

Effect of Ethanol-Gasoline Blends on Corrosion Rate in the Presence of Different Materials of Construction used for Transportation, Storage and Fuel Tanks

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ABSTRACT

Due to spiraling for possible options of blending alternate fuels such as ethanol and biodiesel in gasoline and diesel respectively. Ethanol (5%) blending in gasoline has become mandatory in specified states in India. There is also proposal to increase ethanol to 10% in gasoline blends. Ethanol blending in gasoline crude oil prices, Oil Companies as well as government is seriously looking will aid in reducing particulate emissions in the compression ignition engines due to more efficient combustion. On the other hand Ethanol blending in gasoline accelerates corrosion susceptibilities of metals during pipeline transportation, storage, car fueling systems etc. due to ethanol's hygroscopic nature and impurities present.

Ethanol/Gasoline blends, due to ethanol's greater affinity to water, can absorb significant amounts of water (0.3-0.5 v/v %) without phase separation. This soluble water in ethanol causes corrosion in metallurgy. Therefore corrosion inhibitors are added into these blends for reducing corrosion during storage, pipeline transportation and also in car fuel tank systems.

The present paper reports effect of ethanol-gasoline blends on corrosion rates in presence of different construction materials viz., carbon steel, brass and copper. Further, the performance of novel organic ethanol based inhibitors were developed in the laboratory scale is also reported.

KEYWORDS

Gasoline, ethanol, corrosion inhibitor, moisture, metallurgy, potentiodynamic polarization

INTRODUCTION

The global fuel crisis has triggered the awareness amongst many countries to focus on the development of alternative fuels. In India 5% Ethanol blending (E5) is

mandatory which is proposed to be 10% (E10) by 2009. Ethanol and gasoline have differences in some critical properties such as octane number, vapour pressure but their blends known as gasohol shows higher vapour pressure and octane compared to base components¹. Typical properties of these blends are shown in Table 1.

Ethanol is not easily transported via pipelines because it has a tremendous affinity to absorb water. Water accumulation during pipeline transport is a normal occurrence and in some cases water enters through refinery tank roofs. In presence of moisture contamination, ethanol-gasoline blends show phase separation, resulting in two layers of product: a layer of gasoline on top and an ethanol layer on the bottom² which can cause problems during tank storage and in vehicles fuel transfer lines. Ethanol can dissolve and carry impurities that are present inside multi-product pipeline systems³, may cause problems for end use applications. Ethanol blended gasoline storage is very critical because its storage requires especially moisture resistant tanks with good internal linings. Some preparatory steps are required to avoid water contamination⁴.

High concentrations of ethanol can lead to internal stress corrosion cracking, which is hard to detect and manage. This may be accelerated at weld joints or "hard spots" where the steel metallurgy has been altered. To overcome these problems selective possibilities of improved post-weld heat treatment and the coating of internal critical zones (at pipeline weld points) has to be explored⁵. Ethanol can accelerate corrosion in steel of storage tanks systems by scouring or loosening deposits on the internal surfaces of tanks and piping⁶. Ethanol is not compatible with soft metals such as zinc, brass, copper, lead, and aluminum. These metals will degrade or corrode in contact with ethanol and possibly contaminate a vehicle's fuel system⁷.

It has been observed that the storage and transportation of ethanol gasoline blend is a critical issue, therefore selection of suitable corrosion inhibitor to match the

material of construction is important. In this paper corrosion studies have been undertaken with ethanol-gasoline blends in presence of moisture and different materials of construction such as carbon steel, brass and copper commonly used in storage tanks, pipelines and fuel tanks and other parts of engine. In addition the development of corrosion inhibitors suitable for different gasohol blends as well as the metallurgy is also discussed. .

EXPERIMENTAL

The experiments were done to determine the corrosivity of ethanol blends with gasoline using different metals like carbon steel, copper and brass.

CHEMICALS & REAGENTS

Ethanol sample collected from blending stations (as per BIS specs.). Gasoline from Retail outlets. Corrosion inhibitor, in-house synthesized (Ref. Internal Report Dec, 07). All reagent used in lab experiments are of analytical grade, Millipore water was used for dilutions

Corrosion MEASUREMENTS

Ethanol blended with gasoline at various percentages from 5, 10, 20 & 100 and the samples will be referred as E5, E10, E20 & E100 respectively.

Weight loss measurements were done using Carbon Steel (CS), Brass and copper coupons according to ASTM G1-90 and ASTM G 31-728. The experimental set-up consisted of a closed reaction vessel and constant temperature bath. Various corrosion coupons were placed with the help of specially designed coupon holders. The temperature was kept 50 + 2°C. The specimens were degreased using acetone and finally dried. The cleaned specimens were weighed before and after the experiments.

For potentiodynamic polarization studies, metal strips were coated with commercially available lacquer with exposed area of 1.0 cm² were used and all the experiments were carried out at temperature (30 ± 1°C). Equilibrium time leading to steady state of the specimens was 30 minutes. Sweep rate in potentiodynamic experiments was kept at 1 mV/sec and an in-house developed (Ref. Internal Report Oct'07) probe was used for the electrochemical measurements.

Development of Corrosion inhibitors

An organic Schiff bases compounds soluble in ethanol were developed (Ref. Internal Report Dec'07) in-house and experiments were conducted on E10 and E20 samples using copper, brass and carbon steel coupons.

The weights of the coupons were measured before and after the test and corrosion rates (CR) were calculated. The inhibition efficiency (IE) of the inhibitors was calculated using the following equation:

$$IE = \frac{CR_0 - CR_i}{CR_0} \times 100$$

Where: CR₀ = Corrosion rate of blank solution; CR_i = Corrosion rate after adding inhibitor

Results & Discussion

The experiments were done using various gasohol blends under accelerated corrosion tests. The blends were tested for effect of different metallurgy, moisture content and effect of corrosion inhibitor on corrosion of metals

CORROSION STUDIES ON GASOHOL BLENDS

(a) Effect of different metallurgy

The experiments were conducted on carbon steel brass and copper with various blends of gasohol. The results are shown in Figure-1. It can be seen that corrosion increases with increase in the ethanol percentage in the gasoline. As corrosion mainly occurs due to presence of water/moisture in the blends so with increasing the ethanol content moisture increases in the blends which results into the increase in corrosion rate. Maximum increase in corrosion rate is observed in case of carbon steel, which is mainly due to higher carbon and iron content in the alloy which makes it more susceptible for corrosion.

(b) Effect of moisture

The effect of moisture on corrosion of carbon steel with E5 blend has been shown in Figure- 2. Carbon steel metallurgy is selected for the study of moisture effect on corrosion rate as it is generally used for pipelines and storage tanks. . It has been shown in figure that with increase in moisture content from 0.3 – 55 Corrosion rate increase from 2.5 to 12 MMPY. Significant decrease in corrosion rate (< 2 MMPY) has been observed after addition of corrosion inhibitor (10-20 ppm).

(C) DOSAGE OF CORROSION inhibitor

The effect of inhibitor was studied with various blends of ethanol & gasoline on metals like carbon steel, copper and brass. The results are shown in Figure 3.

It has been observed from the results that inhibitor shows a significant decrease in corrosion rate on all the metals with all blends. In E5 and E10 blends significant decrease in corrosion rate (< 1 MMPY) has been observed with 10 ppm inhibitor dosage. On higher blends (from E50 onwards) required inhibitor dosage increases up to 25 ppm. Corrosion inhibitor has shown good inhibition efficiency (95%) in all the blends with all metals.

(D) Potentiodynamic polarization studies

The electrochemical parameters like corrosion current density (I_{corr}), Corrosion potential (E_{corr}) and inhibition efficiency (IE) for all the ethanol-gasoline blends on carbon steel, copper and brass metals. Results are given in Table -2

It is evident from the results that I_{corr} values of all the inhibited metal coupons are lower than uninhibited coupons. In case of E5 blend the required quantity of the

inhibitor is 10 ppm which has shown 95% inhibition efficiency with all the metals, whereas in case of E10 and E20 increased concentration of inhibitor (15 ppm) has shown good inhibition efficiency (94-95%). The result show that there is no significant change in Ecorr value after the addition of inhibitor with all the metals, it indicates that the inhibitor is mixed type, i.e., it protects corrosion on both anodic and cathodic sites of the metals¹⁰.

CONCLUSIONS

The following conclusions can be drawn from the above study;-

- Corrosion in ethanol gasoline blends increases on increasing the ethanol concentration because moisture susceptibility also increases on increasing ethanol quantity
- Different metals has shown variation in corrosion rates with increasing ethanol concentration in the blends
- Carbon steel has shown maximum corrosion rate among all studied metals
- Corrosion rate of Gasoline ethanol blend increase with increase in moisture content because of phase separation and it can be reduced by dosing adequate amount of corrosion inhibitor.
- In-house synthesized corrosion Inhibitor has shown good performance on all the metals with all blends of gasoline–ethanol by potentiodynamic polarization methods

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Table -1 Comparison of properties of ethanol, gasoline and gasohol blends

Properties	Gasoline	Ethanol	Ethanol blends	
			E10	E20
Density	0.72 - 0.78	0.794	0.73-0.76	0735-0.765
Reid Vapour pressure kpa	44-78	17	64	63.4
Oxygen content (% wt)	0	34.7	3.5	7.0
Water solubility (%)	Nil	100	>0.5	>0.7
Stoichiometric Air to fuel ratio	14.6	9.0	14.0	13.5

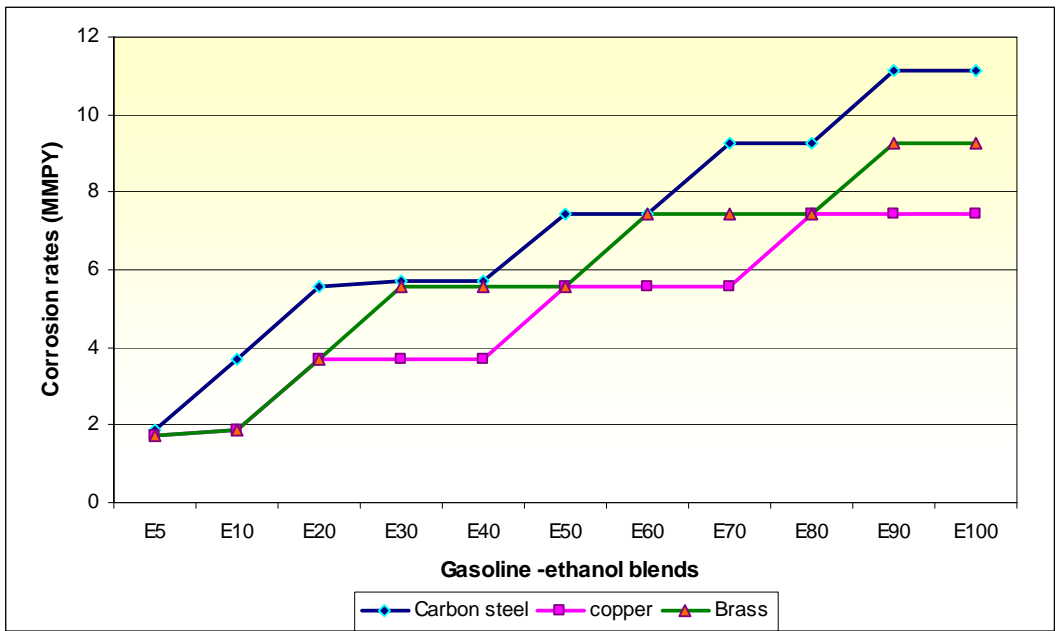


Figure-1: - Effect of corrosion rates of carbon steel, copper and brass

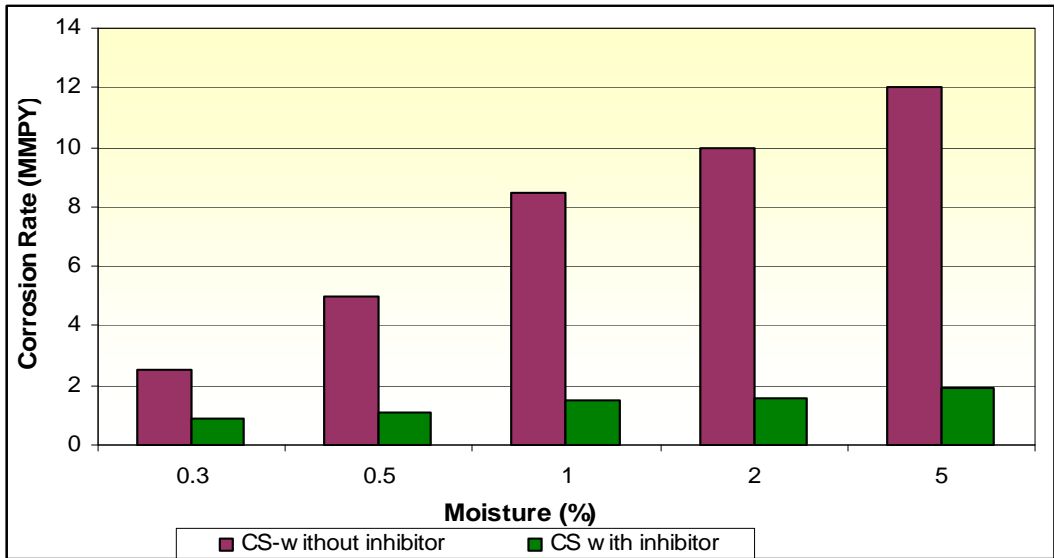


Figure -2:- Effect of moisture on corrosion of gasohol blends with Carbon steel

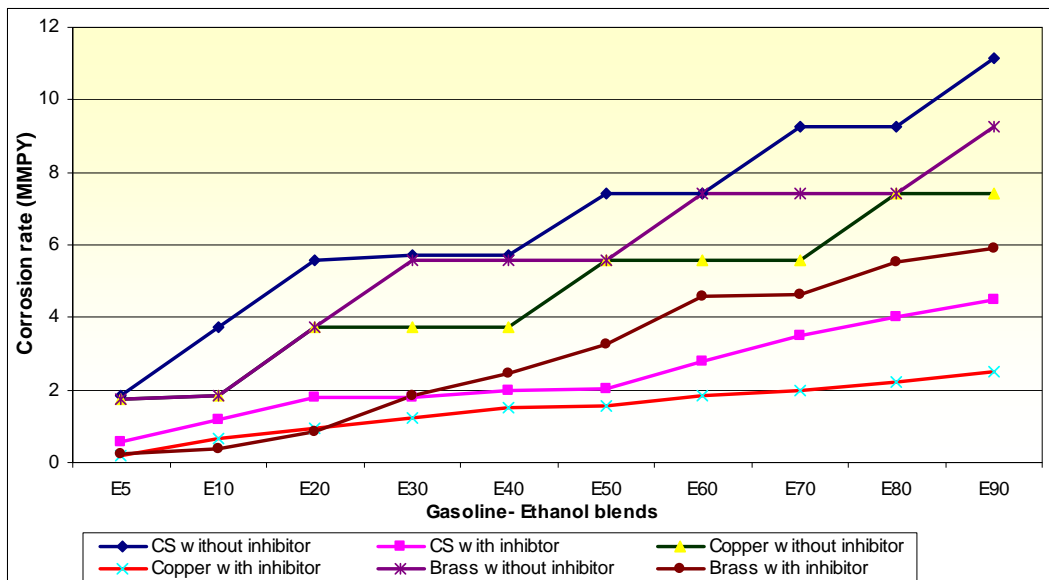


Figure -3: Effect of corrosion inhibitor on various metals in gasoline ethanol blends

Metallurgy	Blend	Inhibitor conc. (ppm)	(E_{corr}) mv	(I_{corr}) ($mA\ cm^{-2}$)	(IE) (%)
Carbon steel	E5	nil	-560	0.20	--
	E5	10	-556	.010	95.0
	E10	nil	-554	0.28	--
	E10	15	-556	0.016	94.3
	E20	nil	-558	0.36	--
	E20	15	-554	0.020	94.4
Copper	E5	nil	-360	0.12	--
	E5	10	-356	.006	95.0
	E10	nil	-346	0.14	--
	E10	15	-344	.008	94.2
	E20	nil	-350	0.16	--
	E20	15	-352	.010	93.8
Brass	E5	nil	-310	0.18	--
	E5	10	-308	0.008	95.6
	E10	nil	-320	0.20	--
	E10	15	-324	.012	94.00
	E20	nil	-328	0.24	--
	E20	15	-330	0.014	94.2

Table 2:- Potentiodynamic Polarization data obtained from different concentration of inhibitor with E5, E10 & E20 blends for carbon steel, brass & copper metals