 0.30	ASTM D 4530
8.	Water and Sediment	% vol	max 0.05	ASTM D 2709 or ASTM D 1796
9.	Distillation Temp 90 % vol	^oC	max 360	ASTM D 1160
10.	Sulfated Ash	% m/m	max 0.02	ASTM D 874
11.	Sulfur Content	ppm-m (mg/kg)	max 100	ASTM D 5453 or ASTM D 1266
12.	Phosphor Content	ppm-m (mg/kg)	max 10	AOCS Ca 12-55
13.	Acid Number	mg-KOH/g	max 0.8	AOCS Cd 3d-63 or ASTM D 664
14.	Free Glycerol	% m/m	max 0.02	AOCS Ca 14-56 or ASTM D 6584
15.	Total Glycerol	% m/m	max 0.24	AOCS Ca 14-56 or ASTM D 6584
16.	Ester Alkyl Content	% m/m	min 96.5	Calculated
17.	Iodine Value	% m/m (g-Iod/100g)	max 115	AOCS Cd 1-25
18.	Halphen Test		Negative	AOCS Cd 1-25

- **Water and sediment** refers to the presence of free water droplets and sediment particles. Water content biodiesel is set at the same level allow for high speed diesel fuel (0.05 % volume).
- **Copper strip corrosion** is used to indicate potential difficulties with copper and bronze fuel system components. The requirement of biodiesel and high speed diesel fuel is set at the same.
- **Carbon residue** gives a measure of the carbon depositing tendency of a fuel to form carbon deposit in an engine.
- **Free and total glycerin numbers** measure the amount of unconverted or partially converted fats and by-product glycerin present in the fuel. Incomplete removal of glycerin can leads to high free glycerin and total glycerin. If these numbers are too high, storage tank, fuel system, and engine fouling can occur. Fuel that exceed these limits are highly likely to cause filter plugging and other problems.
- **The T90 distillation** was incorporated to ensure that fuel have not been contaminated with high boiling materials such as used engine oil. The atmospheric boiling point of biodiesel generally ranges from 330^{o}C to 360^{o}C.

III. LUBRICITY MEASUREMENT

High frequency reciprocating rig (HFRR) is used to measure lubricity of diesel fuel. HFRR uses a hardened steel ball oscillating transversely in loaded contact with a hardened steel plate immersed in the test fuel. It was design to give negligible hydrodynamic film formation and low frictional heating. Contact temperature can be controlled as an independent test variable, enabling assessment of temperature-dependent effect. Figure 2 shows the general arrangement of the HFRR apparatus.

The HFRR procedure has been written in conformity with ASTM D 6079. Results of the HFRR are based on comparison of wear scar diameter with that of reference fuel, usually after test runs at temperature level, typically 60°C. The unit of wear scar diameter (WSD) is in micron, WSD correspond to lubricity. The lower WSD shows better lubricity compare to the higher WSD.

IV. EXPERIMENTAL

Biodiesel was used in this study is FAME of palm oil and diesel fuel samples are taken from three refineries, they are called refinery R1, R2 and R3. Observation of lubricity change was done by adding 1%, 5% and 10% volume of FAME into diesel fuel samples. Characteristics of diesel fuel, FAME and their mixture samples were analysis using ASTM test method.

VI. RESULTS AND DISCUSSION

A. *Diesel Fuel Refinery R1*

Test results of diesel fuel from refinery R1, FAME and their mixtures is shown in Tale 3. Test results of diesel fuel refinery R1 (0% vol FAME) characteristics meet Diesel Fuel 48 specification and its lubricity is 300 mm, it is lower than lubricity specified in Diesel Fuel 51 specification (460 mm) and FAME characteristics (100 %vol FAME) meet biodiesel specification. Adding 1%, 5% and 10% volume FAME into diesel fuel cause fuel characteristics change. All characteristics change still in the range of Diesel Fuel 48 specification.

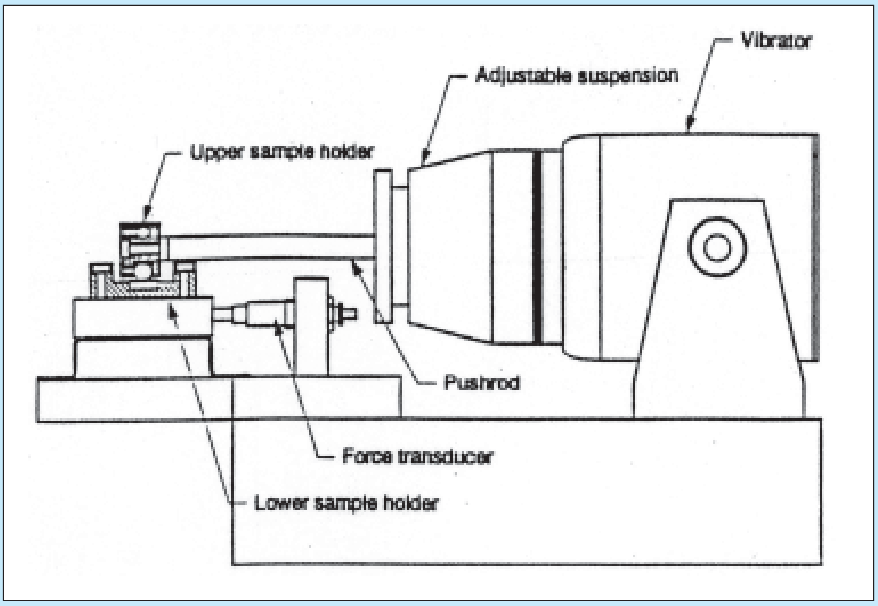

Figure 2
Schematic of the HFRR Test Apparatus[3)]

Table 3
Test results diesel fuel refinery R1, FAME and their mixtures

Characteristics	Unit	Concentration of FAME in Diesel Fuel (%vol)					Test Method ASTM
		0	1	5	10	100	
Density at 15°C	kg/m^3	851	852	853	854	876	D 1298
Cetane number		56	56,4	56,9	56,9	67,4	D 613
Flash Point, PMcc	°C	78	78	79	80	>110	D 93
Cu strip corrosion	No.	1a	1a	1a	1a	1a	D 130
Sulfur content	% m/m	0,3	0,297	0,285	0,27	Nil	D 1226
Viscosity @ 37,8°C	cSt	3,57	3,58	3,68	3,83	5,08	D 445
WSD/Lubricity	µm	300	287	256	245	242	D 6079

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Table 4
Test results of diesel fuel refinery R2, FAME and their mixtures

Characteristics	Unit	Concentration of FAME in Diesel Fuel (%vol)					Test Method ASTM
		0	1	5	10	100	
Density at 15°C	kg/m^3	849	850	851	852	876	D 1298
Cetane namber		57,4	57,4	57,8	59,2	67,4	D 613
Flash point, PMcc	°C	67	68	70	72	>110	D 93
Cu strip corrosion	No.	1a	1a	1a	1a	1a	D 130
Sulfur content	% m/m	0,25	0,248	0,238	0,225	Nil	D 1226
Viscosity @ 37,8°C	cSt	4,15	4,16	4,22	4,26	5,08	D 445
WSD/Lubricity	µm	620	363	287	264	242	D 6079

Table 5
Test results of diesel fuel refinery R3, FAME and their mixtures

Characteristics		Concentration of FAME in Diesel Fuel (%vol)					Test Method ASTM
	Unit	0	1	5	10	100	
Density at 15°C	kg/m^3	849	850	851	852	876	D 1298
Cetane namber		60,8	61,2	61,3	61,5	67,4	D 613
Flash point, PMcc	°C	86	86	87	88	>110	D 93
Cu strip corrosion	No.	1a	1a	1a	1a	1a	D 130
Sulfur content	% m/m	0,23	0,228	0,219	0,207	Nil	D 1226
Viscosity @ 37,8°C	cSt	5,42	5,36	5,33	5,34	5,08	D 445
WSD/Lubricity	µm	311	310	291	283	242	D 6079

Blending biodiesel with diesel fuel decrease wear scar diameter (WSD), it is mean increase lubricity. Adding 1%, 5% and 10% FAME into diesel fuel from refinery R1 WSD decrease from 300 µm to 287 µm, 256 µm, 245µm respectively. It is mean the higher FAME concentration, the higher lubricity increase.

B. *Diesel Fuel Refinery R2*

Test results of diesel fuel from refinery R2, FAME and their mixtures is shown in Tale 3. Test results of diesel fuel refinery R2 (0% vol FAME) characteristics meet Diesel Fuel 48 specification and its lubricity is 620 mm, it is higher than lubricity specified in Diesel Fuel 51 specification (460 µm) and FAME characteristics (100% vol FAME) meet biodiesel specification. Adding 1%, 5% and 10% volume FAME into diesel fuel cause fuel characteristics change. All characteristics change still in the range of Diesel Fuel 48 specification.

Blending biodiesel with diesel fuel decrease wear scar diameter (WSD), it is mean increase lubricity. Adding 1%, 5% and 10% FAME into diesel fuel from refinery R2 WSD decrease from 620 mm to 363 mm, 287 µm, 264 µm respectively. It is mean the higher FAME concentration, the higher lubricity increase.

C. *Diesel Fuel Refinery R3*

Test results of diesel fuel from refinery R3, FAME and their mixtures is shown in Tale 3. Test results of diesel fuel refinery R3 (0% vol FAME) characteristics meet Diesel Fuel 48 specification and its lubricity is 311 µm, it is lower than lubricity specified in Diesel Fuel 51 specification (460 µm) and FAME characteristics (100 %vol FAME) meet biodiesel specification. Adding 1%, 5% and 10% volume FAME into diesel fuel cause fuel characteristics change. All characteristics change still in the range of Diesel Fuel 48 specification.

Blending biodiesel with diesel fuel decrease wear scar diameter (WSD), it is mean increase lubricity. Adding 1%, 5% and 10% FAME into diesel fuel from refinery R3 WSD decrease from 311 µm to 310 µm, 291 µm, 283 µm respectively. It is mean the higher FAME concentration, the higher lubricity increase.

The increasing of lubricity diesel fuel from refinery R1, R2 and R3 is summarized in Table 6 and Figure 3. The WSD of diesel fuels from refinery R1 and R3 are lower than WSD specified in Diesel Fuel 51 specification (460 µm). Both of these diesel fuels no need to be added with lubricity additive. Diesel fuel from refinery R2 has higher WSD (620 µm). This diesel fuel need to be added with lubricity additive to bring WSD lower than 460 µm.

VII. CONCLUSION

From the analysis of test results and foregoing discussion it can be concluded as follow:

- Hydrotreating process for desulfurization of diesel fuel simultaneously decreasing components that provide good natural lubricity, when sulfur content is reduced, the risk of inadequate lubricity increase. To enrich lubricity of diesel fuel needed to be added with lubricity additive
- Biodiesel has wear scar diameter (WSD 242 µm) much lower than WSD specified in Diesel Fuel 51 (460 µm) can be used as an additive to improve lubricity of diesel fuel. The higher effect of increasing lubricity of diesel fuel, when it is blended with poor lubricity diesel fuel.

Table 6
Resume of lubricity change of diesel fuel

FAME	Lubricity of Refinery (µm)		
(% vol)	R1	R2	R3
0	300	620	311
1	287	363	310
5	256	287	291
10	245	264	283

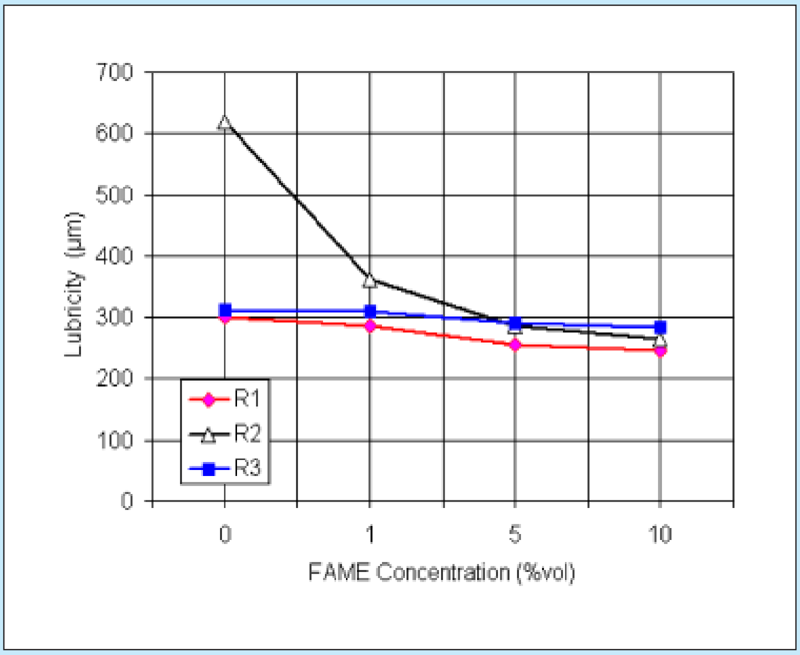

Figure 3
Resume of lubriity change of diesel fuel

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