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RESEARCH ARTICLE

USE OF USED PALM OIL AS BIOFUEL AND ITS CORROSION BEHAVIOUR ON A FEW INDUSTRIAL METALS

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ABSTRACT

Biofuel is a renewable and environmentally friendly alternative fuel that can be used in diesel engines with little or no modification. Low cost feed stocks such as waste oils, used cooking oils and animal fats are important sources of biofuel production. Use of waste cooking oil as a biofuel offers the possibility of transforming a pollutant waste into a sustainable and renewable energy source. During production, transportation and usage, biofuels come in contact with materials at various stages. Therefore it is important to understand the influence of biofuels on materials. The corrosive nature of biofuels can be more aggravated if free water and free fatty acid are present in it. Hence the present study aimed to investigate the corrosion behavior of aluminium, mild steel and copper in used palm oil in comparison with that in aqueous medium by various methods. Surface morphology was examined by optical microscope. The negligible corrosion rate in 100% oil for all three metals indicates that the oil may be used as alternate fuel alone or in blends with petrodiesel. The measured contact angle is obtuse for the three metals suggesting that oil preferably wets the metals and thereby preventing corrosion.

INTRODUCTION

The renewable sources of energy are emerging as a need to ensure sustainable development for current and future society. As one of the potential renewable energy, bio-energy is not a new invention since Rudolf diesel had already developed a diesel engine which was run with vegetable oil in 1900 (Hameed *et al*., 2009). There are many vegetable oils (Devan and Mahalakshmi, 2009; Meenakshi *et al*., 2011), which can be used as fuels in diesel engines and their chemical composition helps in reducing the emission of unwanted components when they are burnt. One of the methods to derive biofuel is the conversion of waste substances to energy. Million liters of oil used for frying foods are discarded each year into sewage systems. Nevertheless, due to the increase of food consumption, increasing amount of waste edible oils has led to significant disposal problems. From a waste management standpoint, producing biofuel from used cooking oils (Charoenchaitrakool and Thiemethangkoon, 2011; Ozsezen and Canakci, 2010) is environmentally beneficial and cleaner way for disposing these products (Farag *et al*., 2011).

Corrosion is one of the topics very relevant to the biofuel compatibility issue. Waste cooking oil becomes more corrosive due to high free fatty acid level. The situation becomes complex due to interplay between different features such as changes in total acid number, increased water content, oxidation product, unsaturated molecules, presence of metal species, etc. Very few research studies are available on the corrosion of metals and biofuels (Anisha *et al*., 2011; Haseeb *et al*., 2011; Wang *et al*., 2010). Systematic laboratory studies should be carried out under wide spectrum of experimental conditions to obtain more data to develop a user-friendly database on the compatibility between metals and biofuels. The objective of this paper is to compare the corrosion behavior of Used Palm Oil (UPO) on industrial metals including aluminium, mild steel and copper.

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MATERIALS AND METHODS

Selection of Metal and Preparation of Metal Sample

Potential problems such as corrosive nature of metals and degradation of biofuel arises from the fact that biofuel degrades through auto-oxidation, moisture absorption, attack by microorganisms etc. during storage and transportation. The exposure of different metals (ferrous and non ferrous metallic materials) in biofuel may aggravate its corrosive nature at different magnitude, thereby makes the situation more complicated. Hence the present paper is aimed to investigate the corrosion behavior of UPO on aluminium, mild steel and copper. The chemical compositions of the metals are presented in Table1. The preparation of the metal coupons and detailed experimental procedure for static immersion test, conductivity measurement, contact angle measurement and linear polarization resistance (LPR) method are given in previous publication (Meenakshi *et al*., 2010).

Biofuel collection and characterization

Used palm oil was collected from a fast food restaurant in Coimbatore, Tamilnadu, India. The characterization of the oil was performed as per ASTM D6751.

Surface Morphology

After the static immersion test in 100% oil (O100) and NaCl for a period of 100 hours, the corroded surface of aluminium, mild steel and copper coupons and their polished samples were characterized by inverted metallurgical microscope KOZO optics model XJM 404T.

RESULTS AND DISCUSSION

Analysis of biofuel

The various parameters for UPO analyzed as per ASTM D6751 are presented in Table 2. The data reveals that most of the properties of oil are comparable with the ASTM standards. The higher viscosity may be attributed to the high molecular weight and large chemical

Table 1. Elemental analysis of metals

Aluminium		Mild Steel		Copper	
Element	% Chemical composition	Element	% Chemical composition	Element	% Chemical composition
Aluminium	99.013	Iron	99.6	Copper	94.907
Copper	0.037	Carbon	0.102	Zinc	5.065
Magnesium	0.299	Manganese	0.222	Manganese	0.006
Silicon	0.285	Silicon	0.011	Aluminium	0.003
Iron	0.194	Phosphorous	0.030	Nickel	0.008
Manganese	0.075	Sulphur	0.026	-	-
Nickel	0.015	Chromium	0.003	-	-
Zinc	0.008	Molybdenum	0.035	-	-
Tin	0.020	Nickel	0.008	-	-
Titanium	0.021	-	-	-	-
Chromium	0.033	-	-	-	-
Density(g/cm^3)	2.73	-	7.87	-	8.96
Equivalent weight	9.09	-	27.92	-	31.77

Table 2. Fuel properties of used palm oil

Parameters	ASTM D6751	Units	Value	Units
Flash point	130.0 min	° C	162	° C
Water and sediment	0.050 max	% vol	0.05	%
Kinematic viscosity 40° C	1.9 – 6.0	mm^2/sec	27	mm^2/sec
Sulfated Ash	0.020 max	% mass	0.01	%
Sulfur content	0.0015 max	ppm	0.0012	ppm
Copper strip corrosion	No 3 max	_	1	_
Cetane	47 min	_	29	_
Carbon Residue	0.050 max	% mass	0.24	%
Acid Number	0.80 max	mg KOH/gm	1.4	mg KOH/gm
Free Glycerin	0.020 max	% mass	0.01	%
Total Glycerin	0.240 max	% mass	0.11	%
Phosphorous contents	0.001 max	% mass	1.6	%
Distillation Temperature, Atmospheric Equivalent temperature, 90 % recovered	360 max	°C	284	°C

Table 3. Mean corrosion rate of various metals in UPO

Medium	Aluminium	Mild steel	Copper
NaCl	3.021	1.539	3.446
O99	0.071	0.054	1.370
O100	0.076	0.037	1.678

structure of the vegetable oil. Used cooking oil is associated with water content in it. As the heating by cooking period increased, free fatty acid content also increases and hence the higher acid number. Low speed engines (100-500 rpm) of ships require heavy oils of high viscosity and cetane number of about 25 (Sivasankar, 2008). Used palm oil could be used safely in low speed engines without any modifications since it has higher viscosity (27 mm^2/sec) and lower cetane number (29). The problem in using UPO in other engines (high speed and medium speed) can be rectified by converting oil into biodiesel and blending of oil with in commercial diesel in proper proportion (Dutra *et al*., 2009).

Static immersion test

Entry of moist air and accumulation of water in the tanks and pipelines create conducive atmosphere for corrosion. A synthetic 3% sodium chloride solution was used to simulate the water phase in all the experiments. The susceptibility of a metal surface to corrosion in the UPO is discussed based on the type of emulsion (o/w or w/o) wettability (water wet or oil wet) and corrosivity in brine (NaCl). The mean corrosion rates of aluminium, mild steel and copper in UPO was determined by mass loss method are presented in Table 3. The corrosion rate of studied metals in O100 is very less when compared to NaCl solution. By the addition of 1% NaCl to the oil (O99), water in oil emulsion is formed. Thus the metal is still in contact with the oil hence the corrosion rate is not affected. Among these three metals, copper was more susceptible to corrosion than aluminium and mild steel. From literature survey, it is cleared that copper was more corroded than other metals in palm biodiesel (Haseeb *et al*., 2013) and poultry fat (Geller *et al*., 2008). Higher corrosion rates of copper may be due to the formation of the corrosion products such as Cu_2O, CuO, $CuCO_3$ and $Cu(OH)_2$ with water, CO_2, $RCOO^-$ etc present in biofuel. This has been proved by Fazal *et al*. (2013) in palm biodiesel.

Wettability

The corrosion of a metal surface in oil in the presence of water depends on the wettability. An oil wet surface is not susceptible to corrosion where as water wet surface is prone to corrosion. One of the methods to determine the wettability is by measuring the contact angle of the water-oil-metal interface through the water phase.

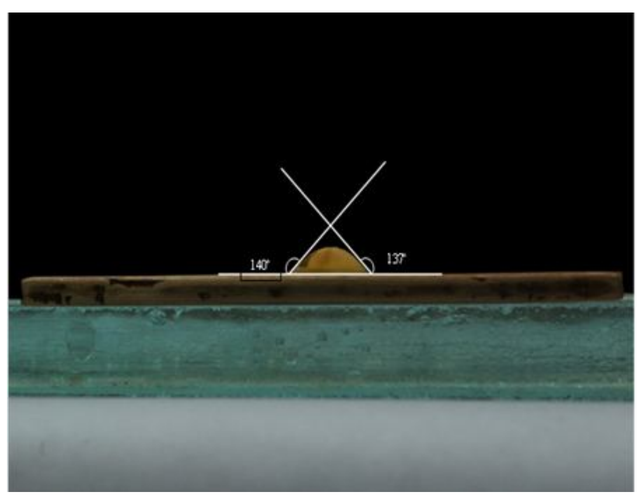

Figure 1. Wettability on copper by contact angle method

The surface is considered as water-wet when the contact angle is acute and oil-wet when the contact angle is obtuse. The contact angle for aluminium, mild steel and copper was found to be 127˚, 118˚and 139˚respectively suggesting that the oil preferably wets on the metal surface. Thus it is found that UPO has a strong affinity towards the metals and isolate the metals from the corrosive environment. Therefore in this case the corrosion process is very slow. A typical contact angle measurement is shown in Figure 1.

Linear polarization resistance method

A similar trend of result as that of mass loss method is noted. As shown in Figure 2, the negligible corrosion rate was measured in O99and O100 than in NaCl. Even though the corrosion rate of O99 and O100 are low, there was a little difference between them. The variation in corrosion rate values obtained via mass loss method and LPR methods may be due to the adaptation of methodology. It should be noted that LPR method measure instantaneous corrosion rates where as mass loss method measures time averaged corrosion rates.

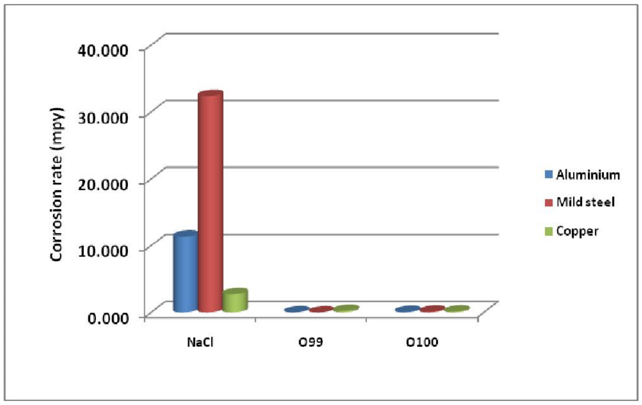

Figure 2. Mean corrosion rates of tested metals - LPR technique

Conductivity measurement

The corrosion of metals in biofuel and its blend occurs by electrochemical mechanism. Hence there is a direct correlation between the corrosivity of the medium and conductance. From Figure 3, it is clear that NaCl has highest conductance while that of O100 is least. Also the addition of 1% NaCl has not increased the conductivity (Anisha *et al*., 2011; Meenakshi *et al*., 2013). This brings out the direct correlation of non-corrosive nature of water/oil emulsion directly with the conductivity. The conductivities of solution after exposure were found to be low for aluminium. This may be due to decrease in the ionic content in the test medium or complex formation of the solution with metal ion. The higher conductance of test solutions in mild steel and copper indicates the increased ionic content of the solution due to corrosion and the absorption of moisture by oil. The conductivities of O100 and O99 remained the same establishing the corrosion resistant nature.

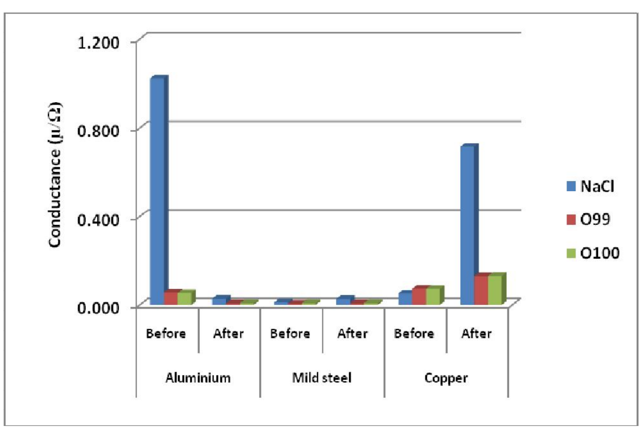

Figure 3. Variation of conductivity - Before and after exposure of metal coupons in various test solutions

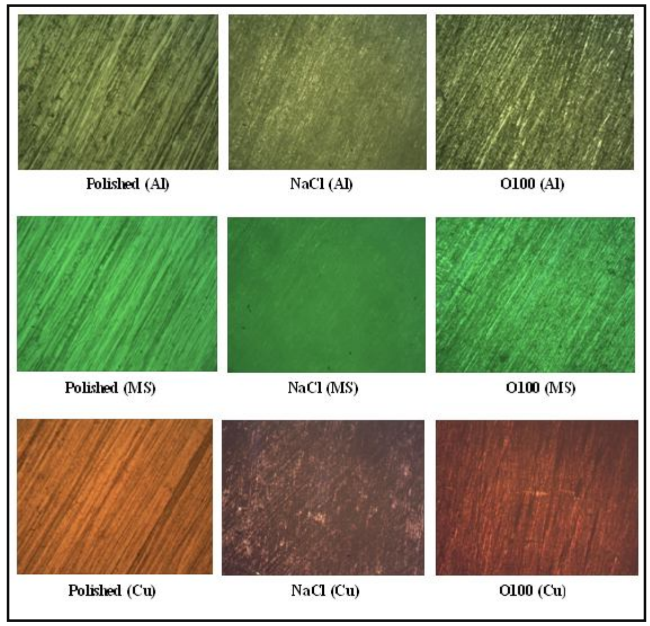

Figure 4. Optical photographs of the polished surfaces of aluminium (Al), mild steel (MS) and copper (Cu) and samples after exposing to NaCl and UPO

Surface morphology

The micrographs of the polished samples and coupons exposed to NaCl and O100 are presented in Figure 4. The polished samples are associated with polishing scratches which may be due to the physical abrasion of the samples with emery paper. Visibly, the samples in NaCl were covered with dark deposits which showed the presence of corrosion product. The coupons exposed to O100 showed little damage to coupon surfaces with occasional pitting, which confirmed that negligible corrosion.

Conclusions

- The used palm oil adhered to most of the fuel properties as per ASTM D6751 standard. The higher viscosity may be attributed to the high molecular weight and large chemical structure of the vegetable oil.
- Used palm oil could be used safely in low speed engines without any modifications since it has higher viscosity (27 mm^2/sec) and lower cetane number (29).
- UPO can be used in high speed and medium speed engines by converting oil into biodiesel and blending of oil with in commercial diesel in proper proportion.
- The corrosion behavior of metals can be predicted based on the wettability. The measured contact angle for the studied metals was found to be obtuse suggesting that the oil wets the metal surface and hence less corrosive.
- The negligible corrosion rates of aluminium, mild steel and copper in the 100% oil indicates that this oil may be used as alternate fuel alone or in blends with petrodiesel as a cost effective measure.
- Highest corrosion rates were observed in copper when compared to aluminium and mild steel in used palm oil.

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