STRUCTURE ELUCIDATION OF 4-VINYLPYRIDINE DIMER AND ACTIVITY TESTS AS CORROSION INHIBITOR FOR MILD STEEL IN CO_2−SATURATED BRINE SOLUTION

(Skripsi)

By

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BANDAR LAMPUNG
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ABSTRACT

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The dimerization of 4-vinylpyridine monomer has been carried out through oxidative coupling method using methanol as a solvent and hydrochloric acid (HCl) as a catalyst. The dimerization product was compared with its monomer using thin layer chromatography (TLC) and fourier transform infrared (FTIR) spectroscopy. Molecular weight screening and compound structure elucidation were carried out using liquid chromatography-mass spectrometry (LC−MS) for identification of 4-vinylpyridine dimer, D(4-VP). D(4-VP) was evaluated as a corrosion inhibitor for mild steel in a brine solution saturated with CO_2 using wheel test method. Mild steel surface morphology analysis was performed using scanning electron microscope (SEM). The D(4-VP) was appeared as a transparent yellow diluted liquid. TLC and FTIR results showed a slight difference between monomer and D(4-VP) by the spots and functional groups, respectively. LC−MS screening result showed that the formation of D(4-VP) identified at retention time of 6.18, 6.59, and 16.22 minutes. The wheel test of D(4-VP) showed a corrosion inhibition activity, where an inhibition efficiency (IE) increased with an increase of D(4-VP) concentration. The highest IE (63.12%) was reached out at the highest concentration used (200 mgL^{-1}). Mild steel protection was also supported by a surface visualization using SEM.

Keywords: mild steel, CO_2 corrosion, corrosion inhibitor, 4-vinylpyridine dimer, oxidative coupling.

ABSTRAK

ELUSIDASI STRUKTUR DIMER 4-VINILPIRIDIN DAN UJI AKTIVITAS SEBAGAI INHIBITOR KOROSI BAJA LUNAK DALAM *BRINE SOLUTION* YANG JENUH CO_2

Oleh

MUHAMMAD FADHIL RAMADITO

Dimerisasi 4-vinilpiridin telah dilakukan dengan menerapkan metode kopling oksidatif menggunakan pelarut metanol dan katalis asam klorida (HCl). Produk hasil dimerisasi dibandingkan dengan monomernya menggunakan kromatografi lapis tipis (KLT) dan spektroskopi *fourier transform infrared* (FTIR). *Screening* berat molekul dan elusidasi struktur senyawa dilakukan menggunakan kromatografi cair−spektrometri massa (LC−MS) untuk identifikasi dimer 4-vinilpiridin, D(4-VP). Senyawa D(4-VP) diuji aktivitasnya sebagai inhibitor korosi terhadap baja lunak dalam *brine solution* yang jenuh CO_2 menggunakan metode *wheel test*. Analisis morfologi permukaan baja lunak dilakukan menggunakan *scanning electron microscope* (SEM). Senyawa D(4-VP) berwujud *liquid* berwarna kuning transparan. Hasil KLT dan FTIR masing-masing menunjukkan adanya sedikit perbedaan antara monomer dan produk dimerisasi berdasarkan identifikasi noda dan gugus fungsi. Hasil *screening* LC−MS menunjukkan bahwa pembentukan senyawa D(4-VP) teridentifikasi pada waktu retensi 6.18, 6.59, and 16.22 menit. Hasil pengujian metode *wheel test* menunjukkan aktivitas inhibisi dari senyawa D(4-VP) terhadap korosi, di mana efisiensi inhibisi (IE) meningkat dengan meningkatnya konsentrasi D(4-VP) yang digunakan. Nilai IE terbesar (63.12%) telah dicapai pada konsentrasi D(4-VP) tertinggi yang digunakan (200 mgL^{-1}). Proteksi baja lunak juga didukung dengan visualisasi permukaan menggunakan SEM.

Kata kunci: baja lunak, korosi CO_2, inhibitor korosi, dimer 4-vinilpiridin, kopling oksidatif.

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By

Muhammad Fadhil Ramadito

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Dengan ini menyatakan dengan sebenar-benarnya bahwa skripsi saya yang berjudul "***Structure Elucidation of 4-Vinylpyridine Dimer and Activity Tests as Corrosion Inhibitor for Mild Steel in CO_2–Saturated Brine Solution***" adalah benar karya sendiri dan tidak keberatan jika sebagian atau seluruh data dalam skripsi tersebut digunakan oleh dosen atau program studi untuk kepentingan publikasi sesuai dengan kesepakatan.

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RIWAYAT HIDUP

Penulis lahir di Tangerang, pada tanggal 10 Desember 2000 sebagai anak pertama dari dua bersaudara, putra dari Bapak Eriyo Budi Susetyo dan Ibu Wahyu Sukmawati. Penulis menyelesaikan pendidikan di Madrasah Tsanawiyah (MTs) Annajah Jakarta Selatan pada tahun 2013−2016 dan SMA Yadika 5 Jakarta Barat pada tahun 2016−2019. Pada tahun 2019, penulis melanjutkan pendidikan sebagai mahasiswa Jurusan Kimia, Fakultas Matematika dan Ilmu Pengetahuan Alam, Universitas Lampung melalui jalur Seleksi Bersama Masuk Perguruan Tinggi Negeri (SBMPTN) dan menyelesaikan studinya pada tahun 2023.

Selama menjadi mahasiswa, penulis aktif dalam Kader Muda pada Himaki tahun 2019, kemudian menjadi pengurus aktif Himpunan Mahasiswa Kimia (Himaki) pada tahun 2020 di bidang Sains dan Penalaran Ilmu Kimia. Pada tahun 2022 penulis pernah menjadi asisten Praktikum Kimia Dasar dan Praktikum Kimia Anorganik-Fisik pada tahun 2023.

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MOTTO

“Success is no accident. It is hard work, perseverance, learning, studying, sacrifice and most of all, love of what you are doing or learning to do”
(Edson Arantes do Nascimento)

“Ability is what you’re capable of doing. Motivation determines what you do. Attitude determines how well you do it”
(Lou Holtz)

“Failure happens all the time. It happens everyday in practice. What makes you better is how you react to it”
(Mia Hamm)

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Bandar Lampung, 09 Juni 2023
Penulis

Muhammad Fadhil Ramadito

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I. INTRODUCTION

1.1 Background and Problem

Corrosion is generally defined as the degradation process of material structure quality due to a chemical oxidation-reduction that occurs when it comes in contact with its surrounding. The reduction and oxidation process between the target material and its environment gradually results in damage in the form of oxide chemical product called rust (Singh, 2017). In recent, corrosion is still often found in every object that uses metal-based materials, both in everyday life as well as in industry and transportation, such as home appliances, airplanes, cars, ships, and pipelines in the oil and gas industry.

Corrosion in the oil and gas industry pipelines occurs due to the presence of water and acid-producing gases such as sulfide acid (H_2S) or carbon dioxide (CO_2) dissolved in oil and gas (Song et al., 2022). H_2S gas reacts with water to form sulfuric acid (H_2SO_4), while CO_2 gas reacts with water to form carbonic acid (H_2CO_3) and corrodes the inner surface of the pipe (Obot et al., 2019). Wang et al. (2019) reported at the same pH, carbonic acid is more aggressive than hydrochloric acid. This reason made CO_2 corrosion as the main issue in industrial processes of oil and gas for many years.

Corroded pipelines cause a degradation in the mechanical properties of materials including the strength, toughness, and ductility, that the longer can result to leakages and leads to the failure of the component (Seghier et al., 2022). Failure of engineering materials is almost an undesirable event for

several reasons, including endangering human lives, disrupting the availability of products and services, and also causing economic losses. According to data reported by the National Association of Corrosion Engineers (NACE) in 2016, corrosion in oil and gas industry can cause significant economic losses, by looking to the total loss that estimated at US$1.371 trillion per year.
The reports also showed that the cost of corrosion in the United States reached US$276 billion per year, equivalent to 3.1% of the country's total gross national product (GNP) (Koch et al., 2016). However, in economic terms, the replacement of corroded components or units is not as impactful compared to indirect losses caused by production shutdown, loss of efficiency, as well as leakage during manufacturing, storage, and product contamination.

The corrosion issues in oil and gas pipelines are able to be controlled through several methods, such as material selection and coating (May et al., 2022), cathodic/anodic protection (Yulianto et al., 2018), and addition of inhibitors (Ilim et al., 2016, 2017 and 2021a; Fawzy and Toghan, 2021). However, there are some disadvantages within those methods. The selection of high-quality materials needs to consider towards the price of the material, coating is not possible to apply into pipelines which located underwater of the subsea, and cathodic/anodic protection has disadvantages in terms of short service life and large amount of external energy consumption. Therefore, the addition of inhibitors would be an alternative way to control the corrosion because it is effective, has a longer shelf life, does not require a large external energy supply, and relatively inexpensive (Abdulazeez et al., 2021).

Corrosion inhibitors have a role as a substance which can inhibit corrosion attack on metal surface by adding them in a small amounts into a corrosive medium. The activity of inhibitor in protecting a corrosion is generated by forming the protective layer through adsorption of inhibitor molecules onto the metal surface. The protective layer will then prevent the diffusion of the corrosive medium towards the metal (Porcayo-Calderon et al., 2022). In general, corrosion inhibitors consist of organic or inorganic compounds having a lone pair of electrons such as oxygen, nitrogen, sulfur and phosphorus (Dawood et al., 2021). Organic inhibitors are mostly used because they are environmentally friendly and biodegradable (Lahrour et al., 2019 and Al-Moubaraki et al, 2022). Previous studies have used several natural and synthetic organic compounds as corrosion inhibitors, such as imidazoline derivatives (Sanchez-Salazar et al., 2021), vinylpiperidine (Ilim et al., 2017), 1,2,4-triazole derivatives (Avdeev et al., 2021), and 4-vinylpyridine oligomer (Ilim et al., 2021a).

Polymer-based corrosion inhibitor is one of a group of compounds known to inhibit corrosion rates and their potential continues to be developed. This is because the polymers can form complexes with metal ions on metal surfaces (Tsoeunyane et al., 2019). Moreover, the presence of heteroatoms, especially oxygen, sulfur, and nitrogen in a compound performs good inhibition. Various polymer compounds containing heteroatoms have been studied for their ability as corrosion inhibitors (Ilim et al., 2016, 2017 and 2021a; Avdeev and Kuznetsov, 2021; Hadisaputra et al., 2021; Ramkumar et al., 2021). Poly(4-vinylpyridine) is one of the polymeric compounds that has been studied as a corrosion inhibitor for mild steel in NaCl saturated with CO_2. The 4-vinylpyridine oligomer can inhibit the corrosion of mild steel in NaCl solution, but the monomer is the opposite one, which promotes the corrosion rate (Ilim et al., 2016 and 2021a).

Previous study (Ilim et al., 2021a) reported that the synthesis and characterization of 4-vinylpyridine oligomer using a 0.25 mole of H_2O_2 initiator generates a product with relatively abundant of oligomers dominated by 4-vinylpyridine dimers. This compound showed higher effectiveness as a corrosion inhibitor when compared to the 4-vinylpyridine oligomer which was synthesized using the 0.33 mole of H_2O_2 initiator with the same highest relative abundance (Ilim et al., 2016). It was found that the amount of initiator H_2O_2 used determines the molecular weight distribution of 4-vinylpyridine oligomers and affects the effectiveness of corrosion rate inhibition, but does not change the relative abundances contained in the oligomers.

Based on the problems and the research results previously mentioned, this research focuses on taking the dimerization method into account to obtain 4-vinylpyridine compounds in the form of two monomeric chain (dimer) and elucidating their structures with the support of several characterization and screening tests. The dimerization of 4-vinylpyridine compound is carried out using oxidative coupling method with the support of a hydrochloric acid (HCl) catalyst which acts as an electrophile to produce the active coupling site in the form of a carbocation (Zahl et al., 2018). A dimerized 4-vinylpyridine product is then evaluated as corrosion inhibitor for mild steel in brine solution saturated with CO_2.

1.2 Research Purposes

The purpose of this research is as follow:

1. Obtain the 4-vinylpyridine (4-VP) dimer synthesized through 4-VP monomer dimerization using methanol solvent and hydrochloric acid (HCl).
2. Analyze the dimer product and its monomeric difference by comparing their chemical in terms of thin layer chromatography (TLC) and functional groups analysis using fourier transform infrared (FTIR) spectroscopy.
3. Identify the 4-VP dimer derivatives formed in the dimer product through molecular weight screening using liquid chromatography−mass spectrometry (LC−MS) and compound structure elucidation.
4. Obtain the inhibition activity value of 4-vinylpyridine dimer compound as corrosion inhibitor of mild steel in a brine solution saturated with CO_2 using wheel test method.
5. Visualize the mild steel surfaces morphology under several conditions and treatments using scanning electron microscope (SEM).

1.3 Research Benefits

The results obtained in this research are expected to provide benefits for adding a new information about the dimerization method applied to obtain 4-vinylpyridine dimer compound as one of the several polymer-based macromolecular derivatives as a corrosion inhibitor for mild steel in a brine solution saturated with CO_2 and providing contribution in efforts to overcome the need for corrosion inhibitors in Indonesia.

II. LITERATURE REVIEW

2.1 Carbon Steel

According to Luo et al. (2019), carbon steel is a mixture of carbon (C) and metal elements, generally most steels contain only carbon with a few other alloys. Carbon steel is classified into three types based on its concentration or elemental content, namely low carbon steel, medium carbon steel, and high carbon steel. The type of carbon steel used in this research is medium carbon steel, which also named as mild steel. The composition of mild steel is shown in Table 1. Mild steel will be used as a research object to see how severe corrosion is formed on the mild steel surface.

Table 1. Chemical composition of mild steel from various references

Element	Fe	C	Si	Mn	Cu	P	S	Reference
Content (%)	98	0.20	0.50	1.60	0.6	< 0.01	< 0.01	Coors et al. (2022)
	99	0.22	0.02	0.74	0.01	0.02	0.014	Ilim et al. (2016)
	98.9	0.22	0.02	0.74	0.01	0.02	0.014	Ilim et al. (2021a)

2.2 Corrosion

Corrosion originates from the Latin *corrodore* which means "a gnaw into pieces". According to Yang (2020), corrosion is defined as the chemical or electrochemical reaction between a material, usually a metal or alloy, and its environment that produces a deterioration of the material and its properties.

This chemical or electrochemical reaction of corrosion occurs spontaneously, that is characterized by a change in free energy that is less than zero ($\Delta G < 0$).
The meaning of the change in free energy is deviation between the free energy of reactants and the free energy of oxidation products. This spontaneous reaction is identical to the corrosion mechanism based on corrosion thermodynamics in terms of the difference in free energy values. So, corrosion is a thermodynamic system of metals with an environment (water, air, soil) that seeks to achieve equilibrium. This system is said to be balanced when the metal has formed a more stable oxide at the lowest energy level (Gapsari, 2017).

Electrochemical corrosion reactions, to be generated, involve an electrolyte environment (ammonia, chloride, acids and bases). This corrosion is generally called as wet corrosion. The definition of electrochemical corrosion is the process of releasing electrons from metals which, if flowing continuously, produce a continuous potential difference. The electrochemical reaction is a half-cell reaction at the anode and cathode site. In anode site occurs oxidation reaction (electron release) and cathode site occurs reduction reaction (electron capture). Corrosion affected by the electrolyte environment is referred to as external corrosion, while corrosion affected by the presence of dissolved gases in water is referred to as internal corrosion. Among these two types, internal corrosion is the most common one (Mazumder, 2020).

2.3 CO_2 Corrosion (Sweet Corrosion)

Carbon dioxide (CO_2) is a dry gas presence in oil and gas caused by the production of CO_2 from a gas reservoir during the exploration process or due to the injection of CO_2 aimed for increasing the enhanced oil recovery (EOR) value. Carbon dioxide is a non-corrosive agent, but if the gas dissolves in water, a spontaneous reaction will occur that produces carbonate ions that can initiate a reaction between the inner metal surface of the pipe and the corrosive salt solution (Owen et al., 2018). The reaction mechanism is as follow:

Dissolution of reacting CO_2 to form carbonic acid (H_2CO_3)

$$CO_{2\,(g)} \longleftrightarrow CO_{2\,(aq)} \tag{1}$$

$$CO_{2\,(aq)} + H_2O_{(l)} \longrightarrow H_2CO_{3\,(aq)} \tag{2}$$

The carbonic acid formed will dissociate into bicarbonate ions and carbonate ions

$$H_2CO_{3\,(aq)} \longrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)} \tag{3}$$

$$HCO_3^-{}_{(aq)} \longrightarrow CO_3^{2-}{}_{(aq)} + H^+_{(aq)} \tag{4}$$

Based on the bicarbonate ion formation scheme above, the corrosion reaction process that occurs is as follow:

Anode: $Fe_{(s)} + HCO_3^-{}_{(aq)} \longrightarrow FeCO_{3\,(s)} + H^+_{(aq)} + 2e^-$ (5)

Cathode: $2\,H^+_{(aq)} + 2e^- \longrightarrow H_{2\,(g)}$ (6)

Total reaction: $Fe_{(s)} + HCO_3^-{}_{(aq)} + H^+_{(aq)} \longrightarrow FeCO_{3\,(s)} + H_{2\,(g)}$ (7)

With the presence of hydrogen ions, the reaction produces an acidic atmosphere and hydrogen ions will attack the iron surface in oil and natural gas pipelines, causing the pipeline to undergo oxidation and erosion. Erosion occurs continuously until the exhaust of hydrogen ions.

2.4 Corrosion Control and Mitigation

2.4.1 Cathodic Protection

Cathodic protection is one of the methods for countering the corrosion by applying electrochemical principles to metal components both buried underground and submerged in water. Cathodic protection is carried out by supplying a certain amount of DC current from external sources on corroded metal surfaces. There are two methods of supplying direct current in cathodic protection, namely the sacrificial anode cathodic protection (SACP) method or the impressed current cathodic protection (ICCP) method.

The SACP method uses the principle of Galvanic cells, which is to protect the target metal structure with other active metals that are more anodic (have a more negative standard reduction potential) so that the target metal can be protected from corrosion at the cathode, while the anodic metal will be damaged at the anode. The ICCP method is carried out by providing direct electric current from an external source between the inert anode and the target metal. The direct current given causes the target metal to be cathodically protected through the supply of electrons produced by the metal (Wasim and Djukic, 2022).

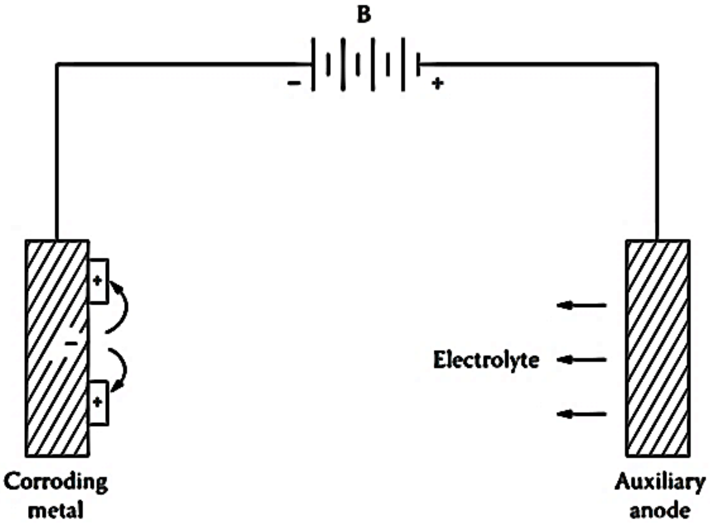

Figure 1. Cathodic protection cells using DC current

2.4.2 Coating

According to Wasim and Djukic (2022), coating is a process of protecting metal surfaces by forming a layer that can minimize contact between the metal surface and its environment so that corrosion attacks on the metal can be prevented.
The most commonly used coating example is liquid protective coating (LPC) or paint. Paint can be interpreted as a liquid or viscous product that when applied to a metal surface will form a thin layer of dryness, cohesion, and have good adhesion to the surface and are able to protect the surface from its environment. Coating is divided into three types; metal plating (electroplating, cladding, hot dip

Galvanizing, thermal spraying, electro-less plating, physical vapor deposition), inorganic coatings (passive coatings, copper coatings, phosphate coatings, chromate filming, anodic control), and organic coatings (sacrificial effect, barrier effect, inhibition effect).

2.4.3 Material Selection

Material selection is based on the suitability with the function of the selected material to a particular environment or medium. The suitability of material functions can be considered through several references such as physical characteristics (material density, ductility, crystal structure), mechanical properties (curve stress strain, hardness, fatigue characteristics), design limitations, fabrication characteristics, and economic characteristics (Cai et al., 2022).

2.4.4 Addition of Inhibitor

Inhibitor comes from the base word "inhibition" which means to inhibit some physical of chemical processes. Corrosion inhibitor is an inorganic or organic chemical compound, which are added in small amounts (mostly in milligram per liter unit) into the corrosive medium to control the corrosion rate, by forming a protection layer through an adsorption process both chemically (chemisorption) and physically (physisorption) to the metal surface (Ilim et al., 2021a).

2.5 Corrosion Inhbitor

Organic or inorganic compounds which when added in relatively small amounts into a corrosive metal-medium system can reduce the corrosion rate of the metal, are referred to as corrosion inhibitors. In general, corrosion inhibitors are divided into two types, namely inorganic inhibitor and organic inhibitor.

Inorganic inhibitors are compounds containing inorganic elements such as chromate, dichromate, nitrite, phosphate, silicate, borate and arsenate. Inorganic inhibitors are called as anodic inhibitors as they have an active group in the form of anions that are useful for reducing corrosion. Inorganic inhibitors are quite effective in inhibiting the rate of corrosion, but there is a disadvantage that they have a high level of toxicity that can pollute the environment and are relatively expensive (Karim and Joseph, 2012; Mardhani and Harmami, 2013).

Organic inhibitors are compounds containing nitrogen, oxygen, phosphorus, sulfur, and other related atoms having a free electron pair. Organic inhibitors are classified into two types, namely synthetic organic inhibitors and natural organic inhibitors. Synthetic organic inhibitors have advantages such as not requiring isolation processes or other separation methods to obtain inhibitor compounds because the process takes a long time, and can be synthesized as desired. One of synthetic organic compound groups having a quite good protective activity is the group of oligomeric compounds such as 4-vinylpiperidine (Ilim et al., 2017) oligomers and 4-vinylpyridine oligomers (Ilim et al., 2021a).

As corrosion inhibitor, organic compounds can protect metal surfaces through the adsorption of inhibitor by metals due to the presence of π and heteroatoms that tend to increase molecular adsorption (Ramkumar et al., 2021). Adsorption occurs will lead to the formation of coordination covalent bonds by donating the inhibitor's free electron pair on the metal’s d orbital. This organic inhibitor forms a hydrophobic protective film layer that is adsorbed on the metal surface and becomes a barrier between the metal and the electrolyte so that the reduction and oxidation reactions in corrosion can be inhibited, with the reaction shown in Figure 2.

The 4-vinylpyridine oligomer inhibitor contains a nitrogen group that donates a pair of electrons on the surface of a mild steel metal when Fe^{2+} ions are diffused into a corrosive solution. Therefore, it is expected that the corrosion products formed have better stability compared to Fe^{2+} only.

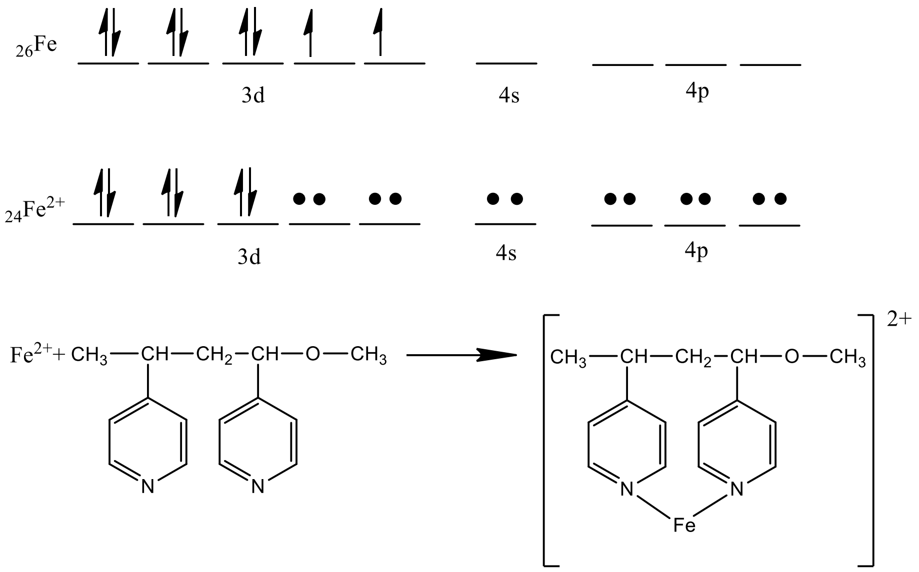

Figure 2. Protection mechanism 4-vinylpyridine inhibitor in forming a complex with Fe (Ilim et al., 2007)

2.6 4-Vinylpyridine Oligomer

4-Vinylpyridine oligomer is a form of 4-vinylpyridine polymer with a lower molecular weight. This compound has been successfully synthesized in previous studies (Ilim et al., 2021a) by reacting 4-vinylpyridine monomers, methanol and water solvents, as well as the initiator H_2O_2 0.25 mole. The molecular weight distribution of the resulting oligomer was confirmed through characterization using ESI−TOF (electrospray ionization-time of flight) mass spectrometer (MS).

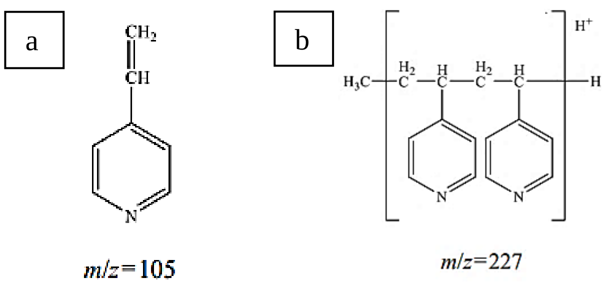

Figure 3. (a) Monomer and (b) dimer structure of 4-vinylpyridine (Ilim et al., 2021a)

Characterization of MS is interpreted through a spectrum which shows the relationship between the mass (m/z) of the x-axis and the relative number of the y-axis. Based on the study, information was obtained through the MS spectrum (Figure 4) that the sample contained a series of components with different molecular weights, ranging from 122 to 994.

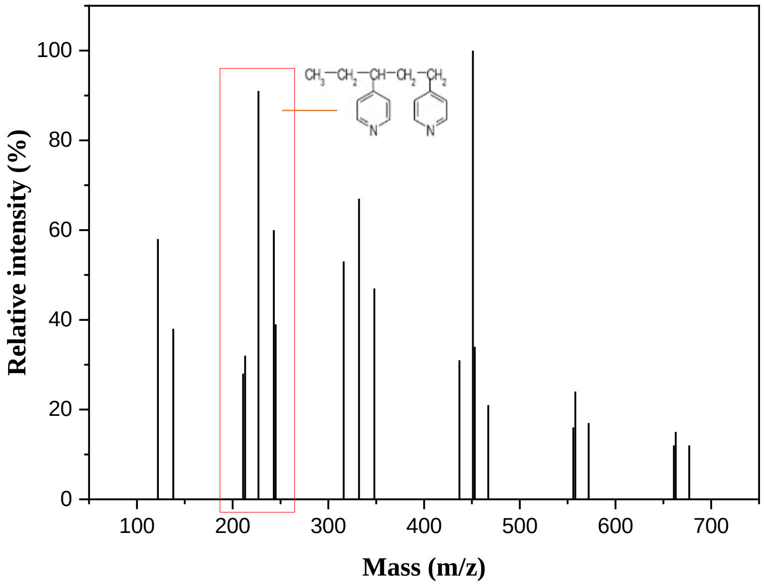

Figure 4. MS spectrum of 4-vinylpyridine oligomer (Ilim et al., 2021a)

The study also provided additional information for the number of monomers in the sample, that another factor causes the molecular weight value of each oligomer to be varied is the difference in the final group of each oligomer compound. Some of the possible end groups are presented in Table 2.

Table 2. The end group mass of 4-vinylpyridine oligomers of various combinations (Ilim et al., 2021a)

End group →	C=C	H	OH	CH_3	OCH_3
Mass ↓	(m=-1)	(m=1)	(m=17)	(m=15)	(m=31)
H (m=1)	0	2			
OH (m=17)	16	18	34		
CH_3 (m=15)	14	16	32	30	
OCH_3 (m=31)	30	32	48	46	62

Based on the two factors underlying the variation in molecular weight, an obtained equation for determining the molecular weight (M_w) of the oligomer is formulated through Equation 1.

$$M_w\ of\ oligomer = n \cdot 105 + m + 1 \tag{8}$$

where:
n: unit number of monomer
m: end group mass, with 1 corresponds to the mass of proton

Table 3. Composition of 4-vinylpyridine oligomer (Ilim et al., 2021a)

Number of monomer unit (n)	Molecular weight (m/z)
1	(122) and (138)
2	(211), (213), (227), (243), and (245)
3	(316), (332), and (348)
4	(437), (451), (453), and (467)
5	(556), (558), and (572)
6	(647), (661), (663), (677), and (693)
7	(766), (768), and (782)
8	(871), (873), and (887)
9	(978) and (994)

Based on Figure 4 and Table 3, it is shown that 4-vinylpyridine oligomers are a mixture of monomers and polymers formed by the range of 2−9 monomer units with dimer (n=2) to tetramer (n=4) dominates the mixture of the synthesized product.

Research conducted by Ilim et al. (2016) reported that the synthesis of 4-vinylpyridine oligomers using H_2O_2 0.33 M as the initiator formed products with molecular weights in the range of 200−2200 g/mol, then their characterization showed dimer (n=2) as the dominating component of the synthesis product. These two studies provide justification for the important role of H_2O_2 initiators in determining the degree of polymerization and dimers that have a highest relative abundance value of the synthesized products. Therefore, this research focuses on optimizing the method of dimerization and application of 4-vinylpyridine dimer as a corrosion inhibitor in a brine solution saturated with CO_2.

2.7 Oxidative Coupling: An Approach to Dimerization Process

Dimerization is the process of covalently coupling the two monomer units through breaking the double bond and forming a new one, longer bond. One type of organic chemical reaction to synthesize dimer compounds is oxidative coupling with the support of chemical catalysts (Barve et al., 2015). The characteristic of catalyst used is that it has a large electrophilicity to abstract a carbon-carbon double bond so that the breaking of π bond occurs and the electron pair is used for the formation of new σ bond (Liu et al., 2015). Some types of catalysts with a large electrophilicity are transition metals such as palladium (Shibahara et al., 2012), copper (Alamsetti et al., 2013), rhodium (Glorius et al., 2012), and mineral acids and Lewis acids such as HCl, HBr, BF_3, and $AlCl_3$ which have been applied to synthesize dimer derivatives of eugenol (Purwono et al., 2010; Wilger et al., 2014).

The formation of dimer via oxidative coupling has the same reaction principle as polymerization in common, both condensation and addition. Addition polymerization is a chain reaction caused by the presence of free radicals or ions, so that addition polymerization can be classified into two groups, namely free radical polymerization and ionic polymerization. In ionic polymerization, the initiation stage takes place in the presence of electrophile species (H^+) which added into monomer molecules to produce a new cation, namely carbocation. Furthermore, carbocation becomes a propagated species through the addition of monomers. The termination stage becomes the final stage where the dimer undergoes termination of chain growth by forming bond variations with end groups to produce stable dimers (Prasetya et al., 2019). Based on the principle, this chemical dimerization method is applied in the current research for conducting a dimerization of 4-vinylpyridine monomer compound.

2.8 Corrosion Rate Measurement

2.8.1 Wheel Test Method

The wheel test method is the most widely used corrosion measurement method. Coupons are metal plates placed in the system and left corroded, in order to determine the corrosion rate (Fitriani, 2020). Corrosion coupons are widely used for construction materials to detect permanent assaults of corrosiveness. Coupons describe corrosion damage over a period of time and are only used on conditions where the increased corrosion rate can be measured. The shape and dimensions of the coupon can be varied according to the test requirements. The coupon test is placed on the test environment for a certain period, then the preconceived corrosion products must be eliminated. The method of removal of corrosion products can be carried out without causing further corrosion. The equation for calculating the corrosion rate is as follows:

$$\mathrm{CR\ (mmpy)} = 10 \times \left(\frac{\mathrm{Wt}}{\mathrm{A}}\right) \times \frac{1}{\mathrm{D}} \times \frac{365}{\mathrm{t}} \tag{9}$$

where:
CR = corrosion rate (mmpy)
Wt = weight (g), the difference in the initial weight and the final weight
A = sample area (cm^2)
D = density (g/cm^3).

The equation for determining the inhibition efficiency of an inhibitor in inhibiting the corrosion rate is as follows:

$$\%\mathrm{IE} = \frac{\mathrm{CR_i} - \mathrm{CR_o}}{\mathrm{CR_o}} \times 100\% \tag{10}$$

where:
IE : inhibition efficiency
CR_o : corrosion rate without inhibitor
CR_i : corrosion rate with inhibitor.

2.8.2 Electrochemical Method

A. Potentiodynamic Polarization

Determination of the corrosion rate on a metal surface can be done by several methods, one of which is the potentiodynamic polarization method (Ilim et al., 2021a). The advantages of this method include that the time required is relatively shorter compared to wheel test method. In addition, this method can be used to analyze the corrosion behavior of a metal (Tsoeunyane et al., 2019).

The potentiodynamic polarization method is based on electrochemical reactions by measuring the relationship between the current and the potential that occurs from an oxidation reduction reaction that will determine the characteristics of them. polarization curve. One method that is often used is the Tafel extrapolation.

The basic principle of measuring the corrosion rate by the Tafel method refers to the theory of mix potential. This method is used to accurately obtain an estimate of the corrosion rate of the metal in solution. The corrosion rate measurement data by Tafel extrapolation is represented in the Tafel plot. The Tafel plot was obtained by polarizing the test object 300 mV in the anodic and cathodic direction of the corrosion potential, E_{corr} with a potential scanning rate of 0.1−1.0 mV/s. The obtained current is plotted on a semilogarithmic scale and the corrosion current, I_{corr}, is obtained from the plot of such Tafel by means of extrapolation of the linear part of the curve against the E_{corr} (Tasliyana and Nofrizal, 2019).

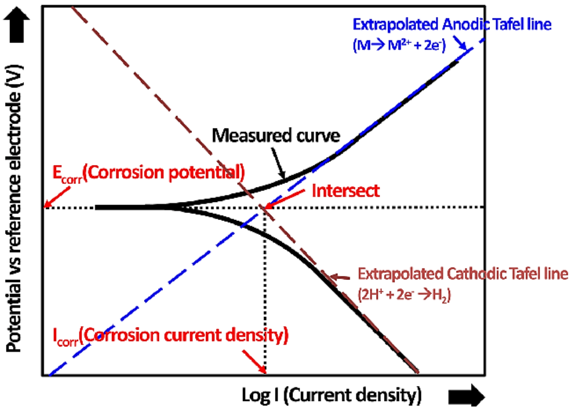

Figure 5. Cathodic and Anodic Polarization Diagrams (Lee et al., 2016)

The corrosion current obtained from the curve is then converted into a corrosion rate using Equation 4.

$$\mathrm{CR} = \mathrm{I_{corr}}\ .\ \wedge . \varepsilon . \left(\frac{1}{\rho . A}\right) \tag{11}$$

Where:

CR = corrosion rate

I_{corr} = corrosion current

A = sample area (1.13 cm^2)

ε = weight equivalent

∧ = constant (1,2866 x 105)

ρ = density (g/cm^3)

The equation used to determine the corrosion current is Stern-Geary Equation (5).

$$\mathrm{I_{corr}} = \left[\frac{1}{(2.303\ R_p)}\right]\left[\frac{\beta_a \beta_c}{(\beta_a + \beta_c)}\right] \tag{12}$$

Where:

I_{corr} = corrosion current

R_p = corrosion resistance ($\Omega.cm^2$)

β_a = anodic Tafel slope (mV/decade)

β_c = cathodic Tafel slope (mV/decade)

The inhibition efficiency (%IE) can be calculated using the following equation.

$$\%\mathrm{IE} = \left(1 - \frac{I_{corr(i)}}{I_{corr(o)}}\right) \times 100\% \tag{13}$$

Where:

IE : inhibition efficiency

$I_{corr(o)}$: corrosion current before addition of inhibitor (blank)

$I_{corr(i)}$: corrosion current with addition of inhibitor

With this method, the activity value of 4-vinylpyridine oligomer inhibitors was 87.8% at a temperature of 70 °C (Ilim et al., 2021a). The polarization curve of the 4-vinylpyridine oligomer as a corrosion inhibitor is interpreted in Figure 6.

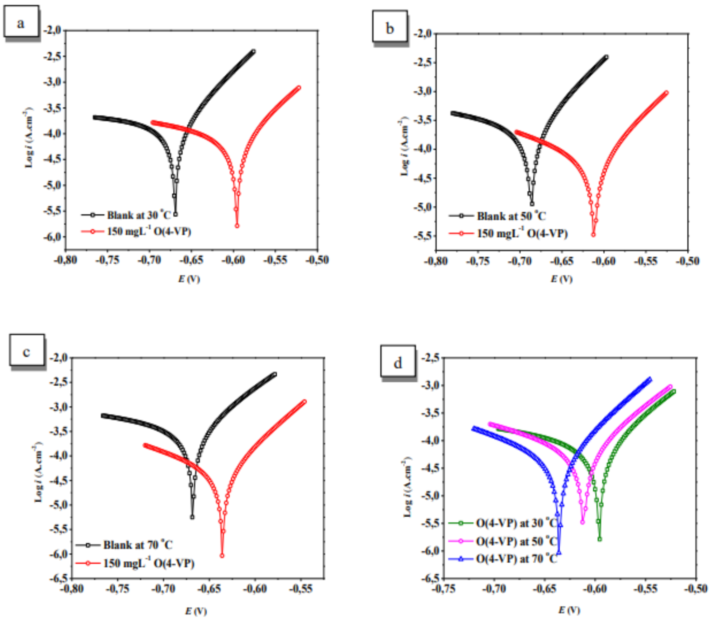

Figure 6. The polarization curve of blank solutions and solutions contain 150 mg L^{-1} oligomer inhibitors of 4-vinylpyridine at (a) 30, (b) 50, (c) 70 °C, and (d) 150 mgL^{-1} inhibitors at temperature variations (Ilim et al., 2021a)

B. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is an in situ analysis technique used to determine electrochemical processes and perform an assessment of corrosion behavior. Furthermore, analysis using EIS has been tested and applied to determine the interface processes occurring in the adsorption of inhibitors against metal surfaces in corrosive environments saturated with CO_2 (Farelas et al., 2010).

In principle, the EIS corrosion analysis is carried out based on electrochemical kinetics, which are determined through several representative parameters including polarization resistance (R_p), solution resistance (R_s), charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}). These parameters were obtained on the Nyquist plot, the output data from the EIS measurements obtained at the open circuit potential (OCP) at ~ -700 mV and then the diagram is formed through the plot of the magnitude of the real impedance (Z_r) against the imaginary impedance (Z_i) (Ilim et al., 2017).

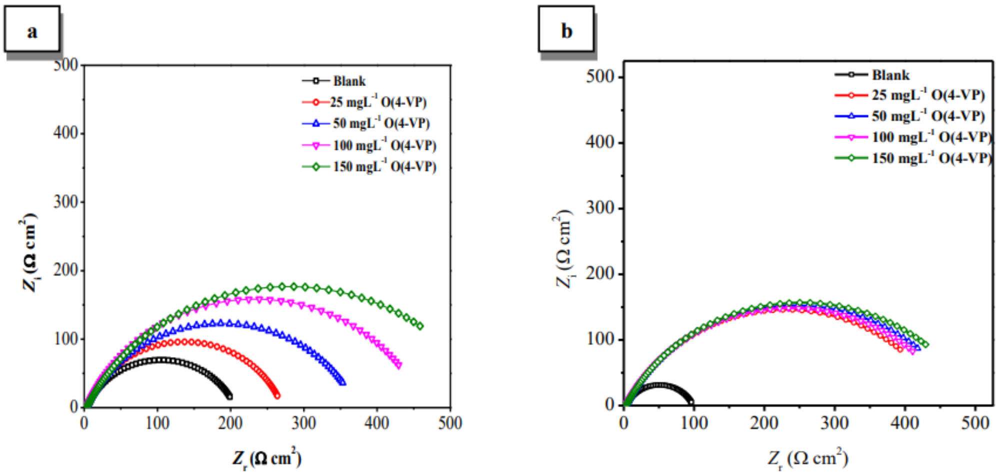

Figure 7. Nyquist plot of blank solutions and solutions containing oligomer inhibitors of 4-vinylpyridine at (a) 30 and (b) 50 °C (Ilim et al., 2021a)

Based on the Nyquist plot, the value of R_p, R_s, and R_{ct} can be determined. The value of R_s is the minimum point of Zr and R_p is the maximum point of Z_r in the area of the formed semicircle. While the R_{ct} value is the difference between the values of R_p and R_s or the magnitude of the diameter of the semicircle resulting from the Nyquist plot. When it is related with inhibition ability, the maximum value of Z_r will be directly proportional to the percent of protection or inversely proportional to the corrosion rate (Ilim et al., 2021a). Equation 7 below is used to obtain an inhibition efficiency based on the EIS parameter.

$$\%\mathrm{IE} = \frac{\mathrm{R_{ct(i)}} - \mathrm{R_{ct(o)}}}{\mathrm{R_{ct(i)}}} \times 100\% \qquad (14)$$

Where:

IE = inhibition efficiency
$R_{ct(o)}$ = charge transfer resistance without addition of inhibitor (blank)
$R_{ct(i)}$ = charge transfer resistance with the addition of inhibitor

The activity of 4-vinylpyridine oligomers as corrosion inhibitor evaluated using this method has the highest percent protection value of 86.5% at a temperature of 50 °C (Ilim et al., 2021a).

2.9 Instrumentation Analysis

2.9.1 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is one of the instrumentation methods that used to identify chemical compounds, both naturally and synthetically. In FTIR analysis, two molecules of compounds with different chemical structures have also different infrared spectra. This is due to the difference in the type of bond and the frequency of vibration.

Although having the same type of the bond, the type of compound is different, as well as the frequency of vibration obtained is different, so that the infrared spectrum in FTIR is a fingerprint of a molecule. If infrared rays are passed through a sample of organic compounds, then there are a number of frequencies that are absorbed and there are that are passed on or transmitted. The absorption of light by molecules depends on the electronic structure of the molecule.
The general setup schematic of FTIR spectroscopy is shown in Figure 8.

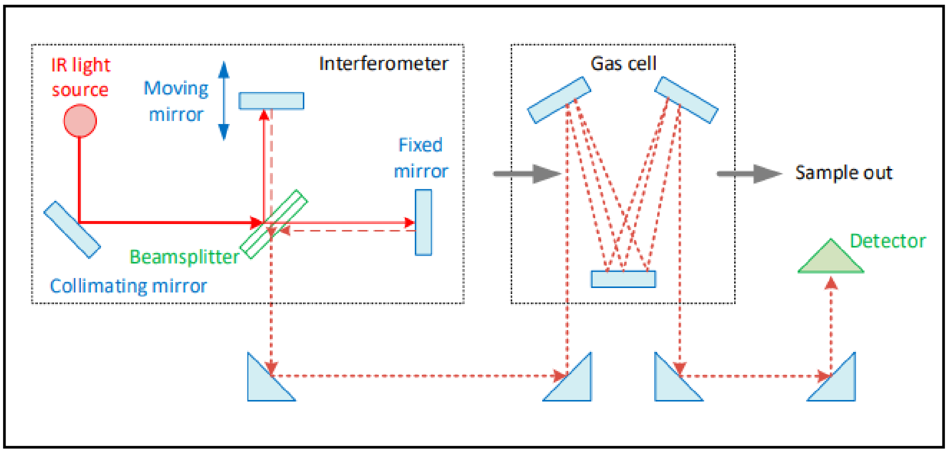

Figure 8. General setup of FTIR spectroscopy (Giechaskiel and Clairotte, 2021)

The absorbed energy by some molecules is about to change a vibrational energy and its rotational energy levels. FTIR will detect a sample at the functional group level. Different bonds such as C−C, C═C, C≡C, CO, C═O, −OH and N−H have their characteristic frequencies as absorption bands in the infrared spectrum.

A functional group in the absorption band in the area of 3550−3200 cm^{-1} that shows the vibrational characteristics of the −OH stretch, an absorption band above 3350 cm^{-1} that indicates the vibrational characteristics of the N−H amine. Other absorption bands that indicate the presence of NH_2 amines vibration are in the 1650−1550 cm^{-1} area which shows NH_2 bending vibration (primary amine), absorption band in the 1250−1000 cm^{-1} area which shows C-N vibration, absorption band at area of 2950-2850 cm^{-1} shows C−H vibrational stretch characteristics, other absorption bands in the 1470−1350 cm^{-1} area which shows C−H bending vibration, and absorption bands in the 1250−1050 cm^{-1} area indicating C-O bending vibration (Guerrero-Pérez and Patience, 2020).

The analysis result of FTIR is an absorbance graph consisting of absorbance values on the Y axis and the number of cm^{-1} waves or frequencies on the X axis.

2.9.2 Liquid Chromatography−Mass Spectrometry (LC−MS)

LC−MS is a chemical analysis technique that combines the physical separation capabilities of liquid chromatography (HPLC) with mass spectrometry (MS) as the detector. LC−MS is an effective qualitative and quantitative analysis technique with a wide range of applications, such as clinical applications (drug therapy monitoring, toxicology, endocrinology, pediatrics, microbiology, proteomics) and industrial applications, including synthetic macromolecular (polymers) materials (Bugsel and Zwiener, 2019; Borrowman et al., 2020).

The principle of LC−MS is based on the mass spectrometry that continues the analysis detection of sample after separation process in HPLC by ionizing its molecules which will then sort and identify ions by mass, according to the fragmentation ratio (m/z). The two important components in this process are the ion source that will produce the ion, and the mass analyzer that detects the ion. LC−MS systems generally use several types of ion sources and mass analyzers that can be adjusted to the polarity of the compounds to be analyzed. Each ion source and mass analysis have some advantages and disadvantages so it needs to be adjusted to the type of information needed (Famiglini et al., 2021).

- Ion source

There is a wide variety of ionization techniques used in mass spectrometry. Things that must be considered in the selection of ionization techniques include the internal energy displaced during the ionization process and the physicochemical properties of ionizable analytes. An evolving ionization method includes; electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric pressure photo-ionization (APPI).

Electrospray ionization is generated by applying a strong electric field in atmospheric pressure to a liquid passing through a capillary tube with a weak flow (1−10 μL min^{-1}). The electric field is obtained by applying a potential difference of 3−6 kV between the capillary tube and the electrode counter separated by a distance of 0.3-2 cm so as to produce an electric field with an order of 106 V/m. This field triggers the accumulation of charges on the surface of the liquid at the end of the capillary pipe and breaks to form droplets (fine grains) with high charges. Then these fine grains by the heated inert gas are removed the solvent molecules left behind, thereby increasing the charge density on the particles resulting in an increase in surface tension, the granules split back to smaller (ion analytes with charge), then the analytes are transferred through the capillary holes to the mass analyzer. Electrospray has the characteristic of being able to produce double-charge ions from large molecules, which can be useful for increasing the sensitivity of the detector. The obtained detection limit reaches the attomole range of 10^{-15} mole.

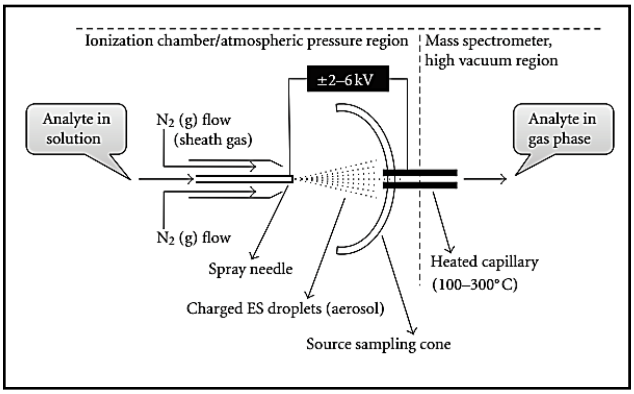

Figure 9. Schematic diagram of ESI source (Banerjee and Mazumdar, 2012)

Atmospheric pressure chemical ionization (APCI) is an ionization technique that uses the reaction of a gas–molecular gas at atmospheric pressure. It is generally used for polar and relatively non-polar compounds, with a medium molecular weight of about 1500 Da and giving a single charge ion. The analyte in the solution is fed into the nebulizer, the solution is converted into thin vapors by high-speed nitrogen. Then it is passed to the corona and ionization occurs, the ions from the ion source react with the analyte and ionize through charge transfer.

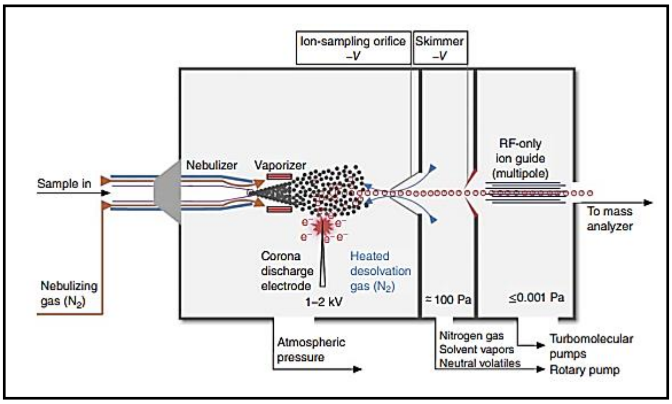

Figure 10. Schematic diagram of APCI source (Ceballos and Niessen, 2017)

Atmospheric pressure photoionization (APPI) is one of the latest developments of ion sources that utilize atmospheric pressure. The principle is to use photons to ionize gas phase molecules. The sample in the solution is evaporated by nebulizer heating similar to the method on APCI. After evaporation, the analyte interacts with the photons emitted by the release lamp. These photons trigger a series of gas-phase reactions that lead to the ionization process of the sample molecule. The difference from the APCI method is the use of photon-emitting lamps. The benefit of this method is that it has the potential to ionize non-polar compounds, efficiently for the analysis of flavonoid class compounds, steroids, pesticides, polyaromatic hydrocarbons (Harmita et al., 2019).

- Mass analyzer

After the gas phase ions are formed, the ions are then separated based on each mass. The physical property of the ions measured by the mass analyzer is the ratio of mass to charge (m/z). Hence, for double-charged ions, the value of m/z is the fractional part of the actual mass. The common mass analyzers used are quadrupoles, ion traps, and time-of-flight (TOF).

A quadrupole analyzer consists of four metal rods (quads) that are circular or ideally hyperbolic, arranged in parallel oppositely. Separating ions in an electric field that is varied against time, the electric field is created using radio frequency voltage (Rf) and constant direct current (DC) voltage and applied to a precision-made set (4 rods) of metal (AB and CD). AB and CD bar pairs are connected with opposite DC source ends so that when CD is negative then AB is positive. The ions that enter the space between the rods are only those that are stable with a certain m/z that reach the detector. If m/z and frequency do not match the requested conditions, the ion oscillates with a wide path causing the ion to collide with the rod or be attracted by vacuum.

Ion traps analyze the ions by trapping them in a chamber that can be detected by rings-shaped electrodes. The electrodes are connected by Rf and DC voltages. The voltage of Rf is applied arbitrarily, which is that if the Rf rises, the orbitals of heavy ions will be stable, while the light ions are unstable and there will be collisions with the electrode walls, then ejected to the detector.

Time-of-flight (TOF) analyzes the ions by collecting liquid chromatography results on spotter plate wells, then the sample is mixed with chromophores such as chrotonic amino acids that absorb light from high-intensity laser shots (using UV lasers) in an ion source. This target molecule then explodes, becoming a gas phase while ionizing it chemically. The fragments go to the flight tube through the focusing lens. The flight time of each fragment depends on its m/z ratio. The lighter fragments arrive at the detector first. To detect m/z fragments, each element of the diode-treated detector is activated only for a specific m/z, which allows selection only at a single mass per explosion (Harmita et al., 2019).

LC−MS is the only liquid chromatography technique that coupled with a mass spectrometer detector. According to Ali et al. (2021), LC−MS technology has some advantages compared to any other analysis methods as mentioned below:

1. Specificity. A typical and specific analysis results are obtained from the use of a mass spectrometer as a detector.
2. Broad application with a practical system. In contrast to GC−MS as a "classic" mass spectrometer, the application of LC−MS is not limited to volatile molecules and able to identify the highly polar components. In addition, sample preparation is quite simple in the absence of derivatization techniques.
3. Flexibility. Different tests can be run and developed with a high degree of flexibility and short time.
4. Rich in information. A number of quantitative as well as qualitative data can be obtained. This is due to the very fast fragmentation of ions with some considerable parameters.

2.9.3 Scanning Electron Microscopy (SEM)

SEM is one of the most commonly used instruments available as a tool for scanning and analyzing the morphology of microstructures. Analysis of SEM interpretation in the form of visualization of the morphology of a material, requires an understanding to the principle of a light optical (Mohammed and Abdullah, 2019). In brief, SEM consists of electron beams that will have a reaction with a sample to produce topology image and relative composition. After in contact with a sample, the electron beams will also produce secondary electron (SE) and backscattered electron, which then detect by each detector and finally visualized in a display computer (Davies et al., 2022).

SEM comprises an electron source, two or more electron lenses, a deflection system, a vacuum system, a control console, and an array of detectors that analyze the generated signals. The electron gun, or source, generates electrons and accelerates them to energy in the range of 0.1–30 kV. An electron gun is a source of electrons with high energy emitted from a filament such as tungsten, which functions as a cathode. This will result in electrons flowing towards the anode. In the principle of SEM measurement, it is known that there are two types of electrons, primary electrons and secondary electrons. Primary electrons are high-energy electrons emitted from a heated cathode. The cathodes used in common are tungsten (W). Tungsten is used as a cathode as they have the shortest lifetime (30–100 hours), largest source size (30–100 μm), widest energy spread (1–3 eV), and lowest brightness (1×10^5 A cm^{-2} sr^{-1}), all of which ultimately lead to the lowest resolution imaging (Davies et al., 2022). Secondary electrons are low-energy electrons, which are released by atoms on the surface, after being subjected by the electron beam of primary electrons. These secondary electrons that the detector (secondary or backscatter) will capture to and convert the signal into an image, known as a micrograph. The micrograph resulting from analysis with SEM provides some information related to the morphology of the sample surface, namely grain size, grain distribution, and surface porosity.

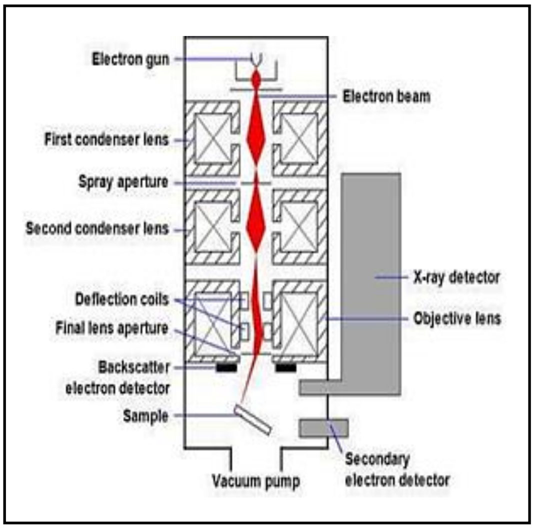

Figure 11. Schematic diagram of SEM (Zhang and Ulery, 2018)

III. RESEARCH METHOD

3.1 Time and Place of Research

This research was conducted in October 2022−April 2023 at the Inorganic/ Physical Chemistry Laboratory, University of Lampung for inhibitor synthesis (dimerization) and wheel test. Thin layer chromatography (TLC) and UV test were carried out at Organic Chemistry Laboratory, University of Lampung. Instrumentation analysis was carried out at the Integrated Laboratory and Technology Innovation Center (LTSIT) University of Lampung for FTIR and SEM, and Integrated Laboratory of Research and Calibration (LPPT) University of Gadjah Mada for LC−MS screening characterization.

3.2 Chemicals and Instruments

Chemicals used in this research were purchased from Merck include monomer of 4-vinylpyridine, methanol, ethyl acetate, n-hexane, ethanol, acetone, Sb_2O_3, $SnCl_2$, HCl 37%, NaCl, aquadest, $NaHCO_3$, anhydrous $CaCl_2$, CO_2 gas, N_2 gas, TLC silica gel 60G F_{254} 25 glass plates (20 cm × 20 cm), silicon carbide paper (grade 200, 400, 600, 800, 1000, and 1200), and mild steel (SAE/AISI Grade 1022) was purchased from Krakatau Steel.

Instruments used in this research include Thermo Nicolet Avatar 360 FTIR and LC-Q Exactive Plus Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Fisher Scientific, Massachusetts, USA), Scanning Electron Microscope (SEM, ZEISS, Oberkochen, Germany), Heidolph VV2000 Rotary Evaporator, Analytical Balance METTLER AE 200, UV lamp 254 nm, magnetic stirrer, micropipette, micrometer, laboratory glassware, and Duran bottles.

3.3 Research Procedure

3.3.1 Dimerization of 4-Vinylpyridine

The dimerization of 4-vinylpyridine using oxidative coupling was carried out by adopted the Botta et al. (2020) method with several modifications. A 0.105 gram of 4-vinylpyridine monomer (1 mmol) was added into a three-neck flask containing 2.05 mL of HCl 37% in 15 mL of methanol equipped with a magnetic stirrer. The system was fed with nitrogen gas and stirred on a magnetic stirrer for 7 hours at room temperature. After 7 hours, the stirring was stopped and the dimerization product was dried with $CaCl_2$ anhydrous. The final stage was concentrating them from the solvent using rotary evaporator. Dimerization process was controlled with TLC analysis at the 1st, 3rd, and 7th hours. Confirmation of the formation of 4-vinylpyridine dimer was carried out through the analysis of functional groups and molecular weight using FTIR with the scan range was about 4000−650 cm^{-1} and LC−MS with the following operational conditions mentioned below.

3.3.2 LC−MS Screening Characterization

The separation of dimerized 4-vinylpyridine product was performed by UPLC BEH C18 reverse-phase column (2.1 × 50 mm, particle size 1.7 µm). The two mobile phases used for gradient elution were: A, water with formic acid 0.1% and B, acetonitrile with formic acid 0.1% v/v), the flow rate was 0.4 µL/min, and the injection volume was 2.5 µL. A full scan mode was achieved in the range of 50–1200 m/z with the following conditions: capillary voltage 3.0 kV, cone voltage 30 V, and ionization source temperature corresponded to 500 °C. The mass spectra were recorded in positive ion mode, $[M+H]^+$. MestReNova© 14.3.2 software (Mestrelab Research, Santiago de Compostela, Spain) was used for identification and structure elucidation of 4-vinylpyridine dimer compounds.

3.3.3 Inhibitor Solution Preparation

15000 mgL^{-1} of inhibitor solution 20 mL was prepared by adding 0.3 gram of 4-vinylpyridine dimer into volumetric flask and diluted with methanol solvent up to the mark. The solution was then homogenized and put into vial bottle. The equation can be shown in Appendix 2.

3.3.4 Mild Steel Sample Preparation

Mild steel specimen (SAE/AISI Grade 1022) were cut with a size of 2×1×0.1 cm, then sanded with silicon carbide paper with a roughness grade of 200, 400, 600, 800, 1000, and 1200. Furthermore, it was cleaned with ethanol solution and then measured the mass as well as surface area.

3.3.5 Corrosion Rate Measurement and Inhibition Test

The corrosion rate measurement and activation test of 4-vinylpyridine dimer as an inhibitor was evaluated by wheel test method. 175 mL of brine solution was put into each of six glass bottles. A certain volume of 15000 mg L^{-1} dimer solution was added from a micropipette into each bottles in order to obtain the dimer concentrations of 50, 100, 150, 200 mgL^{-1} (Appendix 2) and the solution was fed with CO_2 gas for 45 minutes. The weighed mild steel coupons were put into each glass bottles and the flow of CO_2 gas was carefully stopped. The bottle was directly closed and left for 24 hours. The coupons were removed from the bottles and cleaned with Clarke's solution (a solution consisting of Sb_2O_3 2% and $SnCl_2$ 5% dissolved with concentrated HCl) for 45 seconds to remove corrosion products from the surface. The coupons were then washed with water and ethanol, then dried. After drying the coupons were re-weighed for corrosion rate measurement.

3.3.6 Mild Steel Surface Morphology Analysis

Morphology of the mild steel surface in a corrosive solution medium saturated with CO_2 gas both without the addition of inhibitor and with the addition of inhibitor were analyzed with scanning electron microscope (SEM).

V. CONCLUSION AND SUGGESTION

5.1 Conclusion

This conducting research has put several points into the following conclusion:

1. The 4-vinylpyridine dimer has been obtained with 12.05% of the yield and appeared to be a transparent yellow diluted liquid.
2. TLC control of the stirred compound has slightly the same spot compared to the monomer sample, while the TLC of dimer product provided a lower spot than the monomer.
3. FTIR comparation between the monomer and the dimerized compound showed the loss of allyl (C=C) group absorption at 1603 cm^{-1} and unsaturated vinyl ($-CH=CH_2$) group at 932 cm^{-1} at the spectrum of the dimerized compound.
4. LC-MS screening analysis and structure elucidation results showed that the formation of 4-vinylpyridine dimer, D(4-VP), identified at retention time of 6.18, 6.59, and 16.22 minutes.
5. Wheel test results demonstrated that D(4-VP) can suppress the corrosion rate (CR). According to the influence on an increase of D(4-VP) concentration, the CR gradually decreased from 5.01×10^{-1} to 1.85×10^{-1} mmpy and the inhibition efficiency (IE) increased from 30.65 to 63.12%.
6. The result of conducting corrosion rate inhibition was also supported by the SEM’s surface image comparation of mild steel both with no presence of inhibitor and with presence of inhibitor, where the evident was that a significant reduction on the number of corrosion pit and crack of mild steel with presence of inhibitor.

5.2 Suggestion

The suggestion for the upcoming research is as follows:

1. Based on the product yield (%) obtained from the oxidative coupling’s dimerization of 4-vinylpyridine using hydrochloric acid (HCl) as catalyst, it is necessary to put an attempt for using another selective type of acid catalyst. For instance, transition metal-based Lewis acid is one of the common used acid catalyst-derived either for homocoupling (dimer synthesis) or heterocoupling (hybrid synthesis).
2. The dimerization must be conducted by paying attention to every step of the process to obtain more selective targeted dimer, as the conducting method can probably produce other macromolecule derivatives such as trimer, tetramer, oligomer, and polymer.
3. The TLC analysis must be carried out by using the same eluent to show a suitability of the dimerization process control and the obtained dimer product comparation to its monomer.
4. The corrosion inhibition activity of 4-vinylpyridine dimer must be conducted under different temperature conditions to obtain the best activity value of 4-vinylpyridine dimer in protecting mild steel over the corrosion.
5. The electrochemical method, as expected to be taken part in this research, was unfortunately not carried out for corrosion inhibition evaluation due to the consideration of instrumentation analysis taking place and limitation of research time schedule. Therefore, the value of 4-vinylpyridine dimer as corrosion inhibitor needs to be progressed by electrochemical evaluation for the upcoming research.

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