Paper Reference ID: RTC 021

MODELLING ASPECT OF CORROSIVE WEAR UNDER BIODIESEL

A.A. Adebisi and M. A. Maleque

Department of Materials and Manufacturing Engineering
International Islamic University Malaysia
53100 IIUM Gombak, Kuala Lumpur, Malaysia
E-mail: debisi1@yahoo.com, maleque@iium.edu.my

ABSTRACT

Biodiesel as an alternative renewable fuel is increasingly been considered as blending components or replacement for conventional petroleum fuel. Although the acceptability of biodiesel in automotive application is relatively a successful story, it is an issue with regards to its materials incompatibility. When compared to diesel, biodiesel is more prone to absorb water and allows the development of electrochemical corrosion. Corrosive wear occurs as a result of chemical reaction on wearing surface. The main aim of this paper is to study the modelling aspect of corrosive wear under biodiesel for automotive application. A systematic review analysis was performed on the corrosive wear, wear of engine component materials using on road engine test, aspect of corrosive wear and also factors affecting corrosive wear of automotive component. A corrosive wear model has been developed with three main domains such as mechanical wear, electrochemical corrosion, and interaction of both processes to evaluate the total corrosive wear of automotive component materials under biodiesel. It was found that modelling aspect play an important role in the measurement of corrosive wear especially under biodiesel.

Keywords: Modelling, corrosive wear, automotive materials, Biodiesel

1. INTRODUCTION

Corrosive wear occurs as a result of chemical reaction resulting from the combination of a wear mechanism and a corrosive environment. The combined effect of the two processes involves mechanical and electrochemical mechanisms which often result to substantial increase in the rate of material loss and degradation [method] when compared to the individual process of wear or corrosion action. The process of interaction among the operating mechanism such as abrasion, impact, rubbing and corrosion etc influences the total material losses and degradation especially in the presence of an aqueous environment. In a study carried out by Dun (1985), corrosive wear has seventeen synergistic relationships between abrasion, impact and corrosion that facilitate significant increase to wear mechanism in wet and aqueous environments. The effect of these relationships can be minimized by acquiring fundamental knowledge of the interaction mechanism and their significant to the specific environment. However, the quantification of the corrosive wear synergism provides information on the required material for reducing total material loss for a particular environment. Also corrosive wear could be minimized by expressing the wear degradation and corrosion in common terms which allows the synergism between the degradation processes qualitatively and quantitatively. Model development for corrosive wear mechanism provides an insight into the behaviour of the synergism by controlling, quantifying and optimizing the process. Madsen (1994) developed a penetration rate equation model for quantifying each of the degradation process for both corrosion and wear by providing useful information on the synergism between the processes. These models are used to quantify the synergism result obtained from the abrasive and sliding wear measurements. Batchelor and Stachowiak (1988), Schumacher (1985); (1993) and Yue et al., (1987) have studied the synergism between wear and corrosion. The main objective of this paper is to study the modelling aspect of corrosive wear under biodiesel for automotive application by utilizing a systematic review analysis.

Different components of the automotive engine parts such as filter, fuel liners, piston rings, fuel pump, fuel injector, gaskets etc made from different materials such as aluminium, copper, brass, zinc, bronze, elastomers have direct contact with fuel (biodiesel). Biodiesel becomes more corrosive during usage or storage due to degradation as a result of oxidation (Monyem, 2001), moisture absorption (Thompson, 2007), attack by microorganism (Klofutar, 2007). Oxidation of biodiesel reconverts esters into different mono-carboxylic acids like formic acid, acetic acid, propionic acid, caproic acid, etc which are responsible for enhanced corrosion. This process also increases the free water content which is undesirable because it may promote microbial growth and corrode fuel system components. Kaul et al, (2007) studied the corrosion characteristics for non edible oils like *Jatropha curcas*, *Pongamia glabra* (Karanja), *Madhuca indica* (Mahua) and *Salvadora oleoides* (Pilu) using long duration static immersion test for engine part like piston metal and piston liner. Biodiesel from *salvadora* showed marked corrosion on the diesel engine compared to neat diesel. Investigations carried out by Geller (2008) showed that copper alloys are more prone to corrosion by biodiesel as compared with ferrous alloys.

The corrosion behavior of aluminum exposed to biodiesel can be compared to the corrosion behavior of aluminum in aqueous solutions. It was also observed that corrosion of aluminum can be used as a quantitative indication of biodiesel purity (Diaz-Ballote, 2009). Maleque et al. (2000) and Kalam and Masjuki (2002) observed that the wear rate in biodiesel was relatively higher due to its oxidative and corrosive behaviors. Corrosiveness and tribological properties of biodiesel also depends on its feedstock (Bu inskas, 2009). Pure biodiesel sample from different origin has better value and lower tribological properties. However, regular diesel fuel has more stable properties compared to pure biodiesel as a result of difference in production process.

2. WEAR ANALYSIS OF BIODIESEL

Biodiesel is a realistic fuel alternative for diesel engines based on its lower energy content, higher cetane number, free of contaminants like sulphur and aromatics and most significantly burns cleaner than conventional diesel fuel. However, its capacity is been limited as a result of feedstock availability. The need of biodiesel for automobile application raises concern on the impact of corrosion wear behaviour on automobile engine when it comes in contact with tribo-component of static and dynamic parts like piston, piston rings etc. The wear rate of materials in the presence of biodiesel occurs in various forms which amount to the evaluation of metal debris generated as a result of wear. Fontaras et al., (2009) investigated the metal particulate concentration in neat soybean oil biodiesel (B100) and its 50 vol% blend with petroleum diesel (B50) on diesel engine passenger car in order to access the biodiesel impact on wear. The analysis of the lubricating oil samples showed that the use of B50 and B100 may lead to increased wear in terms of higher amounts of metallic elements, originated from the different moving parts.

Investigations on wear in automobile engine for biodiesel derived from different sources like rapeseed, palmoil, and soybean were carried out for both static engine test and on-road engine test which involves static (fuel tank, filter, fuel pump injector housing, fuel line, exhaust system, cylinder liner etc) and dynamic (piston, piston rings, inlet and exhaust valve, fuel pumps and filters plunger, connecting rod) components. The dynamic components are mostly metals and they slide against each other and also on the static part during operation which results in the generation metal debris due to wear. Table 1 summarizes the test conducted by analyzing the concentration of the metal debris in the lubricant oil after running the engine for a particular period of time. The wear rate, source of element and engine condition provided relevant information from the test conducted. Biodiesel enhances better lubricity than diesel fuel as a result of its inherent properties and the presence of components such as free fatty acids, monoglycerides; diglycerides found in the biodiesel fuel which improves the lubricity of the fuel (Knothe, 2005). Oxygen containing compounds such as free fatty acids, esters are superior wear and friction reducing agents (Haseeb et al., 2010). These compounds adsorb or react on rubbing surfaces to reduce adhesion between contacting asperities and thereby limit friction, wear and seizure.

Table 1 elemental analysis for on-road engine test results on wear in biodiesel as compared with diesel

Sources	Biodiesel	Engine Operation Hour	Wear elements						References
			Al	Cr	Cu	Fe	Pb	Zn	
Ethyl soyate	B100	200	H	L	H	L	H	-	Clark et al. (1984)
Methyl soyate	B100	200	L	S	L	L	H	-	Clark et al. (1984)
Rapeseed	B20	512	L	L	L	L	L	-	Agarwal et al. (2003)
Rapeseed	B100	1000	L	L	-	L	L	-	Perkins et al. (1991)
Rapeseed	B50	1000	L	L	-	L	L	-	Perkins et al. (1991)
Palm oil	B100	1000	H	H	H	S	H	-	Prateepchaikul and Apichato (2003)
Palm oil	B7.5	100	L	-	L	L	L	-	Kalam et al., (2002)
Palm oil	B15	100	L	-	L	L	L	-	Kalam et al., (2002)
Palm oil	B7.5	300	-	-	L	L	L	H	Hu J. et al. (2005)
Linseed oil	B20	500	-	L	L	L	L	L	Agarwal et al. (2003)

L = less wear; S = similar wear; H = higher wear

3. CORROSION OF BIODIESEL

Biodiesel is a vegetable based oil or animal fat-based diesel fuel consisting of saturated and unsaturated long chain fatty acid alkyl (methyl, propyl or ethyl) esters and are produced chemically by reacting lipids e.g., vegetable oil, animal fat (tallow) with alcohol. The presence of free fatty acid which may exist as a consequence of incomplete transesterification reaction and the ability of the biodiesel to absorb moisture (hygroscopic nature) increase the corrosiveness of the fuel. Moreover, the auto-oxidation of biodiesel can also catalyze the corrosion characteristics. Transesterification (also called alcoholysis) reaction of the fat or oil triglyceride with an alcohol forms esters and glycerol. Figure 1 shows the transesterification reaction of triglycerides. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. The reaction results in a compound called fatty acid alkyl ester (biodiesel) and a by product, glycerol. From the resulting reaction, hygroscopic biodiesel may be formed due to persistence of mono and di glycerides left over from an incomplete reaction process. Biodiesel degrades through the process of oxidation, moisture absorption and attack by microorganism during storage or use. The oxidation of biodiesel reconverts esters into different mono-carboxylic acids like formic acid, acetic acid, propionic acid, caproic acid, etc which are responsible for enhanced corrosion (Tsuchiya, 2006).

This process also increases the free water content which is undesirable because it may promote microbial growth and corrode fuel system components. Several investigation have been carried out to determine the corrosiveness of different biodiesel and the corrosion effect on material compatibility for automotive component materials like aluminium, copper, stainless steel and leaded bronze using static immersion test (Fazal et al., 2010 and Haseeb et al., 2010) In automobile fuel system application, components made from aluminium are piston (100%), engine block (19%), cylinder head (70%) etc. Other components made from stainless steel include valve bodies, fuel filter, nozzle and pump ring.

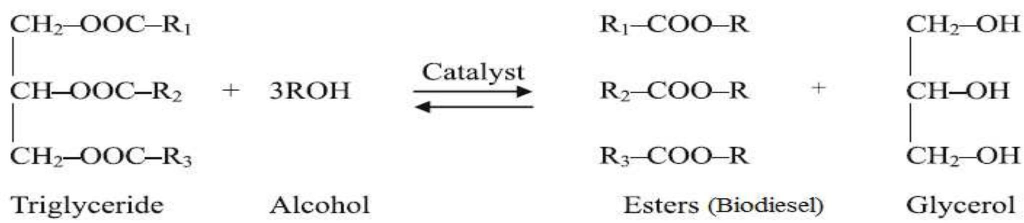

Fig. 1 Transesterification reaction of triglycerides

Moreover, copper and its alloy are used to manufacture injector, pump and bearing (Fraer, 2005). All these component parts made from different materials come in contact with fuel which undergoes chemical reactions and thereby deteriorate the material as well as degrade the fuel properties too. Kaul et al., (2007) investigated the corrosiveness of different biodiesel (i.e. Jatropha curcas, Karanja, Mahua and Salvadora) as compared to that of diesel fuel. They found that biodiesel from Jatropha curcas and Salvadora were more aggressive for both ferrous and non-ferrous metal. Geller et al., (2008) observed that copper alloys are more prone to be attracted by corrosion in fat based biodiesel as compared with ferrous alloys. It was also reported that pitting corrosion was found on sintered bronze filters in oil nozzle after 10 h of operation with biodiesel at 70 °C (Sgroi et al., 2005). In another study, corrosion attack was also reported even for lower biodiesel (2%) blend levels (Tsuchiya, 2006). The corrosive and oxidative nature of biodiesel relatively increases wear rate (Haseeb et al., 2010).

Research conducted to determine the extent of corrosion on automotive component materials utilized weight loss measurement and change in surface morphology (Fazal et al., 2010). The data obtained from the weight loss were analyzed and converted into corrosion rate by using the equation;

$$\text{Corrosion rate}\,(mpy) = \frac{w \times 534}{D \times T \times A} \qquad (1)$$

where corrosion rate 'mpy' stands for mils (0.001 in.) per year, W is the weight loss (mg), D is the density (g/cm^3), A is the exposed surface area (square inch) and T is the exposure time (h). Haseeb et al. (2010) investigated the corrosion behaviour of commercial pure copper and lead bronze in automotive fuel system for static immersion test in B0, B50, B100 at room temperature for 2640hrs and B0, B100, B100 (oxidized) at 60°C for 840hrs. The result shows that pure copper was more susceptible to corrosion in biodiesel compared to leaded bronze. In another study, Fazal et al, (2010) studied the corrosion comparison of aluminium, copper and stainless steel in both diesel (B0) and biodiesel (B100) using immersion test at 80°C for 1200hrs. They observed that the effect of corrosion and change in fuel properties upon exposure to metal is more in biodiesel than diesel. They concluded that copper and aluminium were susceptible to attack by biodiesel whereas stainless steel was not.

4. FACTORS AFFECTING CORROSIVE WEAR

4.1 Materials properties

The properties of all the materials involved in the tribological contact and the reaction products formed on the rubbing surface and surrounding environment are of relevance to determine the material behaviour. In the absence of corrosion, wear resistance of a material depends on properties such as hardness, rigidity, ductility and yield strength. The relationship between these properties on corrosive wear rate requires an in depth study for better understanding of the synergistic mechanism. Published research has tried to study the synergistic effects between wear and corrosion processes which result in accelerated material loss and in some cases actually decelerate material loss.

4.2 Mechanical operation

The rate of corrosive wear for a given metal environment combination depends on the applied forces and the type of contact sliding, fretting, rolling or impact. The other factors include sliding velocity, type of motion, shape and size of contacting bodies, alignment, vibration etc. For example, in the case of fretting corrosion, there are small amplitude oscillations occurring in a corrosive environment. Contact geometry involving shape and size of contacting surfaces is another important parameter in corrosive wear, as it determines the size of the contact zone and the alignment of the rubbing surfaces. Different mechanical processes have different parameters affecting the process, like in case of erosion the energy and the angle of incidence of the impacting particles and their shape are critical variables.

4.3 Solution and environment

The environmental variables/parameters and contact conditions (metal pair or non-metal pair), play an important role in corrosive wear. Its influence is in the form of the medium at the interface i.e., solid, liquid or gaseous and its corresponding properties like viscosity, conductivity, pH, corrosivity, temperature etc. For example, the metals exposed to air, the relative humidity will determine whether a thin liquid electrolyte film may form at the surface changing the corrosion mechanism. In case of aqueous systems, concentration of oxygen, pH and concentration of certain anions like chloride ions influences corrosivity. In case of high temperature applications, the physical nature of the scales formed is critical. Certain corrosion products containing sulphur have a relatively low melting point, which can lead to the formation of highly corrosive molten salts on the surface.

4.4 Electrochemical parameters

In corrosive wear system, the corrosion monitoring is analyzed by using basic electrochemistry process. Basic parameters applied are potential, ohmic resistance, passive film growth, active dissolution etc, as shown in Fig. 2. The electrochemical aspect is considered mainly because corrosive wear phenomena have been studied for many years by electrochemists and tribologists. Electrochemists have concentrated their attention on the study of kinetics of repassivation of metal surfaces activated by scratching, whereas tribologists have been interested as to how surface oxidation during rubbing affects the rate of mechanical wear.

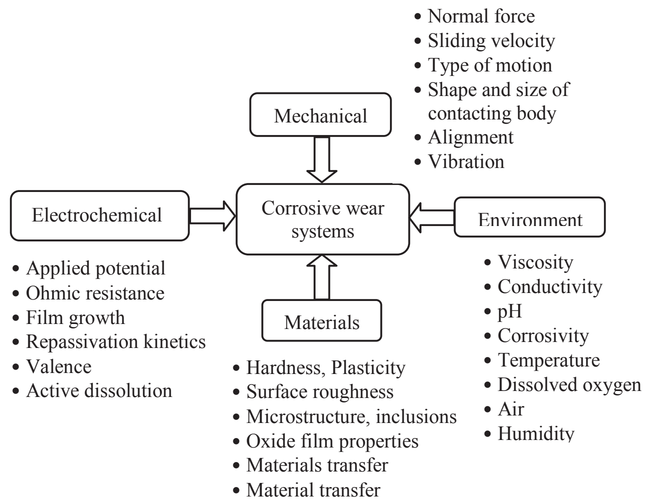

Fig. 2 Factors influencing corrosive wear

5. CORROSIVE WEAR MODEL

5.1 Corrosive wear interactions

Corrosive wear interactions can be expressed as wear-corrosion, where the total damage, *T*, is given by (i.e. sliding or abrasive wear):

$$D_T = W_M + C_S + S_I \quad (2)$$

where, W_M is the mass loss due to wear, C_S is the solids free flow corrosion rate and S_I is the synergistic or interactions term. Total damage under erosion–corrosion, D_T, can be represented as:

$$D_T = C_M + C_S + S_I \quad (3)$$

where C_M is the corrosive wear material loss,
There are numerous interactions between wear and corrosion and many ways to experimentally quantify them. Mostly these interactions are referred to as synergistic (two or more parameters interacts together to produce a result) and as attain the level of synergy. Synergy is the difference between wear-corrosion and the summation of its two parts and can be expressed by equation (4).

$$S_I = D_T - (C_M + C_S) = (\Delta C_W + \Delta M_W) \quad (4)$$

where D_T, C_S and C_W are typically gravimetric terms relating to wear-corrosion, electrochemical corrosion and mechanical wear mechanisms, respectively. The interactive processes can be simplified into two components, ΔC_W and ΔM_W, where ΔC_W is the corrosion-enhanced wear and ΔM_W is the mechanical/wear-enhanced corrosion. Recent literature has defined ΔC_W as the synergy term and ΔM_W as the additive term.

The synergistic effect (interactive term), S_E, is referred to as ΔC_W or ($\Delta M_W + \Delta C_W$) depending on the literature source and under what conditions C_S has been obtained. Synergistic levels for different materials must be carefully understood when using multiple sources of literature. The ASTM G119-93 standard is a very useful guide to measure and evaluate synergy (Ponthiaux et al., 2004).

5.2 Proposed Model for corrosive wear

The corrosive wear laboratory setup model needs to be properly configured in other to provide an accurate and reliable result. Figure 3 shows the proposed model which consist of a combined system, the tribometer to measure evolution of wear depth (linear wear) and the electrochemical set up to monitor the corrosion rate from the model system. The electrochemical set up consists of three electrodes as indicated by (c), (e) and (g). The sample is operating as the working electrode. The proposed model clearly shows that the corrosion phenomenon and the mechanical wear of the material under or in the presence of biodiesel can be measured simultaneously or concurrently and therefore provide the information on corrosive wear.

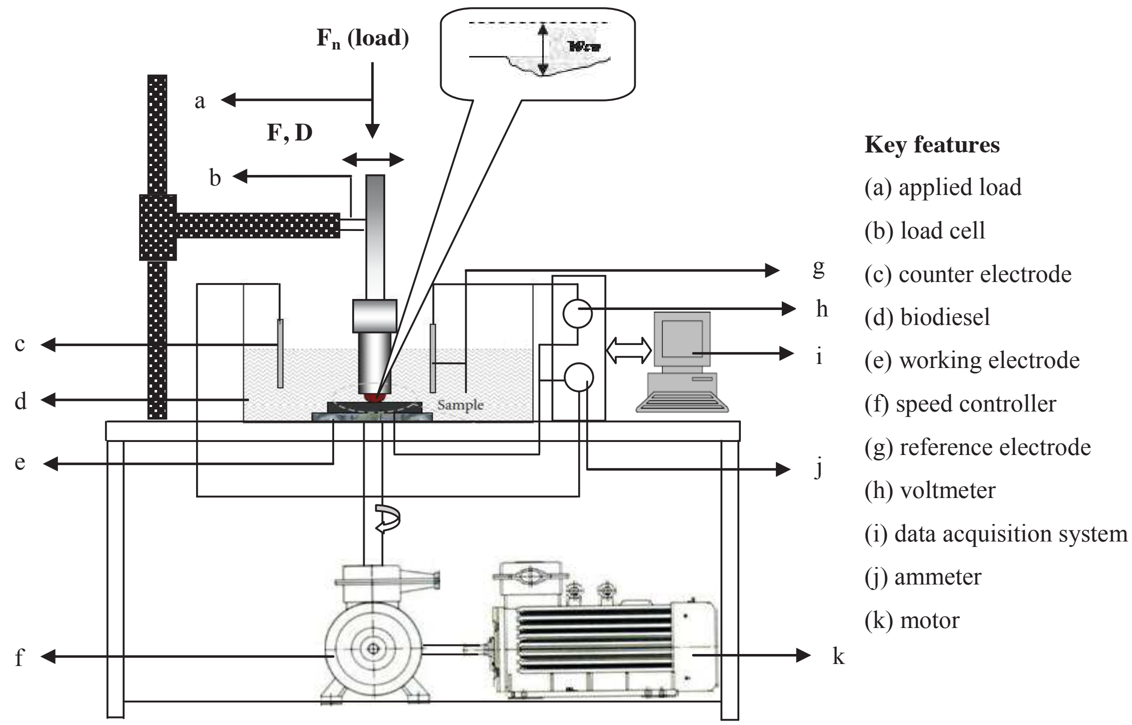

Fig 3 Proposed model for corrosive wear study of biodiesel

From the above it can be said that corrosive wear consist of three main domain, wear due to mechanical action, wear due to corrosion and wear due to the interaction of both corrosion and mechanical action under synergistic conditions.

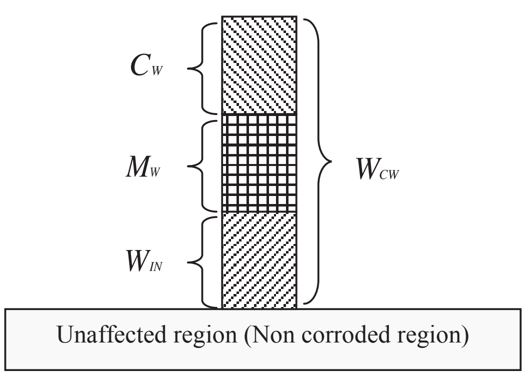

Fig 4 Model of sectioned profile of corrosive wear

Figs. 4 illustrate sectioned profile of corrosive wear in presence of biodiesel. Relative to a non- corroded region on a datum surface, the total corrosive wear can be expressed as;

$$W_{CW} = C_W + M_W + W_{IN} \quad (5)$$

Where,

$$W_{IN} = \Delta M_W + \Delta C_W \quad (6)$$

Therefore,

$$W_{CW} = C_W + M_W + (\Delta M_W + \Delta C_W) \quad (7)$$

Where W_{CW} = total corrosive wear
C_W = wear due to corrosion
M_W = wear due to mechanical action
W_{IN} = wear due to corrosion and mechanical action

It is expected that the total corrosive wear, w_{cw} can be measured using equation 7 and prediction can be made for the safe use of automotive component materials under biodiesel.

6. CONCLUSION

Based on the current study along with the proposed corrosive wear model the following conclusion can be drawn from the analysis;

i. The current study has been able to provide a general knowledge about the field of corrosive wear.

ii. Corrosive wear system is significantly influenced by factors such as mechanical action, material properties and the environmental condition.

iii. It is established from the study that corrosive wear mechanism has three domains such as wear due to mechanical action, wear due to corrosion and wear due to the interaction of both corrosion and mechanical action under synergistic conditions.

iv. The successful development of the model shows that the total corrosive wear can be obtained from the model set up.

Acknowledgement

This work was supported by FRGS research grants scheme No. FRGS10-026-0145 from Ministry of Higher Education, Malaysia. Authors are grateful to the International Islamic University Malaysia (IIUM) which made this study possible.

REFERENCES

Agarwal, A., J. Bijwe, et al. (2003). "Wear assessment in a biodiesel fueled compression ignition engine." Journal of engineering for gas turbines and power 125: 820.

Batchelor, A. and G. Stachowiak (1988). "Predicting synergism between corrosion and abrasive wear." Wear 123(3): 281-291.

Bu inskas, V. and R. Suba ius (2009). "Tribological Properties of Biodiesel Fuel and Its Mixtures with Diesel Fuel."

Clark, S., L. Wagner, et al. (1984). "Methyl and ethyl soybean esters as renewable fuels for diesel engines." Journal of the American Oil Chemists' Society 61(10): 1632-1638.

Díaz-Ballote, L., J. López-Sansores, et al. (2009). "Corrosion behavior of aluminum exposed to a biodiesel." Electrochemistry Communications 11(1): 41-44.

Dunn, D. (1985). "Metal removal mechanisms comprising wear in mineral processing." Wear of Materials 1985: 501-508.

Fazal, M., A. Haseeb, et al. (2010). "Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials." Fuel Processing Technology 91(10): 1308-1315.

Fontaras et al., T. T., L. Ntziachristos, and Z. Samaras (2009). Biodiesel (soy-bean FAME) effect on particulate and gaseous pollutants from a passenger car. European Aerosol Conference. Karlsruhe, Germany: 4.

Fraer, R., H. Dinh, et al. (2005). "Operating Experience and Teardown Analysis for Engines Operated on Biodiesel Blends (B20)." SAE Technical Paper: 01-3641.

Geller, D. P., T. T. Adams, et al. (2008). "Storage stability of poultry fat and diesel fuel mixtures: specific gravity and viscosity." Fuel 87(1): 92-102.

Haseeb, A. S. M. A., H. H. Masjuki, et al. (2010). "Corrosion characteristics of copper and leaded bronze in palm biodiesel." Fuel Processing Technology 91(3): 329-334.

Haseeb, A., S. Sia, et al. (2010). "Effect of temperature on tribological properties of palm biodiesel." Energy 35(3): 1460-1464.

Hu, J., Z. Du, et al. (2005). "Study on the lubrication properties of biodiesel as fuel lubricity enhancers." Fuel 84(12-13): 1601-1606.

Kalam, M. and H. Masjuki (2002). "Biodiesel from palmoil--an analysis of its properties and potential." Biomass and Bioenergy 23(6): 471-479.

Kaul, S., R. Saxena, et al. (2007). "Corrosion behavior of biodiesel from seed oils of Indian origin on diesel engine parts." Fuel Processing Technology 88(3): 303-307.

Klofutar, B. and J. Golob (2007). "Microorganisms in diesel and in biodiesel fuels." Acta chimica slovenica 54(4): 744-748.

Knothe, G. and K. R. Steidley (2005). "Lubricity of components of biodiesel and petrodiesel. The origin of biodiesel lubricity." Energy & Fuels 19(3): 1192-1200.

Madsen, B. "Standard guide for determining amount of synergism between wear and corrosion." ASTM

G119-93, 1994 Ann. Book ASTM Stand 3: 507-512.

Maleque, M., H. Masjuki, et al. (2000). "Effect of mechanical factors on tribological properties of palm oil methyl ester blended lubricant." Wear 239(1): 117-125.

Monyem, A. (2001). "The effect of biodiesel oxidation on engine performance and emissions." Biomass and Bioenergy 20(4): 317-325.

Perkins, L., C. Peterson, et al. (1991). Durability testing of transesterified winter rape oil (Brassica napus L.) as fuel in small bore, multi-cylinder, DI, CI engines, Society of Automotive Engineers.

Ponthiaux, P., F. Wenger, et al. (2004). "Electrochemical techniques for studying tribocorrosion processes." Wear 256(5): 459-468.

Prateepchaikul, G. and T. Apichato (2003). "Palm oil as a fuel for agricultural diesel engines: comparative testing against diesel oil." Songklanakarin Journal of Science and Technology 25(3).

Schumacher, W. (1985). "Corrosive wear synergy of alloy and stainless steel." Wear of Materials 1985: 558-566.

Schumacher, W. (1993). "Corrosive wear principles." Materials Performance;(United States) 32(7).

Sgroi, M., G. Bollito, et al. (2005). "BIOFEAT: Biodiesel fuel processor for a vehicle fuel cell auxiliary power unit:: Study of the feed system." Journal of power sources 149: 8-14.

Thompson, et al. (2007). "Moisture absorption in biodiesel and its petro-diesel blends." Applied Engineering in Agriculture 23(1): 71-76.

Tsuchiya, T., H. Shiotani, et al. (2006). "Japanese Standards for Diesel Fuel Containing 5% FAME: Investigation of Acid Generation in FAME Blended Diesel Fuels and Its Impact on Corrosion." SAE Technical Paper: 01-3303.

Yue, Z., P. Zhou, et al. (1987). "Some Factors Influencing Corrosion--Erosion Performance of Materials." Wear of Materials 1987. 2: 763-768.