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UTILIZATION OF PALM SHELL LIQUID SMOKE AS A CALCIUM CARBONATE SCALE FORMATION INHIBITOR

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ABSTRACT

This study evaluates the effectiveness of palm shell liquid smoke and ethylenediaminetetraacetic acid as inhibitors of calcium carbonate crystal growth at solution concentrations of 0.0250 – 0.0500 M using the unseeded experiment method. The chemical composition of palm shell liquid smoke was characterised using IR and GC-MS, while crystal characterisation was performed using PSA, SEM, and XRD to observe particle size, morphology, and crystal phase. The results showed that palm shell liquid smoke inhibited crystal formation by 28-41%, with optimal performance at a 25% concentration, while ethylenediaminetetraacetic acid reached 79-84%. The addition of inhibitors resulted in smaller crystals and a more uniform particle size distribution. SEM indicated changes in crystal morphology, and XRD confirmed a phase shift from calcite to aragonite and vaterite. This demonstrates that palm shell liquid smoke effectively disrupts crystallisation and has potential for preventing scale in industrial applications.

Keywords: Calcium Carbonate, Green Scaling Inhibitor, Ethylenediaminetetraacetic Acid, Crystal Growth Inhibition, Palm Shell Liquid Smoke.

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INTRODUCTION

The formation of calcium carbonate ($CaCO_3$) scale is a common problem encountered in piping systems, industrial equipment, and water treatment facilities.[1-7] Scale deposits on equipment surfaces can obstruct flow, reduce thermal efficiency, and increase operational and maintenance costs.[8-11] Various efforts have been made to address this issue, one of which is the use of scale inhibitors. Inhibitors function to prevent or inhibit scale formation, thus maintaining optimal equipment performance.[12-16] In modern industries, chemical-based inhibitors like Ethylenediaminetetraacetic acid (EDTA) are often used due to their high effectiveness in preventing scale formation. EDTA works by binding calcium ions, preventing them from combining with carbonate ions to form scale. However, the use of synthetic chemicals like EDTA raises environmental concerns, as they are not environmentally friendly and can be toxic to aquatic ecosystems.[17] With growing environmental awareness, many studies are shifting towards utilising natural materials as eco-friendly alternatives for scale inhibitors.[18] One abundant and potentially useful natural resource is waste from the palm oil industry. Palm shell waste is plentiful and can be further processed into liquid smoke, which may be applied as an inhibitor for $CaCO_3$ scale formation. Additionally, charcoal produced from pyrolysis can serve as an adsorbent. This study aims to explore the potential of palm shell liquid smoke as an inhibitor for $CaCO_3$ scale formation and to compare its effectiveness with EDTA. It is hoped that the results of this study will contribute to more environmentally friendly scale management solutions while optimising the utilisation of abundant palm oil industry waste.

EXPERIMENTAL

Material and Methods

The materials used in this study include anhydrous $CaCl_2$, Na_2CO_3, distilled water, palm shells, and EDTA. All chemicals were sourced from Merck, Germany. The palm shells were obtained from PT.

Kalirejo Lestari in Central Lampung. The equipment used in this study includes standard laboratory glassware, a water bath, plastic bottles, a magnetic stirrer, a spinbar, an oven, an analytical balance, filter paper, a digital pH meter (Metrohm, 827 pH Lab), a Particle Size Analyzer (PSA) (SZ-100V2 made in Japan), a Scanning Electron Microscope (SEM) (JSM 6360 LA, JEOL, Japan), an X-Ray Diffraction (XRD) machine (Panalytical Xpert 3 Powder, England), a Fourier Transform Infrared (FTIR) Spectrophotometer (Bruker, Alpha II, USA), and Gas Chromatography-Mass Spectrometry (GC-MS).

General Procedure

Palm shell liquid smoke was obtained through a pyrolysis process at a temperature of 200-250℃ for 5-8 hours. After obtaining the liquid smoke from condensation, it was left to settle and then filtered. The characterisation of the obtained liquid smoke was performed using an IR Spectrophotometer to identify the functional groups present in the palm shell liquid smoke and GC-MS to determine its chemical composition.[19] In this study, palm shell liquid smoke was used at concentration variations of 5%, 15%, 25%, 35%, and 45%. The preparation of the EDTA inhibitor solution with a 5% concentration was done by taking 5 grams of EDTA, then diluting it with distilled water in a 100 mL volumetric flask, and homogenising it. The same procedure was followed for preparing inhibitor solutions with concentrations of 15%, 25%, 35%, and 45%.

Testing Inhibitors in Inhibiting the Growth Rate of $CaCO_3$ Crystals

Determination of $CaCO_3$ Growth Rate without Adding Inhibitors: To prepare a 0.0250 M $CaCO_3$ growth solution, 300 mL of 0.05 M $CaCl_2$ and 0.05 M Na_2CO_3 solutions were mixed and homogenised for 15 minutes under magnetic stirring at 90°C. After stirring, the pH of the mixture was measured. Then, the $CaCO_3$ solution (50 mL) was transferred into five plastic bottles and immersed in a 90°C water bath. Observations were made every 20 minutes for the first bottle and every 10 minutes for the subsequent bottles. The crystals obtained were filtered and dried at 105°C for 3-4 hours, then weighed until their weight became constant. The experiment was repeated for $CaCO_3$ crystallisation solution concentrations of 0.0375 M and 0.0500 M.

Determination of $CaCO_3$ Growth Rate with the Addition of Inhibitors: The growth solution was prepared from 300 mL of 0.0500 M anhydrous $CaCl_2$ and 0.0500 M Na_2CO_3, with the addition of palm shell liquid smoke and EDTA. The solution was continuously stirred at 90°C for 15 minutes, and the pH was then measured. The resulting mixed solution was divided into five plastic bottles, each containing 50 mL, and placed in a water bath at 90°C. Observations were made every 20 minutes for the first bottle and every 10 minutes for the subsequent bottles. The crystals formed in each plastic bottle were filtered with filter paper and dried in an oven at 105°C for 3-4 hours, then weighed until the weight became constant. The experiment was repeated with variations in the $CaCO_3$ growth solution concentrations of 0.0375 M and 0.0500 M, as well as variations in palm shell liquid smoke and EDTA.

Detection Method

The growth rate of calcium carbonate scale was analysed using MS Excel based on the data of weight changes of the precipitate over time, both without and with the presence of inhibitors and growth solutions at varying concentrations. The morphology of the $CaCO_3$ scale was analysed using SEM, the particle size distribution was analysed using a particle size analyser (PSA), and the crystal structure of $CaCO_3$ was analysed using XRD.[20] The effectiveness of the inhibitor (% EI) was calculated using the Patel and Finan Equation (Eqn.-1).[21]

$$\text{Inhibitor Effectiveness (\%)} = 100\% \times \frac{(Ca - Cb)}{(Cc - Cb)} \qquad (1)$$

Where:

Ca = Weight of $CaCO_3$ after the addition of the inhibitor at a state of equilibrium (g)

Cb = Weight of $CaCO_3$ without the inhibitor at a state of equilibrium (g)

Cc = Initial weight of $CaCO_3$ (g)

RESULTS AND DISCUSSION

Analysis of Palm Shell Liquid Smoke Content

An IR spectrophotometer is used to identify organic and inorganic compounds through molecular vibration and rotation spectra, helping to identify functional groups. Meanwhile, GC-MS analysis integrates gas chromatography (GC) for separation with mass spectrometry (MS) for identification and quantification, with high-accuracy analysis of components in complex mixtures[22], such as in palm shell liquid smoke. The IR analysis of palm shell liquid smoke provides in-depth information about the chemical structure of compounds that may be involved in the mechanism of inhibiting calcium carbonate scale. By identifying functional groups such as carboxylates, phenols, and carbonyls, IR spectroscopy helps in understanding how components in the liquid smoke interact with calcium ions to inhibit scale formation. Fig.-1 shows the characterisation of palm shell liquid smoke, indicating absorption bands present in the liquid smoke. The band at 3265.1 cm^{-1} indicates a strong intensity hydroxyl (O-H) alcohol group.[23] The band at 2087.3 cm^{-1} suggests the presence of an alkyne (C≡C) group with low intensity.[24] The band at 1640.0 cm^{-1} indicates a medium intensity carbonyl (C=O) group from carboxylic acid.[25] The band at 1394.0 cm^{-1} indicates the presence of a phenol O-H group[26], and the band at 1274.7 cm^{-1} suggests the presence of an ether (C-O-C) group[27], both with low intensity. The band at 1013.8 cm^{-1} shows the presence of a primary alcohol (O-H) group [28] with low intensity. The results of the IR spectrophotometer analysis in Fig.-1 indicate that palm shell liquid smoke contains several functional groups that may inhibit the formation of calcium carbonate scale. The liquid smoke contains phenol O-H groups, carboxylate (C=O) groups from carboxylic acids, ether (C-O-C) groups, and primary alcohol (O-H) groups (Table-1). The IR data support the analysis results obtained using GC-MS. GC-MS was used in the characterisation of palm shell liquid smoke to identify and quantify the chemical compounds contained within it. The liquid smoke contains various volatile organic compounds such as acids, phenols, aldehydes, ketones, esters, and aromatic hydrocarbons. GC-MS is capable of separating and accurately identifying these compounds. By using GC-MS, the profiling of the main components of liquid smoke can be performed. This is important for understanding the composition of compounds that may provide functional properties, such as scale inhibitors, antimicrobial activity, or preservative qualities. Liquid smoke is produced from the pyrolysis of palm shells, breaking down biomass components (such as cellulose, hemicellulose, and lignin) into simpler chemical compounds. GC-MS can detect pyrolysis products, including aromatic compounds and organic acids. In other words, GC-MS is a crucial tool for in-depth analysis of the chemical composition of liquid smoke, which may have implications for its use as an inhibitor of calcium carbonate scale formation. GC-MS analysis of palm shell liquid smoke used as a calcium carbonate ($CaCO_3$) scale inhibitor provides information about the chemical compounds responsible for its ability to inhibit or prevent calcium carbonate scale formation. Table-2 shows the results of the chemical component analysis of palm shell liquid smoke using GC-MS. Fig.-2 shows the results of the chemical component analysis of palm shell liquid smoke using GC-MS. The analysis results reveal the presence of 24 chemical components in palm shell liquid smoke, marked by the appearance of 24 peaks. The GC-MS analysis results (Table-2) show that the chemical composition of palm shell liquid smoke is dominated by phenol derivatives (59.22%), phenol (11.37%), catechol (4.83%), guaiacol (3.16%), 4-methylpentenoic acid (2.13%), and palmitic acid (1.45%). The presence of organic acids in liquid smoke, as shown in Table-1, contributes to its preservative properties and the acidity level (pH) of the liquid smoke, which ultimately plays a role in inhibiting calcium carbonate scale formation.

Table-1: Functional Groups of Palm Shell Liquid Smoke from IR Analysis

Functional Groups	Compounds	Bond Type	Wave Number (cm^{-1})
O-H	Alcohol	Stretch	3265.1
C≡C	Alkyne	Stretch	2087.3
C=O	Carboxylic Acid	Stretch	1640.0
O-H	Phenol	Bend	1394.0
C-O-C	Ether	Stretch	1274.7
O-H	Primary Alcohol	Stretch	1013.8

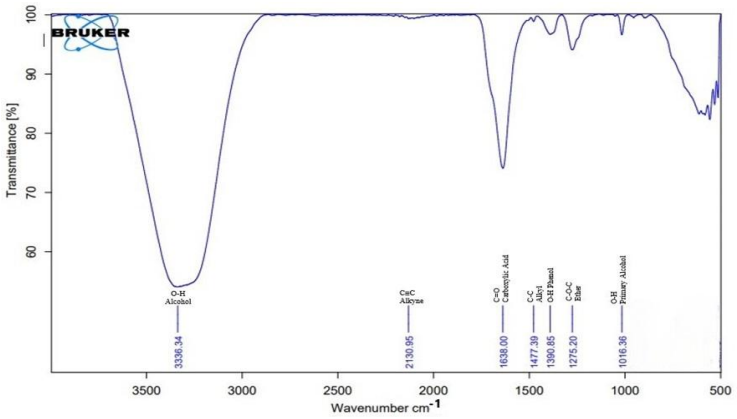


Fig.-1: FTIR Spectrum of Palm Shell Liquid Smoke

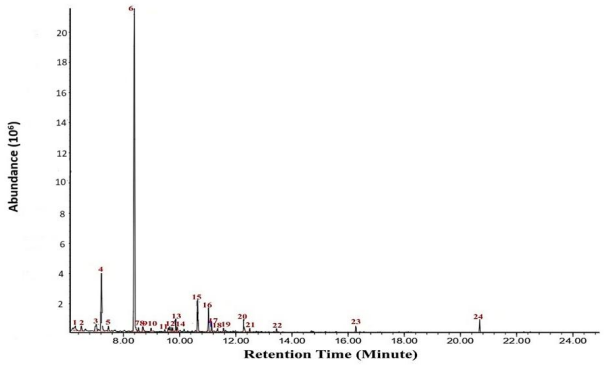


Fig.-2: Chromatogram of GC-MS Analysis of Palm Shell Liquid Smoke

Table-2: Chemical Components of Palm Shell Liquid Smoke

Peak	Retention Time	Percent Area	Compound Name
1	6.23	1.60	Butyrolactone
2	6.50	1.06	3-methylbutanoic acid
3	7.03	2.13	4-methylpentenoic acid
4	7.22	11.37	Phenol
5	7.47	1.03	Furfuryl alcohol
6	8.39	59.22	Phenol derivatives
7	8.55	0.62	Benzyldimethylsilyl(+/-)-2-phenylbutanoate
8	8.70	1.32	Hexanoic acid
9	8.99	0.52	2-methoxyphenol
10	9.64	1.36	Levulinic acid
11	9.70	0.64	3-pyridinol
12	9.76	0.56	m-cresol
13	9.87	1.83	2-carboxyloxolenic acid
14	9.92	0.59	p-cresol
15	10.65	4.83	catechol
16	11.04	3.16	guaiacol
17	11.14	1.45	4-hydroxylbutanoic acid
18	11.36	0.61	Benzoic acid
19	11.57	0.64	6-methylheptanoic acid
20	12.30	2.13	Catechol derivatives

21	12.50	0.56	Butanoic acid
22	13.46	0.56	2,3-dimethoxyphenol
23	16.28	0.77	4-hydroxylbenzoic acid
24	20.68	1.45	Palmitic acid

Effect of Inhibitors on $CaCO_3$ Scale Growth

The pattern of $CaCO_3$ crystal growth rates, both without and with the presence of inhibitors at a calcium carbonate growth solution concentration of 0.050 M, can be observed in Figs.-3 and 4. Fig.-3 shows the $CaCO_3$ crystal growth rate with the addition of palm shell liquid smoke at concentration variations of 0 – 45%. Fig.-4, on the other hand, illustrates the $CaCO_3$ crystal growth rate with the inclusion of EDTA at the same concentration variations as with palm shell liquid smoke. Figs.-3 and 4 show that the addition of palm shell liquid smoke and EDTA effectively slowed down the rate of $CaCO_3$ crystal growth. When comparing the effectiveness of palm shell liquid smoke and EDTA in inhibiting $CaCO_3$ crystal growth, EDTA's ability is slightly higher than that of palm shell liquid smoke at the same concentrations. A more detailed observation of the effectiveness of both inhibitors in inhibiting $CaCO_3$ crystal growth can be seen from the Inhibitor Effectiveness Percentage (% EI) using Equation 1, as presented in Tables-3 and 4. Table-3 shows the effectiveness of palm shell liquid smoke as an inhibitor in preventing $CaCO_3$ crystal growth at growth solution concentrations of 0.0250, 0.0375, and 0.0500 M, with inhibitor concentration variations from 0 to 45%. Meanwhile, Table-4 presents the effectiveness of EDTA as an inhibitor in preventing $CaCO_3$ crystal growth at the same solution concentrations with the same inhibitor concentration variations. Tables 3 and 4 also display the pH values of the solution before and after the addition of the inhibitor. Table-3 indicates that the highest %EI (40.56%) for palm shell liquid smoke occurred at a growth solution concentration of 0.0250 M with the addition of 25% liquid smoke. A similar condition occurred with the addition of EDTA inhibitor (Table-4), where the highest %EI (83.82%) was achieved at a growth solution concentration of 0.0250 M with the addition of 25% EDTA solution. Based on Tables-3 and 4, the optimal effectiveness of palm shell liquid smoke and EDTA was observed at a growth solution concentration of 0.0250 M, with %EI values of 40.56% and 82.83%, respectively, with an inhibitor concentration of 25%. In this case, increasing the inhibitor concentration beyond 25% did not correspond with increased inhibitor effectiveness in preventing $CaCO_3$ scale growth. The scale inhibition ability does not always increase proportionally with inhibitor concentration, as observed in this study. This is due to two factors: (a) after reaching saturation, all active binding sites for the inhibitor on scale-forming ions are occupied, so further addition of the inhibitor does not enhance the inhibitory effect; and (b) at high concentrations, the inhibitor can form complexes with scale-forming ions (in this case, calcium ions). However, if the concentration is too high, the inhibitor may compete with itself for binding to these ions, potentially reducing its efficiency. Each inhibitor has an optimal concentration point, which is the amount at which scale inhibition effectiveness is maximised. If the inhibitor concentration exceeds this optimal point, any further increase in inhibition effect becomes minimal, or the effectiveness may even decrease. This optimal point is highly dependent on the type of inhibitor, the type of scale-forming ions, and the system conditions (such as temperature, pressure, and pH). Therefore, it can be concluded that inhibitor effectiveness does increase with concentration up to a certain limit. However, after reaching the optimal point, its effectiveness will no longer increase significantly and may even decrease. Thus, determining the optimal inhibitor dosage is key to achieving maximum effectiveness in scale prevention while maintaining cost efficiency and avoiding adverse effects on the system. This occurred in this study, where adding liquid smoke beyond 25% did not further enhance its ability to inhibit calcium carbonate crystal growth.

In Tables-3 and 4, it can be observed that the addition of liquid smoke and EDTA causes a decrease in the pH of the growth solution from the initial pH of the solution without inhibitors, which ranged from 9 to 10, to a range of 3 to 5 after the addition of inhibitors, depending on the concentration of the growth solution. pH plays an important role in influencing $CaCO_3$ crystal growth[29-31], especially when palm shell liquid smoke and EDTA are added. This is related to changes in the chemical composition of the solution, the availability of ions in the solution, and the interaction of active compounds with the crystal surface. Here are some reasons why pH affects calcium carbonate crystal growth in the context of adding liquid smoke and EDTA.

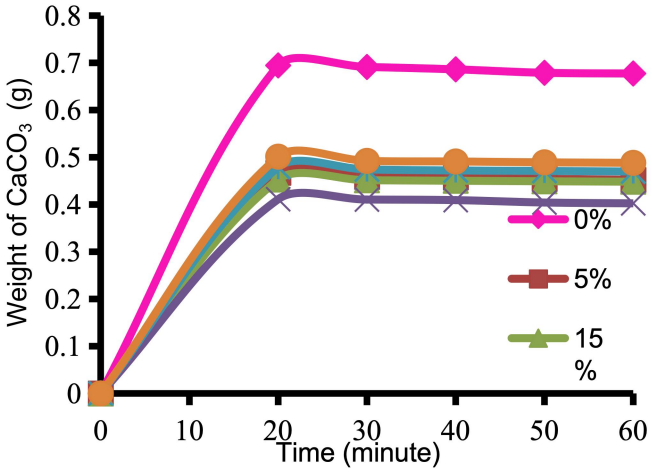


Fig.-3: Graph of $CaCO_3$ Crystal Growth Rate with the Inclusion of Palm Shell Liquid Smoke at a Crystallisation Solution Concentration of 0.0250 M

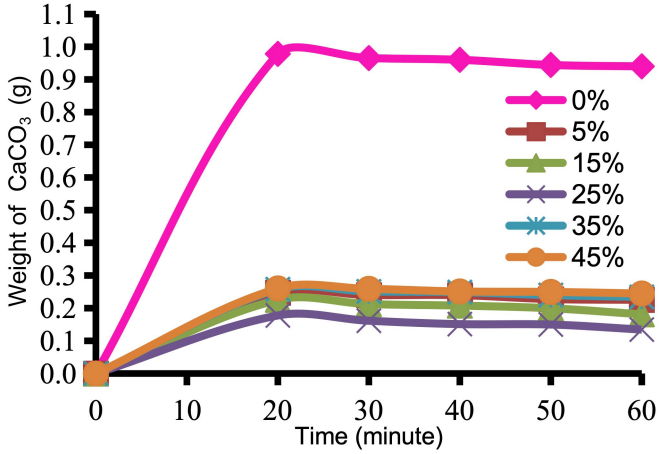


Fig.-4: Graph of $CaCO_3$ Crystal Growth Rate with the Inclusion of EDTA in a Crystallisation Solution with a Concentration of 0.0250 M

The Solubility of Calcium Carbonate is Affected by pH

Calcium carbonate ($CaCO_3$) has solubility that depends on pH. At low pH (acidic conditions), $CaCO_3$ tends to dissolve more readily due to its reaction with H^+ ions, producing calcium ions (Ca^{2+}) and carbon dioxide (CO2) as shown in the following reaction:

$$CaCO_3\ (s) + 2H^+\ (aq) \rightarrow Ca^{2+}\ (aq) + CO_2(g) + H_2O\ (l)$$

At higher pH (basic conditions), the solubility of $CaCO_3$ decreases, allowing more carbonate ions (CO_3^{2-}) to combine with calcium ions (Ca^{2+}) and form $CaCO_3$ crystals. The addition of liquid smoke or EDTA, which affects the solution's pH, can shift this solubility balance, either enhancing or inhibiting crystal formation.

Acidic Components in Liquid Smoke and EDTA

EDTA in the growth solution is acidic, and palm shell liquid smoke also contains organic acids, which lower the pH of the solution, creating an acidic environment. At low pH, $CaCO_3$ is more soluble, and crystal growth is inhibited because fewer crystal-forming ions are available in solid form. By lowering the pH through the addition of liquid smoke and EDTA, calcium carbonate crystal growth can be inhibited, as the formation of $CaCO_3$ scale becomes more difficult in a more acidic environment. If the pH decreases,

$CaCO_3$ will tend to dissolve, while at higher pH (basic conditions), crystal growth may increase because the solubility of carbonate decreases, making the scale-forming ions more available to combine.

Table-3: The Effectiveness of Palm Shell Liquid Smoke as an Inhibitor in Preventing $CaCO_3$ Crystal Growth

No.	Addition of Inhibitors (%)	pH	0.0250 M	pH	0.0375 M	pH	0.0500 M
			Inhibitor Effectiveness (%)		Inhibitor Effectiveness (%)		Inhibitor Effectiveness (%)
1	0	9.20	0.00	9.47	0.00	10.24	0.00
2	5	5.19	33.18	5.22	24.01	5.40	17.08
3	15	5.19	34.31	5.22	28.46	5.38	20.35
4	25	5.15	40.56	5.20	35.31	5.36	27.67
5	35	5.21	30.97	5.23	26.02	5.42	15.96
6	45	5.22	28.18	5.23	23.38	5.43	12.62

Table-4: The Effectiveness of EDTA as an Inhibitor in Preventing $CaCO_3$ Crystal Growth

No.	Addition of Inhibitors (%)	pH	0.0250 M	pH	0.0375 M	pH	0.0500 M
			Inhibitor Effectiveness (%)		Inhibitor Effectiveness (%)		Inhibitor Effectiveness (%)
1	0	9.20	0.00	9.47	0.00	0.24	0.00
2	5	3.97	75.35	3.98	72.47	4.02	62.57
3	15	3.96	78.56	3.97	74.88	4.01	64.86
4	25	3.92	83.82	3.91	80.03	3.93	78.78
5	35	3.97	74.28	3.99	70.68	4.01	59.43
6	45	3.98	73.58	3.99	68.06	4.02	58.22

Particle Size Analyser (PSA) Analysis

The PSA was applied to characterise the size and distribution of $CaCO_3$ particles prior to and following the addition of palm shell liquid smoke inhibitor, to monitor how the presence of the inhibitor (palm shell liquid smoke) affects the size of $CaCO_3$ crystals. Inhibitors can inhibit growth or slow down crystal aggregation, which should be reflected as changes in the particle size distribution. If the particle size is smaller after the addition of the inhibitor, it indicates that the liquid smoke successfully prevented larger crystal growth or particle agglomeration. PSA provides particle size distribution, allowing identification of whether the addition of the inhibitor makes the particle size distribution more uniform. An effective inhibitor will result in more homogeneous particle sizes because it prevents uncontrolled crystallisation and the formation of large agglomerates. Overall, PSA provides quantitative data on the changes in particle size and distribution caused by the addition of the inhibitor, helping evaluate the effectiveness and mechanism of scale inhibition by palm shell liquid smoke. PSA can measure particles ranging from nanometers to micrometres, making it a valuable tool in various applications. The PSA analysis was conducted on the $CaCO_3$ scale with and without the addition of palm shell liquid smoke inhibitor, as shown in Fig.-5. The addition of EDTA in the $CaCO_3$ growth solution was not analysed, as the amount of $CaCO_3$ crystals produced after the addition of EDTA was very small, insufficient for PSA analysis. The graph in Fig.-5 shows a comparison of the $CaCO_3$ crystal particle size distribution at a growth solution concentration of 0.0250 M, without and with the addition of palm shell liquid smoke inhibitor (25%). The average particle size without the inhibitor was 3642.2 nm, and upon the addition of palm shell liquid smoke, it reduced to 471.7 nm. This indicates that the addition of palm shell liquid smoke effectively inhibited $CaCO_3$ crystal growth and reduced the distribution of $CaCO_3$ crystal sizes. An effective inhibitor results in more homogeneous particle sizes, as it prevents uncontrolled crystallisation and the formation of large agglomerates.[32] The $CaCO_3$ particle size distribution became smaller and more uniform after the addition of palm shell liquid smoke, due to the influence of organic compounds present in the liquid smoke. Palm shell liquid smoke contains various active organic compounds, such as phenols and organic acids, which act as crystallisation inhibitors. These compounds disrupt the calcium carbonate crystal

growth process by binding to the growing crystal surfaces. When these organic compounds bind with Ca^{2+} or CO_3^{2-} ions, they inhibit these ions from incorporating into the calcium carbonate crystal lattice, thereby slowing down the crystal growth rate. As a result, the formed particles tend to be smaller and are unable to grow into larger crystals.

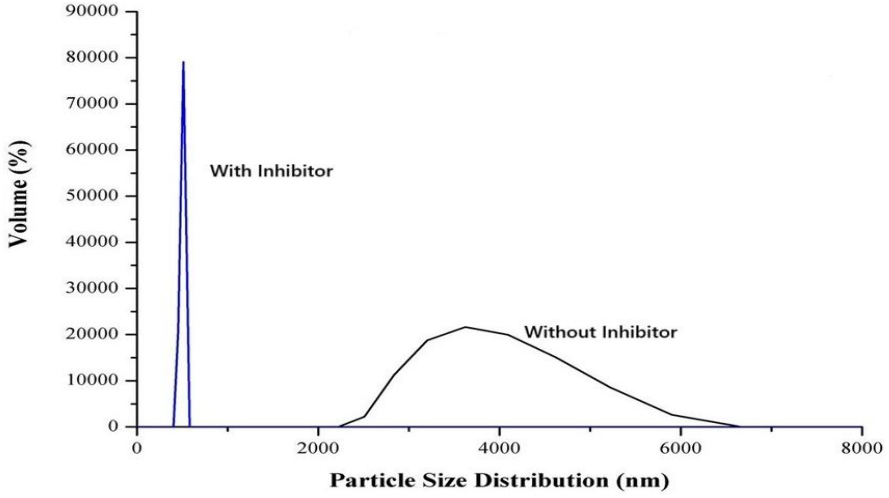
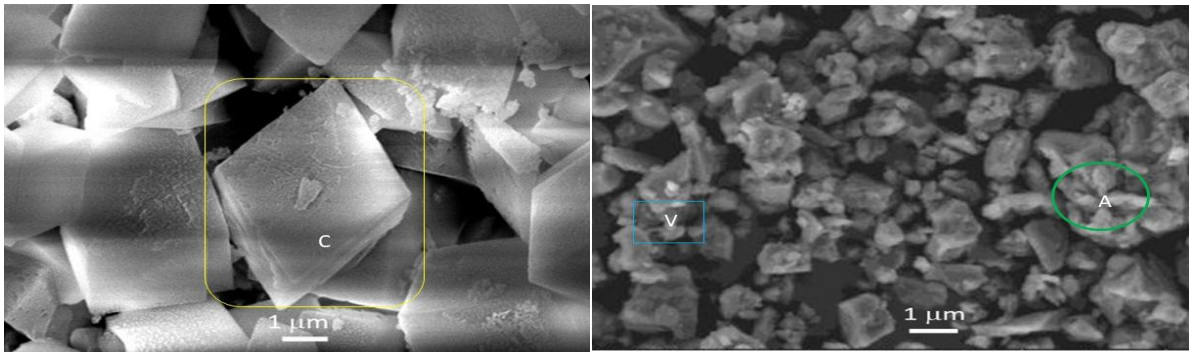


Fig.-5: Calcium Carbonate Particle Size Distribution with and without the Presence of Inhibitors

Moreover, at a concentration of 0.0250 M, palm shell liquid smoke contains sufficient inhibitory compounds that effectively hinder both nucleation (the initial formation of crystal seeds) and crystal growth. These inhibitors work by adsorbing onto the crystal seed surfaces or altering the crystal surface structure, thereby impeding crystal growth. Organic compounds can cover the functional sites located on the crystal surface, preventing the crystals from accumulating more ion-building blocks. Due to this growth inhibition, the calcium carbonate crystals formed remain small, and the particle size distribution becomes more uniform and smaller.[33-35]

Scanning Electron Microscopy (SEM) Analysis

SEM analysis was used to observe the differences in the structure of the $CaCO_3$ scale with and without the addition of inhibitors. This analysis was conducted on $CaCO_3$ crystals without the addition of inhibitors at a growth solution concentration of 0.0250 M, and with the addition of palm shell liquid smoke inhibitor at a 25% concentration in a 0.0250 M growth solution, using the unseeded experiment method. The SEM analysis results are shown in Fig.-6. The addition of the inhibitor caused a dramatic change in the morphology and size of the $CaCO_3$ crystals. After the addition of the palm shell liquid smoke inhibitor (Fig.-6b), the $CaCO_3$ crystal size generally became smaller compared to the crystals without the inhibitor (Fig. 6a). This data supports the observations made using PSA (Fig.-5) and the inhibitor's efficiency data in inhibiting calcium carbonate crystal formation. Therefore, it can be concluded that palm shell liquid smoke acts as an inhibitor in slowing the rate of calcium carbonate crystals. SEM observations show the differences in calcium carbonate crystal morphology between the solution without the inhibitor and the solution with the addition of palm shell liquid smoke at the same growth solution concentration (0.0250 M). The liquid smoke inhibitor works by disrupting crystal growth, altering the size and shape of the crystals, and affecting the crystal surface, which is clearly visible through SEM analysis. These results provide visual evidence that strengthens the growth rate and PSA data analysis regarding calcium carbonate crystal growth with or without the addition of inhibitors. When palm shell liquid smoke is added, the size of the $CaCO_3$ crystals is smaller compared to the crystals without the inhibitor. Organic inhibitors from liquid smoke, such as phenols and organic acids, disrupt crystal growth, resulting in smaller crystals. SEM observations without the inhibitor (Fig.-6a) show that the calcium carbonate crystals formed are relatively large, with more regular and well-defined shapes. With the addition of the inhibitor (Fig.-6b), the crystals appear smaller and more uniform in size, with clear inhibition of crystal growth.



(a) (b)

Fig.-6: Morphology of $CaCO_3$ Scale at 10,000x Magnification (a) without Inhibitor and (b) with Palm Shell Liquid Smoke Inhibitor

Fig.-6 also shows changes in the structure of $CaCO_3$ crystals before and after the presence of the inhibitor. Fig.-6a shows that $CaCO_3$ crystals without the inhibitor are larger and more regular, forming calcite (C) crystals, which have cubic or rhombohedral shapes with sharp edges and a more orderly structure (Fig. 6a). After the addition of the inhibitor (Fig.-6b), the calcium carbonate crystal morphology becomes more irregular, forming vaterite (V) or aragonite (A), which are polymorphic forms of $CaCO_3$ that are less stable than calcite, and these forms become more dominant. With the inhibitor, the crystal morphology appears more amorphous, with rounded edges, or forms less stable vaterite or aragonite. This occurs because the organic compounds in the inhibitor disrupt the arrangement of calcium and carbonate ions in the crystal lattice. Thus, the inhibitor has proven effective in inhibiting crystal growth, altering the morphology, reducing crystal size, and preventing the formation of hard-to-remove scale. Without the inhibitor, $CaCO_3$ crystals are dominated by calcite (C), a hard-scale type that is difficult to clean (Fig.-6a). Meanwhile, after the addition of the inhibitor, the morphology of the $CaCO_3$ crystals changes from calcite (C) to aragonite (A) and vaterite (V), which are soft-scale types that are softer and easier to remove (Fig.-6b).[36-38]

X-Ray Diffraction (XRD) Characterisations

XRD characterization of $CaCO_3$ crystals with and without the addition of palm shell liquid smoke inhibitor was conducted to identify and analyse the crystal structure and phases of the formed calcium carbonate, thereby supporting the SEM and PSA data. XRD provides information about polymorphism, crystal size, and crystal quality, which may be affected by the addition of inhibitors. The characterisation results are shown in Fig.-7. Calcium carbonate can form in several polymorphic structures: calcite, vaterite, and aragonite, each having a different crystal structure. Calcite is the most stable and common polymorph, while vaterite and aragonite are more metastable polymorphs, whose formation is typically easier to inhibit with inhibitors. In the samples analysed, calcite (C) dominated in the $CaCO_3$ crystals without the addition of palm shell liquid smoke, whereas vaterite (V) and aragonite (A) were found after the addition of the inhibitor (Fig.-7). The presence of vaterite and aragonite, with the addition of the liquid smoke inhibitor, indicates that the inhibitor effectively disrupts $CaCO_3$ scale growth. The $CaCO_3$ phase, such as calcite, is thermodynamically more stable compared to vaterite and aragonite. Organic inhibitors from liquid smoke promote the formation of metastable phases (vaterite and aragonite), as detected by XRD. This is significant because metastable phases tend to be less dense and easier to remove, making them more favourable for reducing the formation of hard, difficult-to-clean scale. These results are visually confirmed by the SEM analysis previously conducted (Fig.-6). This transformation suggests that the inhibitor not only prevents excessive scale formation but also modifies the crystal structure, reducing the size and adhesion of scale deposits, making them easier to remove. Studies have confirmed this effect, showing that inhibitors can induce the formation of aragonite and vaterite, contributing to effective scale management in industrial systems.[35,38]

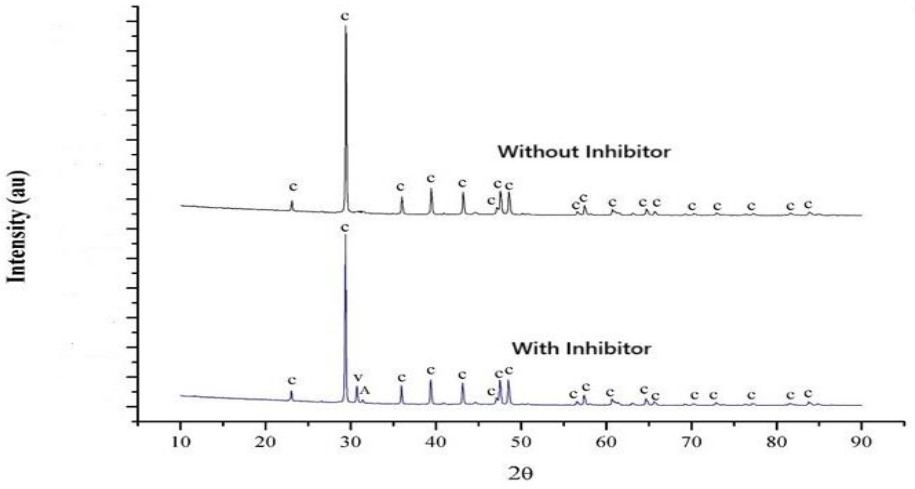


Fig.-7: XRD Spectrum of $CaCO_3$ Crystals with and without the Addition of an Inhibitor

Comparison of the Two Inhibitors

Calcium carbonate scale is a common problem in piping systems, boilers, and water coolers because it can reduce system efficiency and increase operational costs.[7-11] To address this issue, various scale inhibitors have been used, both synthetic and natural. Two of them are EDTA and liquid smoke derived from palm shell biomass, each of which has its own advantages and limitations. Chemically, EDTA is a synthetic chelating agent that is highly effective in binding calcium ions (Ca^{2+}), thus preventing the formation of calcium carbonate crystals. The effectiveness of EDTA has been widely demonstrated in numerous studies and industrial applications. Even at low concentrations, EDTA can suppress scale growth efficiently and consistently. Therefore, in terms of technical effectiveness, EDTA remains the primary choice as an inorganic scale inhibitor. Nevertheless, a sustainability-based approach shifts attention toward more environmentally friendly alternatives. One promising candidate is liquid smoke produced from the pyrolysis of palm shell, a type of agricultural biomass waste abundantly available in Indonesia. This liquid smoke contains phenolic compounds, organic acids, and carbonyl groups that can disrupt the crystallisation process of $CaCO_3$. Although its effectiveness is not as high as that of EDTA, liquid smoke still shows potential as a scale inhibitor through different mechanisms, such as localised pH alteration and adsorption on the crystal nucleation surface. The main advantage of liquid smoke lies in its sustainability and environmental profile. Derived from renewable agricultural waste, liquid smoke is biodegradable and does not lead to the accumulation of hazardous chemical residues. In contrast, EDTA is poorly biodegradable and can contaminate aquatic environments while mobilising heavy metals from sediments. Therefore, liquid smoke is considered safer for long-term applications that are sensitive to ecotoxicity.

Additionally, it has antimicrobial properties, providing dual protection against biofilm formation or microbiological corrosion within water systems. From an economic and availability standpoint, liquid smoke also has advantages. Because it can be produced locally from palm shell waste, the cost is relatively low and supports the principle of a circular economy. This is especially important in developing countries like Indonesia, where synthetic chemicals such as EDTA may be expensive and less accessible. Thus, although EDTA excels in terms of effectiveness, liquid smoke from palm shells offers an environmentally friendly, low-cost, and locally sourced alternative solution. Innovations in formulation, increasing active concentration, or combining liquid smoke with other additives may further enhance its performance as a natural scale inhibitor in the future.

Although the effectiveness of liquid smoke derived from palm shell in inhibiting the formation of calcium carbonate scale is generally still lower than that of EDTA, preliminary studies indicate that this liquid smoke has significant potential to improve its inhibition efficiency to over 70% through optimisation of the pyrolysis process, particularly by employing temperatures above 400°C. In fact, the use of palm shell-derived liquid smoke produced through pyrolysis at 450°C has demonstrated an inhibition efficiency

exceeding 100% relative to the untreated control, indicating a highly effective suppression of $CaCO_3$ scale formation.[39] At higher pyrolysis temperatures, there is an increased decomposition of lignocellulosic compounds in the palm shell biomass, resulting in liquid smoke with higher concentrations of phenolic compounds, organic acids, and active carbonyls. These compounds play a crucial role in the mechanism of scale inhibition, either by disrupting the crystallisation process, lowering the local pH, or adsorbing onto the nucleation surface of $CaCO_3$ crystals. Therefore, pyrolysis at temperatures above 400°C can significantly enhance the content of active components in the liquid smoke, thereby strengthening its inhibitory capacity. Consequently, further research focusing on pyrolysis temperature optimisation and the characterisation of active components in the liquid smoke is essential to develop a competitive, environmentally friendly, and locally producible natural scale inhibitor.

CONCLUSION

Palm shell liquid smoke has the potential as an inhibitor for calcium carbonate ($CaCO_3$) scale formation, with an effectiveness slightly lower than that of EDTA, which is commonly used as a commercial inhibitor. The study results show that palm shell liquid smoke in the unseeded experiment method is optimal at a 25% concentration, with an %EI (inhibitor effectiveness) of 28-41% at growth solution concentrations of 0.0250 – 0.0500 M. In comparison, the EDTA inhibitor under the same conditions provided a %EI of 79-83% at growth solution concentrations of 0.0250 – 0.0500 M. The addition of palm shell liquid smoke inhibitor alters the morphology and size of $CaCO_3$ crystals. The particle size distribution of $CaCO_3$ crystals becomes smaller with the addition of liquid smoke, confirmed by PSA and SEM analysis. Furthermore, the morphology of $CaCO_3$ crystals after the addition of the inhibitor undergoes a phase transformation from calcite to vaterite and aragonite, confirmed by SEM and XRD analysis. Thus, palm shell liquid smoke can be used as an eco-friendly inhibitor to inhibit calcium carbonate scale growth, which poses a challenge in industries, particularly at moderate growth solution concentrations, especially in industries using boilers.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6: Clean Water and Sanitation*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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