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Lubricity Improvement of the Ultra-low Sulfur Diesel Fuel with the Biodiesel

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Abstract

Ultra-low sulfur diesel fuel is essential requirement as per the emission regulation. With the adoption of hydrodesulfurization (HDS) process, the diesel fuel loses its inherent lubricity, however certain amount of lubricity of diesel fuel is needed to save several engine components from wear and failure. Though the loss of lubricity of the diesel fuel is observed with the removal of sulfur, it is mainly due to the loss of nitrogen and oxygen based polar trace compounds which are also removed in the HDS process. Unrefined biodiesels having little amount of monoglycerides (<0.8%) and free fatty acids also show better lubricity and fuel properties to be used as fuel lubricant. Biodiesel are also considered as the suitable blending compound with the diesel. This study found that the biodiesel blends up to 20% with the diesel fuel can effectively reduce both the wear of the tribo-contact surfaces as well as the friction coefficient. The use of biodegradable fuel lubricant has set away the threat of environment pollution by the diesel additives which are derived chemically. The oxidation stability and the low temperature properties of both the biodiesel and the vegetable oils can be improved with some chemical modification. It can be concluded that the use of biodiesel with the diesel fuel can be an appropriate option for effective engine lubrication system where only the fuel has to provide the required lubricity.

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Keywords: ULSD; hydrodesulfurization; biodiesel; monoglycerides; biolubricant;fuel lubricity.

1. Introduction

Friction/traction and wear are the obvious requirement when one substance is moving over another substance. In engine fuel system, the relevant components experience the friction with the fuel flow activities. The useful work is obtained from the engines only when the produced energy can overcome the

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friction of these moving parts. Reportedly, more than 30% of the mechanical energy (i.e. ~38% of total thermal energy produced by the engine) is lost due to friction in the engine and other moving parts to move the vehicle [1-3]. Figure 1 is schematically demonstrating the energy distribution after being produced in an engine due to fuel combustion. On the other hand, lubricity of a fluid is the indication of how much it can protect two mating surfaces from wear or scarring due to motion between that two mating bodies [4]. Fuel lubrication is necessary to the engine components to reduce the friction between the mating components. If the fuel does not contain enough lubricating ingredients, it is considered as a "dry fuel" for its incapacity of lubricating the components like fuel delivery and injection system, cylinder liners, etc. [5, 6]. Tung and McMillan [7] mentioned that to perform under acceptable ranges, different components experiences various lubrication regimes, e.g. hydrodynamic (HDL), elasto-hydrodynamic (EDHL), boundary (BL) and Mixed (ML) lubrication. The fuel guards the metallic parts away from rapid wear by forming HDL films (function of fuel viscosity) or BL films (function of di-aromatic constituents) in between the solid surfaces [6, 8].

Automotive lubricants solely can be burnt in high temperatures in presence of oxygen and turn into acidic in nature to increase the rate of corrosion and wear of the mating components. They require some alkaline type anticorrosion additives to abate this burnout, which combinedly create a fluid film in those mating surfaces. The lubricant must withstand variable loads along with high temperature conditions to by reducing the friction or traction. Due to presence of high-pressure pump in the fuel flow system, the diesel engine's mechanical frictional losses (i.e. piston-crank, piston ring-combustion cylinder-fuel pump liner, various auxiliary assemblies, etc.) are higher than petrol engines. Besides, about 1.5-2.5% fuel consumption can be reduced if the mechanical frictional losses are reduced by 10% [9]. Since the amount of frictional energy losses is comparable to the exhaust emission, reduction of frictional energy loss can increase the overall efficiency.

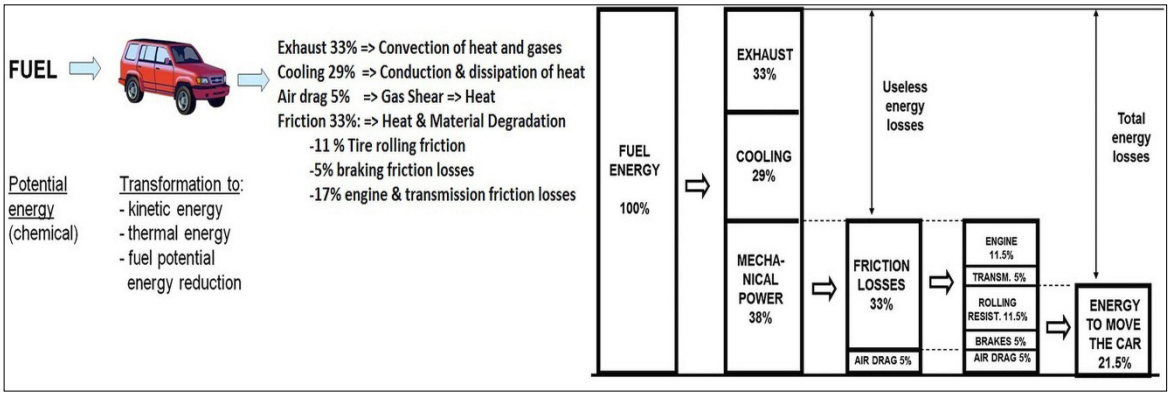

Fig. 1. Distribution of energy losses produced by an engine from combustion of fuel [3]

The inherent lubricity quality of the diesel fuel was in a reserve capacity level prior to the effect of stringent emission standard mandates on diesel fuel sulfur content (Table 1) for the purpose of reducing the environment pollution [4, 10]. Indeed, the fuel lubricity is not a function of sulfur content in it [8]. Because, the naturally available trace level complex polar substances (e.g. oxygen-, nitrogen-, aromatics, and olefinic contents) which used to be in the diesel fuel and created protective layers on the metal surfaces as a natural lubricant are also destroyed in the hydro-desulfurization process [6, 11].

Typically the number 1 diesel has lower lubricity than that of number 2 diesel [4]. Viscosity and the lubricity are not the interlinked parameters; highly viscous fluid can consume more energy to flow through a system, whereas, highly lubricious fluid can protect the contacting surfaces from wear and help in

withstanding the load [12, 15]. Schumacher and Howell [12] observed that the addition of biodiesel into the diesel fuel improves the fuel's lubricity property. They found that the addition of at least 20% biodiesel can effectively improve the lubricity of low sulfur diesel fuel. Moreover, the biodiesel fuel can reduce the emission contents for better environment [16]. Hence, the biodegradable fuel, biodiesel, can effectively reduce the necessity of adding more chemical additives in the diesel fuel for the same purpose.

In this article, the lubricity property improvement of diesel fuel with the addition of various biodiesels and vegetable oils is studied. Since the ultra-low sulfur diesel is obvious option for environment protection from the engine emission, the use of biodiesels or vegetable oils as bio-lubricant can be a great potential in this case.

Table 1: Sulfur content mandates of on-road transport vehicle diesel fuels

Fuels	USA [12, 13]		Australia [14]	
	Sulfur content	Year	Sulfur content	Year
Diesel fuel	5000 ppm	Until 1993	5000 ppm	Before 2002
Low sulphur diesel fule	≤ 500 ppm	1993	≤ 500 ppm	2002
Ultra-low sulphur diesel fuel	≤ 15 ppm	2006	≤ 50 ppm	2006
	-	-	≤ 10 ppm	2009

2. Improvement of fuel lubricity

2.1. Anti-wear additive mechanism

The lubricity of the diesel fuel can be improved by adding some chemical substances as additives. Arkoudeas et al. [17] mentioned that, the lubricity of number 1 diesel and number 2 diesel fuel appears to rise from very small quantities of polar, to quite high boiling point components. Agarwal et al. [6] described that, lubricity additives comprise a range of surface active chemicals. They have an affinity for metal surfaces and form boundary films that prevent metal – metal contact, which otherwise could have led to wear under light to moderate loads. When different additives are simultaneously present in a fuel, their surfactants can competitively react with the metal of friction surfaces. Surfactants of other additives can be sorbed on the friction surfaces, forming boundary layers capable of preventing the metal from reacting with the anti-wear additive. They have observed that the 1-amino glycerol mixed with diesel fuel as an additive gives less wear scars than that of glycerol compounds. Moreover, when the organic compounds are used as anti-wear additives, the polar parts are dissolved in the hydrocarbon fuels so that the polar/non-polar effects are balanced. As a result, the mixed compound is adhered on the rubbing metal surfaces in the form of boundary lubrication to reduce the wear [18].

2.2. Use of Biodiesel and Vegetable Oils

The biodiesels can be considered as lubricity property enhancer for diesel fuel. And the vegetable oils can be considered as alternative to the mineral/synthetic lubricant basestocks. Use of biodiesel-diesel blends thus reduces the use of further anti-wear additives in the fuel. Also, such blends are considered as effective alternative fuels for diesel engines.

2.2.1. Lubricity of Biodiesels

Biodiesel is one of the alternative clean transport fuels to be used in unmodified diesel engine. It is sure that the tribological properties of a fuel are not the sole parameters for overall quality assessment of the fuel. But, if the fuel possesses lower level of lubricity, it is not encouraging to use that fuel for internal combustion engines without further chemical treatment. Hu et al. [19] observed that both the monoglycerides (MG,<0.8% w/w) and the fatty acid methyl esters (FAME, >96% w/w) content ascertain the lubricity level of the standardized biodiesel. The researchers also observed that the free fatty acid contents (FFA, <0.4% w/w (oleic acid as typical FFA)) and diglycerides (DG, <0.4% w/w) can have moderate effect on the lubricity property of the biodiesel, but the triglycerides (TG, <0.4% w/w) do not have that capacity. Though the amount of %wt of MG is too small in the biodiesel, variation of its concentration can markedly change the lubricity property of the biodiesels produced from various feedstocks. Only unrefined biodiesels can retain these glycerides, thus show some lubricity properties in the diesel-biodiesel blends. Since, biodiesel is an oxygen rich fuel, Knothe et al. [20] found that the oxygen moieties in the biodiesel has the lubricity ability (by HFRR test) in the order of COOH > CHO > OH > COOCH3 > C=O >C-O-C. The fatty acids in the biodiesel contain polar-imparting O atoms, which offer better lubricity of the fuel. Also, the biodiesels rich in oxygen (in terms of aliphatic fatty acids) can lower the friction and wear in comparison to diesel [21]. Moreover, hydroxylated FAME significantly enhances the lubrication quality of diesel fuel than that of the non-hydroxylated FAME [20, 22].

Haseeb et al. [23] mentioned that the same lubricant experiences increased wear and friction with temperature rise in the contact surfaces. They found less wear rate for 50% blend of palm biodiesel, i.e. though the wear rate increases with the temperature, the increased biodiesel content reduces the friction and wear rate. The test was conducted in a four-ball tribometer. Bhatnagar et al. [24] found almost 45% reduction of WSD for inedible feedstocks derived biodiesel from *Jatropha curcus, Pongamia glabra, Madhuca india and Salvadora oleoides* compared to the high speed diesel fuel in a HFRR test rig. They found that up to 20% blend of these biodiesel fuels exhibited improved lubricity. On the other hand, Demirbas [25] and Knothe et al. [20] mentioned that the ultralow-sulfur diesel (ULSD) fuel blended with at least 1% biodiesel can exhibits about 30% improvement in its lubricity.

Since the ULSD experiences the loss of oxygen, nitrogen and polar compounds during the removal of sulfur, it possesses a very poor level of lubricity. So a small amount of biodiesel shows the significant improvement in the fuel lubricity. Moreover, the lubrication property of biodiesel can reduce the long-time engine wear by 50% in comparison to the ULSD fuel [20]. Sulek et al. [26] used 5% rape seed methyl ester as an additive to fuel oil and found that the friction and wear reduced about 20% and 50% respectively in comparison to the fuel oil due to formation of a durable lubricant film in the tribo-contact surfaces. Biodiesel can contribute in reducing the pollutant emissions from engine combustion and effectively contribute to improve the diesel-biodiesel blend fuel's lubricity. Therefore, it can be considered as a lubricity enhancer of diesel fuel.

2.2.2. Vegetable oil based lubricants

Vegetable oils (both edible and non-edible) possess effective lubricant properties along with their biodegradability and non-toxic attributes. They do not expose any threat to environment during disposal like the synthetic or mineral lubricants mixed with additives [27]. Shahabuddin et al. [28] investigated the Jatropha oil with the SAE40 lubricant in various proportion from 10 to 50. Their investigation has shown that the 10% Jatropha oil mixed lubricant blend (JBL10) can demonstrate almost similar anti-wear property of base lubricant. Both the wear scar diameter (WSD) and coefficient of friction (COF) were found as 0.35mm and 0.045 respectively with the JBL10, which are within the standard limits. Zulkifli et al. [29] investigated

lubricant capacity of palm-oil-derived trimethylolpropane ester (TMP) in various lubrication regimes, i.e. BL, HDL, etc. They found that the 3% TMP mixed with ordinary lubricant can reduce the WSD and COF by 30% in BL regime. Whereas, in HDL regime, 7% TMP mixed ordinary lubricant showed 50% reduction of the friction.

Several researchers [27, 30] have mentioned that because of higher viscosity index (i.e. less response of viscosity changing with temperature), lower volatility, higher flash-point, and better contact lubrication properties with comparison to the mineral/synthetic base oils, the vegetable oil based lubricant could be also used as a lubricant basestock. But they need some chemical treatment to overcome the oxidation instability (due to bis-allylic protons) as well the low temperature property issues. Cavalcante et al. [31] mentioned that the oleic acid ($C_{18:1}$) content in the biodiesel, which is a monounsaturated fatty acid and abundantly found in both edible and non-edible sources, can be effectively used to produce biolubricants. Due to unsaturation quality, it is good in cold flow property but vulnerable to the oxidation stability. Erhan et al. [32] have demonstrated that the blend of two chemical additives (2% zinc-diamyl-dithiocarbamate (ZDDC) and 2% antimony-dialkyl-dithiocarbamate (ADDC)) and 20% diluent polyalphaolefin (PAO) in the high-oleic vegetable oils (i.e. oils of less polyunsaturated fatty acids) significantly increased the oxidation stability of the vegetable oils by as much as 35%. The oils used in their tests were alkali refined soybean oil (SB), a high-linoleic soybean oil (HLSB), a mid-oleic soybean oil (MOSB), a high-oleic soybean oil (HOSB), a high-oleic sunflower oil (HOSF) and a high-oleic sunflower oil (HOSN).

The ZDDC is an excellent antioxidant to vegetable oils [33], whereas, the ADDC exhibits antiwear, extreme pressure additive as well as antioxidant properties [32]. Besides, the cold flow properties of the vegetable oils can be improved by using 1%PPD and 20%PAO diluent in these vegetable oils. Quinchia et al. [34] also observed better cold flow properties for other vegetable oils using 1%PPD. With the improved oxidation stability and cold flow properties, the vegetable oil based lubricant basestock can be the appropriate option for better lubricity in the moving components. Indeed, the biolubricants outperform the mineral lubricants with such modifications. Better use of lubricants can reduce the consumption of fuel up to 1-2% [35, 36].

3. Discussion

The hydrodesulfurization (HDS) or hydtrotreating has been considered to remove the sulfur content from the fuel to meet the stringent emission standards of the fuel combustion. In that sense, the reason of reduction of lubrication properties of the ULSD fuels is sometimes considered as due to sulfur removal. But the process also removes other compounds like nitrogen and oxygen based polar substances, which governs the lubricity of the diesel fuel. Uses of chemical additives are found in order to improve the lubricity of the fuel. But the chemical additives are not ecofriendly. On the other hand, unrefined biodiesel can exhibits some inherent lubricity due to presence of MG, DG, FFA, etc., which in a small portion mixed with the diesel fuel can effectively enhance the fuel's overall lubricity. The monounsaturated fatty acid ester content of the biodiesel has been found to be effective in improving the fuel's lubricity.

The biodiesel is biodegradable and non-toxic to the environment, which encourages use/production of more ecofriendly biodiesel fuel. The engine durability tests with biodiesels have proved that the fuel is appropriate to degrade the metal surfaces and the fuel distribution system of the enigne. Moreover, the crude oil (vegetable oil) of the biodiesel possesses a lot of MG along with their fatty acid contents for which it can be considered as lubricant basestocks. Indeed, the biolubricants outperform the mineral lubricants with such modifications. Better use of lubricants can reduce the consumption of fuel up to 1-2%. Hence, the uses of biodiesel as biolubricant with the diesel fuel can commercially and environmentally be a suitable option.

4. Conclusion

Use of biodiesel with the diesel fuel, especially with the ULSD, can serve as a lubricity improver along with the proven qualities of emission and combustion performances. Though 1% addition of biodiesel can enhance the ULSD's lubricity by 30%, the use of up to 20% biodiesel in the diesel fuel can serve in best way as clean alternative. The lubricity order has been found as COOH > CHO > OH > COOCH3 > C=O >C-O-C. The polar-imparting O atoms of the fatty acids offer better lubricity of the fuel. Also, the biodiesels rich in oxygen (in terms of aliphatic fatty acids) can lower the friction and wear in comparison to diesel. Moreover, hydroxylated FAME significantly enhances the lubrication quality of diesel fuel than that of the non-hydroxylated FAME. So, mixing the biodiesel can be better alternative to the chemical additives to enhance the fuel lubricity. The vegetable oils also possess better quality with some chemical treatment to be considered for lubricant basestocks. The quantity of additives is also very low. Hence, the ULSD fuel can be well accepted by the diesel engines without further contribution of pollutants in the environment due to the chemical additives.

5. Copyright

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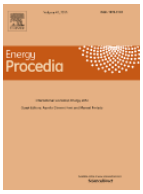

Biography

M.A. Hazrat is currently enrolled in PhD program in the School of Engineering & Technology, Central Queensland University, Australia. He has a keen interest on applied engineering analysis in the areas of thermofluid, thermodynamics and energy engineering. At present, he is pursuing research on alternative fuel processing, properties determination and application in the automotive engines.