4 RESULTS AND DISCUSSION

The studies on interaction between of *Jatropha curcus* biofuel/diesel blends and metals under storage and transportation conditions are discussed under the following heads.

4.1 Characterization of jatropha biofuels

From the chemical point of view, oils from different sources have different fatty acid composition. The fatty acids vary in their carbon chain length and in the number of unsaturated bonds they contain. Fats and oils are hydrophobic substances made up of one mole of glycerol and 3 moles of fatty acids and are commonly referred to as triglycerides. Fully saturated triglycerides lead to excessive carbon deposits in engines. By the process of transesterification, the organically derived oils are combined with alcohol to form fatty esters - the biodiesel. Chemically, biodiesel consists of alkyl esters instead of alkanes and aromatic hydrocarbons in petroleum derived diesel.

Oil, ester and diesel have different number of carbon and hydrogen compound. Diesel having no oxygen compound is a good quality of fuel. On the other hand in the case of vegetable oils, oxidation resistance is markedly affected by the fatty acid composition. The large size of vegetable oil molecules and the presence of oxygen in the molecule suggest that some fuel properties of vegetable oils would differ markedly from those of hydrocarbon fuels. The various fuel properties of *Jatropha curcus* biodiesel and the neat oil taken for investigation in the present work was analyzed as per ASTM D6751 and compared with the standard values and is given in Table 6.

The standard for petrodiesel ASTM D975 is also presented in Table 6 for comparison.
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### Table 6. ASTM standards for diesel, biodiesel and fuel properties of *Jatropha curcus* biofuels

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM D975</th>
<th>ASTM D6751</th>
<th>UNITS</th>
<th>Biodiesel</th>
<th>Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash Point</td>
<td>52 min</td>
<td>130.0 min</td>
<td>°C</td>
<td>169</td>
<td>240</td>
</tr>
<tr>
<td>Water and Sediment</td>
<td>0.050 max</td>
<td>0.050 max</td>
<td>% vol</td>
<td>0.05</td>
<td>0.028</td>
</tr>
<tr>
<td>Kinematic Viscosity 40° C</td>
<td>1.9 - 4.1</td>
<td>1.9 - 6.0</td>
<td>mm²/sec</td>
<td>5.4</td>
<td>12.2</td>
</tr>
<tr>
<td>Sulfated Ash</td>
<td>0.01 max</td>
<td>0.020 max</td>
<td>% mass</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Sulfur (S 500 grade)</td>
<td>0.05 max</td>
<td>0.05 max</td>
<td>% mass</td>
<td>0.0006</td>
<td>0.0018</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td>No 3 max</td>
<td>No 3 max</td>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cetane</td>
<td>40 min</td>
<td>47 min</td>
<td>---</td>
<td>53</td>
<td>51</td>
</tr>
<tr>
<td>Carbon Residue</td>
<td>0.050 max</td>
<td>% mass</td>
<td>0.058</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Acid Number</td>
<td>0.80 max</td>
<td>mg KOH/gm</td>
<td>3.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Free Glycerin</td>
<td>0.020 max</td>
<td>% mass</td>
<td>0.02</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Total Glycerin</td>
<td>0.240 max</td>
<td>% mass</td>
<td>0.25</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Phosphorus Content</td>
<td>0.001 max</td>
<td>% mass</td>
<td>0.0001</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Distillation Temperature, Atmospheric</td>
<td>282 - 338</td>
<td>360 max</td>
<td>°C</td>
<td>330</td>
<td>295</td>
</tr>
<tr>
<td>Equivalent temperature, 90 % recovered</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromaticity</td>
<td>35 max</td>
<td>-</td>
<td>% vol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.1.1 Commercial diesel, Jatropha biodiesel and oil: FT-IR analysis

The FT-IR spectra in the mid-infrared region have been used to identify the functional groups and the bands corresponding to various stretching and bending vibrations in the samples of diesel, jatropha biodiesel and jatropha oil and the spectra are given in the Figure 7, 8 and 9 respectively.

The position of carbonyl group in FT-IR is sensitive to substituent effects and to the structure of the molecule. The spectral regions between 1700-1800 cm\(^{-1}\) corresponds to the characteristic absorptions of biodiesel and diesel and distinguishes diesel with biodiesel or neat vegetable oil. Diesel absorbs in 2750–3000 cm\(^{-1}\), which corresponds to the stretching modes of CH\(_2\) and CH\(_3\), in 1350–1500 cm\(^{-1}\), which correspond to angular deformation of CH\(_2\) and CH\(_3\) and at 720 cm\(^{-1}\), which is assigned to asymmetric angular deformation in the plane of CH\(_2\).

In the spectra of biodiesel, stretching vibration of carbonyl bands appear around 1750 cm\(^{-1}\), peaks in the 1000–900 cm\(^{-1}\) region are assigned to symmetric angular deformation (out of plane) of the C–H bonds of olefins, peaks around 1200 cm\(^{-1}\) are assigned to the asymmetric stretching band of C–C (O)–O bonds of the ester group, and peaks around 1183 cm\(^{-1}\) are assigned to the asymmetric stretching band of O–C–C bonds.
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Figure 7. FT-IR spectra of commercial diesel
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Figure 8. FT-IR spectra of jatropha biodiesel
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Figure 9. FT-IR spectra of jatropha neat oil
The band at 1378 cm\(^{-1}\), which corresponds to the location of bending vibration of C–H groups is very important for the detection of methyl groups in diesel. The absorbance peak of 1700–1800 cm\(^{-1}\) (ester peak) for biodiesel clearly differentiates biodiesel from diesel fuel.

The biodiesel may be distinguished from neat oil by measuring the FTIR area (1446 – 1428 cm\(^{-1}\)) under the methyl (O-CH\(_3\)) peak (1436 cm\(^{-1}\)), which accounted for the methyl esters of all types of fatty acids in the biodiesel. The FTIR spectra of biodiesel showed a C-O stretching band at 1743 cm\(^{-1}\) that are consistent with the presence of saturated aliphatic esters and C–O bands at 1252, 1200, and 1175 cm\(^{-1}\). The appearance of new bands at 1436.22 cm\(^{-1}\), 1196.67 cm\(^{-1}\) and 1171.17 cm\(^{-1}\) in the spectrum of biodiesel and the disappearance of peaks at 958 cm\(^{-1}\) distinguishes biodiesel from oil.

4.2. Corrosivity of biofuels under storage and transportation condition

4.2.1 Water contamination

Biodiesel is considered chemically stable in pure form, but it can become more corrosive during storage, transportation and utilization, when it degrades through moisture absorption, microbial oxidation and other contaminants. Moreover, the fatty acid methyl esters undergo oxidative degradation over time, mainly influenced by temperature and oxygen. According to Tsuchiya et al. (2006), 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. The corrosive nature of biodiesel is more aggravated if free water and free fatty acids are present in it. Water enters the tanks from various sources. Water contamination due to condensation is considered as one of the main corrosion factors for storage containers and pipelines. Whatever be the source of water, when it comes in contact with the metal surface, it becomes susceptible to corrosion which may be due to the corrosive ions that may hydrolyze the methyl esters and produce more corrosive fatty acids.
4.2.2 Controlling factors

The susceptibility of a metal surface to corrosion in the presence of water and oil is primarily controlled by three factors:

1. type of emulsion of the oil and water
2. the wettability on the metal surface
3. the corrosivity of brine in the presence of oil

Emulsion and wettability are two important properties that govern pipeline corrosion. A biofuel may hold a lot of water, but as soon as the inversion point occurs the surface may become water-wet immediately. On the other hand, an inversion point may occur at a very low water-cut, but the surface may not become water-wet until a very high water-cut is reached. The difference in behavior is due to the fact that the emulsion depends on liquid-liquid (oil-water) interaction whereas wettability depends on the balance between two solid-liquid (metal-oil and metal-water) interactions.

Figure 10. Predicting influence of biofuel on internal corrosion of pipelines (ASTM G 205)
Corrosivity of water-phase becomes important only in the presence of either an o/w emulsion or free water, and on a water-wet or mixed-wet surface. The corrosivity of water-phase also depends on the chemical species contained in the biofuels. The factor responsible for one property may or may not influence other properties. For this reason, all three properties (emulsion, wettability, and corrosivity) should be determined independently under the pipeline operating conditions. A flow chart to predict the influence of biofuels on the corrosion of pipelines is presented in Figure 10.

4.2.2.1 Type of emulsion

Due to non ionic nature, biofuel does not mix with water, but at low concentrations it forms emulsion. There are two kinds of emulsion; oil-in water (O/W) and water-in-oil (W/O). In a W/O emulsion, oil is the continuous phase, therefore has low conductivity and is non-corrosive. In an O/W emulsion, water is the continuous phase, hence high conductivity and is corrosive. The percentage of water at which W/O converts to O/W is known as the emulsion inversion point (EIP). As long as w/o emulsion is formed, the aspect of corrosivity does not arise because the water is trapped inside the oil phase.

The emulsion inversion point, for both Jatropha biodiesel and Jatropha oil occurred at 80% water cut (Figure 11).
4.2.2.2 Wettability

The presence of free water, or of o/w emulsion, does not necessarily lead to corrosion. Under this condition, wettability of the biodiesel on the metal determines corrosivity. Based on the wettability, oil can be classified into three categories:

- **Oil-wet surface**: On an oil-wet surface, the oil has a strong affinity to be in contact with metal. Oil-wet surfaces physically isolate the pipe from the corrosive environment and, under such conditions, corrosion does not occur.

- **Water-wet surface**: On a water-wet surface, the oil does not have affinity to be in contact with metal; in fact the oil may not be in contact with the metal at all, even when it is the only phase. A water-wet surface (in the presence of oil) is highly susceptible to corrosion. The probability is higher than in the absence of any oil, because the engulfing oil layer above the water layer facilitates localization.

- **Neutral-wet surface**: On a neutral-wet surface, the oil does not have any preference to be in contact with metal. The oil may be in contact with the metal surface as long as there is no competing phase present.

The tendency of a biodiesel to displace water from metal can be estimated by considering the relative surface energies of all the interfaces involved. A water-metal interface will be replaced by an oil-metal interface if the energy of the system decreases as a result of this action. Therefore it follows that displacement of water by oil should be expected when the contact angle is between 90° and 180°, while the displacement of oil by water should be expected when the contact angle is between 0° and 90°. The surface is
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considered water-wet when the contact angle is between 0° and 90°, and oil-wet when the contact angle is between 90° and 180°.

**Figure 12. Contact angles of oil drops and water on metal surface as per ASTM G 205**

The contact angles of the various metals studied in the presence of JBD and JO measured through the water phase is given in the figure 13.

The contact angles for all the metals studied were found to be between 90° and 180° suggesting that the oil preferably wets on the metal surface. Thus it is found that jatropha biofuels have a strong affinity to be in contact with the metal and isolates the metal from the corrosive environment. This allows the safe use of the studied metals for the storage of jatropha biofuel and for transportation conditions.

### 4.2.2.3 Corrosivity of brine

Corrosive nature of biodiesel seems to be attributed to its free fatty acid components and impurities remaining after processing. In addition, biodiesel is hygroscopic in nature and can absorb moisture from air and thereby can increase the water content (*Fazal et al., 2010*). In the presence of free water or o/w emulsion and on a water-wet surface, oil can influence the incidence of
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4.3 Influence of Jatropha curcus biodiesel and neat oil on the selected metals

The influence of Jatropha curcus biodiesel and neat oil on the selected metals – aluminium, copper, brass, carbon steel I and carbon steel II has been studied under four different conditions: static, flow, deaerated and at different temperatures. 3% Sodium chloride is used in this investigation to imitate water.

4.3.1 Static immersion test

Most corrosion issues of biodiesel have been observed during storage. As the fuel tank is emptied, air enters through the vent pipes to displace the fuel in the tank. Free water may enter from carry-over from the fuel distribution system or leakage through the fill cap or spill containment wall or pipelines. Entry of moist air and accumulation of water in the tank creates favorable conditions for corrosion occurrence. Under stagnant conditions, the water drop will form a separate phase at the bottom of the biodiesel container. Therefore the formation of the water drop on the metal surface may push the majority of biodiesel away but leave a thin layer of water biodiesel mixture on the metal surface. The water drop itself will facilitate the anodic reaction and corrode the metal surface. Hence corrosion rates of the five chosen metals in B100, B99 and NaCl by static mass loss method were determined.

4.7 Surface Analysis
The optical micrographs of the five different metals exposed to fossil diesel, jatropha biodiesel and neat oil are presented in the Figure 31.

Figure 31. Optical micrographs (4x) of the selected metals

a. CD   b. B100   c. O100
4.8 Behavior of metals under long term exposure

Biofuels become unstable when they exhibit a net increase in any insoluble formation, acid number and viscosity. The time to reach unacceptable levels of such features varies with the biofuel sample but they become “old” fuels in a span of 4 - 8 weeks of storage. These stored fuels lead to aggressive peroxides that may oxidize storage tanks, pipes and pressure vessels, and the diesel engine parts. Compatibility of biofuels with storage and engine part materials is still an open issue. Only few works can be found in the literature with detailed studies on the materials surface change after prolonged contact with biofuels (Geller et al., 2008 and Maru et al., 2009). Hence, the interaction between jatropha biofuels and the selected industrial metals were studied by static mass loss method and scanning electron microscopy for a period of 8784h.

4.8.1. Static mass loss method

The behavior of aluminium, copper, brass and mild steel I in CD, B100, O100 and NaCl was determined after the exposure for 8784h. The data obtained was compared with that of the corrosion rate for 100h exposure period and is presented in Table 31. Coupons were also subjected to normal environmental conditions for the same period (8784 h) and the corrosion rate was determined.

It is obvious from the table that the corrosion rates of all the metals under long term exposure is increased compared to that of at 100h period in all the test media. Carbon steel I was found to be the most corroded in CD when compared to other metals. As in the case of 100h exposure, the corrosion rate of the metals followed the order

**Carbon steel I> Copper> Brass> Aluminium.**

In general, the metal degradation was higher in biodiesel when compared to those samples exposed to environmental condition. This may be due to the fact that, in addition to environmental factors, the degradation of biofuel occurs under long term storage which inturn enhances the corrosion of
the metals in contact. A perusal of the literatures reveal that increased acidity and increased peroxide value as a result of oxidation of biodiesel can cause enhanced corrosion of fuel system components (Monyem et al., 2001). It was reported that the corrosiveness of biofuel increases with time when compared to diesel fuel due to the presence of free fatty acid, more oxygen moieties and water content, impurities remaining after processing (Fazal et al., 2010).