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THE USE OF LIGNOSULFONATE FROM EMPTY FRUIT BUNCHES AS CORROSION INHIBITOR

ISSHAM ISMAIL[1*], MOHD. AZIZI CHE YUNUS[2], AHMAD SHAMSULIZWAN ISMAIL[3] & AMIR AKMAL IBRAHIM[4]

Abstract. Corrosion is a natural process that can affect the performance of facilities in oil and gas industry. This gives a serious view of pollution to the ocean especially during production, transportation, storage process, transmission pipelines and other activities on offshore platforms. This paper discusses the effectiveness of lignin extracted from *Jatropha Curcas'* empty fruit bunch (EFB) as a corrosion inhibitor agent. *Jatropha Curcas* empty fruit bunch was used in this study as it is a good source of lignin where it contains 25% of lignin. Lignin had been extracted from the *Jatropha Curcas* empty fruit bunches using Klason Lignin method and the purity of treated lignin was verified using the Fourier Transform Infrared Spectroscopy (FT-IR). Extracted lignin then went under sulphite processes to change its characteristic into lignosulfonate. A performance comparison work was carried out in the laboratory with and without commercial inhibitor and lignosulfonate EFB using carbon steel in brine solution to determine its optimum concentration. The commercial inhibitor used was Sodium Benzotriazole (BTA-S). Experimental results revealed that lignosulfonate EFB could give a better performance as corrosion inhibitor compared to BTA-S. The optimum concentration for lignosulfonate EFB was 20% with inhibitor efficiency was 70%. These findings show that EFB lignosulfonate has the potential to be a good corrosion inhibitor.

Keywords: Corrosion; empty fruit bunch; inhibitor efficiency; Jatropha Curcas; klason lignin method; sulphite process

Abstrak. Kakisan ialah proses semula jadi yang boleh menjejaskan prestasi kemudahan minyak dan gas. Keadaan ini boleh menyebabkan berlakunya pencemaran terutama semasa pengeluaran, penghantaran, proses penstoran, pengaliran melalui talian paip dan aktiviti lain di pelantar luar pesisir luar. Artikel ini mengetengahkan keberkesanan lignosulfonat yang diekstrak daripada tandan buah jarak (EFB) sebagai agen perencat kakisan. Tandan buah jarak digunakan dalam kajian ini kerana tandan terbabit mengandungi sekitar 25% lignin. Lignin diekstrak daripada

[1&3] Department of Petroleum Engineering, Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru

[2] Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru

[4] Schlumberger, Rohas Perkasa, Kuala Lumpur

* Corresponding author: issham@petroleum.utm.my

tandan menggunakan kaedah Klason Lignin dengan ketulenannya dinilai menerusi ujian Spektroskopi Lampau Merah Jelmaan Fourier (FT-IR). Lignin yang dihasilkan kemudiannya menjalani proses sulfit bagi mengubah sifat-sifatnya kepada lignosulfonat. Kajian pembandingan dilakukan di makmal yang melibatkan penggunaan perencat kakisan komersial dan lignosulfonat EFB dan tanpa perencat kakisan terbabit, menggunakan keluli karbon dalam larutan air garam bagi menentukan kepekatan optimumnya. Agen perencat kakisan komersial yang digunakan ialah Sodium Benzotriazole (BTA-S). Hasil kajian menunjukkan bahawa lignosulfonat EFB boleh memberikan prestasi yang lebih baik berbanding BTA-S. Kepekatan optimum lignosulfonat EFB ialah 20% dengan kecekapan perencatannya ialah 72%. Penemuan ini membuktikan bahawa lignosulfonat EFB berpotensi menjadi agen perencat kakisan yang baik.

Kata kunci: Kakisan; tandan buah jarak; kecekapan perencatan; Jatropha Curcas; kaedah klason lignin; proses sulfit

1.0 INTRODUCTION

Corrosion is a natural process that occurs when a metal deteriorates due to chemical action. It damages the surface of a metal either by oxidation or chemical combination. As a metal is corrosively deteriorating, its properties efficiency also will degrade. Generally, corrosion can be classified by the form it manifests itself where each type can be identified by mere visual observation [1]. In few occasions, magnification may be required. An examination or a careful observation of the failed equipment before executing cleaning procedures is of utmost importance in order to acquire valuable information for the solution of a corrosion problem.

There are two groups of corrosion coatings: organic coatings and inorganic coatings. But it is widely known that the mechanisms of inhibition can be complex. Inhibitors affect either anodic or cathodic sites and stifle the corrosion current. Use of inhibitors is favored in closed systems because the required concentration of inhibitors can easily be maintained. There are four types of inhibitors, namely anodic inhibitors, cathodic inhibitors, mixed inhibitors, and volatile corrosion inhibitor. Inhibitor is always considered to be the first line of defense against corrosion [2, 3].

In this research work, the lignin extracted from *Jatropha Curcas* [4, 5] that underwent sulfonation process to become EFB lignosulfonate was used as a corrosion inhibitor. Laboratory research done by Lau and Ibrahim [6] found that this kind of lignosulfonate can be categorized under organic group. Lignin [7] that was used in this study can be described as chemical compound that is most commonly derived from wood and is an integral part of the cell walls of plants, especially in tracheids, xylem, fibres, and sclereids. Lignin is second most abundant organic compound found on the earth after cellulose. Lignosulfonates or sulfonated lignin is water-soluble and is by products from the production of wood pulp using sulfite pulping.

According to Payer [8], lignin is one of the abundant naturally occurred polymers. He highlighted that 30% of carbon in organic matter forms lignin. Lignin is widely used in paper industry and also may be used as solid fuel in heat generation. But in recent research findings, it is found that lignin from wood can interact with conducting polymers forming conductive films on the surface of the metal or steel. According to Hatakeyamas [7], however, for a better corrosion protection activity, natural lignin needs to improve the interfacial deposition amid its amphiphilic nature.

According to Timonin [9], corrosion environment is referred to any surrounding or ecology that can cause corrosion. This is important because there is a significant relation between corrosion and environment. Generally, there are three types of corrosion environment, namely physical, chemical, and biological, where each of them produces different type of pollution. It is very unfortunate to disclose that the problems of corrosion and ecology were never investigated simultaneously.

In the oil and gas industry, corrosion problems always occurs in at least three general areas: production, transportation and storage, and refinery operation. In those operations, a tremendous amount of iron and steel pipe are used for structures fabrication. As time passes by, corrosion may occur and this phenomenon causes leaks in the facilities which will lead to loss of oil and gas. In a more severe situation, it will cause million dollars of loss due to maintenance and replacement. Many chemical-based commercial inhibitors are used to overcome or mitigate this problem [10]. This paper discusses on the use of lignin extracted from *Jatropha Curcas'* empty fruit bunch (EFB) as a corrosion inhibitor agent. This research work was initiated to maximize the use of waste from natural resources – an effort which can contribute positively towards environment's sustainability.

2.0 MATERIALS AND METHODS

This section highlighted the extraction of lignin from the empty fruit bunch of *Jatropha Curcas*. It also detailed out the process of confirming the purity of lignin using the Fourier Transform Infrared Spectroscopy Test (FTIR) and the application of lignosulfonate, which has been sulfite processed from lignin, as a corrosion inhibitor agent. Thus, an experimental work on corrosion tests with and without lignosulfonate was carried out using carbon steel in brine solution at different lignin concentrations. The commercial inhibitor used in this study was sodium benzotriazole (BTA-S), which was used for performance comparison with lignosulfonate extracted from empty fruit bunches. The formula from Standard ASTM G46 (1980) was used to calculate the corrosion rates and the calculation of inhibitor efficiency.

2.1 Preparation of the Material

The *Jatropha Curcas'* empty fruit bunch used in this study was obtained from BIONAS and the material was cut into 1 × 1 inch pieces, dried, and stored in a sealed plastic bag. This research work used the sun-dry mechanism.

2.2 Preparation of Lignin

The dried EFB of *Jatropha Curcas* was weighed and placed in the extraction thimbles. Each sample of 7 gm of *Jatropha Curcas* was placed in the Soxhlet Extraction units to undergo a solid-solid extraction process, which used 200 ml ethanol-toluene mixture as a dilute solution. After 18 hours of extraction process, the thimble wash sample with ethanol was taken out to ensure there was no chlorophyll or other residue left on the sample. Sample was then placed in the vacuum oven overnight at temperature of 90°C for 24 hours. Sample was weighed repeatedly until there was no longer any change in the mass of the sample before and after the drying process.

2.3 Klason Lignin Method

A 200 mg of processed sample was placed into a 100 ml conical flask, followed by 1 ml of 72% (w/w) H_2SO_4.The mixture was then stirred and dispersed thoroughly with a glass rod before it was placed in water bath at 40°C for 60 minutes. This process was followed by the introduction of 56 ml of distilled water into the heated sample before being kept in an autoclave at 121°C, 15 psi for 15 minutes. Sample was placed in the autoclave to pressurize aqueous solutions and heated them above their boiling points – a process which would cause the solution to get sterilized. After 15 minutes, the sample was removed from the autoclave and lignin was filtered off using the buchner funnel and glass microfiber filter paper. The residue was washed thoroughly with hot water and dried in the vacuum oven at 100°C overnight.

2.4 Fourier Transform Infrared Spectroscopy Test (FTIR)

Infrared spectroscopy test was used to verify the purity of the lignin extracted from EFB of *Jatropha Curcas*. The identification characteristic of absorption bands caused by different functional groups was used for the interpretation of infrared spectra. The content of the functional group in lignin was determined using the standard method. Powdered lignin sample was mixed with potassium bromide (KBr) at ratio 1:100. The mixture was then compacted for 10 minutes using compactor to produce a flat transparent plat and tested using FT-IR spectroscopy machine to verify the purity of the treated lignin as compared to the commercial lignin.

2.5 Sulfonation Process

Sulfonate is one of the organic inhibitors that are commonly used in the oil and gas industry due to its water solubility. Thus for lignin, its water solubility characteristic was improved by undergoing the sulfonation process and this process would also change the pH of lignin from 11 down to 2, i.e. from alkaline to acidic lignosulfonate.

According to Zaki [2], sulfonation of lignin is a process to improve the water solubility and this criteria is of utmost importance for a corrosion inhibitor. Corrosion inhibitors are known to be effective in systems in which they are soluble but are less effective in systems in which they are insoluble.

The following procedures was the sulfonation process. A 100 gm of crude lignin was dispersed in 3 liter of water and the lignin dissolved while heating in the presence of 10 gm NaOH and 16 gm of sodium sulfite. The solution was then precipitated while stirring dilute hydrochloric acid to decrease the pH from 11 to about pH 2. The suspension was then filtered immediately using a glass microfiber filter paper and the filter cake was rinsed with warm water to wash off the excess salt. The filter cake of lignin was then dried in a vacuum oven for 24 hours to ensure all the impurities was removed.

2.6 Corrosion Specimen Preparation

Specimen that was used in this experiment must be cleaned to remove the impurities and dirt from the surface of the sample. Carbon steel of 5 cm × 5 cm was used in this research work. The method for cleaning and weighing the specimen before the corrosion test was based on the ASTM G1 (1979). The methods were as follows:

(1) An abbrasive paper was used to scrub the carbon steel specimen to remove all the impurities and dirt from the specimen surface.
(2) The carbon steel specimen was then washed using fresh water.
(3) Specimen was dried and weighed using electronic balance of four decimal points.

After the completion of the corrosion test, the following cleaning process was used:

(1) A bristle brush was used to scrub the carbon steel specimen lightly under running water.
(2) The specimen was then dried and weighed using an electronic balance of four decimal points.

2.7 Electrolyte Solution Preparation

Electrolytes is the fluid which reflects the environment condition for corrosion to occur. According to Oberndorfer and Thayer [3], 3% concentration of NaCl was sufficient in preparing an electrolyte solution which simulates the actual chloride concentration in a natural brine solution. Thus, 3 gm of sodium chloride (NaCl) powder was added into 100 ml of distilled water, and the solution was then stirred until all sodium chloride powder has dissolved in water.

2.8 Corrosion Inhibitor Test

The research works comprised nine sets of test: four tests using lignosulfonate EFB of *Jatropha Curcas* and the other four using Sodium Benzotriazole (BTA-S), and the final one as the controlled experiment which used only 3% NaCl as electrolyte and carbon steel. This test followed the ASTM STP 866 (1985). Each of those experimental works was prepared as follows:

(1) 3% concentration of NaCl electrolyte was prepared. This formulation was used as the controlled condition.
(2) 3% concentration of NaCl electrolyte was added with 5% of lignosulfonate as a corrosion inhibitor.
(3) 3% concentration of NaCl electrolyte was added with 10% of lignosulfonate as a corrosion inhibitor.
(4) 3% concentration of NaCl electrolyte was added with 20% of lignosulfonate as a corrosion inhibitor.
(5) 3% concentration of NaCl electrolyte was added with 40% lignosulfonate as a corrosion inhibitor.
(6) 3% concentration of NaCl electrolyte was added with 5% of BTA-S as a corrosion inhibitor.
(7) 3% concentration of NaCl electrolyte was added with 10% of BTA-S as a corrosion inhibitor.
(8) 3% concentration of NaCl electrolyte was added with 20% of BTA-S as a corrosion inhibitor.
(9) 3% concentration of NaCl electrolyte was added with 40% of BTA-S as a corrosion inhibitor.

Carbon steel specimens were placed in the mixture of each of those samples for 720 hours. After 720 hours, specimens were cleaned using the method suggested by ASTM G1 (1979), and weighed. The optimum lignin concentration, corrosion rate, and corrosion inhibitor efficiency could then be identified.

3.0 RESULTS AND DISCUSSION

This section discusses the purity of the lignin extracted from *Jatropha Curcas'* EFB and its performance as compared to BTA-S. Generally, BTA-S is one of the commercial inhibitors that are widely used in the oil and gas industry.

3.1 Verification of Lignin Purity

Commercial lignin was used as the reference to verify the purity of lignin which was extracted from the EFB of *Jatropha Curcas*. Fourier transform infrared spectroscopy was used to do this verification process. The curve of spectrum for lignin sample (Figure 1) that was extracted from *Jatropha Curcas* showed a similar trend as the commercial spectrum (Figure 2). This research findings revealed that all the significant points for functional components on the curves were in the same range, thus EFB lignin shows it has the potential to be used as a corrosion inhibitor.

As shown in Figure 4.1, the the hydroxide (OH) group for the commercial lignin has been shown by the strong and broad band at 3430.22 cm^{-1} with a peak of 2929.28 cm^{-1} for identified C-H bond stretching of the methylene group. The conjugated carbonyl is shown with value of 1709.38 cm^{-1} while a band at 625.15 cm^{-1} represents the C-H deformation and also the ring vibration.

The FTIR spectrum for lignin extracted from empty fruit bunch of *Jatropha Curcas*, as shown in Figure 2, reveals that the characteristic of hydroxide was shown by the a strong and broad band at 3427.22 cm^{-1} with a peak value of 2918.06 cm^{-1} which is the identification of C-H bond stretching of the methylene group. There is a stretch of the conjugated carbonyl with a value of 1704.36 cm^{-1} for the lignin EFB while a band at 629.13 cm^{-1} represents the C-H deformation and also the ring vibration.

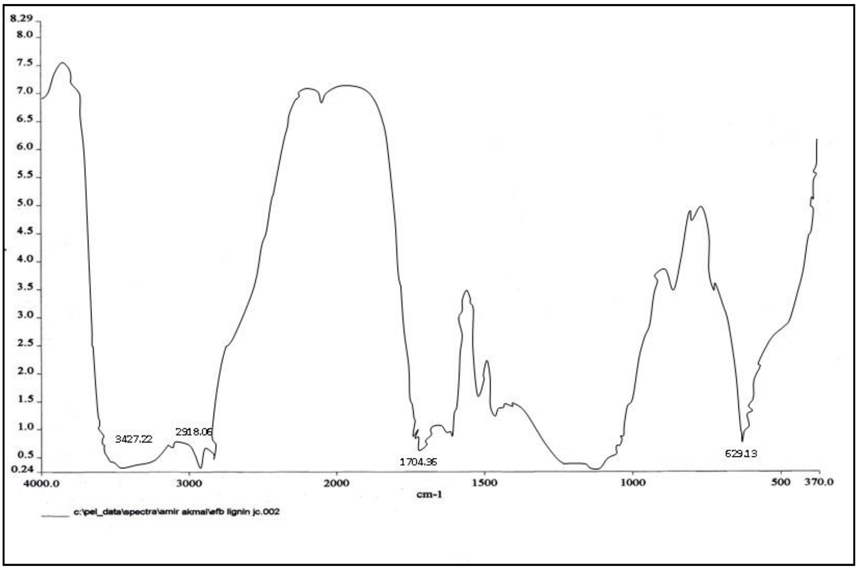

Figure 1 FTIR graph of lignin extracted from *Jatropha Curcas*

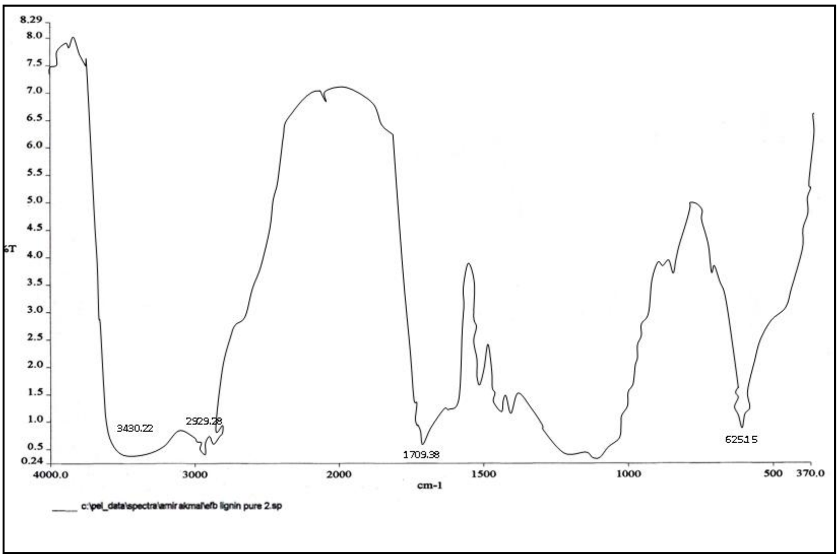

Figure 2 FTIR graph of commercial lignin

3.2 Performance of EFB Lignosulfonate

The EFB lignosulfonate and the commercial inhibitor, sodium benzotriazole (BTA-S), which both can be classified as organic inhibitors form a layer of protection on a metal's surface to protect it from corrosion. In this research work, the BTA-S was used as standard in the comparison of corrosion inhibition performance at room temperature.

After 720 hours of exposing the carbon steel to the 3% NaCl solution at room temperature, an analysis was done to determine the corrosion inhibitor efficiency. Figure 3 shows the red line curve for EFB lignosulfonate while the blue line is for BTA-S which was the commercial inhibitor. It shows that EFB lignoulfonate appeared to be the better corrosion inhibitor compared to BTA-S. It was found that their efficiency increased with concentration. Corrosion rate also showed the least for EFB lignosulfonate for every concentration (i.e., 5%, 10%, 20%, and 40%) that was used.

The experimental results showed that the optimum concentration for EFB lignosulfonate was 20%. The optimum concentration could be determined from the point when the corrosion rate curve starts to become constant after it reduces gradually.

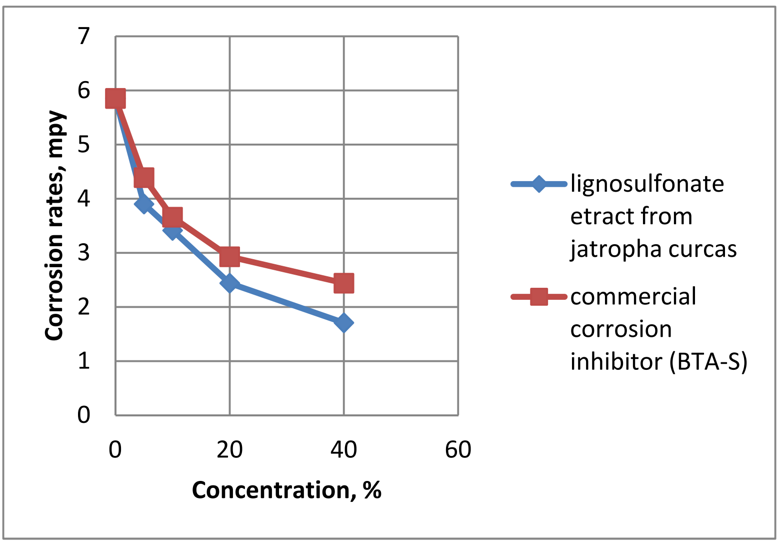

Figure 3 Corrosion rate versus concentration for EFB lignosulfonate and BTA-S

A performance comparison between EFB lignosulfonate and BTA-S (commercial inhibitor) also was done to determine the effectiveness of EFB lignosulfonate as a corrosion inhibitor. Figure 4 shows that EFB lignosulfonate gave a better performance than BTA-S. It shows that the inhibitor efficiency of EFB gave an increasing trend for all the concentrations (i.e., from 5 to 40% concentrations).

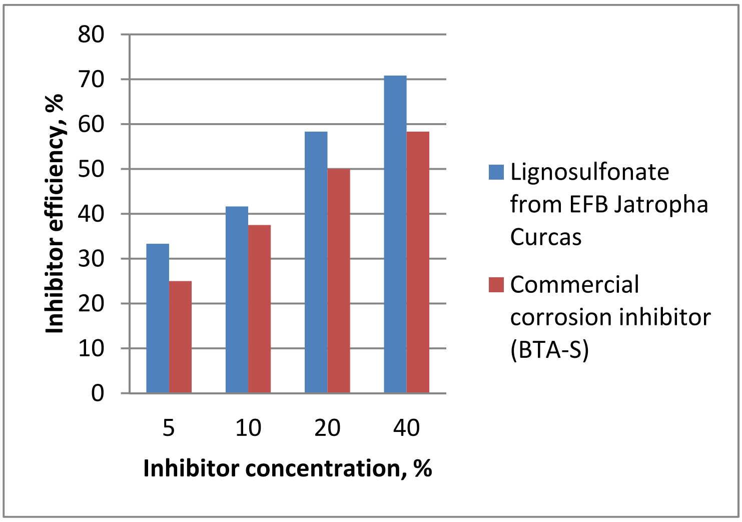

Figure 4 Inhibitor efficiency versus concentration for EFB lignosulfonate and BTA-S

4.0 CONCLUSIONS

Based on this research work, several conclusions could be drawn out accordingly:

(1) The EFB lignosulfonate extracted from the lignin of *Jatropha Curcas* has the potential to be used as a corrosion inhibitor.

(2) The EFB lignosulfonate has been successfully produced from EFB lignin through the sulfonation process.

(3) Lignin from *Jatropha Curcas'* empty fruit bunch was succesfully extracted using Klason Lignin method and it showed a comparable characteristics as commercial lignin as revealed by the Fourier Transform Infrared Spectroscopy test.

(4) The EFB lignosulfonate and commercial lignin were found both comprising hydroxide (OH) group, C-H bond (ethylene group), conjugated carbonyl (ether stretching), and also C-H deformation and ring vibration.

(5) The EFB lignosulfonate gave a better performance as a corrosion inhibitor as compared to BTA-S as it produced higher corrosion inhibition efficiency (i.e., 70%) than BTA-S (i.e., 59%) at room temperature.

(6) The optimum concentration for EFB lignosulfonate to reduce corrosion rate at room temperature was 20%.

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