

**COMPATIBILITY OF GALVANIZED IRON WITH USED
GROUNDNUT OIL AND ITS BLEND WITH
COMMERCIAL DIESEL.**

KARTHIKA.B

11PCMO4

A thesis submitted to the

**AVINASHILINGAM INSTITUTE FOR HOME SCIENCE
AND HIGHER EDUCATION FOR WOMEN,
COIMBATORE-43**

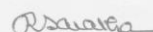
In partial fulfillment of the requirements for the

MASTER'S DEGREE IN CHEMISTRY

MAY-2013



**Signature of the
Head of the department**



Signature of the Supervisor

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LIST OF ABBREVIATIONS

mpy : Miles per year

hrs : Hours

NaCl : Sodium Chloride

- LPR** : **Linear Polarization Resistance**
- UGNO** : **Used groundnut oil**
- EIP** : **Emulsion Inversion Point**
- h** : **Height**
- CD** : **Commercial Diesel**
- R_p** : **Polarization Resistance**
- ASTM** : **American Standards for Testing Materials**

1. INTRODUCTION

Biofuel

Rapid growth in population coupled with industrial and technological developments is leading towards the depletion of limited fossil fuel resources of the world. Hence alternative fuel sources are needed to decrease the demands on fossil fuel. The development of new technologies for processing and using biofuel is steadily progressing.

Biofuels are derived from living plants, animals or their byproducts, which are not more than 20-30 years old. Biofuels contains stored solar energy and are renewable sources of energy, since the plants are grown again. Bioenergy is the energy derived from biofuels.

Biodiesel

Biodiesel is the diesel replacement fuel, that is the manufactured from vegetables oils, recycled oils or animal fats. The biodiesel manufacturing process converts oils and fats into chemicals called long chain mono alkyl esters or biodiesel that are also referred to as fatty acid methyl esters (AAME) or fatty acid ethyl ester. 'Biodiesel is defined in ASTM D6751, as a fuel comprised of mono alkyl esters of long fatty acids derived from vegetables oils or animal fats designated B100'.

Biodiesel contains carbon, hydrogen and oxygen .The color of biodiesel is golden and dark brown. The color and C/H ratio depends on the feedstock. It is immiscible with water, and has density of 0.88 g/cm^2 .It has virtually no sulphur. It is often used in additive to Ultra Low Sulphur Diesel fuel.

The difference between the biodiesel and diesel fuel is the quantity of oxygen content.

Biodiesel is used in standard diesel engines and thus distinct from the vegetable and waste oils used in fuel converted diesel engines. Biodiesel can be used alone, or blended with petro diesel.

Scientific research advices that the use of biodiesel has less harmful effect on human health. Whereas if the ordinary fuel is used, the compounds emitted during their combustion is very harmful but in the case of biodiesel the emission of those compounds reduced by 15%.The

presence of oxygen in the fuel leads to a reduction in emissions of hydrocarbons (HC), and toxic compounds, carbon mono oxide (CO), particulate matter (PM) when biodiesel blends are burned in diesel engines.

Biodiesel production

The process of manufacturing biodiesel involves widely understood and well-documented basic chemistry. Biodiesel can be made from any vegetable oil or fat through a chemical reaction called TRANS ESTERIFICATION. In this reaction, the oil or fat is mixed with a chemical catalyst called methoxide (which itself is a mixture of base catalyst and methanol) in the presence of heat. The methoxide “breaks the oil into two final products, methyl esters (or biodiesel) and glycerol (also referred as glycerin).

These two products are then separated and the biodiesel is washed to remove excess amount of ethanol and unreacted oils, and any remaining glycerol. After washing, the remaining water is removed from the biodiesel product and it is ready for use as a perfect substitute for conventional diesel.

Biodiesel in India

Analysis from Frost & Sullivan, Strategic analysis of the Indian biofuels industry, reveals that the market is an emerging one and has a long way to go before it catches up global competitors.

The government is currently implementing an ethanol-blending program and considering initiatives in the form of mandates for bio-diesel. Due to these strategies, the rising population, and the growing

energy demand from the transport sector, bio-fuels can be assured of a significant market in India.

Advantages of biodiesel

- Pure Biodiesel is non-toxic, biodegradable and greenhouse gas neutral.
- As a blended addition to Ultra Low Sulphur Diesel (ULSD) Biodiesel reduces pollution, particulates (soot) and hydrocarbons and restores lubricity lost due to the reduction of sulphur compounds in ULSD (thereby reducing engine wear..
- Both Biodiesel and mineral diesel have similar energy and power content and have proven to be of a similar retail value at the pump.
- Mineral diesel fuel is produced from mineral crude oil, whereas, biodiesel is produced from a variety of feed stocks including used vegetable oil, tallow from meat processing and vegetable oils, including but not limited to rape, canola, soy, and linseed, palm, coconut, mustard and cotton oils.
- It is fully degraded in a waterway environment within approximately 28 days.
- Significant lubricant characteristics enabling a reduction in wear and extended efficiency for injectors and for all engines using ULSD, resulting in lower maintenance costs.
- It can also be manufactured from tallow oil and used cooking oils
- Virtually zero sulphur content.
- Zero aromatic content (toluene and benzene).

- Similar energy and power content to ULSD.
- Significant reduction in particulates (soot) and hydrocarbons.
- Reduces pollution, as there is a 70 per cent. Reduction of carbon monoxide emissions in diesel exhausts.

Biodiesel-world scenario

Biodiesel has emerged as a realistic and desirable alternative, or blended addition, to mineral diesel and is becoming an increasingly valuable contributor to the world's drive to reduce greenhouse gas emissions. It has been in general pure use for the last 10 years in continental Europe. However, the majority of UK Biodiesel production is expected to be used as a 5-20% blend with mineral diesel. In the UK, a 5% Biodiesel blend is currently being marketed on forecourts; Petro plus, a significant diesel refiner, markets "Bio plus" and Greenergy, a significant distributor of green fuels (25 % owned by Tesco plc.), markets "Global Diesel". Biodiesel, when added to ULSD, restores lubricity lost due to the reduction of sulphur compounds of sulphur, as well as adding environmental benefits to the blend.

A number of key diesel engine producers and commercial vehicle manufacturers including Volkswagen, Audi, Seat and Skoda have confirmed to their customers that pure biodiesel (provided it meets minimum standards set out by those manufacturers) is suitable for use in certain of their vehicle engines. A number of manufacturers of plant and machinery such as John Deere, Caterpillar and Cummins have also given similar confirmations.

Biodiesel emission characteristics in internal emission characteristics

Biodiesel reduces emissions of carbon monoxide (CO) by approximately 50 % and carbon dioxide by 78 % on a net lifecycle basis because the carbon in biodiesel emissions is recycled from carbon that was already in the atmosphere, rather than being new carbon from petroleum that was sequestered in the earth's crust. (Sheehan, 1998).

Biodiesel contains fewer aromatic hydrocarbons" aromatic hydrocarbons: benzofluoranthene: 56 % reduction; Benzopyrenes: 71 % reduction. It also eliminates emissions of sulphur (SO₂), because biodiesel does not contain sulphur. Biodiesel reduces the emission of particulate, by as much as 65 % of small particles of solid combustion products. This reduces cancer risks by up to 94 % according to testing sponsored by the US Department of Energy.

Biodiesel has a flash point of 160 °C, and is classified as a non-flammable liquid by the US Occupational Safety and Health Administration. This property makes biodiesel relatively safe to produce, resulting in higher safety margins for storage and transfer. Also vehicles fuelled by pure biodiesel are far safer in Car accidents than ones powered by petroleum diesel or the explosively combustible gasoline.

Ecofriendliness & suitability for future

Biodiesel is biodegradable and non-toxic, in fact an average 60 kg person would need to consume more than 3 liters of Biodiesel to cause death 50% of the time, making biodiesel ten times less toxic than Sodium chloride table salt. In addition it is as biodegradable as sugar, and has

significantly fewer emissions than petroleum-based diesel (petro-diesel) when burned.

The factors that make it one of the main candidates to replace fossil fuels as the world's primary transport energy source are: it is a renewable, clean-burning fuel that can deliver benefits both to the environment and to vehicle engines. Biodiesel can be distributed using today's infrastructure, and its use and production is increasing rapidly (especially in Europe, the United States, and Asia). Fuel stations are making biodiesel available to consumers and in Germany for example there are 1600 stations nationwide, and a growing number of transport fleets use it as an additive in their fuel. Our Biodiesel will be available in a blend of 5 per cent Biodiesel to 95 per cent mineral diesel (B5), and 100% pure Biodiesel (B100), so no changes are required to the logistics of the fuel supply chain infrastructure or to vehicle engines. It's good for engines and the environment.

It improves engine lubrication, it burns more completely thereby reducing emissions, it is virtually sulphur free and can deliver increased engine life. Biodiesel has combustion properties very similar to mineral diesel and can replace it in most uses. Biodiesel is most often used blended with mineral diesel. Using it in a blend also extends existing fossil fuel reserves.

PEANUTOIL



Figure. 1(a) Groundnut oil



Figure. 1(b) Groundnut seed

Peanut oil, also known as groundnut oil or arachis oil, is a mild tasting vegetable oil derived from peanuts. The oil is available in refined, unrefined, cold pressed, and roasted varieties, the latter with a strong peanut flavor and aroma, analogous to toasted sesame oil.

It is often used in Chinese, South Asian and Southeast Asian cuisine, both for general cooking, and in the case of roasted oil, for added flavor. Peanut oil has a high smoke point relative to many other cooking oils, so is commonly used for frying foods. Its major component fatty acids are oleic acid (46.8% as olein), linoleic acid (33.4% as linolein), and palmitic acid (10.0% as palmitin) The oil also contains some stearic acid, arachidic acid, arachidonic acid, behenic acid, lignoceric acid and other fatty acids.

Antioxidants such as Vitamin E are sometimes added, to improve the shelf life of the oil. Peanut oil will make medicine .Peanut oil, as with other vegetable oils; can be used to make soap by the process of saponification. The oil is safe for use as massage oil.

Biodiesel

At the 1900 Paris Exhibition, the Otto Company, at the request of the French government, demonstrated that peanut oil could be used as a source of fuel for the diesel engine; this was one of the earliest demonstrations of biodiesel technology.

Bio diesel from peanut oil is compatible with fossil fuel based biodiesel and can be mixed in any combination. Compared to fossil fuel based biodiesel, there will be a 2% to 5% reduction in miles per gallon with either soy or peanut oil based fuel.

Geller says peanut biodiesel is less toxic to the atmosphere and has a cleaning effect on diesel engines. Running peanut biodiesel cleans residue from diesel engines. This can be good and bad, because the particulates tend to clog up the filter on an engine. After cleaning the filters a few times, peanut biodiesel actually runs much cleaner than biodiesel.

Waste cooking oil as fuel

Waste cooking oil is a promising alternative for biofuel production because it is cheaper raw materials and avoids the cost of waste product disposal and treatment. Also it reduces the land used for the biofuel production crops.

Health issues in reused oil

Recent research confirms that the use of reused cooking oil in a number of times will affect human health. A research carried out by Spanish researchers found that people used any type of oil that had been reused many times will have very high blood pressure than people whose cooking oils were changed more frequently. The reuse of deep fried oil will cause allergic reactions in digestive tract, growth retardation, increased weight of liver and kidneys. Food fried in reused oil causes Necrosis, dark red patches and it affects the blood serum level.

Advantages of using waste cooking oil as fuel

- ❖ Free of cost, easily available
- ❖ It produces fewer greenhouse emissions
- ❖ The conversion of vegetable oil into fuel is a cheap process
- ❖ It does not require any special storage
- ❖ Safer to handle compared to petroleum diesel

Corrosion issues in biofuel

Corrosion is defined as “deterioration” of metals .corrosion normally occurs in metals and alloys when they exposed to air and moisture. Galvanized iron is widely employed in most of the industries due to their low cost and availability and ease of fabrication of various reaction vessels such as storage tank, cooling tower tank.

Mostly corrosion is observed in fuel storage tank. Entry of moisture and accumulation of water in the, tank leads to condensation of water thus creating conditions susceptible of corrosion.

In order to limit the contamination of air in the tank, biofuels is not stored in partially filled tanks for prolonged duration.to decrease the

probability of creating conditions for corrosion ,tanks are designed with a bottom valve to drain water accumulated at the bottom of the tank.

Hence the present work is proposed to predict the extent of service life of the galvanized iron in groundnut oil which shall be used as a biofuel in internal combustion engines with the following objectives:

OBJECTIVES

- ❖ To characterize the used groundnut oil and compare with ASTM 6751 standard.
- ❖ To find out the composition of metal.
- ❖ To conduct a systematic study to the corrosivity of reused groundnut oil on galvanized iron sheet.
- ❖ To evaluate the corrosion rate of galvanized iron sheet in 3% NaCl.
- ❖ To evaluate the corrosion rates of galvanized iron sheet in reused groundnut oil and its blend with commercial diesel for a period of 100 hours at room temperature by mass loss method.
- ❖ To measure the conductivity of test solutions before and after exposure of galvanized iron sheet in the solutions.
- ❖ To carry out the linear polarization studies to evaluate the corrosion rate continuously for a period of 24 hours for galvanized iron sheet.
- ❖ To compare the corrosion rate obtained by mass loss method with that obtained by linear polarization method.
- ❖ To determine the wettability of oil on galvanized iron sheet using contact angle method.
- ❖ To determine the emulsion inversion point by conductance measurements of oil and brine solution.

- ❖ To analyze the surface morphology of the metal coupons using inverted metallurgical microscope.
- ❖ To determine the emulsion inversion point by conductance measurements of oil and brine solution.

2. REVIEW OF LITERATURE

- ❖ . The production of methyl ester fuels from non-edible oil like castor oil by using different catalysts such as NaOH, H₂SO₄, and the effects of various parameters like temperature, residence time, catalyst concentration on yield of biodiesel and the physical properties like viscosity, specific gravity and acid value have been studied by **Deshpande et al., 2012**
- .
- ❖ . **Mishra S.R et al., 2012** have investigated the transesterification of Simarouba glauca oil with ethanol using KOH as a catalyst at a temperature .the characterization of biodiesel is done by using TLC techniques and they compared the properties of biodiesel with diesel.
- ❖ . **Surendhiren .D et al., 2012** have studied the biodiesel production from micro algae as a raw material due to its mass productivity and faster lipid production. The study also investigated the technical improvements in cultivation of different micro algal species and lipid content in various algal species.
- ❖ . **V.Maniyan et al., 2013** have investigated the parameters such as specific fuel consumption, and brake thermal efficiency and emissions such as oxides of nitrogen, CO, hydrocarbon, smoke density, exhaust gas temperature using Exhaust gas recirculation Technique. In diesel engine with B20 biodiesel as fuel, obtained from Madhua.
- ❖ .The groundnut oil contains high amount of free fatty acid was pretreated with HCl as catalyst and anhydrous CH₃OH at a molar ratio of 9:1 to reduce its free fatty acid to 1.5%.the characterization of oil and its biodiesel were investigated by **E.I Bello et al ., 2012**
- ❖ **Anisha Anand et al., 2011** have investigated corrosion aspect of Jatropha oil on various such as carbon steel. Aluminium, copper brass. Results

showed that all metal surfaces are wetted with Jatropha oil. All the metals exhibited lower corrosion rates and it is found that corrosivity of Jatropha oil is lower than that of biodiesel obtained from Pongamia Pinnata.

- ❖ **Guzatto et al., 2011** have aimed to produce the biodiesel from waste cooking oil soybean oil and linseed oil and compare the performance of the resultant biodiesel fuel. Transesterification which involves double step process results in high conversion and products with satisfactory yields. The reduction of the concentration of catalyst in basic and acidic steps did not reduce the conversion of the reaction. A comparison of the results demonstrated that a final washing and drying procedure was necessary for satisfactory results

- ❖ The effects of operating process conditions to oil molar ratio, reaction temperature and catalyst loading on biodiesel production in presence of Sr/ZrO₂ were investigated by **Won Nor Nadyaini Wan Omar et al., 2011**.

- ❖ **Wang et al., 2011** have found that the use of surfactants and detergent fractionation to improve the cold flow properties of biodiesel from waste cooking oil. The required loading of these surfactants was considerably lower than the other surfactants. Furthermore detergent fractionation was introduced to remove fractions with high melting points from biodiesel.

- ❖ . Biodiesel can be produced from renewable sources such as vegetable oil, animal fat and used cooking oil (**Math et al., 2010**). The cost of biodiesel can be reduced by using low cost feedstock such as animal fat and used cooking oil. The fuel properties and biodiesel from used cooking oil were also reviewed and compared. Results showed that

biodiesel produced from used cooking oil can be used in diesel engines without any engine modification

-
- ❖ . **Fazal** *et al.*, 2010 have aimed to compare the corrosion behavior of aluminium, copper and stainless steel in both petroleum diesel and palm biodiesel. Immersion tests in biodiesel (B100) and diesel (BO) were carried out at 80°C for 12hrs. At the end of the test corrosion characteristic was investigated by weight loss measurements and changes on the exposed metal surface. Surface morphology was examined by optical microscope.
- ❖ **Meenakshi** *et al.*, 2010 have studied the corrosion rates of aluminium copper, brass and carbon steel in biodiesel obtained from *Pongamia Pinnata*. Result showed that the corrosion rates of all metals in biodiesel are insignificant. However the conductivities of biodiesel after the experiment in most cases increased by about one order of magnitude. Addition of 1% NaCl does not increase the corrosion rates of biodiesel significantly the biodiesel preferentially wets all the metal surfaces studied.
- ❖ The electrochemical / Corrosion experiments studied by **Deniz** *et al.*, 2010. The anaerobic microbial metabolism of biodiesel in coastal seawater samples accelerated the rate of pitting corrosion in carbon steel.
- ❖ **Singh** *et al.*, 2009 have reviewed the source of production and characterization of vegetable oils and their methyl ester as the substitute of the petroleum fuel and future possibilities of biodiesel production

- ❖ The effects of different operating variables of waste cooking oil (WCO) for the production of biodiesel through chemical methods has been studied by **Banerjee *et al.*, 2009**. The production of biodiesel from WCO with high FFA content, esterification of the FFA using acid type catalyst should be carried out first before alkaline transesterification of the catalyst should be carried out first before alkaline transesterification of the triglycerides for overall improvement of the biodiesel yield especially for WCO.
- ❖ **.Y.C.Sharma *et al.*, 2008** have described that the bio-diesel is an environmentally viable fuel. Direct use and blending, micro-emulsions, most commonly used methods transesterification, of vegetable oils, fats waste oils.
- ❖ **. Shyamala *et al.*, 2008** have investigated the development of new technologies for processing and using biofuels is steadily progressing. Biofuels are being increasingly used with fossil fuel. All fuels are susceptible to contamination at various points.
- ❖ The experimental investigation on regulated and unregulated emission of diesel engine fueled with ultra-low sulfur diesel fuel blended with bio-diesel from waste cooking oil was studied by **Yoge Di *et al.*, 2008**.
- ❖ **. L.Diaz-Ballote *et al.*, 2008** have found that corrosion behavior of aluminium in bio-diesel contaminated with alkalis is similar to the corrosion behavior of aluminium in aqueous solution. In addition, it was demonstrated that corrosion of aluminium can be used as a quantitative indication of bio-diesel purity.

- ❖ **Geller-Daniel.Pet et al.**, 2008 examined the corrosion effects of poultry fat and diesel full mixtures on vacuum metals. It was found that Brass and copper were susceptible to attack by these fuels whereas 316 stainless steel and carbon steel were not.

- ❖ **R.Shyamala et al.**, 2008 have investigated the development of new technologies for processing and using biofuels is steadily progressing. Biofuels are being increasingly used with fossil fuel. All fuels are susceptible to contamination at various points.

- ❖ **. Demirbas et al.**, 2007 have studied the economic, social and politic contribution of biodiesel to the transportation sector and analysis of the effect of biodiesel on the exhaust emissions from diesel powered vehicles. Biodiesel emissions showed decreased levels of polycyclic aromatic hydrocarbons and nitride PAH compounds which have been identified as potential cancer causing compounds.

- ❖ The laboratory evaluation, often referred to as residual analysis provides quick monitoring of the adequacy of treatment levels of corrosion inhibitors in different applications, time of dispersion through fluids as well as efficiency of inhibitor is done by **Adelina.J.Son** 2007

- ❖ **. S.Murillo et al.**, 2006 have investigated the biodiesel alone or blended biodiesel can be used in compression ignition outboard engines there by providing alternative to diesel. Special attention should give while using the biodiesel in boats and rivers, which are vulnerable to pollution.

- ❖ **Savitha Kaul. R.C Saxena** *et al.*, 2006 have investigated the corrosion behavior of biodiesel obtained from non-edible oil such as *Jatropha curcas* .*Pongamia glabra* (karanja), *Mahuca indica* (Mahua).

- ❖ Influence of physical and chemical properties of feedstock oils on the alkaline catalyzed transesterification process have been studied by **D.Y.C Leung** *et al.*, 2006 and they determined the optimal transesterification reaction conditions that produce the maximum ester content and yield .

- ❖ **Mangesh G.Kulkarni** *et al.*, 2006 reviewed the methods of transesterification of waste cooking oil and the performance of biodiesel obtained from WCO in a diesel engine is also studied.

- ❖ **Park** *et al.*, 2005 have examined the effects of dissolved oxygen on the corrosion properties of aluminium cast alloy, A384, in bio-ethanol blended gasoline fuel at 100°C.

3. MATERIALS AND METHODS.

To determine the outcome of any research work, selection of method and materials are vitally important. Following are the material chosen and methodology adopted in the present work.

3.1. Selection of sample

Galvanized iron sheet is chosen due to its low cost, and wide range of applications and availability. Galvanized iron sheet is used because of its high corrosion resistance ability due to the presence of zinc. Structural components made from galvanized iron used in many applications such as air ducts and trash cans.

3.2. Preparation of sample

The sheet of cold rolled galvanized iron sheet, which is commercially available in the market, were machined into coupons of area 34.01cm^2 . Holes were drilled on the center of the one side of all the coupons for suspension. These coupons were degreased, cleaned with emery paper and washed with distilled water. The panels were stored in desiccators in the absence of moisture before their use for the investigation.

The elemental analysis of the galvanized iron sheet is carried out by Si'Tarc SCIENTIFIC AND INDUSTRIAL TESTING AND RESEARCH CENTRE, COIMBATORE.

Testing laboratory by using ARL Spark analyser. The composition of galvanized iron sheet used in the investigation is given in **Table .1**

Table.1**Composition of galvanized iron**

S.No	Element	% of chemical Composition.
1	CARBON	0.065
2	SILICON	0.002
3	MANGANESE	0.24
4	PHAHOROUS	0.009
5	SULPHUR	0.009
6	NICKEL	0.014
7	CHROMIUM	0.023
8	MOLYBDENUM	0.014
9	VANADIUM	0.001
10	COPPER	0.02
11	TUNGESTON	0.013
12	TITANIUM	0.0007
13	TIN	0.002
14	COBALT	0.003
15	ALUMINIUM	0.049
16	LEAD	0.003
17	BORON	0.0002
18	ANTIMONY	0.003
19	NIOBIUM	0.011
20	ZIRCONIUM	0.001
21	BISMUTH	0.003
22	CALCIUM	0.00006
23	MAGNESIUM	0.0002
24	ZINC	0.007
25	CERIUM	0.002
26	LANTHANUM	0.008
27	IRON	99.39

3.3. Oil characterization procedure

Reused groundnut oil was collected from a restaurant at Coimbatore. The characterization of the oil was performed as per ASTM D6751 in IND-AG INSPECTION AND TESTING LABORATORY COIMBATORE.

3.4. Techniques adopted for corrosion rate measurements

3.4.1. Mass loss method

Metals were accurately weighed in an electronic balance (SHIMADZUAUW220D) and fully immersed in 200ml of test media for a period of 100 hours. The various test media used for the study is as follows **Table.2**

Table 2

Test media for mass loss method

Test media	Constituents
O100	100% oil
O99	99 % of oil + 1% of 3% NaCl
NaCl	3% NaCl
CD	Commercial Diesel (CD)
O5	5 % of oil +95 % of CD
O10	10 % of oil +90 % of CD

Specimens were removed after a set of intervals of time. They were washed with distilled water, dried and reweighed. The mass loss was

determined in triplets in each test media. The corrosion rate was calculated from the following equation.

$$\text{Corrosion rate (mpy)} = \frac{3.45 \times 10^6 \times \text{mass loss (in grams)}}{\text{Density (g/cm}^3\text{)} \times \text{Area (cm}^2\text{)} \times \text{Time (hours)}}$$

3.4.2 Conductivity measurements

The conductivity of various test solutions were was measured using conductivity meter (EQIPTRONICS Model NO EQ-660A) before and after exposure of coupons and wiped off the excess oil. The coupons were cleaned with trichloroethylene and then immersed in ammonium chloride solution for half an hour.

3.4.3 Linear polarization resistance method

A frequency response analyzer 1280B (SOLATRON) and an IBM personal computer which automatically controls linear polarization was used for the polarization study. The data were analyzed by using computer software. The cell for the polarization studies was a glass beaker containing the aerated unstirred test solution with a platinum electrode as the counter electrode, and saturated calomel electrode as a reference electrode and the galvanized iron sheet as the working electrode.

The metal coupons (of same composition in the mass loss method) were degreased, cleaned with fine quality emery sheet washed with distilled water. The linear polarization measurements were carried within the potential range of -0.02 V to +0.02 V (scan ratio 0.1667 m V/s) with respect to open circuit potential. The corrosion rate was measured

every hour for 24 hours. From the polarization resistance (R_p) values, the corrosion rates were calculated.

$$I_{\text{corr}} = \frac{1}{R_p} \left(\frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \right)$$

Where

β_a - Anodic Tafel Slope

β_c - Cathodic Tafel Slope

Assuming value of 120V for both β_a and β_c and the above equation is reduced to

$I_{\text{corr}} = 26/R_p$. From the corrosion current, corrosion rate was calculated using the ASTM G5 STANDARD.

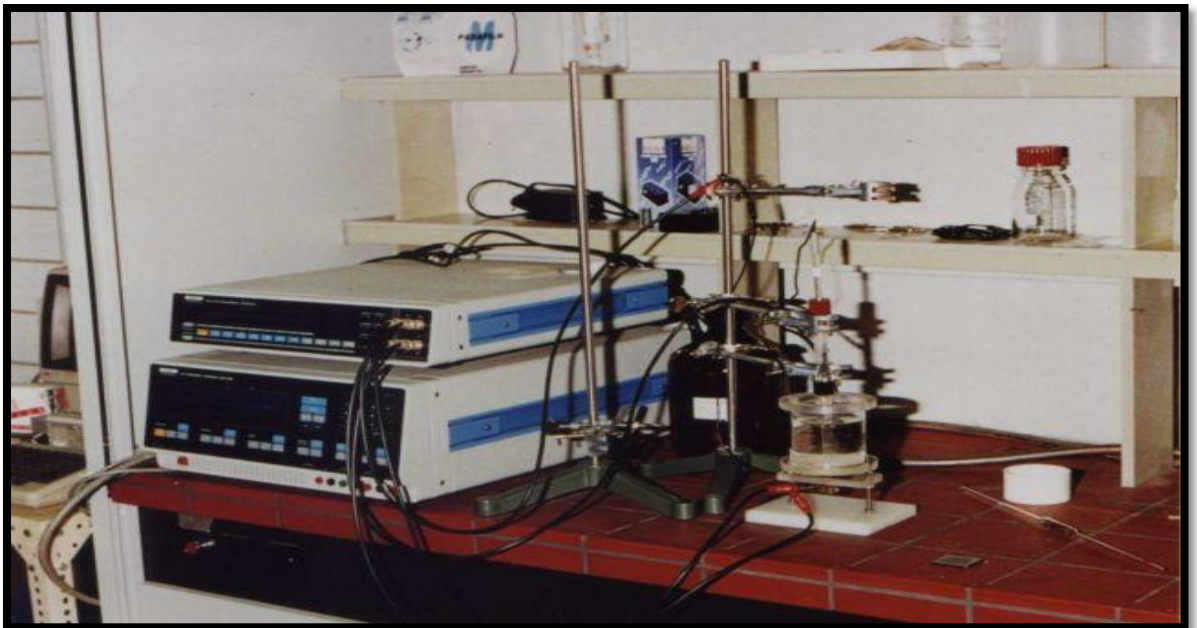


Figure.2 Linear polarization set up (SOLATRON)

3.4.4. Wettability-contact angle method

Metal samples were polished and cleaned first with distilled water and with ethanol. The samples were then placed in a non-reflecting rectangular glass tank containing distilled water and the oil was injected through a syringe into the water so that it would adhere to the sample surface. The contact angle was measured through the water phase. The photograph of the oil droplet on the metal surface was taken. On a printed photograph a horizontal line was drawn at the base of the droplet with the metal surface two tangents were drawn. The two exterior angles between the base and the tangents are measured with a protractor.

3.4.5. Surface morphology

The changes in surface morphology of galvanized iron exposed to various test media was characterized by inverted metallurgical microscope KOZO optics model XJM404T.



Figure.3 Metallurgical microscope KOZO

3.4.6. Emulsion inversion point - (EIP)

EIP was determined by measuring the conductivity of the solution. Oil has a high resistance in composition to NaCl and thus the emulsion inversion point can be determined by finding the point at which the resistance of the emulsion drops. Test solution was placed in an electromagnetic stirrer and continuously stirred for 20 minutes. The conductivity was measured at 2 minutes interval. These steps were repeated with different oil/NaCl ratio, starting with 100% oil and progressively increasing the water content in steps of 10% until 100% NaCl was reached.

4 .RESULTS AND DISSCUSSION

The purpose of the present work is to test the corrosion of the galvanized iron sheet in the reused groundnut oil and their blends with Commercial diesel and the results are discussed in the following sections.

4.1. Biodiesel quality and the standardization of biofuel

Standards are of high significance for producers, suppliers and users of biodiesel for the assessment of safety, risks, and environmental pollution. The mostly used standard is ASTM D6751. To meet the ASTM D 6751 standard a biodiesel sample should satisfy specifications of a sequence of tests including: Flash point water and sediment viscosity, sulfur content, sulfated ash, copper strip, Cetane number, cloud point, carbon residue, acid number, free glycerin, total glycerin, phosphorous content, and distillation temperature.

In this study reused groundnut oil is used as a biofuel. The characterization of reused groundnut oil as per ASTM D 6751 is given in **Table.3**

Table.3**Characterization of reused groundnut oil as per ASTM D 6751.**

Parameters	ASTM D 6751	Value	Units
Flash point	100-170	153	°C
Water and sediment	0.055 max	0.04	%
Kinematic viscosity 400°C	1.9-6.0	3.1	mm ² /sec
Sulphated ash	0.02 max	0.02 max	%
Sulphur content	0.05 max	0.05 max	mg/kg
Copper strip content	No 3 max	No.3 max	-
Cetane	47 min	34	
Carbon residue	0.050 max	0.21	Mass
Acid number	0.80 max	1.7	mg KOH/g
Free glycerin	0.002 max	0.020 max	% mass
Total glycerin	0.240 max	0.14	% mass
Phosphorous content	0.001 max	0.001 max	% max
Distillation temperature	360 max	260	°C

Most of the properties of reused groundnut oil, well satisfy with ASTM D 6751 standard specifications of biofuel.

4.2. Corrosivity of brine solution in the presence of groundnut oil.

The corrosion of metals in NaCl in biodiesel and biodiesel blends under storage and transportation condition is electrochemical in nature. Hence the present work is proposed to deal with the corrosion rate of

galvanized iron in reused groundnut oil was investigated under the following conditions given in **Table 2**.

4.3 Mass loss method

Generally corrosion studies used weight loss measurement as the traditional method to characterize the corrosion rate of metal. In the present work too metal coupons were exposed to various test media. The results of the mass loss method given in **Table.4**

It is evident from the **Table.4** the corrosion found in NaCl is high as expected, (the highest corrosion rate of metal is observed in 3 % NaCl), whereas corrosion is very less in O100. Addition of 1% of 3 % NaCl to the oil i.e. O99, does not much alter the corrosion rate of galvanized iron.

As long as the galvanized iron is in contact with the reused groundnut oil, the corrosion seldom occurs. Since the non-ionic nature of oils and the presence of hydrocarbons are non-corrosive

The very low corrosion rate found in reused oil may be due to the absorbed moisture. During the storage of biodiesel in steel tanks the oil wets the steel surface since it has a long affinity with the carbon steel, the oil wet surface isolate the tank thereby prevents corrosion.

At low concentration of water i.e. an addition of 1 % of 3 % NaCl to the groundnut oil can form “emulsion” to water. At this condition, oil is the continuous phase and water is entrapped inside the oil. Thus the metal is still in contact with the oil and hence a non-corrosive stage prevails.

Under this condition, two types of “emulsions” formed. The emulsion formed by the addition of little amount of water to oil is said to be water/oil type.

Corrosion rates of galvanized iron in NaCl, O100 and O99 by mass loss method

Medium	Specimen	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mpy)	Conductance (Ω^{-1})	
						Before immersion	After immersion
NaCl	1	35.6258	35.5381	0.0877	11.3027	1.835	0.13
	2	35.3599	35.2865	0.0734	9.4597	1.509	0.16
	3	35.6051	35.5180	0.0871	11.2253	1.397	0.12
O99	1	35.4487	35.4412	0.007	0.9666	0.083	0.260
	2	35.4900	35.4846	0.0054	0.6959	0.090	0.242
	3	34.7674	34.7577	0.0097	1.2501	0.088	0.240
O100	1	35.5682	35.5647	0.0033	0.4253	0.135	0.257
	2	34.9066	34.9058	0.0008	0.1031	0.150	0.254
	3	35.4395	35.4355	0.004	0.5155	0.135	0.267

According to **Table .4**, the conductance of NaCl is found to be high and least in the in O99 the conductance does not vary much by the addition of 1 % of 3 % NaCl to 99 % of oil. This shows the direct correlation of non-corrosive nature of water/oil emulsion with the conductivity.

Table.5 Corrosion rates of galvanized iron in O5, O10, O20, O100 and CD by mass loss method

Medium	Specimen	Initial Weight (g)	Final Weight (g)	Mass Loss(g)	Corrosion Rate (mpy)	Conductance ($\mu\Omega^{-1}$)	
						Before Immersion	After Immersion
O5	1	35.4413	35.4379	0.0033	0.4305	0.117	0.249
	2	35.4851	35.4816	0.0035	0.4463	0.113	0.246
	3	34.7572	34.7540	0.0032	0.4098	0.121	0.252
O10	1	34.9058	34.9015	0.0043	0.5606	0.109	0.285
	2	35.4340	35.4287	0.0052	0.6727	0.107	0.283
	3	35.2510	35.2456	0.0054	0.6972	0.113	0.287
O20	1	35.5811	35.5734	0.0078	1.0000	0.124	0.255
	2	35.0715	35.0653	0.0063	0.8055	0.121	0.272
	3	34.9831	34.9749	0.0082	1.0568	0.171	0.275
O100	1	34.8043	34.7982	0.0061	0.7887	0.122	0.258
	2	35.5346	35.5294	0.0052	0.6895	0.127	0.273
	3	35.6726	35.6673	0.0054	0.6895	0.128	0.265
CD	1	35.0235	35.0210	0.0026	0.3299	0.125	0.302
	2	35.6333	35.6296	0.0037	0.4743	0.127	0.259
	3	35.5740	35.5716	0.0024	0.3119	0.132	0.269

4.4. Linear polarization resistance method (LPR method)

The corrosion rate of galvanized as a function of time in reused groundnut oil and 3 % NaCl is obtained by LPR method and is given **Table.6** and depicted in the **Figure.4**

Table.6 corrosion rates of galvanized ion in NaCl, O100 and O99 as a function of time by LPR method

Time in hours	Corrosion rate (mpy)		
	NaCl	O99	O100
1	21.228	4.3413	0.62003
2	20.576	6.629	0.96855
3	26.981	5.4025	0.98348
4	35.368	2.6313	0.9223
5	42.864	4.6087	0.44727
6	52.082	2.6634	0.89184
7	60.118	0.82699	0.91407
8	59.118	0.32083	0.83837
9	64.294	0.30393	0.10852
10	66.153	0.29003	0.10514
11	65.734	0.78853	1.7006
12	66.663	0.18616	0.34248
13	66.951	0.32077	0.15309
14	67.382	0.28588	1.4858
15	68.254	0.071904	0.53537
16	69.656	0.14808	0.87066
17	69.763	0.20114	0.92043

18	70.115	1.7638	0.26634
19	68.984	0.1241	0.78322
20	68.952	1.7337	0.12438
21	65.618	0.52616	0.40513
21	64.852	1.3732	0.95162
23	62.779	0.41932	0.48451

The corrosion rate observed in O100.O99 is less, when compared to NaCl. Similar trend of result noted in mass loss method.

Corrosion rates of galvanized iron in NaCl, O99 and O100 as a function of time by LPR method

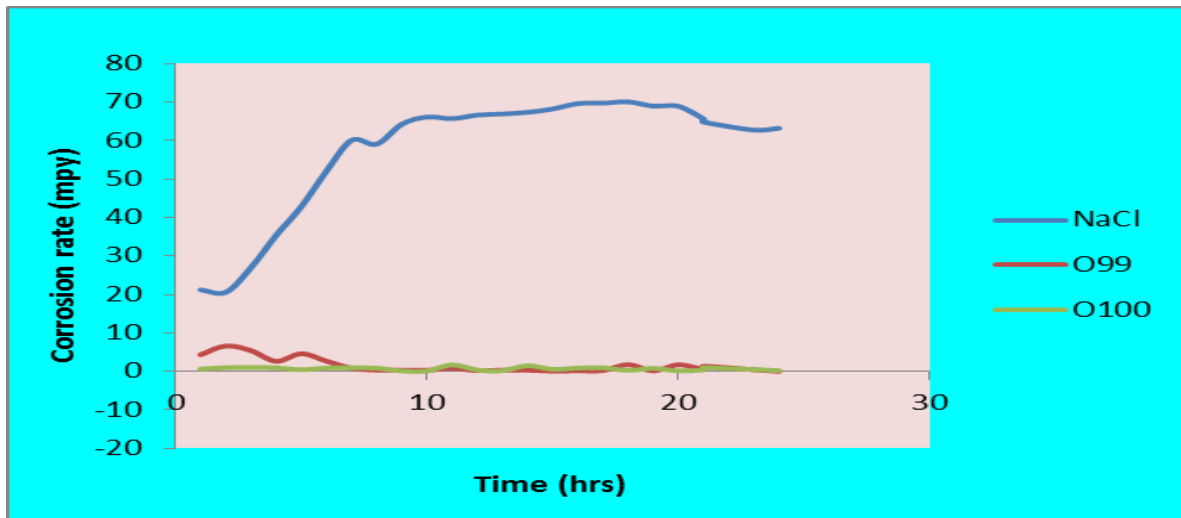


Figure .4

Corrosion rates of galvanized iron in commercial diesel and its blend with biofuel is given in Table.7

Times in hours	Corrosion rate (mpy)				
	CD	O5	O10	O20	O100
1	0.2278	0.3972	1.6871	0.2058	0.6200
2	0.7835	0.7848	0.5344	0.4177	0.9686
3	0.3996	0.2070	1.7836	0.1603	0.9835
4	0.2821	0.1859	1.6446	0.2845	0.9223
5	0.1663	1.348	0.1019	0.0910	0.4473
6	0.3859	0.1002	0.7760	0.6629	0.8918
7	0.7304	0.4607	0.3519	0.2782	0.9141
8	0.0190	0.0851	1.244	0.0684	0.8384
9	0.2135	0.1970	1.5294	0.5065	0.1085
10	0.2082	1.1404	0.0828	0.3408	0.1051
11	0.5756	0.9699	1.49	0.9329	1.7006
12	0.8826	1.1704	0.2480	0.1072	0.3425
13	0.0022	1.029	0.6051	0.2146	0.1531
14	0.2195	0.6896	0.8605	0.8414	1.4858
15	0.5005	0.3325	0.0542	0.7343	0.5354
16	0.1842	0.1852	1.6045	0.7849	0.8707

17	0.2050	0.2840	1.0917	0.2337	0.9204
18	0.0707	1.206	0.5750	0.0182	0.2663
19	0.2100	1.3522	0.6586	1.0913	0.7832
20	0.1218	0.3094	0.4761	1.3247	0.1244
21	0.1477	1.2164	0.0145	1.3115	0.4051
22	-	0.36377	0.1922	1.15	0.9516
23	-	0.5936	0.1664	1.7884	0.4845
24	-	0.1669	0.2883	1.4564	0.2007

Corrosion rates of galvanized iron in O5, O10, O20, O100 and CD as a function of time by LPR method and the is shown in Figure .5

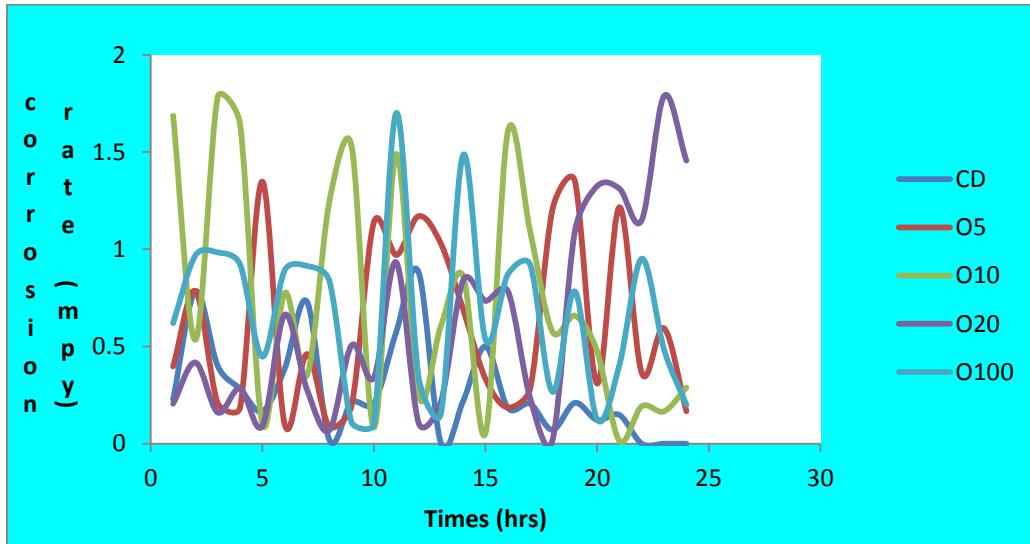


Figure.5

4.5 Wettability contact angle method

The presence of free water or O/W emulsion does not necessarily lead to corrosion. Based on the wettability of oil or water on a metal surface determines susceptibility to pitting corrosion, according to the above oil wet surface is non-corrosive, but water wet surface is corrosive.

Wettability is characterized by measuring the contact angle (Papavinasams et al., 2007). In the present study contact angle was measured through the water phase. The contact angle of used groundnut oil is measured from the following **Figure.5** and presented in **Table.8**. The values 131° and 132° confirms that the used groundnut oil wets the metal surface thereby making the surface non corrosive.

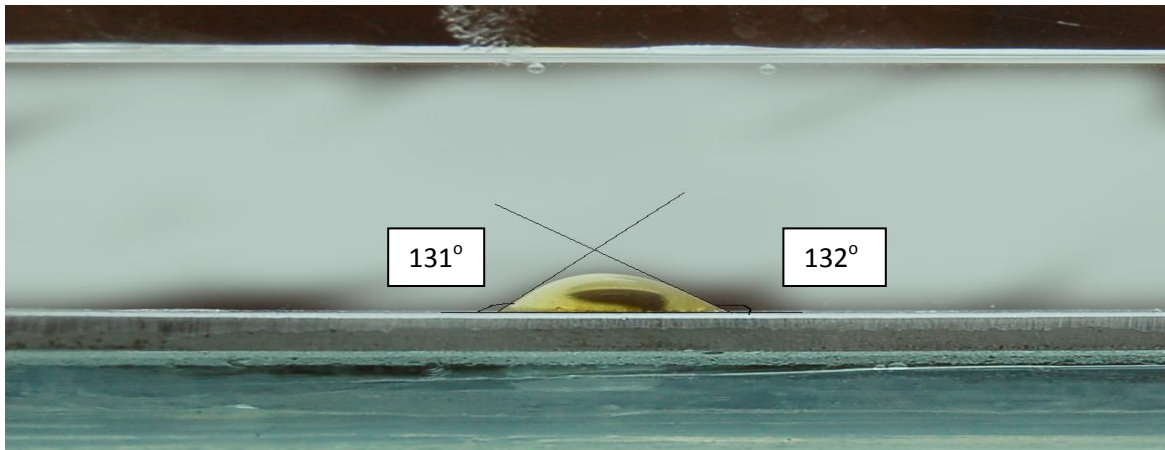


Figure.6

Table.7Wettability of groundnut oil on galvanized iron-contact angle method.

Metal	Contact angle in degree	
Galvanized iron	131°	132°

4.6 Emulsion Inversion Point - (EIP):

Type of emulsion formed with brine solution in the presence of biofuel, is one of the way to know the influence of biodiesel on the corrosion process.

There are two different types of emulsions

1. Oil in water (O/W)
2. Water in oil (W/O)

The percentage of water at which water in oil converts to oil in water type is known Emulsion Inversion Point (EIP) Corrosivity of water phase becomes important only in the presence of either oil in water emulsion or free water depending on the chemical species contained in the oil. Hence EIP is very significant in the corrosion studies of biodiesel. In the present study, EIP was determined by measuring the conductivity of 100% groundnut oil and progressively increasing water content in steps of 10% until 100% NaCl is reached

The results are shown in the **Table.8** and also shown in **Figure. (4)**

Table.8

Medium	Conductance(Ω^{-1})
O100	0.0577
O90	0.0575
O80	0.0561
O70	0.0595
O60	2.2
O50	1
O40	2.2
O30	1.4
O20	1.6
O10	1.5

Variation of conductance with concentration.

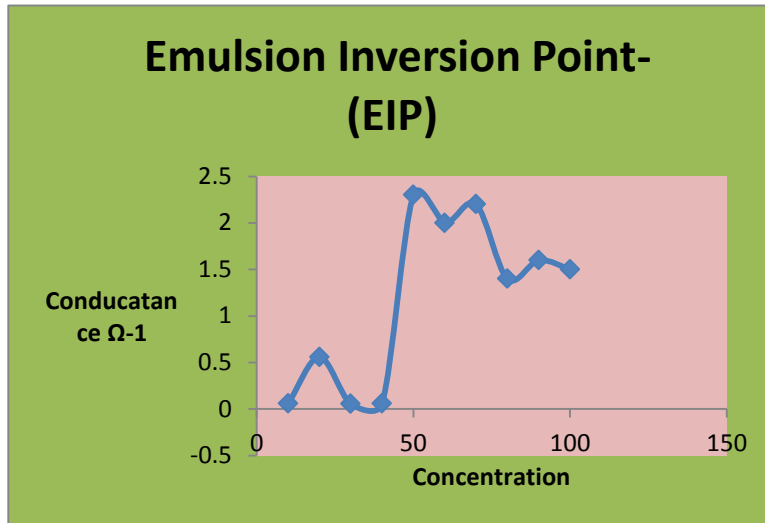


Figure.7

4.7 Corrosion behavior in reused groundnut oil

Biofuel can be used in its pure form or its conventional blend with petrodiesel fuels. The lower conductivities of solution after exposure than before in NaCl indicates that there was no degradation. The increased conductivities in commercial diesel and its blends are due to the absorption of moisture from its environment. The corrosion rate of galvanized iron in reused groundnut oil is negligible and this is same as CD. Hence reused groundnut oil is used as a storage tank material and blending component for diesel engines, thereby decreasing the usage of crude oil and reducing the emissions of greenhouse gases.

The comparison of corrosion rates obtained by mass loss and LPR method are shown in **Figure8(a)** and **9(b)**.

The corrosion rates of galvanized iron in CD and its blend obtained by mass loss method is compared with LPR method.

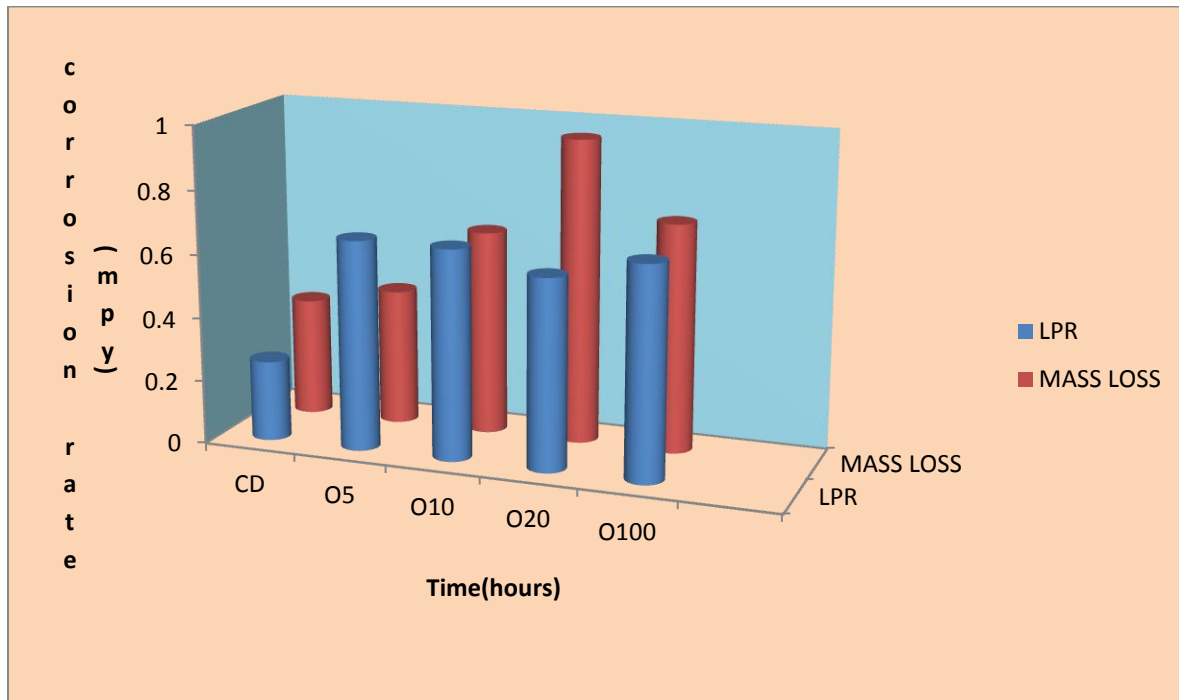


Figure.8 (a)

Corrosion rates of galvanized iron in NaCl, O100 and O99 obtained by mass loss method is compared with LPR method.

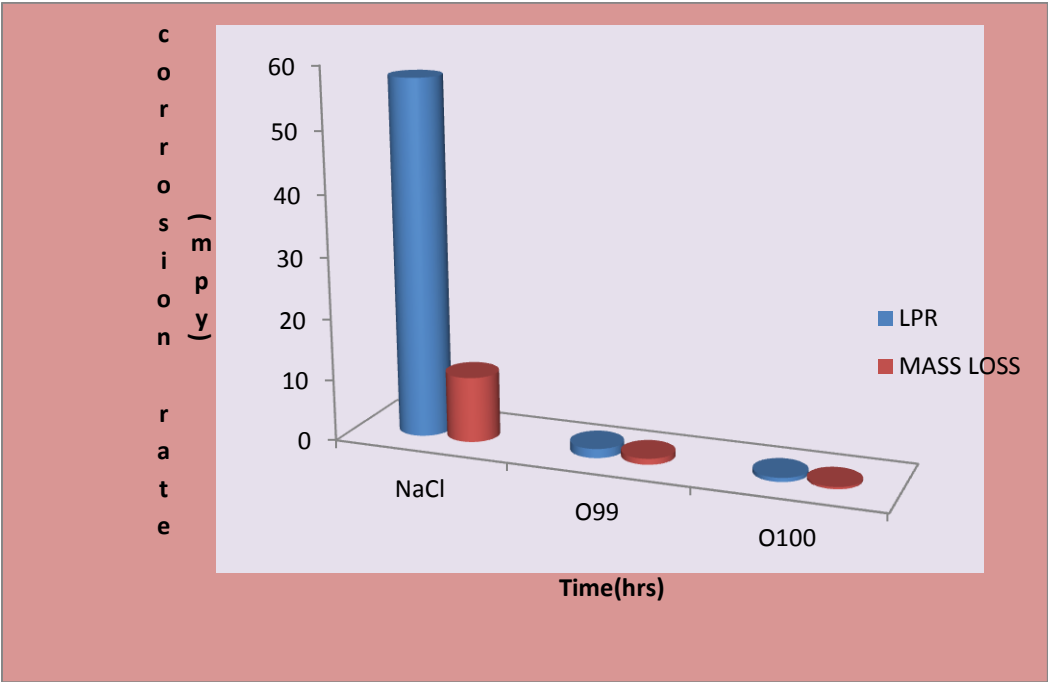


Figure.8 (b)

In these two methods the trend in corrosion rate is same whereas the magnitude is different. This is due to that LPR method gives an instantaneous corrosion rates while as the mass loss method measures only a time averaged corrosion rate.

4.8 Surface morphology

Figure 9 and **10** shows the photomicrographs of mild steel sample exposed to various test solution for a period of 100 hours.

Figure 9 (a), shows the polished surface before exposure to the test solution which is associated with polishing scratches. Metal in NaCl was covered in dark deposits which are showed in the presence of corrosion product. **Figure9(d)**

In the case of metal in O99, a little pitting has been observed **figure 9(c)** which due to water contamination. No significant change is found for the surface of galvanized iron exposed in O100,CD and its blends figure **10(b),10(c), 10(d), 10(e)**, when compared to polished sample. The absence of corrosion products allows the usage of galvanized iron for the storage of biofuel

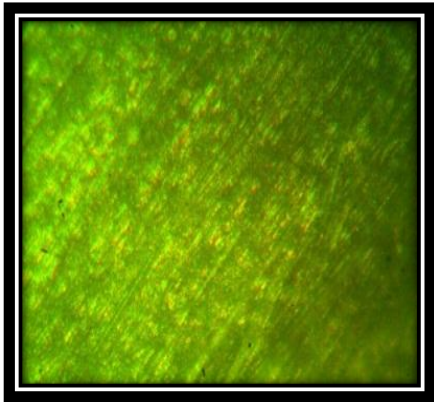


Figure.9 (a) Polished metal

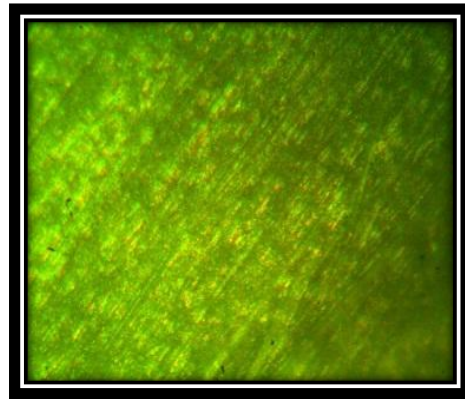


Figure.9 (b) O100

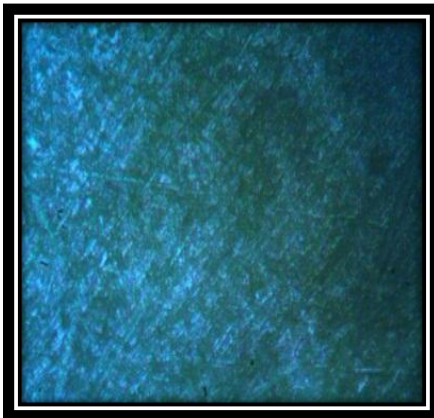


Figure.9(c) O99

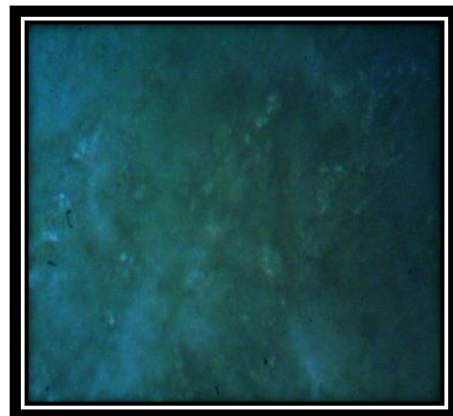


Figure.9 (d) NaCl

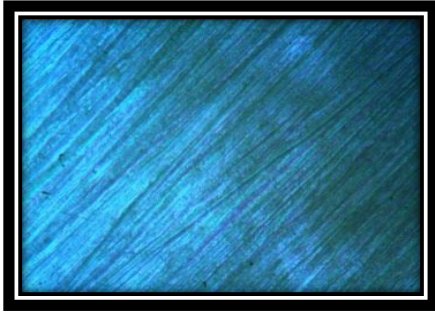


Figure.10 (a) Polished metal

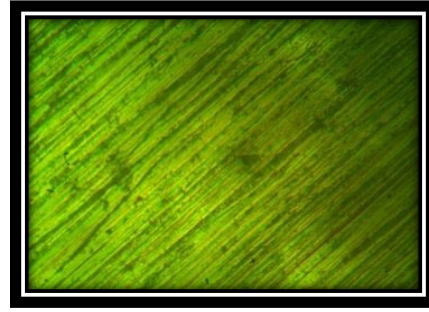


Figure.10 (b) O5

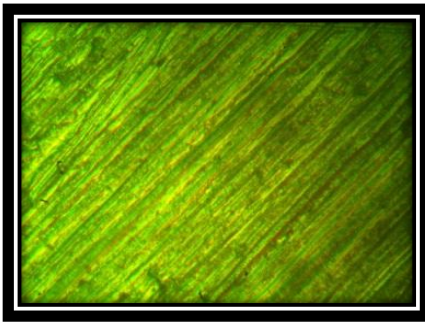


Figure.10 (d) O20

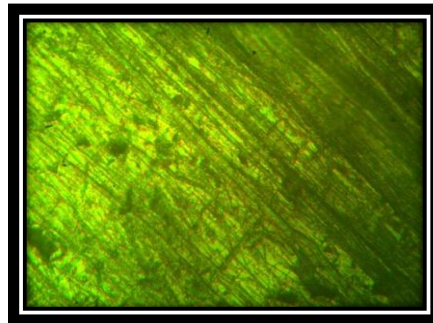


Figure.10(c) O10

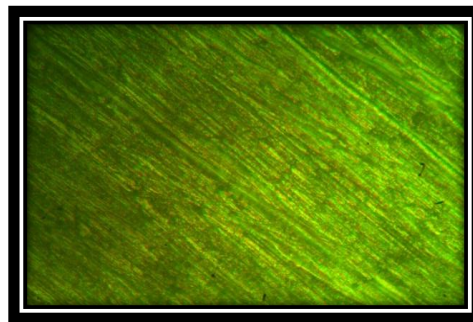


Figure.10 (e) CD

SUMMARY AND CONCLUSION

The present work carried out on the corrosive property of galvanized iron in used groundnut oil and it can be summarized as follows.

- ❖ The used groundnut oil has been characterized as per ASTM D 6751 and most of the properties were found to be similar with the standard.
- ❖ The corrosion behaviours of galvanized iron sheet in UGNO as biofuel was studied by mass loss measurement and linear polarization measurements.
- ❖ The corrosion rates of galvanized iron in O100 were compared with O99 and NaCl. It was found that corrosion rates are maximum in NaCl and the values are least in O100. The corrosion rate in O99 is slightly increased when compared to the corrosion rate in O100. The low corrosion rates of galvanized iron may be attributed to the non-ionic nature of reused groundnut oil.
- ❖ The conductance of test solutions were measured before and after the exposure of metals in test solutions, and it was found that there was no regular change in the conductance before and after the immersion.
- ❖ The corrosion rates of galvanized iron in Commercial Diesel and its blend was studied.
- ❖ The observed difference in the corrosion rate between mass loss and LPR method due to the methodology adopted.
- ❖ The corrosivity of metals can be predicted by contact angle method, for which galvanized iron is found to be obtuse suggesting that oil wets the metal surface and hence is less prone to corrosion.
- ❖ Emulsion inversion point used biodiesel water system was found to be at 90% water cut.

❖ Surface morphology of galvanized iron in various test media was done and found that, NaCl has deposit in it showed that the presence of corrosion. Less deposit was found in O99. No significance change was found in O100, CD and its blends.

Biodiesel is important due to its ecofriendlyness and non –toxicity, hence we can conclude that the reused groundnut oil can be used as an alternative to fuel.

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