Deterioration of rubbers in Waste Cooked oil Bio-diesel(COBD) and HSD fuel used in Indian Railways.

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Abstract - Bio-diesel is a highly oxygenated renewable liquid clean burning alkylester based fuel and as an efficient substitute of fossile fuels (HSD oil) used in Indian Railways. But due to difference in chemical compositions between bio-diesel and fossile fuels,the resistance of different elastomers may not be same as that of high speed diesel oil as per IS: 1460/2010 used in Indian Railways.The present study aims to investigate the impact of waste cooked oil bio-diesel (COBD) and HSD oils on the degradation behavior of elastomers such as Nitrile rubber(NBR), Silicon rubber and viton rubber. A static immersion tests in B0(HSD oil) and B100 (pure Bio-diesel) made from waste cooked oil already used in DG set of IRIMEE,Jamalpur were carried out at room temperature (25^{0}C) and at 40^{0}C for 200 hours. At the end of immersion test, degradation behavior were investigated by measuring % loss or gain in mass as well as hardeness .The exposed elastomers surface was studies by Scanning Electron Microscope (SEM). Fourier Transform Infrared (FTIR) spectroscopy was also used to identify the chemical and structural changes in the elastomers.Results showed that the extent of degradation was higher in case of Nitrile (NBR) i,e 29.3% loss where as in case of Silicon rubber there is a gain of 13.8%,while viton exhibited good resistance in all the case by only gaining of 1.5% by mass and was least attacked /effected by COBD. Hence, found to be comparatively more suitable under the given experimental condition.

Keywords – Waste Cooked oil Bio-diesel (WCOBD), HSD oil, Indian Railways (IR) and Nitrile (NBR), Elastomers.

I. INTRODUCTION

Indian Railways (IR), has already taken a decision to adopt alternative source of energy (BIO-DIESEL) to meet its fuel requirements as well as to overcome the air pollution problems. Biodiesel fuel has become more attractive because of its environmental benefits[1]., better lubricity ,reduces the carbon footprint and are renewable source of energy. Biodiesel has a higher cetane number than diesel fuel, no aromatics, no sulphur, and contains 10-11% more oxygen by weight[2,3].The use of waste cooked oil as biodiesel feed stock in Indian Railways [4] reduces the cost of biodiesel production, since the feedstock cost constitutes approximately 70-95% of the overall cost of the biodiesel production[5]. Hence a considerable work has been done by Indian Railways at Research Design and Standards Organization (RDSO) and IRIMEE to assess the suitability of Bio-diesel for the Indian Railways application as an alternative to power the diesel locomotives,diesel generators as well as in road vehicles.[6] .

In the present research work, bio-diesel was manufactured at IRIMEE, Jamalpur through the process of transesterification by using waste cooked oils as a feed stock , collected from Queens road hostel, Eastern Railway, Jamalpur .and also study about the effects of these bio-diesel (COBD) on the degradation of different rubbers collected from the store of diesel maintenance shop and tested at CMT Laboratory,locoworkshop,Eastern Railway, Jamalpur.

In diesel engine, fuel comes into contact with a wide variety of materials (Rubbers , metal –rubber bonded and other materials). Material compatibility in biodiesel is different from Petro-diesel (HSD oil) [7], because petrodiesel is a mixture of hydrocarbons while biodiesel is a mixture of fatty acid esters [8]. The compatibility of seal, gaskets, hose materials commonly used in automotive as well as in rail transport systems using high speed diesel, has already been established. However, no information are available on the compatibility of elastomers with waste cooked oil biodiesel (WCOB). It has been reported that degradation of certain elastomers is one of the main issues related to material compatibility in biodiesel [7, 9]. In general, Nitrile (NBR) types are considerably more resistant to a much wider variety of fuels and lubricants than any of the rubbers as pointed out by A.S.M.A. Haseeb et al. [7].

The principle behind the swelling of the elastomers with liquid fuel is based on **"like dissolves like".** There is a general rule describing the fact that polar substances are more likely to dissolve in polar solvents and non-polar substances are more likely to dissolve in non-polar solvents. For instance natural rubbers are disintegrated by straight hydrocarbon fluids such as gasoline and kerosene. The polar polymers are virtually unaffected by straight chain hydrocarbons. Conversely, natural rubber (NR) and SBR (Styrene butadiene rubber) which are non-polar polymers, are unaffected by strong polar solvents such as acetone and methyl ethyl ketone while the polar rubber swells severely .

Hence it is extremely important that design engineers and manufacturers should take into consideration the type of fluid that is going to be used in a particular service and specify the rubber, which is the least affected by that fluid, is discussed in this research paper.

II. MATERIALS AND METHODS:

2.1 Manufacturing of Bio-diesel

Due to non-availability of sustainable feed stocks ,waste cooked oil was collected from queen's road hostel, Jamalpur and convert it into the bio-diesel through the process of transesterification reaction as mentioned in Fig-1 and used it in DG set of IRIMEE, Jamalpur . This process has been widely used to reduce the viscosity of vegetable oils (triglycerides). The process for bio-diesel production is shown in figure-2 Where R', R'' and R''' are different types of fatty acid chains associated with the oil. Triglycerides are readily transesterified in the presence of a catalyst at atmospheric pressure and at a temperature of approximately 60 to 66^{o}C with an excess of methanol. The mixture at the end of reaction is allowed to settle. The lower glycerol layer is drawn off, while the upper methyl ester layer is washed to remove entrained glycerol and is then processed further for removal of excess methanol and moisture.

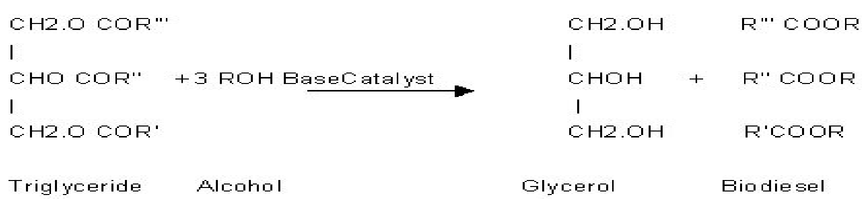

Figure 1. General equation for thansesterification reaction.

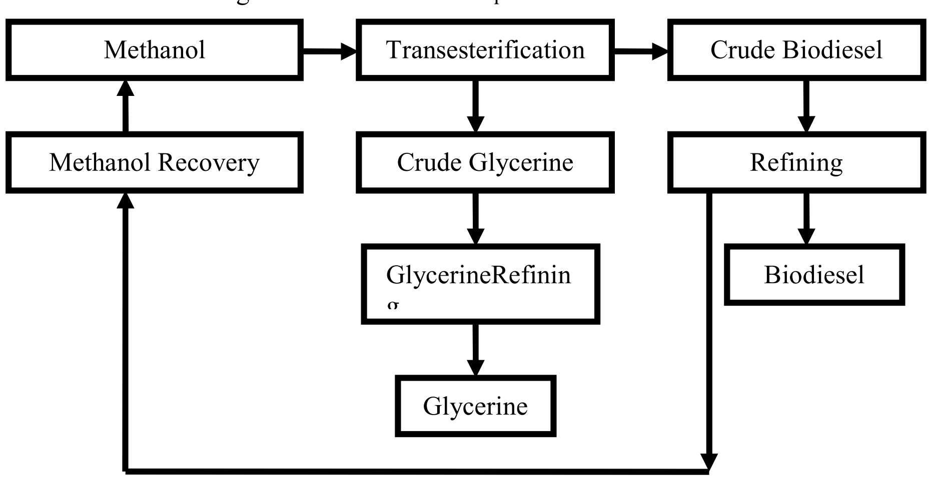

Figure-2Schematic Process for biodiesel production

The biodiesel obtained from COBD was tested for its elastomer compatibility. Table no. 2&3 , show the swelling studies in HSD and COBD. State immersion tests in HSD and COBD were carried out at room temperature & at 40^{o}C for 200h for various rubbers like Buna-N, Viton and Silicon. At the end of immersion test, degradation behavior was investigated by measuring mass and hardness. The exposed elastomer surface was also investigated by SEM to identify the morphological changes. Similarly FTIR spectrum was also used to identify the structural changes in the eleastomers.

2.2 Hardness test: Hardness of different elastomer sample was measured using a Rubber Hardness Tester, SHR-Mark III. It confirms to ASTMD-1706-61 in "A" Scale. Reported hardness values are the average of reading taken at five different locations on each sample at room temperature. Hardness measurement was conducted before and after the fluid emersion.

2.3 Swelling test:

Swelling test was performed to determine the swelling behaviour (by mass) of three different types of elastomers in diesel and COBD at 40^{o}C for a total time of 200 hours.

2.3 Fourier Transform Infrared Spectroscopy (FTIR) & SEM analysis:

The FTIR spectrum was run in Shimadzu IR Prestige 21 instrument in a range of 4000 – 400 cm^{-1} wave number. FTIR of biodiesels and diesel are furnished in Figure 3 (a) & (b). and the comparative features are tabulated in Table -4. FTIR Spectrum of silicon and viton rubber were taken to identify the change in structure before and after swelling. Due to heavy deterioration of Nitrile rubber in COBD ,it was not possible to obtain spectrum of swelled Nitrile rubber Similarly the exposed elastomer surface was investigated by by SEM to identify the morphological changes.

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III. Experiment and Result

Analysis of the result given in Table 2 & 3 shows that in case of Nitrile (NBR) rubber, Viton and silicon rubber, the % of gain were 26.8, 1.1 and 37.1, respectively. However, in case of use of COBD, NItrile rubber(NBR) shows 29.3% loss indicating unsuitability for its commercial use. On the other hand, in case of Viton and silicon, the % of gain were 1.5 and 13.8. Viton rubber found to be comparatively suitable under given experimental condition as the % gain is quite acceptable which can be attributed to the C – F bonding present in the structure which adds polarity to the molecule.
The hardness test was carried out using Rubber Hardness Tester, before and after the fluid immersion. It shows that the Nitrile rubber sample exhibit most overall reduction in hardness in test fluid(COBD).

FTIR spectrum analysis:

The FTIR spectra of HSD oil and COBD are furnished in figures -3 (a) & (b), where as FTIR of viton and silicon rbbers are furnished in Figures 4 (a),(b),(c) & (d). The FTIR spectra of silicon rubber show the presence of –Si-O-Si at 900 – 1100 cm^{-1} range. Additionally O-H_{str} and C-H_{str} frequency is noted at 2960 and 1257 cm^{1}. Similarly viton rubber shows characteristic peaks of C-H_{str} and C-H_{str} at 2918 and 1399 cm^{-1}. These structural features do not show any significant difference before and after use of biodiesel and diesel indicating the stability of functional groups in the material. However, only some morphological changes in the materials are, evident from SEM studies.

SEM analysis:

The morphological features of elastomers such as Silicon and Viton rubber are furnished in Figures 5.(a) ,(b),(c) and (d). They show a uniform surface characteristic. Upon immersion in diesel for 200 hours, no change was observed in surface characteristics. However, upon immersion in COBD, the morphology changes as evident from Figure 5(c) & 5(d), a number of lines indicating the swelling characteristics. Therefore, it may be concluded that the use of COBD may not be suitable for prolonged use.

On the other hand, the surface morphology of viton rubber is presented in Figures 5 (c), and 5(d). No change in structural feature was noted in case of use of COBD but use of HSD changes the morphological feature to some extent.

Table -1 Specification of Selected Elastomer

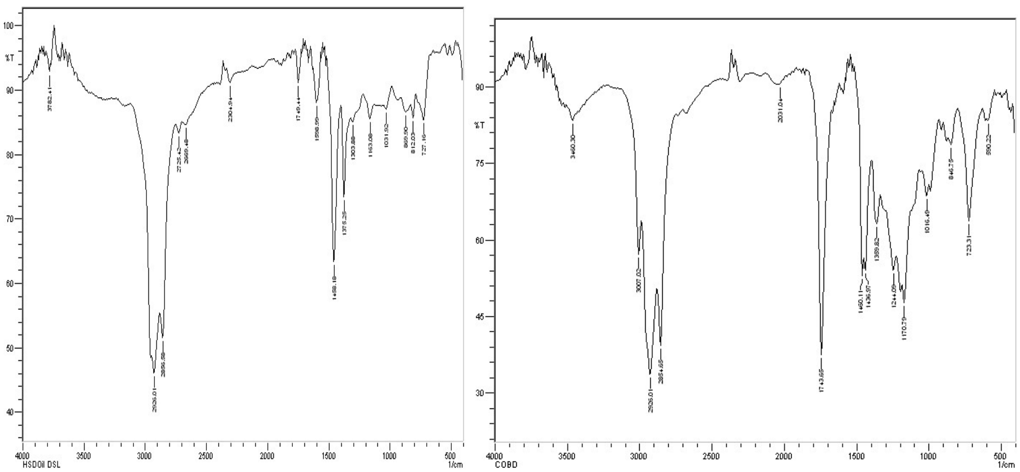
Sl..No.	Diesel Locomotive Workshop (DLW) Specification	Elastomers
1.	D 58632	Nitrile rubber or Buna-N
2.	D 58681	Silicon rubber
3.	D 58695	Viton rubber

Table 2. Swelling % of different types of rubbers in oils

Sl.no.	Types of rubbers	Diesel Oil (HSD Oil)	COBD (Cooked oil Bio-diesel)
1.	Buna-N or Nitrile	26.8% Gain	29.3% Loss
2.	Viton	1.1% Gain	1.5% Gain
3.	Silicon	37.1% Gain	13.8% Gain

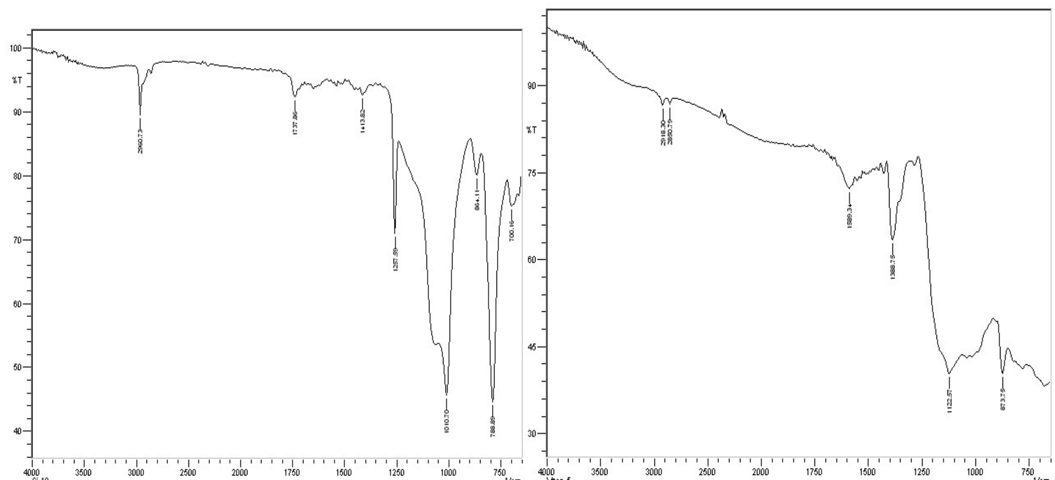
Table 3: Effect of hardness after swelling of rubber polymers in oils.

Sl.no.	Types of rubber polymers	Initial hardness	Hardness after swelling in Diesel	Hardness after swelling in COBD
1.	Buna-N or Nitrile	70	56	54
2.	Viton	78	78	76
3.	Silicon	74	52	61

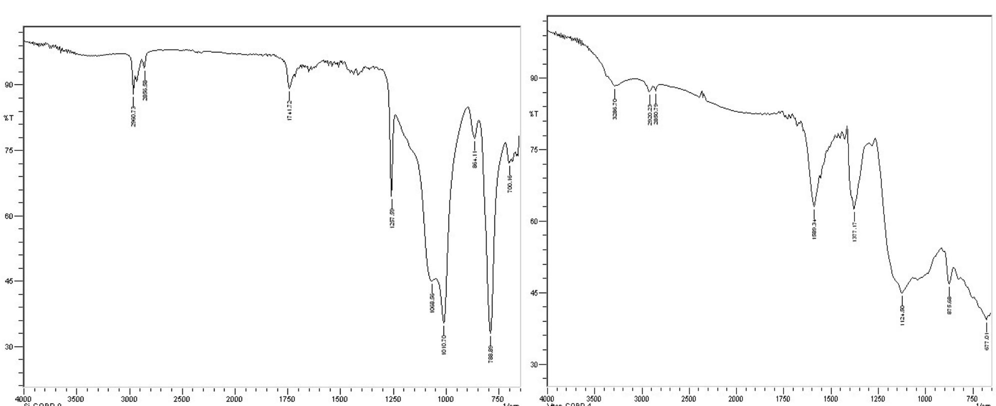


(a) (b)

Figure 3 (a) FTIR Spectra of (HSD Oil) Diesel (b) FTIR Spectra of Cooked Oil Bio-diesel

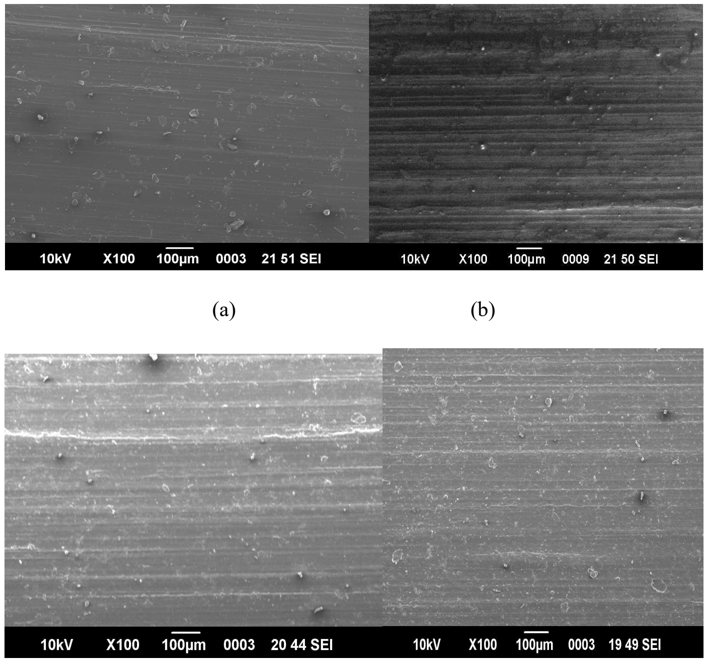


(a) (b)



(c) **(b)**

Figure 4. (a) FTIR Spectra of Silicon rubber without swellin (b) FTIR Spectra of Viton rubber without swelling (c) FTIR Spectra of Silicon rubber in COBD Watermarked image (d)) FTIR Spectra of Viton rubber in COBD



(a) (b)

(c) (d)

Figure 5. (a) SEM of Silicon rubber (without swelling)
(b) SEM of exposed surface of Silicon rubber in COBD after 200hours.
(c) SEM of Viton rubber (without swelling).
(d) SEM of exposed surface of Viton rubber in COBD after 200hours.

IV.CONCLUSION

Based on the experimental investigation with special reference to degradation behavior of elastomers in waste cooked oil bio-diesel(COBD), the following conclusion can be drown.

1. The degradation behavior analysis confirmed that viton rubber is comparatively more suitable under the given set of experimental condition.
2. Nitrile rubber showed greater affinity for COBD than HSD oil used in IR application.
3. Nitrile rubber swelled,and lost its mechanical properties by biodiesel (specially in case of COBD)

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