Journal of Chemical Natural Resources Vol. 03, No. 01, 2021 | 35 – 42

talenta PUBLISHER

JCNaR
Journal of Chemical Natural Resources

Synthesis 2-((Furan-2-yl) Methylene)-1-Phenilhydrazone from Furfural Results of Corn Isolation and Its Utilization as Corrosion Inhibitor in Zinc (Zn) Metal

Dewi Shinta[1], and Herlince Sihotang[2*]

[1,2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jalan Bioteknologi No.1 Kampus USU Medan 20155, Indonesia

Abstract. Synthesis of 2-((furan-2-yl) methylene)-1-phenylhydrazone has been carried out by reaction of condensation of furfural aldehyde groups obtained from the isolation of corn cobs with phenylhydrazine. Furfural condensation with phenylhydrazine was carried out by refluxing in ethanol solvent for 1 hour. Of the 9.6 g (0.1 mol) furfural which was condensed with 5.4 g (0.05 mol) phenylhydrazine obtained yield of 10.54 g (67.02%) phenylhydrazone which was then analyzed by FT-IR spectroscopy showing the presence of vibration C = N in the area around 1597 cm-1. Fenilhidrazone was tested for inhibitor with 78.47% and compared with furfural as much as 58.18%, and phenylhydrazine as much as 50.04%. The results obtained by phenylhydrazone were more efficient at inhibiting the results of 78.47% while furfural and phenylhydrazine were only 58.18% and 50.04%.

Keywords: Corrosion, Corrosion Inhibitor, Furfural, Phenylhydrazine, Phenylhydrazone

Received [10 December 2020] | Revised [11 January 2021] | Accepted [22 February 2021]

1 Introduction

Corn cobs are plant waste and after taking the seeds, the corn cobs are generally thrown away, so that it will only increase the amount of waste, even though the corn cobs are used by rural residents as fuel after being dried first. Even though corn cobs can still be used to extract furfural because corn contains pentosan. Pentosan is a compound that is classified as a polysaccharide that when hydrolyzed will break down into monosaccharides containing 5 carbon atoms called pentosan .

If the hydrolysis is continued by heating dilute sulfuric acid or hydrochloric acid within 2-4 hours, dehydration and cyclization will occur to form a heterocyclic compound called furfural. Therefore, in this study, corn cobs will be used as the basic material for making furfural.

*Corresponding author at: Department of Chemistry, Faculty of Mathematics and Natural Sciences Universitas Sumatera Utara, Medan, Indonesia.

E-mail address: herlince@usu.ac.id

Journal Homepage: http://jcnar.usu.ac.id

Journal of Chemical Natural Resources Vol. 03, No. 01, 2021 | 35 – 42

Furfural is a colorless liquid, which is used as a raw material for the manufacture of furan compounds, tetrahydrofuran, funeral, the manufacture of plastics, as auxiliary material in the synthetic rubber industry, and others. Furfural can be made from all materials containing pentosans such as agricultural waste, including rice husks, sawn wood, wheat husks, corn cobs, bagasse, and others. Corn cobs are estimated to contain 20-22% pentosan (Kirk and Othmer, 1995). Chemically, furfural is classified as an aldehyde so it is possible to convert it into other functional groups, for example in the Schiff base.

Schiff base is an amine compound with C=N bond characteristics. These derivatives can be obtained by condensation of primary amines with carbonyl compounds such as aldehydes or ketones. Many commercial inhibitors include aldehydes or amines, but the presence of C=N bonds in Schiff bases is more efficient in many cases, one of which is as a corrosion inhibitor. The principle of interaction between the inhibitor and the metal surface is chemical adsorption (Ashraf et al., 2011). In everyday life, many tools are used which are made of metal materials such as zinc, copper, iron, and various other metals.

Corrosion is a metal destruction process, where the metal will experience a decrease in quality (degradation) because it reacts with the environment either chemically or electrochemically at the time of use (Siti, 2008). Indonesia is a tropical country with high levels of rainfall and humidity as well as air pollution, and industry will accelerate the corrosion process (Fajar, 2013). Corrosion occurs in all metals, especially those in direct contact with corrosive air and liquids. The Schiff base test was carried out on zinc metal. The zinc plate is used because metallic zinc is an active metal with many industrial applications and is mostly used for corrosion protection of steel (Shah et al., 2011). Therefore, protection against metallic zinc is very important (Eddy, 2010).

Several previous researchers have conducted research on furfural with variations in heating, there is also research on the effect of hydrolysis of corncob cellulose with 1% HCl on glucose for bioethanol. They have studied that Schiff base which is the result of condensation of aldehyde compounds with primary amines, namely compounds containing the RCH=NR group. As a corrosion inhibitor including N-(salicylaldehyde) 4-methoxy aniline to mild steel it can provide a corrosion inhibitor efficiency of 97% in 2 N HCL solution (Upaclhyay and Marthur, 2007). And Schiff's base of some dianilined derivative compounds against hard steel provides a corrosion inhibitor efficiency of 80 to 97% in 1 M H2SO4 media (Eddy, 2010).

Based on the description above, the researchers were interested in synthesizing Schiff base by utilizing furfural obtained from corn cobs followed by the efficiency test of Schiff base obtained as a corrosion inhibitor against zinc metal in 0.1 N HCL media.

Journal of Chemical Natural Resources Vol. 03, No. 01, 2021 | 35 – 42

2 Materials and Methods

2.1 Equipments

The equipments used in this research include: a ball condenser, hotplate stirrer, vacuum apparatus, sandpaper, analytical balance, FT-IR spectrophotometer, desiccator, and glassware.

2.2 Materials

The materials used in this research include corn cobs, aquadest, 0.1 N HCl, ethanol, phenylhydrazine, zinc steel plate, furfural, concentrated H2SO4, chloroform, aniline, and ice cubes.

2.3 Corn Cobs Preparation

The material used in the study was arbitrary corn cobs. The corn cobs are then cut into small pieces and then dried for 3 days, then cleaned off the wrapping leaves that are still attached to the corn cobs.

2.4 Synthesis of Furfural

A total of 100 g of dry corn cobs were put into the flask then added 100 g of NaCl then added 10% H2SO4 until it was set and stirred until homogeneous. Next, the distillate was assembled and then refluxed for 5 hours at 106ºC. Furfural and water will be condensed into a distillate flask and then dripped and accommodated in an Erlenmeyer glass containing chloroform. Furfural will dissolve in chloroform while water will separate to form bilayers (the top layer is water and the bottom layer is furfural/chloroform). Then filtered, to separate the remaining corn cobs then the filtrate is distilled at a temperature of 560 – 670ºC and there are residues and distillates where the residue is furfural and the distillate is chloroform. Furfural identification was carried out by brick red color test, then analyzed by FT-IR spectroscopy.

2.5 Synthesis of (Z)-2-((furan-2-yl) methylene)-1-phenylhydrazone by Condensation Reaction Between Furfural and Phenylhydrazine

A total of 9.6 g (0.1 mol) of furfural was put into a 250 mL two-neck flask and then dissolved with 25 mL of absolute ethanol. Next, a reflux device was assembled with a magnetic bar, thermometer, and water trap then added 5.4 g (0.05 mol) of phenylhydrazine which had been dissolved with 25 mL of absolute ethanol through a dropper funnel slowly while stirring and refluxed for 1 hour at 78 – 83ºC. Then the solvent was evaporated using a rotary evaporator, there were residues and distillates where the distillate was ethanol. The residue was evaporated by the solvent and excess furfural by vacuum distillation, then there were residues and distillates where the distillate was furfural. The residue was dried in a desiccator and weighed and then analyzed by FT-IR spectroscopy.

Journal of Chemical Natural Resources Vol. 03, No. 01, 2021 | 35 – 42

2.6 FT-IR (Fourier Transform-Infrared) Spectroscopy Analysis

For Schiff base which is in solid form, it is ground with anhydrous KBr and then molded to form a transparent pellet, then its spectrum is measured using an FT-IR spectrophotometer.

2.7 Determination of Inhibitor Efficiency

Specimens of zinc steel plate with a length of 5 cm and a width of 1.5 cm smoothed the surface using iron sandpaper. The smooth surface was washed with distilled water and dried and then weighed.

2.8 Determination of Inhibitor Efficiency

A solution of 0.1 N HCl corrosion medium was prepared by diluting 8.3 mL of 37% HCl in a 1000 mL volumetric flask to the mark with distilled water.

2.9 Preparation of Inhibitor Master Solution

Corrosion inhibitor solution Schiff's base 10,000 ppm with 0.1 N HCl solution. The solution is prepared by dissolving 1 g of Schiff's base with 0.1 N HCl in a 100 mL volumetric flask to the limit line. The desired inhibitor solution was prepared by diluting the 10000 ppm mother liquor using 0.1 N HCl solution with various inhibitor concentrations of 1,000 ppm, 3,000 ppm, 5,000 ppm, and 7,000 ppm.

2.10 Inhibitor Efficiency Test

The zinc plate immersion solution was taken from 50 mL of 1,000 ppm inhibitor solution, 50 mL of which was put into a glass container. The zinc plate that has been sanded and weighed is then immersed in the solution for 24 hours. The zinc plate was removed from the corrosion medium, washed carefully using a soft brush, rinsed with methanol, removed, and then allowed to dry for 5 minutes and weighed the final weight.

3 RESULT AND DISCUSSION

3.1 Furfural Formation Reaction

For the manufacture of furfural from pentosan from corn cobs in the early stages, a hydrolysis process from pentosan to pentose occurs by HCl solution, then dehydration of pentose by sulfuric acid becomes furfural. HCl in this case is obtained from the reaction of NaCl with excess H_2SO_4 then the excess H_2SO_4 functions as a dehydrator to form furfural. The reaction has been formed with the support of data from the analysis using FT-IR spectroscopy which shows C-H sp^2 vibrations from the furfural ring, in the wave number region of 3132.4 cm^{-1}, C-H from the aldehyde group in the wave number region 2846.93 to 2816.07 cm^{-1}, C=O group in the wave number area of 1674.21 cm^{-1} and the presence of C-O-C ether in the wave number area of 1280.73 cm^{-1} (figure 1)

Journal of Chemical Natural Resources Vol. 03, No. 01, 2021 | 35 – 42

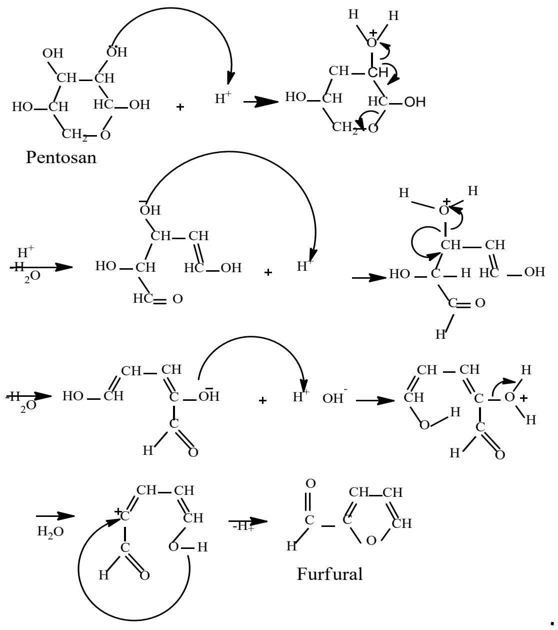

Figure 1. Furfural formation reaction

3.2 Color Test with Aniline Acetate Reagent

The color test is a test of the chemical properties of furfural. The reagent used is aniline-acetate which is used to detect the presence of furfural. Aniline acetate is prepared by mixing aniline with acetic acid in a ratio of 1:1. Each result of the furfural yield variable was tested for color by adding aniline acetate in the same amount as the amount of furfural used. Theoretically, the addition of furfural with aniline acetate causes furfural to have a dark red color. The following are the results of the synthetic furfural color test. Based on the observations of the furfural color test from the distillation of corn cobs, it shows that the color produced in the test is the same as the theoretical furfural test color, namely furfural which was originally clear yellow after the addition of aniline-acetate to dark red, this indicates the yield tested is furfural.

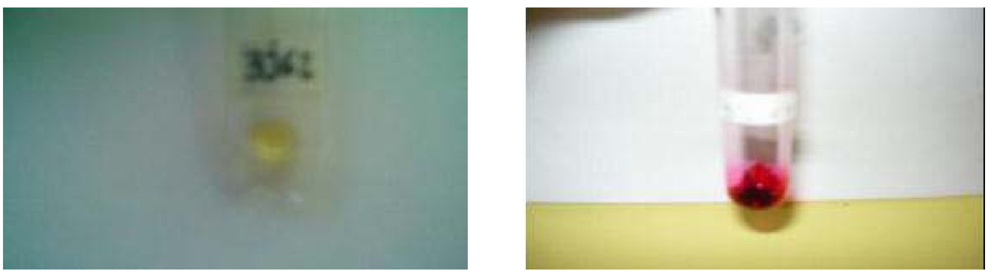

Figure 2. a). Furfural before dripping with aniline-acetate, b). Furfural after dripping with aniline-acetate.

The dark red color is caused by a condensation reaction between furfural and aniline to form dianyl hydroxyglutaconate dialdehyde compounds. This compound is what forms the red color in the reaction.

Journal of Chemical Natural Resources Vol. 03, No. 01, 2021 | 35 – 42

Standard Fe calibration curves are made with standard concentration variations, namely 0.0; 2.0; 3.0; 4.0; 5.0 ppm of $Fe(NO_3)_3$ salt. The measurement results are shown in Table 3

3.3 Synthesis of 2-((furan-2-yl) methylene) 1-phenylhydrazone by Condensation Reaction Between Furfural and Phenylhydrazine

The reaction for the formation of phenylhydrazone from furfural condensation with Phenylhydrazine hypothetically gives the following reaction:

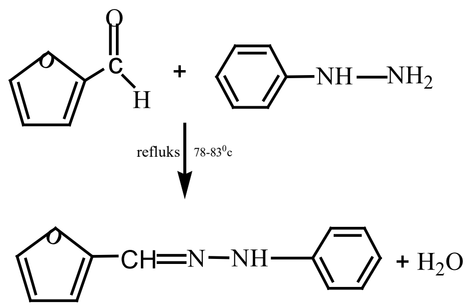

Figure 3. Formation reaction of 2-((furan-2-yl)methylene)-1-feniyhydrazon

Schiff base formation reaction is with primary amine wherein, the reaction between furfural and phenylhydrazine begins with the attack of NH_2 from phenylhydrazine as the primary amine, the C atom of the aldehyde of furfural and the O atom of the aldehyde attacks 1 H atom of the primary amine group. Furthermore, the O atom attacks 1 more H atom and separates releasing water resulting in the formation of a Schiff base, while the NH secondary amine from phenylhydrazine only has 1 H atom so it cannot form a C=N group. The reaction has been formed with the support of data from the analysis using FT-IR spectroscopy which shows the appearance of the C=N stretching at the absorption peak of the wave number 1674.21 cm^{-1} and supported by the C=N stretching at the wave number 1134.14 cm^{-1}. As for the vibration in the wave number region of 3124.54 cm^{-1}, it shows a typical absorption for stretching vibration (C-H) sp^2 which is supported by bending vibrations of C-H sp^2 in the wave number area of 1496.76 cm^{-1}. C=C of aromatic compounds in the wave number region of 1365.6 cm^{-1} and the presence of C-O-C ether in the region of wave number 1257.59 cm^{-1}. After being synthesized into a Schiff base between furfural and phenylhydrazine, $–NH_2$ the primary amine does not appear again at a wave number of 1566.2 cm^{-1} because it has reacted completely to produce a Schiff base.

In the Schiff base formation reaction to produce these compounds, excess furfural is used with a mole ratio (2:1) and a reflux time of 1 hour. It is hoped that the amine group of phenylhydrazine can react completely to produce Schiff's base, while the unreacted furfural can be separated easily by vacuum distillation.

Journal of Chemical Natural Resources Vol. 03, No. 01, 2021 | 35 – 42

3.4 Synthesis of 2-((furan-2-yl) methylene) 1-phenylhydrazone by Condensation Reaction Between Furfural and Phenylhydrazine

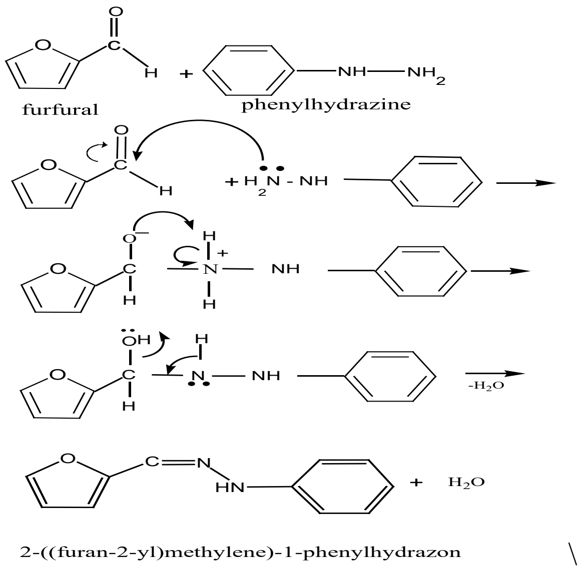

Figure 4. Mechanism of Reaction Formation of (Z)-2 ((furan-2-yl) methylene)-1-phenylhydrazone

3.5 Synthesis of 2-((furan-2-yl) methylene) 1-phenylhydrazone by Condensation Reaction Between Furfural and Phenylhydrazine

Determination of the efficiency of corrosion inhibitors was carried out by immersion in 0.1 N HCl medium for an interval of 24, 48, 72, 96, and 120 hours with various inhibitor concentrations of 1000 ppm, 3000 ppm, 5000 ppm, and 7000 ppm. The inhibitor efficiency test was carried out on zinc metal because zinc metal is an active metal and is widely used in industrial applications. The metal will undergo oxidation and reduction reactions with the following reactions:

$$Zn \rightarrow Zn^{2+} + 2e^- \quad \text{(Oxidation)}$$
$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(Reduction)}$$
$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

From the reaction, it can be concluded that the greater the concentration of hydrochloric acid used, the more Zn atoms are released from the metal so that corrosion will increase. The possible stages of the corrosion process in metals proposed by Trethewey and Chamberlain (1991), are as follows: first, aggressive substances such as sulfates are expected to reduce the bond strength between metals in the presence of these aggressive substances, so that the energy used in binding aggressive ions by metal atoms will reduce the bond energy between the atoms. Second, metal corrosion is caused by the reduction of hydrogen ions that takes place in the solution. The hydrogen molecules formed are adsorbed by the metal causing the bonds between

Journal of Chemical Natural Resources Vol. 03, No. 01, 2021 | 35 – 42

the metals on the zinc plate to weaken or weaken. In testing the efficiency of corrosion inhibitors the method used is the weight loss method. Where the principle of the weight loss method is that the smaller the difference in the weight of the loss of the zinc plate without the addition of an inhibitor and the weight of the loss of the zinc plate with the addition of the inhibitor, will be the greater the efficiency of the inhibitor.

4 Conclusion

Based on this study, it can be concluded as follows:

1. Synthesis of 2 - ((furan - 2 - yl) methylene) -1-phenylhydrazone between phenylhydrazine and furfural obtained from corn cobs have been successfully synthesized, producing Schiff base with a yield of 67.02%.
2. 2-((furan-2-yl) methylene)-1-phenylhydrazone has a higher inhibitor efficiency of 78.47% compared to furfural 58.18% and phenylhydrazine 50.04%.

References

Ashraf, M.A. Karamat, M., and Abdul, W. 2011. Synthesis, Characterization and Biological Activity of Schiff Bases. IPCBEE Vol.10. Singapore: IACSIT Press.

Eddy, N. O. 2010. Electrochim. Port.Acta 28.

Fajar, M.S. 2013. Analisa Korosi dan Pengendaliannya. Baruna Slawi: AKademi Perikanan Baruna Slawi.

Kirk, R. E. and Othmer, D., 1955, Encyclopedia of Chemical Technology, Vol. 10, pp. 237-250, The Interscience Encyclopedia Inc., New York.

Shah, M.D., Patel, A.S., Mudaliar, G.V. and N.K. Shah.2011. Schiff Bases of Tryethylenetetramine as Corrosion Inhibitors of Zinc in Hydrochloric Acid. Chemistry. Departement.School Of Science, Gujarat University: Ahmedabad.

Siti, C. 2008. Efektifitas Penggunaan pelapisan Epoxy dalam Ketahanan Korosi Pipa Baja ASTM A53 di dalam Tanah. Depok: Universitas Indonesia.

Upaclhyay, R. K and Marthur, S. P. 2007. Effect of Schiff's Bases as Corrosion Inhibitors on Mild steel in Sulphuric Acid, E-Journal at Chemistry. Vol 4(3). 408-414.