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Paracetamol as an Inhibitor Corrosion of Low Carbon Steel in Gasoline Environment

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Abstract-Paracetamol contains organic compounds that are safe to use in the environment and are commercially available. Both of these are the reasons for using this drug as a corrosion inhibitor for low carbon steel. Corrosion inhibition of low carbon steel in the gasoline environment by paracetamol drugs was investigated by weight loss and FT-IR. The value of the corrosion rate of low carbon steel and inhibitor efficiency was obtained from the weight loss test for eight weeks of immersion with the variation of paracetamol concentration ranging from 0-100 ppm. While the mechanism of inhibition of paracetamol drug is proved by FT-IR test and isothermal adsorption calculation. The addition of 50 ppm paracetamol inhibitor can lower the corrosion rate of low carbon steel to 0.61 mpy with the efficiency of inhibitor value is 72.41% at the sixth week of immersion. The FT-IR test proves that the paracetamol drug inhibiting mechanism in low carbon steel acts as a mixed inhibitor capable of adsorbed on the steel surface and lowers the corrosivity of gasoline. In the calculation of isothermal adsorption, paracetamol drug adsorbed on the steel surface follows the Langmuir isotherm theory. From the calculation of the adsorption enthalpy energy can be concluded the drug paracetamol adsorbed physically on the surface of steel or called physisorption.

Index Terms *: Adsorption isotherm, corrosion, gasoline, inhibitor organic, paracetamol*

1 Introduction

Corrosion is the process of material degradation both in quality and quantity due to the reaction with the environment [1]. Corrosion is a chemical phenomenon in metallic materials which is essentially a metal reaction into ions on metal surfaces that are in direct contact with the aqueous and oxygen environments [3]. Corrosion reaction will cause a material to change the properties (both physically and chemically) tend to be lower or can be said the ability of a material or metal when exposed to corrosion will experience a decrease in quality and quantity. To modify the environment, inhibitors play a role in changing the environmental properties of the material becomes more immune to corrosion. While the adsorption inhibitor works by forming a coating both physically and chemically useful blocking the metal for direct contact with the environment so that the corrosion rate decreases. The adsorption inhibitor is associated with the presence of hetero (N, O, and S) atoms and the presence of many aromatic group bonds or rings [8]. Anodic inhibitors have two types of characteristics, one requiring dissolved oxygen to be effective, eg molybdate, silicate, phosphate, and borate, while others are oxidizing agents [3]. An example of a commonly used organic inhibitor on the market is a chemical group that normally forms a coordinate bond with metals like amino ($-NH_2$), carboxyl (-COOH), and phosphonate ($-PO_3H_2$) [5]. The absorption depends on the structure of the inhibitor, the charge present on the metal surface and the electrolyte. The processes undertaken to protect metals are carried out by physical adsorption, chemisorption and film formation [2].

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Paracetamol or acetaminophen is an anti-inflammatory drug widely used to relieve pain and fever. Organic compounds are safe and capable of inhibiting corrosion in metals [9]. One drug containing organic compounds capable of reducing the corrosion rate of steel in sulfuric acid and acetic acid to 85% [7]. In addition to adsorbed, paracetamol can decrease the corrosivity of the environment against metals [4]. The use of steel in automotive has been widely applied, for example as raw materials for fuel tanks on cars. One method of steel protection in a fuel-gasoline environment is to add inhibitors in gasoline. The addition of ascorbyl palmitate as an inhibitor in the gasoline environment mixed with 10% ethanol and 1% water can decrease the corrosion rate of carbon steel up to 96.5%. Efficiency increases with the addition of inhibitor concentration and decreases with increasing working environment temperature. The ascorbyl palmitate adsorption on the carbon steel surface follows the isotherm of the Langmuir [6].

2 Experimental Methods

2.1. Materials and solutions

The material used is low carbon steel with composition (%); Mn (0.21), Al (0.21), Si (0.87), Cr (0.87), Ni (0.22), Cu (0.75), Zn (0.19), C (0.26), Co (0.78), and Fe (95.67). Materials are cut into coupons, with dimensions 1.5 cm x 1.5 cm x 0.2 cm for each coupon. Each coupon is immersed in a pickling solution (HCL 30%) to degrade corrosion products formed before immersion. Each coupon will be immersed in a gasoline solution. The gasoline used is a type of pertalite with RON (Research Octane Number) 90. This means the gasoline contains 90% iso-octane and 10% n-heptane. Each gasoline solution will also be given an additional paracetamol drug with a concentration range of 0 to 100 ppm.

2.2 Weight Loss Tests

The corrosion rate can be calculated using ASTM G1[11],

$$CR = \frac{K \times W}{D \times A \times T} \qquad (1)$$

where

CR: corrosion rate
K: corrosion constant
W: mass difference
D: density
A: Surface area
T: immersion time

A corrosion inhibitor must not only reduce the corrosion rate but also be compatible with its environment. Usually, a corrosion inhibitor is assessed by its inhibition efficiency defined as follows:

$$IE = \frac{CR_0 - CR_I}{CR_0} \times 100\% \qquad (2)$$

where

IE: efficiency of inhibitor
CR_0: corrosion rate without inhibitor
CR_I:corrosion rate with the inhibitor

2.3 Infrared Spectrum Analysis

The mechanism inhibition of paracetamol against steels in a gasoline environment can be identified through the FT-IR test. There was four material which done by FT-IR test, is a paracetamol drug, low carbon steel before immersion, low carbon steel after immersion without inhibitor, and low carbon steel after immersion with the addition of paracetamol inhibitor (best concentration). Peaks identified from the FTIR test, interpreted and then analyzed to determine the differences and their similarities.

3 RESULT AND DISCUSSION

3.1. Effect Of Consentration

The effect of variation of concentration of paracetamol in gasoline to corrosion rate of steel has been studied by using weight-loss test. From the graph of corrosion rate of steel to time (see fig. 1.), the highest corrosion rate was found in low carbon steel without the addition of inhibitor (2.29 mpy) at the first week of immersion. Meanwhile, low carbon steel with the addition of 50 ppm paracetamol inhibitor experienced the lowest corrosion rate, ie 0.61 mpy sixth week of immersion. Steel without inhibitors has shown a trend of higher corrosion rate than other variations from the first week to the eight-week.

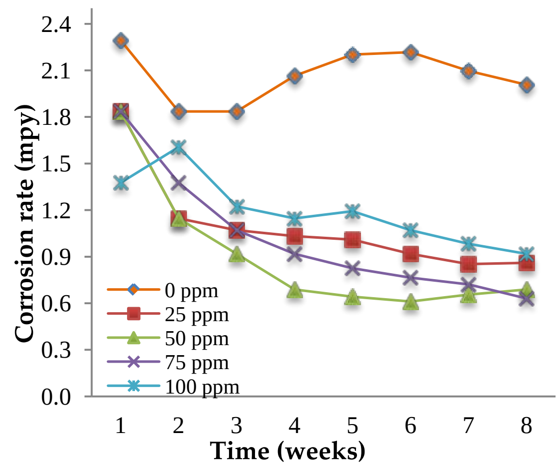

Fig. 1. *Graph of low carbon steel corrosion rate with variation in concentration of paracetamol inhibitor*

In immersion without inhibitor, the corrosion rate of steel without inhibitor in the first week was 2.29 mpy. In the second week, the corrosion rate of steel decreased to 1.83 mpy while in the third week the value of the corrosion rate was equal to the second week. The corrosion rate of steel went back up to the sixth week, where the value of the sixth-week corrosion rate was 2.21 mpy. The value of corrosion rate again decreased until the eighth week, with the value of the eighth-week corrosion rate of 2.00 mpy. From the fig. above, it can be observed that the maximum value of corrosion rate of steel without inhibitor is reached in the first week and the minimum value of corrosion rate of steel in the second and third weeks. The corrosion rate of steel with the addition of 25 ppm paracetamol inhibitor. The value of the first-week corrosion rate of 1.83 mpy at the same time becomes the peak value of the steel corrosion rate. The corrosion rate of steel decreased to the seventh week, where the corrosion rate was 0.85 mpy during the week. In the eighth-week, the rate of corrosion increased slightly to 0.86 mpy.

The rate of corrosion of steel with the addition of paracetamol inhibitor (50 ppm) the first week of 1.83 mpy. The corrosion rate of steel then decreased until the sixth week, with a 0.61 mpy corrosion rate in the sixth week. Then the corrosion rate increased until the eighth week, with a corrosion rate value of 0.68 mpy in the eighth week. In the graph above, it can be seen the maximum and minimum value of steel corrosion rate with the addition of paracetamol (50 ppm) that is 1.83 mpy the first week and 0.61 mpy sixth week. Given the rate of corrosion of steel with the addition of 75 ppm paracetamol inhibitor in the first week of 1.83 mpy. The corrosion rate of steel decreased until the eighth week to 0.63 mpy. From the fig., it is known that the maximum corrosion rate occurs in the first week while the minimum corrosion rate in the eighth week. The corrosion rate of steel with the addition of 100 ppm paracetamol inhibitor the first week was 1.37 mpy. The corrosion rate of steel increased to 1.60 mpy the second week. The decline in corrosion rate occurred until the fourth week with a value of 1.14 mpy corrosion rate per week. In the fifth-week, the corrosion rate again increased with the corrosion rate value to 1.19 mpy. While the sixth week until the eighth week of corrosion rate decreased again with a value of 0.91 mpy at eighth-week.

In many references, the increasing concentration of inhibitors in the metalworking environment, the decrease in the corrosion rate of metals is greater. There is an abnormality in the decrease of the corrosion rate of low carbon steel on the addition of paracetamol with concentrations of 75 and 100 ppm. the corrosion rate of low carbon steel at 75 and 100 ppm inhibitors are still greater than the corrosion rate with the addition of 50 ppm inhibitor. because of the addition of 75 and 100 ppm occurs the formation of protective layers on the surface of low carbon steel. The protective layer further covers the surface as the length of immersion time increases. The process of forming a protective layer resulted in increased corrosion rate. If we observe again the graph of the corrosion rate of steel over time (see fig. 1.), then the corrosion rate of steel with the addition of 75 and 100 ppm inhibitor showed a tendency to decrease until the eighth week. The number still has the possibility to keep it down if the immersion time is extended again. So that in longer immersion does not rule out the corrosion rate of steel with the addition of 75-100 ppm inhibitors lower than 50 ppm. The following table categories of corrosion resistance in low carbon steel with various inhibitor variations.

Tabel 1. *Category of corrosion resistance of low carbon steel in gasoline environment*

Concentration of inhibitor	The average corrosion rate (mpy)	Category
Blank	2.06	Excellent
25 ppm	1.09	Excellent
50 ppm	0.89	Outstanding
75 ppm	1.01	Excellent
100 ppm	1.18	Excellent

In table 1, steel without the addition of inhibitors falls into the excellent category. This shows that the pertalite is less reactive in steel, so the corrosion rate of steel is low so corrosion resistance of steel is the excellent category. Whereas, the steel with the addition of inhibitor can decrease the corrosion rate but remain in the excellent category, except for the addition of 50 ppm paracetamol inhibitor. The addition of 50 ppm paracetamol inhibitor in the gasoline solution, can increase the resistance of steel to corrosion and into outstanding category.

When discussing the performance of inhibitors, it is closely related to the efficiency of the inhibitor to lower the corrosion rate of low carbon steels.

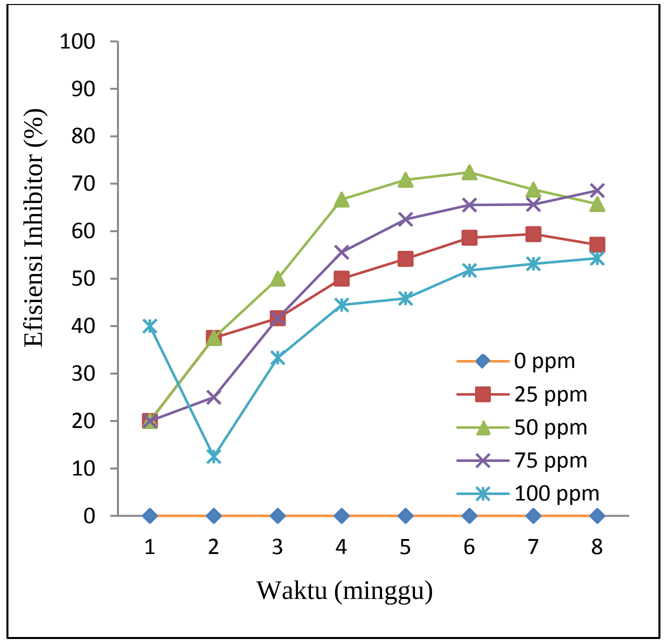

Fig. 2 *Graph efficiency of paracetamol inhibitors on steel in a gasoline solution*

From the graph of inhibitor efficiency in low carbon steels (see fig. 2.), Efficiency of 25 ppm paracetamol inhibitor on steel in the first week by 20%. The Efficiency of inhibitors showed an increase until the seventh week, reaching 59.37% in the week. Then the value of efficiency decreased in the eighth week to 57.14%. From the picture above can be seen that inhibitor paracetamol with 25 ppm concentration works well until week seven and decrease in eighth-week, with the highest efficiency value reach 59,37%.

The addition of 50 ppm paracetamol inhibitor to the steel has an efficiency rate of inhibitor in the first week of 20%. The value of inhibitor efficiency showed an increase until the sixth week, reaching 72.41% in the sixth week. The efficiency of the 50 ppm paracetamol inhibitor on steel decreased in the seventh and eighth weeks, with each efficiency value reaching 68.75% in the seventh week and 65.71% in the eighth week. The Efficiency of inhibitors has increased from the first week to sixth. There was a decrease in the efficiency values of the seventh and eighth week, but the value was still higher than the efficiency of 25 ppm paracetamol inhibitor in the steel.

Steel with the addition of 75 ppm paracetamol inhibitor showed the value of inhibitor efficiency in the first week by 20%. The value of inhibitor efficiency increased until the eighth week reaching 68.57%. The performance of paracetamol inhibitors at this concentration showed an increase until the eighth week, although the maximum efficiency value of the inhibitor was not higher than that of steel with the addition of

50 ppm paracetamol inhibitor. The maximum value at this concentration reached 68.57%.

The 100 ppm paracetamol inhibitor of steel has an efficiency value of 40% inhibitor in the first week. There was a decrease in efficiency value in the second week to 12.5%. After the second week, the performance of 100 ppm paracetamol as a steel inhibitor increased to eight weeks. The maximum value of inhibitor efficiency was in the eighth week of 54.28%.

The addition of paracetamol inhibitors (25 ppm, 50 ppm, 75 ppm, and 100 ppm) can inhibit the low corrosion rate of steel alloys. This is evidenced by the value of inhibitor efficiency greater than zero (steel efficiency without inhibitor), for all variations of paracetamol inhibitor addition (25 ppm, 50 ppm, 75 ppm, and 100 ppm). The lowest efficiency value was found in the paracetamol inhibitor 100 ppm in the second week at 12.5% and the maximum efficiency of the inhibitor at the concentration of paracetamol 50 ppm in the sixth week was 72,41%.

In the first week of immersion, the highest efficiency was in a 100 ppm paracetamol inhibitor (40%). However, in the following week, paracetamol inhibitors with concentrations of 50 ppm showed the best performance compared to other concentrations from the second week to the seventh week (68.75%). While in the eighth week, paracetamol inhibitor with 75 ppm of concentration showed the best performance compared to other concentration (68,57%).

Seen from the graph above, it can be seen that the performance of 50 ppm paracetamol inhibitor has the tendency of the line in the top position, it shows the best performance is in the variation, followed by the sequence of steel with the addition of inhibitor paracetamol 75 ppm, 25 ppm and 100 ppm.

3.2 Adsorption Isotherm

To know the mechanism of inhibition of paracetamol in steel, isothermal adsorption calculation. The approach model is isotherm Langmuir. The graph above is the relationship between inhibitor concentrations in units of M (x-axis) and concentration ratio with one-hundredth of inhibitor efficiency (y-axis) based on isothermal Langmuir theory (see fig. 3.), where the value of R^2 on the isothermal Langmuir is 0,964. The value of R^2 shows the relationship between the x-axis and the y-axis.

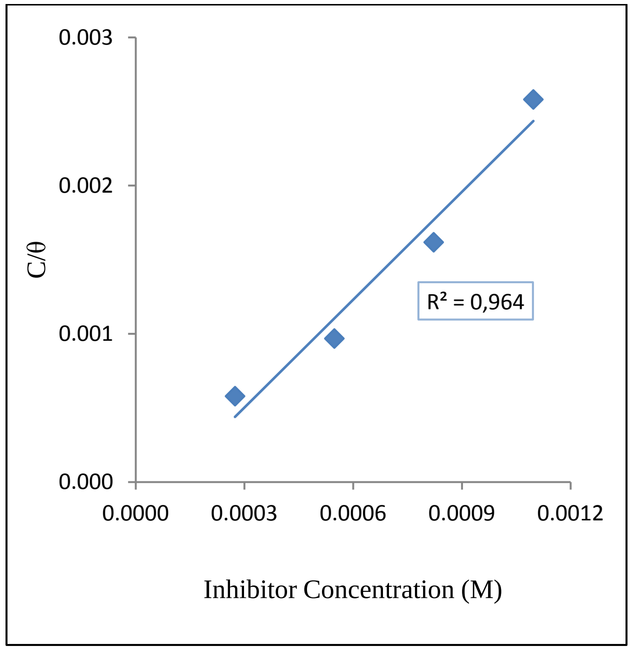

Fig. 3 Graph isotherm Langmuir of paracetamol inhibitor on low carbon steel *in gasoline environment*

The closer to the number one, the relationship between the two axes is stronger and the resulting error is lower. In the isothermal adsorption Langmuir, the inhibitor forms a single layer above a homogeneous metal surface so that the tendency for adsorption in each surface is equal to the same enthalpy value on each side of the surface [8].

After that, thermodynamic calculations were performed by finding the value of the adsorption coefficient (K_{ads}) based on the Langmuir theory. The following is the coefficient of adsorption

$$\text{Kads} = \frac{\theta}{C - C\theta} \qquad (3)$$

From K_{ads} value can be obtained of ΔG_{ads} value (enthalpy of adsorption) using equations

$$\Delta\text{Gads} = -\text{RT}\ln(55{,}5\ \text{Kads}) \qquad (4)$$

The purpose of calculating the value of ΔGads is to determine the process of the formation of adsorbate, either physisorption or chemisorption. If the value of ΔGads ≤40 kJ / mol, then the adsorption that occurs is chemisorption. Whereas if ΔGads above -20 kJ / mol until before -40 kJ / mol, then the adsorption is physisorption [11],[12].

Tabel 2. *The value of K_{ads} dan ΔG_{ads}* on steel in gasoline with the addition of paracetamol inhibitor

Inhibitor concentration	K_{ads} (M^{-1})	ΔG_{ads} ($kJ.mol^{-1}$)
25 ppm	3274.35	-30.51
50 ppm	2378.86	-29.70
75 ppm	1256.61	-28.09
100 ppm	673.77	-26.52

From the value of K_{ads} and ΔG_{ads} on steel in gasoline with the addition of paracetamol inhibitor concentration (see table 2.), it is known that the value of adsorption coefficient decreases with increasing concentration of paracetamol in steel in gasoline. It affects the energy value of freedom (enthalpy) the occurrence of adsorption on the surface of steel becomes higher. From the enthalpy value obtained, it is known that the enthalpy of steel with the addition of 25 ppm paracetamol is the smallest enthalpy value in steel that is -30.51 kJ / mol. While the largest enthalpy value is in the addition of 100 ppm that is equal to -26.52 kJ / mol. The more concentration of paracetamol inhibitor the adsorption value on the surface of steel approaches the value of -20 kJ / mol.

The inhibitor with the working mechanism is adsorbed on the surface of the metal, generally forming two types of layers. Passive layers formed from chemical bonds between inhibitors and metals (chemisorption) and the physically formed protective layers of metal (physisorption) due to electrostatic forces or Van der Walls forces [8].From the calculation of isothermal adsorption Langmuir which then obtained the value of the surface adsorption enthalpy steel by paracetamol compound, theoretically, the layer formed on the surface of the metal is physisorption. Physisorption–shaped, a low-alloy steel protective layer has a weak, easy-to-break bonding type of steel surface.

3.3 IR Test of Paracetamol Drug and Steel

In the analysis of IR data on paracetamol drugs (see fig. 4.), it was detected that paracetamol tablets contained three main groups, namely amine groups, hydroxyl groups, and aromatic groups. In addition, there is also one group but quite weak compared to the other three groups, namely the carbonyl group. The hydroxyl contained is a type of phenols compound which is a hydroxyl bond with a phenyl ring. In the amine group, there are several compounds containing the group, ie amine hydrohalide, primary amine, and hydroxylamine. While the aromatic group detected some compounds containing the group, namely aromatic amine and benzene.

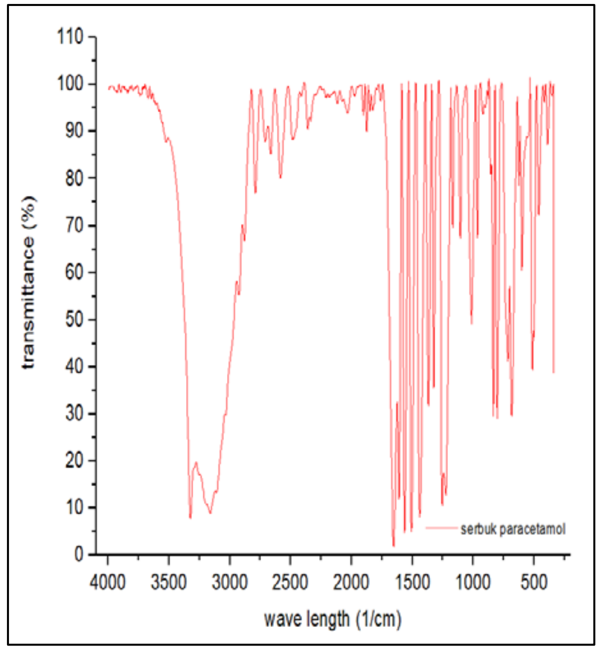

Fig. 4 Graph FT-IR of paracetamol

The FT-IR test is also performed on three low carbon steel coupons. Each one voucher represents three different treatments, ie before immersion, after immersion without inhibitor, and after immersion with the addition of 50 ppm paracetamol inhibitor.

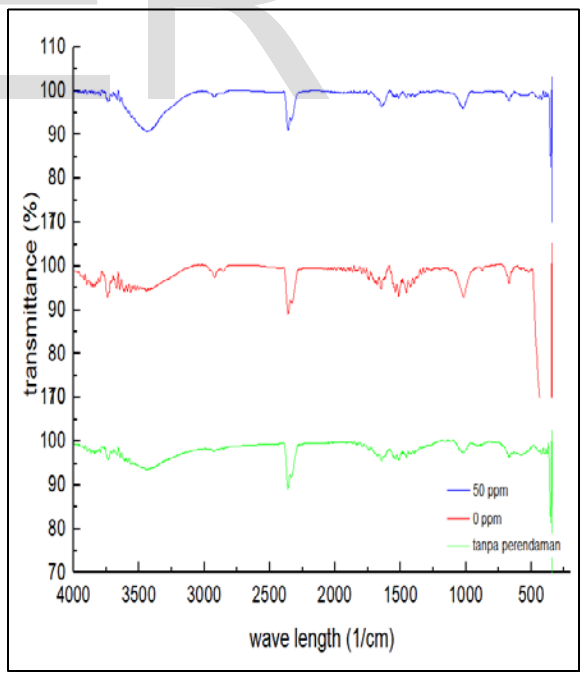

***Fig. 5 G**rafik FT-IR low carbon steel*

From the FT-IR test results (fig. 5.), it is evident that there are compounds of paracetamol adsorbed on the steel. Steel with the addition of 50 ppm paracetamol inhibitor was identified to have more OH (hydroxyl group) compounds than in steel before immersion and after immersion without inhibitors. This is because one of the peaks contained in the steel with the addition of 50 ppm inhibitor (3441 cm-1), appears steeper and the peak absorption region is wider than the other two types of steel treatment. The hydroxyl group of steels with the addition of 50 ppm inhibitors is increased by obtaining hydroxyl donors from paracetamol inhibitors.

In the FT-IR test results, there are known phenyl compounds (C_5H_5) only detectable on steel without inhibitor. The compound is absent in the steel with the addition of 50 ppm inhibitors and is also absent in the steel before immersion, proving that with the addition of paracetamol inhibitors are able to inhibit the formation of compounds derived from gasoline to bond with Fe or other elements contained in the steel. It is characteristic of paracetamol as an inhibitor capable of affecting the metal environment. The environment diminishes its corrosivity in steel with the addition of paracetamol inhibitors.

Fewer compounds are not even present in low carbon steels with the addition of 50 ppm inhibitors compared to low carbon steels prior to before immersion and after immersion without inhibitors, proving paracetamol can make the compound bind to the compounds present in the solution. The presence of hydroxyl ions can precipitate the compounds so as not to bind or dissolve on the metal surface [3]. Consequently, there are compounds that are supposed to bind to the metal, being non-bonded or fixed bonded but in lesser amounts. The compounds that are reduced or even unidentified in the presence of steel surfaces after the addition of 50 ppm paracetamol inhibitors are $Fe_2(CO_4)_2$, $LM(CO)H_2$, ferrocenes, Al-O, and chromate.

In addition, the hydroxyl groups in paracetamol are also capable of inhibiting the binding of other compounds or elements on the surface of the metal so that the presence of the previously fairly heavily deformed compounds in steel prior to before immersion, becomes less present in steels by the addition of 50 ppm paracetamol inhibitors. Both of these are characteristic of cathodic inhibitors. Given these dual functions, the paracetamol inhibitor acts as a mixed inhibitor for steels in a gasoline environment.

4 CONCLUSIONS

The existence of a paracetamol inhibitor in gasoline environment can lower the corrosion rate of low carbon steels. The concentration of paracetamol in the gasoline solution has the best performance at 50 ppm concentration by decreasing the corrosion rate to 0.61 mpy and the inhibitor efficiency reaching 72.41% on the sixth week of immersion.

The calculation of isothermal adsorption indicates a suitability of the isothermal Langmuir adsorption theory, with the type of adsorption being physisorption. Physisorption shows that a protective layer on steel is formed through the Van der Walls force so that the type of bonding layer formed is quite weak.

The hydroxyl groups of paracetamol have been shown to be adsorbed on the steel surface through the FT-IR test. In addition, from the FT-IR test results, it can be known in the presence of paracetamol in the gasoline solution capable of inhibiting the formation of some steel surface compounds and also shed or bind the compounds present in the steel so that the presence of the compound is reduced in steel. This suggests that paracetamol becomes a mixed inhibitor capable of adsorbed on the surface of the steel and decreases the corrosivity of the environment.

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