

Liquid smoke of coconut shell as green inhibitor of calcium carbonate scale formation

Suharso*, Eka Setiososari, Agung Abadi Kiswandono, Buhani, Heri Satria

Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Lampung, Jl. Soemantri Brojonegoro No. 1 Bandar Lampung, Indonesia, 35145, Tel. +62(721)-7625088; Fax: +62(721)-704625; email: suharso_s@yahoo.com (Suharso)

Received 27 January 2019; Accepted 15 July 2019

ABSTRACT

In this study, a liquid smoke of coconut shell (grade 3) was used as an inhibitor of calcium carbonate scale formation by applying a seeded experiment method at 80°C. Experiments were carried out in the various concentration of CaCO₃ growth solution from 0.05 to 0.125 M with the addition of the liquid smoke from 0 to 350 ppm. Characterization of liquid smoke was performed by using infrared spectroscopy (IR) and gas chromatography–mass spectrometry (GC-MS), while the characterization of CaCO₃ crystals was carried out by scanning electron microscopy (SEM), particle size analyzer (PSA), and X-ray diffraction (XRD). The results of GC-MS and IR confirmed that the liquid smoke of coconut shell (grade 3) consists of large amounts of methanol (11.16%), acetic acid (54.15%), and phenol (15.12%). The results of scaling inhibition test showed that the liquid smoke inhibits the growth of CaCO₃ crystal. The effectiveness of the liquid smoke in inhibiting the formation of CaCO₃ crystal is 31%–273% depending on the used growth solution concentration and the added inhibitor concentration. The results of analysis with SEM, PSA, and XRD indicated changes in the morphology, size, and phase of CaCO₃ crystal.

Keywords: Scale inhibitor; CaCO₃ crystal; Liquid smoke; Coconut shell

1. Introduction

The inorganic compound deposition process in industrial equipment such as steam generators, boilers, cooling towers, pipes, and other equipments used in the water–solid process is a worrisome problem [1–7]. Industries involved with this issue should spend additional funds to address this issue. The Indonesian Geothermal Industry (PT Pertamina) has expended US \$ 6–7 million to accomplish the issue in its geothermal industry to regenerate the installation of the geothermal pipeline within 10 years [8–11]. Some researchers have tried to overcome this issue by adding additives that act as inhibitors to inhibit the growth of these unwanted inorganic materials [12–16].

The selection of additives as inhibitors derived from natural or synthesized materials to inhibit the growth of

inorganic materials has recently become an interesting environmental issue [17–25]. Additives are not only capable of acting as inhibitors to inhibit the formation of unwanted inorganic materials but must also be environmentally friendly and inexpensive. Therefore, research on the green inhibitors continues to grow and develop rapidly in order to find inhibitors that are environmentally friendly, effective, and inexpensive.

In this research, it has been studied a liquid smoke from coconut shell as green inhibitor to prevent the scale formation of calcium carbonate by employing seeded experiment method. The utilization of liquid smoke as an inhibitor of calcium carbonate scale formation has not been reported by researchers, whereas the raw material for liquid smoke from coconut shells is very abundant, especially in Indonesia as a tropical country. The liquid smoke from coconut shell is

* Corresponding author.

rich in chemical compounds and the main ones are groups of ketones, aldehydes, acids, phenols, and furanes [26–28]. These compounds are believed to play a role in inhibiting the growth of calcium carbonate scale.

2. Experimental procedure

2.1. Preparation of liquid smoke from coconut shell

The coconut shells were taken and selected from coconut plantations around in Bandar Lampung area. The selected coconut shells were cleaned and washed by water. Before they were processed, they were air dried for 8 h under the sun. Then they were placed into the reactor of pyrolysis process and heated by a smoke generator controlled heating at the temperature of 450°C. The production of liquid smoke was discontinued when the coconut shells were pyrolyzed totally [26]. The liquid smoke obtained from this procedure was classified as grade 3 (Fig. 1). The liquid smoke of the grade 3 was characterized by infrared spectrometer (FTIR spectrometer, Agilent Cary 630, made in USA) to identify the functional groups and gas chromatography–mass spectrometry (GC-MS, Shimadzu GC2010 MSQP 2010S, made in Japan) to investigate the chemical composition contained in the liquid smoke of the grade 3.

2.2. Seed crystal preparation

Preparation of CaCO_3 crystal was performed by mixing 100 mL of CaCl_2 anhydrate solution (1 M) and 100 mL of Na_2CO_3 solution (1 M) in a glass beaker at a temperature of 90°C. The two mixed solution were stirred by magnetic stirrer for 15 min and left in room temperature for 2 h to result seed crystals. The obtained seed crystals were separated from the liquid by filtration using a 0.45 μm Millipore filter, cleaned thoroughly with water, and dried in the oven at temperature of 100°C. This procedure was repeated



Fig. 1. Liquid smoke of grade 3 from coconut shell.

for several times to obtain the seed crystals of CaCO_3 in sufficient quantities to do the experiment. The CaCl_2 anhydrate and Na_2CO_3 applied were produced from commercial products of Merck, Germany.

2.3. Calcium carbonate crystals growth

The precipitation of calcium carbonate was performed with mixing 200 mL of CaCl_2 anhydrate solution (0.100 M) and 200 mL of Na_2CO_3 solution (0.100 M) into 500 mL Nalgene polypropylene bottles continued by shaking to obtain a homogeneous solution. This experiment was destined to produce the growth solution of CaCO_3 with the concentration of 0.050 M. The homogeneous solution obtained was filtered by a 0.45 μm Millipore filter. The filtered solution was placed into 250 mL Nalgene polypropylene bottles consisted of seven bottles with each bottle containing 50 mL of filtered solution. All the bottles were placed to the bottle-roller bath followed with adding simultaneously 100 mg of the seed crystals of CaCO_3 into each bottle. The temperature and the rotating of the bottle-roller bath were adjusted at the 80°C and 40 rpm. The experiment lasted for 90 min, for every 15 min each bottle was taken one by one. The crystals produced were rinsed thoroughly with water and put in the oven adjusted temperature of 105°C for one night. The weight of the CaCO_3 precipitation produced for each bottle was identified and the amount of CaCO_3 crystals was calculated to be plotted as function of time.

For each precipitation experiment, a blank containing in the absence of inhibitor was carried out simultaneously with the presence of an inhibitor to compare the effectiveness of the inhibitor. The same procedure was performed for various concentrations of each 0.075, 0.100, and 0.125 M for CaCO_3 growth solution.

Based on the similar procedure performed for the CaCO_3 growth solution concentration of 0.050 M, a growth solution concentration of 0.075 M CaCO_3 was prepared by blending 200 mL of CaCl_2 anhydrate solution (0.150 M) and 200 mL of Na_2CO_3 solution (0.150 M), a growth solution of 0.100 M CaCO_3 was produced by combining 200 mL of 0.200 M CaCl_2 anhydrate solution and 200 mL of 0.200 M Na_2CO_3 solution, and a growth solution of 0.125 M CaCO_3 was obtained by merging 200 mL of 0.250 M CaCl_2 anhydrate solution and 200 mL of 0.250 M Na_2CO_3 solution.

2.4. Effect of liquid smoke on the crystallization of CaCO_3 crystals

The addition of inhibitor into the growth solution of CaCO_3 to investigate the effect of the inhibitor to the growth rate of CaCO_3 seed crystals was performed in the similar treatment in the experiment of the calcium carbonate precipitation without the addition of inhibitor. The addition of inhibitor was carried out at various concentrations of inhibitor from 0 to 350 ppm (0, 50, 150, 250, and 350 ppm) and at various concentrations of CaCO_3 growth solution from 0.050 to 0.125 M (0.050, 0.075, 0.100, and 0.125 M). The weight of the crystals produced in these experiments was identified and the amount precipitated was calculated to study the influence of the inhibitor toward the growth rate of the CaCO_3 seed crystals and compared with in the absence of inhibitor.

2.5. Characterization of CaCO₃ crystal

In order to study the effect of the inhibitor in inhibiting the growth rate of CaCO₃ seed crystals, the CaCO₃ seed crystals obtained were investigated by a scanning electron microscopy (SEM; Zeiss EVO MA10, made in Germany) to observe the morphology of the CaCO₃ crystals, a particle size analyzer (PSA) (the Beckman Coulter LS 13 320 MW, made in USA) to identify particle size distribution of CaCO₃ crystals, and an X-ray diffraction (XRD, Philips Analytical, made in Netherlands) to characterize the crystal structure of CaCO₃ with and without the addition of the inhibitor.

3. Results and discussion

3.1. Characterization of liquid smoke

Liquid smoke was made using coconut shell based material by pyrolysis conducted for approximately 6–8 h. The smoke from the pyrolysis goes into the condensation process, which then becomes liquid. The obtained liquid smoke (grade 3) has passed through the filtration process, then the liquid smoke can be used as a CaCO₃ scale inhibitor. The spectrum of the liquid smoke characterized by infrared (IR) is displayed in Fig. 2 and the analysis results of chemical compound composition by gas chromatography–mass spectrometry (GC-MS) can be seen in Table 1.

The IR spectrum of the liquid smoke shows a number of absorption bands appearing in the wave number regions as shown in Fig. 2. The existence of O–H group in the liquid smoke is signed with the absorption band of 3,339.7 cm⁻¹ showing the stretching vibration of O–H and this is amplified by the bending vibration of O–H at 1,394.0 cm⁻¹. The functional groups correspond to a common component of the liquid smoke, a phenol compound which is rich in hydroxyl groups. The vibrations of the hydroxyl group (O–H) appearing in Fig. 2 have broad bands of uptake at 3,339.7 cm⁻¹ indicating the presence of hydrogen bonds. The hydrogen bonds present in the liquid smoke are due to the presence of hydrogen bonds between molecules or intra molecules. The presence of the carbonyl group (C=O) is indicated by the appearance of absorption bands at the wave number 1,640.0 cm⁻¹ indicating the presence of aldehyde, ketone, carboxylic or ester groups. In addition to the presence of O–H and C=O groups, the liquid smoke also contains an

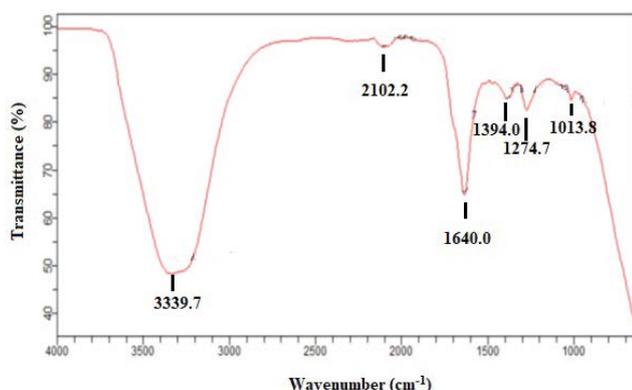


Fig. 2. Infrared spectrum of liquid smoke of grade 3.

ester (C–O) group with an uptake of 1,274 cm⁻¹. Based on the results of the analysis using the IR spectrophotometer it can be stated that the liquid smoke has a compound containing functional groups which can act as the inhibitor of CaCO₃ scaling.

Chemical analysis from liquid smoke grade 3 using GC-MS is shown in Table 1. This table shows the separation of chemical components displayed from chromatogram peaks in GC. The peaks start at a retention time of 2.336 to 60.242 min. The results of chromatogram peak analysis show that coconut shell liquid smoke has 16 chemical components as listed in Table 1. The most abundant content of coconut shell liquid smoke is methanol (11.16%), acetic acid (54.15%), and phenol (15.12%). This result is consistent with IR data (Fig. 2) obtained with the functional groups found in liquid smoke of grade 3, namely hydroxyl, aldehyde, ketone, carboxylic, or ester group. In general, chemical composition of liquid smoke from this experiment is not so different with the chemical composition of commercial liquid smoke products [29].

3.2. Scale inhibition by liquid smoke

The amount of CaCO₃ deposits formed vs. times at various concentrations of growth media of calcium carbonate namely 0.050, 0.075, 0.100, and 0.125 M is displayed in Fig. 3. From Fig. 3, it can be seen that the growth of CaCO₃ crystal seeds has increased along with the increase in the concentration of growth solution from 0.050 to 0.125 M. The higher the concentration of CaCO₃ growth solution the greater the growth rate of crystal CaCO₃. The data shown in Fig. 3 are a reference to observe the effect of liquid smoke as an inhibitor in inhibiting the formation of CaCO₃ scale.

The effect of the addition of liquid smoke at different concentrations on inhibiting the formation of CaCO₃ deposits in the concentration of growth solutions 0.050, 0.075, 0.100,

Table 1
Chemical analysis of liquid smoke (grade 3) by GC-MS

No.	Retention time (min)	% Area	Chemical compound
1.	2.336	11.16	Methanol
2.	2.531	3.71	2-Propanone
3.	2.650	2.22	Methyl acetate
4.	3.338	54.15	Acetic acid
5.	3.793	2.43	1-Hydroxy-2-propanone
6.	4.180	0.42	Propanoic acid
7.	6.025	0.53	Methyl acetaldehyde
8.	7.620	7.08	2-Furancarboxaldehyde
9.	10.317	0.26	Cis-1-methylbutadiene
10.	10.552	0.56	Dihydro-2(3H)-furanone
11.	12.515	0.29	5-Methyl-2-furancarboxaldehyde
12.	13.349	15.12	Phenol
13.	14.874	0.87	1,2-Cyclohexanedione
14.	17.203	0.88	2-Methoxy-phenol
15.	59.600	0.10	Exo-2-hydroxybicyclo[3.3.1]nonane
16.	60.242	0.22	Octadecanoic acid

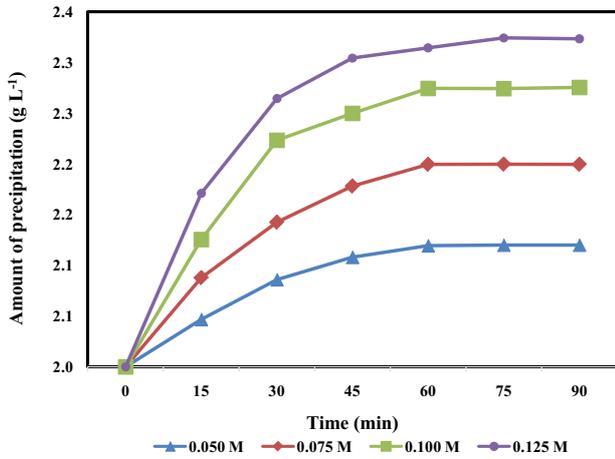


Fig. 3. Amount of CaCO₃ precipitation vs. time at different growth solution concentration.

and 0.125 M is shown in Figs. 4–7. At the concentration of CaCO₃ growth solution of 0.050 (Fig. 4) and 0.075 M (Fig. 5), liquid smoke does not only inhibit totally the growth rate of CaCO₃ crystal seeds but is also capable of dissolving CaCO₃ crystal seeds. At the concentration of 0.050 M growth solution, the addition of liquid smoke as much as 250 and 350 ppm resulted in partially dissolved CaCO₃ crystal seeds. The dissolution of CaCO₃ crystal seeds occurs up to 0.075 M concentration of the growth solution with the addition of liquid smoke of 350 ppm. While the addition of liquid smoke is 350 ppm at the concentration of growth solution of 0.100 and 0.125 M, the inhibitor is only able to inhibit the growth of CaCO₃ crystals close to 100%.

Calculation of the effectiveness of inhibitors (% EI) in inhibiting the formation of calcium carbonate scale can be calculated based on Eq. (1) which has been done by previous researchers [13,30]. The results of calculations using Eq. (1) are shown in Tables 2–5.

$$\text{Effectiveness of inhibitor (\%EI)} = 100 \times \frac{(C_a - C_b)}{(C_c - C_b)} \quad (1)$$

where C_a = the amount of CaCO₃ precipitation in the presence of liquid smoke at equilibrium (g L⁻¹); C_b = the amount of CaCO₃ precipitation in the absence of liquid smoke at equilibrium (g L⁻¹); C_c = the amount of CaCO₃ precipitation in the initial state (g L⁻¹).

Based on the data in Tables 2–5, it can be stated that the effectiveness of inhibitors in inhibiting the growth of CaCO₃ crystals can exceed 100%. This occurs in the concentration of 0.050 M growth solution with the addition of liquid smoke 250–350 ppm and 0.075 M with the addition of liquid smoke 350 ppm. Thus, in the concentration of growth solution of 0.050 and 0.075 M, the liquid smoke with a dose of 250–350 ppm is able to totally inhibit the growth rate of CaCO₃ crystal seeds with the effectiveness of inhibitors of 154%–273%. Even in these situations, the liquid smoke can dissolve the CaCO₃ crystal seeds that are available. Increasing the concentration of CaCO₃ growth solution and decreasing the dose of liquid smoke added to the growth

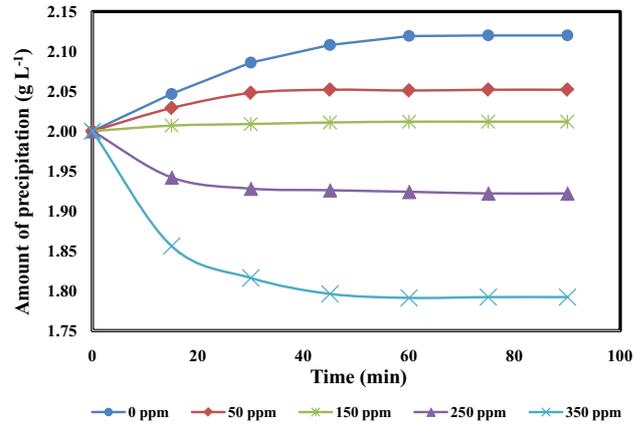


Fig. 4. Amount of CaCO₃ precipitation vs. time with the addition of various inhibitor concentrations at the growth solution concentration of 0.050 M.

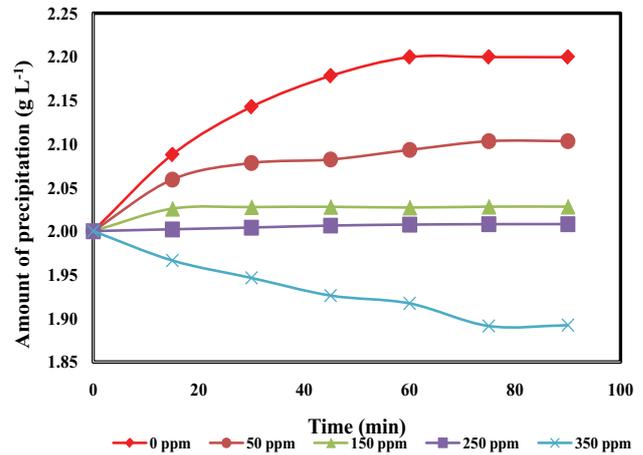


Fig. 5. Amount of CaCO₃ precipitation vs. time with the addition of various inhibitor concentrations at the growth solution concentration of 0.075 M.

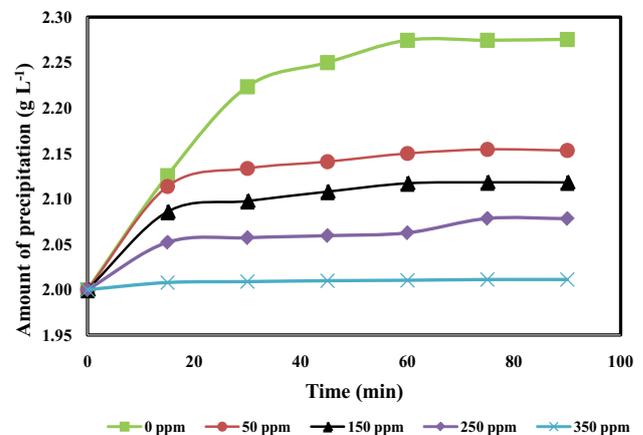


Fig. 6. Amount of CaCO₃ precipitation vs. time with the addition of various inhibitor concentrations at the growth solution concentration of 0.100 M.

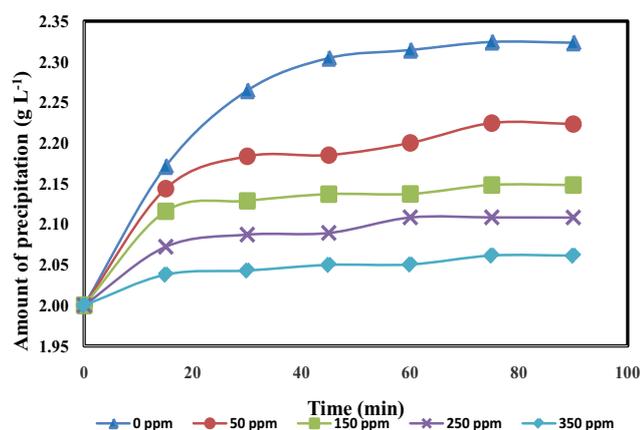


Fig. 7. Amount of CaCO₃ precipitation vs. time with the addition of various inhibitor concentrations at the growth solution concentration of 0.125 M.

Table 2
Effectiveness of inhibitor in inhibiting the scale formation of CaCO₃ at the growth solution concentration of 0.050 M

Inhibitor concentrations (ppm)	Effectiveness of inhibitor (% EI)
0	0.00
50	56.70
150	90.01
250	164.95
350	273.19

Table 3
Effectiveness of inhibitor in inhibiting the scale formation of CaCO₃ at the growth solution concentration of 0.075 M

Inhibitor Concentrations (ppm)	Effectiveness of Inhibitor (% EI)
0	0.00
50	48.30
150	85.92
250	95.94
350	154.06

solution will gradually reduce the ability of the liquid smoke to inhibit the growth of CaCO₃ crystal seeds. The lowest inhibitor effectiveness occurred at the concentration of 0.125 M growth solution with a dose of the liquid smoke added at 50 ppm which was 31% (Table 5).

The effectiveness of liquid smoke grade 3 as inhibitors was compared with other materials and is given in Table 6. From the table, it can be seen that the liquid smoke has the highest effectiveness in inhibiting the growth rate of CaCO₃ crystals. Even the ability of liquid smoke as an inhibitor in inhibiting the growth of CaCO₃ crystal seeds exceeds 270%.

Table 4
Effectiveness of inhibitor in inhibiting the scale formation of CaCO₃ at the growth solution concentration of 0.100 M

Inhibitor Concentrations (ppm)	Effectiveness of Inhibitor (% EI)
0	0.00
50	44.37
150	57.12
250	71.64
350	95.97

Table 5
Effectiveness of inhibitor in inhibiting the scale formation of CaCO₃ at the growth solution concentration of 0.125 M

Inhibitor concentrations (ppm)	Effectiveness of inhibitor (% EI)
0	0.00
50	30.98
150	54.21
250	66.57
350	81.08

This occurs in the addition of 350 ppm liquid smoke in the CaCO₃ growth solution of 0.05 M.

3.3. Characterization of CaCO₃ crystals

To verify that the liquid smoke works in inhibiting the growth of CaCO₃ crystal seed, the crystals obtained were observed using SEM. The results of observations using SEM are shown in Fig. 8. The figure shows that the morphology of CaCO₃ crystals changes dramatically after the addition of liquid smoke (Fig. 8b) compared with the absence of liquid smoke (Fig. 8a). The crystal size of CaCO₃ obtained also becomes smaller after addition of liquid smoke (Fig. 8b) compared with without the addition of liquid smoke (Fig. 8b). Data obtained from SEM analysis are a visual evidence that the liquid smoke can inhibit the growth of CaCO₃ crystals and change the morphology of CaCO₃ crystals.

Further proof of the ability of the liquid smoke as an inhibitor of CaCO₃ crystal growth is by observing the particle size distribution of CaCO₃ using PSA. Fig. 9 displays the particle size distribution of CaCO₃ before and after the presence of liquid smoke. Observations using PSA show that the particle size distribution of CaCO₃ has changed significantly. The addition of liquid smoke has made the CaCO₃ particle size distribution to be much lower than without the presence of liquid smoke. The average of the CaCO₃ particle size distribution without the addition of liquid smoke is 5.146 μm and after the addition of liquid smoke, it drops to 2.897 μm. Thus the results of the analysis using PSA strengthened the results of analysis using SEM and the data of the inhibitor effectiveness in inhibiting the growth of CaCO₃ crystals.

The structure and composition of the CaCO₃ produced before and after the addition of liquid smoke were investigated

Table 6
Comparison of inhibitor effectiveness with other researches

No	Materials	Concentration of Ca ²⁺ in growth media (M)	Inhibitor concentration (ppm)	Inhibitor effectiveness (%)	Literature studied
1	Liquid smoke grade 3	0.050–0.125 in water	50–350	31–273	This work
2	Tobacco rob extract	0.010 in artificial seawater	30–140	18–92	[1]
3	Gambier extract modification	0.100–0.600 in water	50–300	12–92	[8]
4	Calix [4] resorcinarene	0.100–0.600 in water	25–75	38–94	[9]
5	Kemenyan extract	0.050–0.100 in water	50–350	12–77	[10]
6	Gambier extracts	0.100–0.600 in water	50–250	60–100	[11]
7	Maleic anhydride/allyloxy poly(ethylene glycol)-polyglycerol-(OH)5 (MA/APEG-PG-(OH)5)	0.006 in water	2–8	16–97	[15]
8	Acrylic acid-allylpolyethoxy carboxylate copolymer	0.016 in clean sea water	5–100	10–95	[17]
9	Homopolymer of polymaleic acid	0.003 in synthetic seawater	4	67	[30]
10	Terpolymer of polymaleic acid	0.003 in synthetic seawater	4	73	[30]
11	Copolymer of polymaleic acid	0.003 in synthetic seawater	4	18	[30]
12	Polycarboxylic acid	0.003 in synthetic seawater	4	70	[30]
13	Pteroyl-L-glutamic acid	0.010 in mix of sea water and formation water (50/50)	80–200	76–100	[36]
14	Modified collagen by multialdehyde acid compounds	0.006 in water	35	61–89	[37]
15	Citric acid	0.002 in water	1–10	25–30	[38]
16	C-methyl-4,10,16,22-tetrametoxycalix[4]arene	0.100 in water	10–100	34–100	[39]
17	Soy-based polymer	0.102 in synthetic brines water	10	17	[40]
18	Casein-based polymer	0.102 in synthetic brines water	10	54	[40]
19	Polyaspartic acid	0.013 in water	12	80	[41]
20	Polyepoxysuccinic acid	0.013 in water	12	90	[41]

by powder XRD analysis. The XRD patterns of CaCO₃ crystals produced in the absence of liquid smoke and in the presence of liquid smoke are displayed in Fig. 10. Based on calcite JCPDS (Joint Committee on Powder Diffraction Standards) Card No. 05-0586, in Fig. 10a, the characteristics of diffraction peaks shown at 23.03°, 29.38°, 31.41°, 35.96°, 39.39°, 43.14°, 45.82°, 47.47°, 48.63°, 58.08°, 60.66°, and 64.66° in the XRD spectrum indicate the formation of calcite phase from CaCO₃ crystals (calcite peaks are marked with "C"). While, based on aragonite JCPDS Card No. 41-1475, as seen in Fig. 10a, the characteristics of diffraction peaks shown at 26.19°, 27.18°, 33.09°, 38.38°, and 52.96° show the formation of aragonite phase from CaCO₃ crystals (aragonite peaks are marked with "A") [1]. It can be observed in Fig. 10 that the mixtures constituted of calcite and aragonite were formed in the presence and in the absence of liquid smoke, but the amount fractions of calcite and aragonite in the deposit obtained are dissimilar. The presence of liquid smoke into the growth solution caused the appearance of new peaks in the XRD pattern of CaCO₃ crystals as shown in Fig. 10b. The appearance of new peaks at 24.85°, 38.41°, 42.86°, 43.78°, and 50.17° indicates the addition of aragonite phase. Thus, the addition of liquid smoke produces CaCO₃ crystal dominated by aragonite phase as seen in Fig. 10. This fact is in accordance with the results of morphological analysis obtained

through SEM (Fig. 8). As seen in this figure, the morphology of CaCO₃ crystal in the absence of liquid smoke is a regular structure with a typical cube-like crystals showing calcite-type of CaCO₃ crystal (Fig. 8a) [31]. Whereas, the form of the CaCO₃ crystal in the presence of liquid smoke was dominated by a typical rod-like as one of the characteristic from aragonite phase (Fig. 8b), which is the least stable polymorph than the calcite polymorph [32,33]. This result is in line with the results obtained by several previous studies [33–35].

3.4. Mechanism of inhibition

In the absence of the liquid smoke, the nucleation and growth of CaCO₃ crystals took place regularly. The regular shaped rhombohedra had been produced and precipitated. Yet in the addition of the liquid smoke into growth solution of CaCO₃, the carboxylate groups existed in the liquid smoke such as acetic, propanoic, and octadecanoic acid adsorbed the Ca²⁺ or the active sites of the CaCO₃ crystal surface, and as a consequence the stereochemical orientation of CaCO₃ growth was altered. The irregular shaped morphology of the typical rod-like as one of the characteristic from aragonite phase was resulted.

The liquid smoke also has the "threshold effect" of CaCO₃ inhibition. Therefore the liquid smoke may absorb the growing

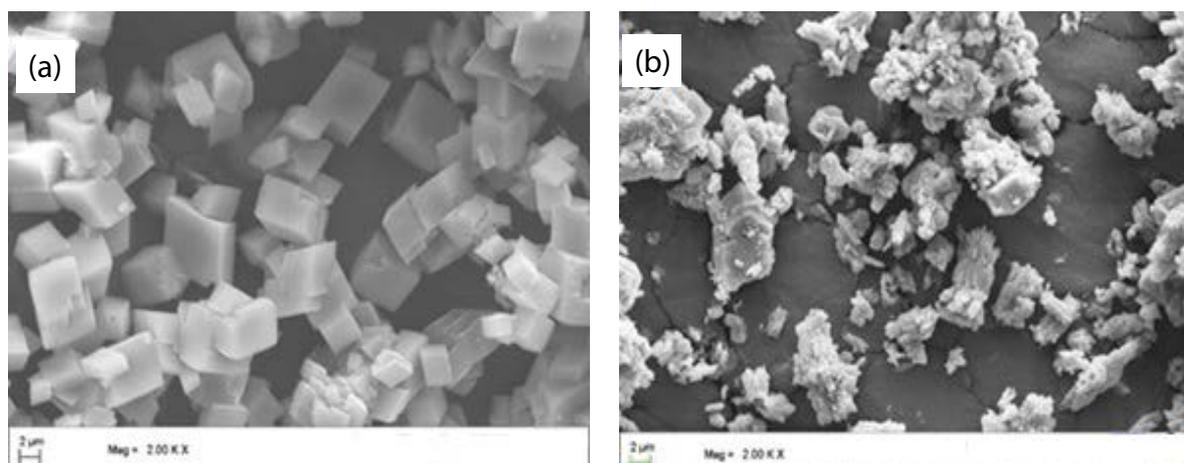


Fig. 8. SEM image of CaCO_3 crystal (a) before and (b) after the addition of 350 ppm liquid smoke at the concentration of 0.050 M CaCO_3 growth solution.

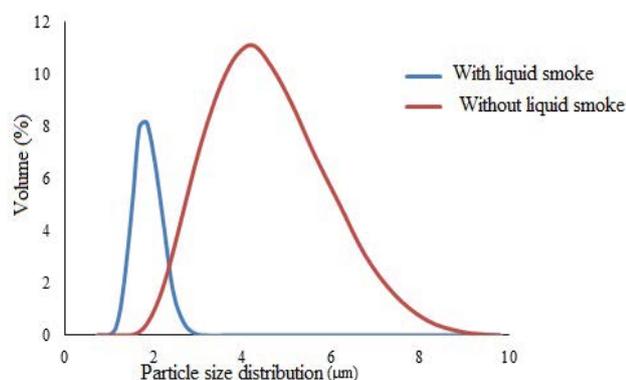


Fig. 9. Particle size distribution of CaCO_3 crystal before and after the addition of 350 ppm liquid smoke at the concentration of 0.050 M CaCO_3 growth solution.

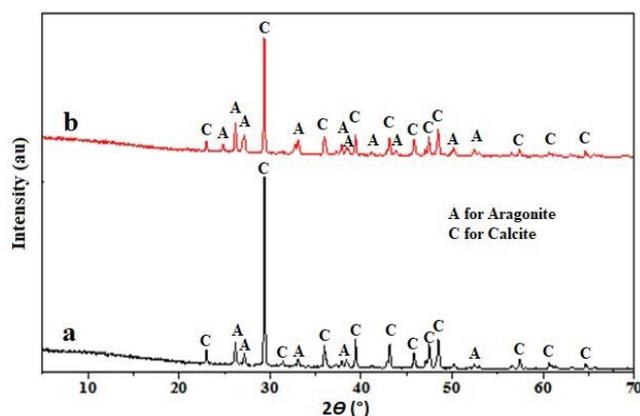


Fig. 10. XRD pattern of (a) CaCO_3 crystal produced in the absence of liquid smoke, (b) CaCO_3 crystal produced in the presence of 350 ppm liquid smoke at the concentration of 0.050 M CaCO_3 growth solution.

crystal phases of the nuclei and avoid aragonite transforming to calcite, which produces in the distortion and retardation of the CaCO_3 crystal growth. This fact was confirmed with the XRD data (Fig. 10). The liquid smoke can also modify the structure of calcium carbonate by adsorbing into the crystal seeds added into growth solution and thus decrease scale formation of CaCO_3 crystals. In addition the liquid smoke can also increase the solubility of calcium carbonate in the solution and dissolve the crystal seeds added into the growth solution especially at the concentration of CaCO_3 growth solution around 0.050–0.075 M. As a consequence of these concentrations of the growth solution, the effectiveness of the inhibitor is above 100%. The similar mechanism of this experiment occurred with the use of polysaccharides [42], hydrolyzed polymaleic anhydride [43], and xanthan [44] as inhibitor of calcium carbonate scale formation.

Besides the carboxylate groups, the existence of hydroxyl groups in the liquid smoke as listed in Table 1 also is able to arrange coordination complex to Ca^{2+} in the growth solution to produce chelates [45,46], which may be adsorbed on the surface of calcium carbonate crystal. The chelation produced has stability and it dissolves in the solution, so it can increase

the inhibition effectiveness of CaCO_3 scale formation. In addition, the liquid smoke also contains several functional groups such as ester group, phenolic and methoxy functionalities and carbonyl. These functional groups may behave as negative charged colloids and have surface-active characteristic, yet they may interact through their hydrophobic aliphatic and aromatic areas bound functional groups with positive growth sites of calcium carbonate scale to inhibit the calcium carbonate scale formation [47]. The ability of inhibitors to inhibit the growth of inorganic material scale is directly proportional to the increase in the number of their functional groups [48]. Thus, in this case the greater the number of functional groups present in the liquid smoke, the greater the ability to inhibit the formation of calcium carbonate scale. The existence of delocalized π -electrons bound to the phenol and methoxy groups attached to the 2-methoxy-phenol also play a role in inhibiting the CaCO_3 scale formation [49], as consequence the liquid smoke has high effectiveness in inhibiting the CaCO_3 scale formation. Even effectiveness of the liquid smoke in inhibiting the

growth of calcium carbonate scale exceeds 200% at concentration of 0.05 M growth solution.

4. Conclusion

The coconut shell liquid smoke of grade 3 can be used as calcium carbonate scale inhibitors. The coconut shell liquid smoke based on GC-MS analysis has 16 chemical compounds. From the 16 chemical compounds, methanol, acetic acid and phenol were the largest fractions in the chemical composition of the coconut shell liquid smoke of grade 3. Effectiveness of the liquid smoke as calcium carbonate scale inhibitor was 31%–273% in the growth solution concentrations of 0.050–0.125 M with the concentrations of the smoke liquid between 50 and 350 ppm. The ability of the liquid smoke to inhibit the growth of CaCO_3 crystals depends on the growth solution used and the concentration of the liquid smoke added. The results of the analysis using SEM and PSA, the presence of liquid smoke in the calcium carbonate growth solution can change the morphology of CaCO_3 crystal and make the average crystal size of CaCO_3 to be smaller than without the addition of the liquid smoke. The results of XRD and SEM analysis also show that CaCO_3 crystals obtained in the presence of inhibitor are more dominated by aragonite polymorph which is the least stable polymorph than the calcite. It can be stated that the inhibition mechanisms of the liquid smoke in inhibiting the CaCO_3 scale formation are threshold inhibition, chelates formation, and dissolution.

Acknowledgments

This project was financially supported by the Directorate of Research and Community Services, Directorate General of Strengthening Research and Development, Ministry of Research, Technology and Higher Education of the Republic of Indonesia (Kemenristekdikti) with contract number: 065/SP2H/LT/DRPM/2019.

References

- [1] H. Wang, M. Gao, Y. Guo, Y. Yang, R. Hu, A natural extract of tobacco rob as scale and corrosion inhibitor in artificial seawater, *Desalination*, 398 (2016) 198–207.
- [2] Y. Gao, L. Fan, L. Ward, Z. Liu, Synthesis of polyaspartic acid derivative and evaluation of its corrosion and scale inhibition performance in seawater utilization, *Desalination*, 365 (2015) 220–226.
- [3] K.D. Demadis, E. Mavredaki, A. Stathoulopoulou, E. Neofotistou, C. Mantzaridis, Industrial water systems: problems, challenges and solutions for the process industries, *Desalination*, 213 (2007) 38–46.
- [4] R. Ikeda, A. Ueda, Experimental field investigations of inhibitors for controlling silica scale in geothermal brine at the Sumikawa geothermal plant, Akita Prefecture, Japan, *Geothermics*, 70 (2017) 305–313.
- [5] M.K. Nayunigari, A. Maity, S. Agarwal, V.K. Gupta, Curcumin-malic acid based green copolymers for control of scale and microbiological growth applications in industrial cooling water treatment, *J. Mol. Liq.*, 214 (2016) 400–410.
- [6] M.K. Jensen, M.A. Kelland, A new class of hyperbranched polymeric scale inhibitors, *J. Pet. Sci. Eng.*, 94–95 (2012) 66–72.
- [7] M. Euvrard, A. Martinod, A. Neville, Effects of carboxylic polyelectrolytes on the growth of calcium carbonate, *J. Cryst. Growth*, 317 (2011) 70–78.
- [8] Suharso, T. Reno, T. Endaryanto, Buhani, Modification of Gambier extracts as green inhibitor of calcium carbonate (CaCO_3) scale formation, *J. Water Process Eng.*, 18 (2017) 1–6.
- [9] Suharso, Buhani, S.D. Yuwono, Tugiyono, Inhibition of calcium carbonate (CaCO_3) scale formation by calix [4] resorcinarene compounds, *Desal. Wat. Treat.*, 68 (2017) 32–39.
- [10] Suharso, N.A. Sabriani, Tugiyono, Buhani, T. Endaryanto, Kemenyan (Styrax benzoin Dryand) extract as green inhibitor of calcium carbonate (CaCO_3) crystallization, *Desal. Wat. Treat.*, 92 (2017) 38–45.
- [11] Suharso, Buhani, S. Bahri, T. Endaryanto, Gambier extracts as an inhibitor of calcium carbonate (CaCO_3) scale formation, *Desalination*, 265 (2011) 102–106.
- [12] Y. Zhao, L. Jia, K. Liu, P. Gao, H. Ge, L. Fu, Inhibition of calcium sulfate scale by poly (citric acid), *Desalination*, 392 (2016) 1–7.
- [13] L. Yang, W. Yang, B. Xu, X. Yin, Y. Chen, Y. Liu, Y. Ji, Y. Huan, Synthesis and scale inhibition performance of a novel environmental friendly and hydrophilic terpolymer inhibitor, *Desalination*, 416 (2017) 166–174.
- [14] Suharso, Buhani, L. Aprilia, Influence of calix[4]arene derived compound on calcium sulphate scale formation, *Asian J. Chem.*, 26 (2014) 6155–6158.
- [15] G. Liu, M. Xue, Q. Liu, Y. Zhou, Linear-dendritic block copolymers as a green scale inhibitor for calcium carbonate in cooling water systems, *Des. Monomers Polym.*, 20 (2017) 397–405.
- [16] A.A. Al-Hamzah, C.M. Fellows, A comparative study of novel scale inhibitors with commercial scale inhibitors used in seawater desalination, *Desalination*, 359 (2015) 22–25.
- [17] G. Liu, M. Xue, H. Yang, Polyether copolymer as an environmentally friendly scale and corrosion inhibitor in seawater, *Desalination*, 419 (2017) 133–140.
- [18] S. Zhang, H. Qu, Z. Yang, C. Fu, Z. Tian, W. Yang, Scale inhibition performance and mechanism of sulfamic/amino acids modified polyaspartic acid against calcium sulfate, *Desalination*, 419 (2017) 152–159.
- [19] A. Martinod, M. Euvrard, A. Foissy, A. Neville, Progressing the understanding of chemical inhibition of mineral scale by green inhibitors, *Desalination*, 220 (2008) 345–352.
- [20] A.O. Saleeh, A.H. Basta, Evaluation of some organic-based biopolymers as green inhibitors for calcium sulfate scales, *Environmentalist*, 28 (2008) 421–428.
- [21] N. Wada, K. Kanamura, T. Umegaki, Effects of carboxylic acids on the crystallization of calcium carbonate, *J. Colloid Interface Sci.*, 233 (2001) 65–72.
- [22] Suharso, Buhani, Efek penambahan aditif golongan karboksilat dalam menghambat laju pembentukan endapan kalsium sulfat, *J. Natur. Ind.*, 13 (2011) 100–104.
- [23] Y. Zhang, H.Q. Yin, Q.S. Zhang, Y.Z. Li, P.J. Yao, Synthesis and characterization of novel polyaspartic acid/urea graft copolymer with acylamino group and its scale inhibition performance, *Desalination*, 395 (2016) 92–98.
- [24] R. Menzri, S. Ghizellaoui, M. Tlili, Calcium carbonate inhibition by green inhibitors: thiamine and pyridoxine, *Desalination*, 404 (2017) 147–154.
- [25] D. Hasson, H. Shemer, A. Sher, State of the art of friendly “Green” scale control inhibitors: a review article, *Ind. Eng. Chem. Res.*, 50 (2011) 7601–7607.
- [26] J. Towaha, A. Aunillah, E.H. Purwanto, Utilization of rubber wood liquid smoke and coconut shell liquid smoke to reduce air pollution in the lump processing, *Bul. RISTRI*, 4 (2013) 71–80.
- [27] F. Swastawati, Quality and safety of smoked catfish (*Arius talassinus*) using paddy chaff and coconut shell liquid smoke, *J. Coast. Dev.*, 12 (2008) 47–55.
- [28] R. Simon, B. de la Calle, S. Palme, D. Meier, E. Anklam, Composition and analysis of liquid smoke flavoring primary products, *J. Sep. Sci.*, 28 (2005) 871–882.
- [29] N. Montazeri, A.C.M. Oliveira, B.H. Himelbloom, M.B. Leigh, C.A. Crapo, Chemical characterization of commercial liquid smoke products, *Food Sci. Nutr.*, 1 (2013) 102–115.
- [30] S. Patel, M.A. Finan, New antifoulants for deposit control in MSF and MED plants, *Desalination*, 124 (1999) 63–74.

- [31] R. Ketrane, B. Saidani, O. Gil, L. Leleyter, F. Baraud, Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: effect of temperature and concentration, *Desalination*, 249 (2009) 1397–1404.
- [32] H. Zhang, X. Luo, X. Lin, P. Tang, X. Lu, M. Yang, Y. Tang, Biodegradable carboxymethyl inulin as a scale inhibitor for calcite crystal growth: molecular level understanding, *Desalination*, 381 (2016) 1–7.
- [33] D.-Z. Zhu, D.-M. Sun, Q.-S. Wu, Assembly of nanosuperstructural aragonite CaCO_3 by living bio-membrane, *J. Exp. Nanosci.*, 6 (2011) 622–630.
- [34] B. Xu, K.M. Poduska, Linking crystal structure with temperature sensitive vibrational modes in calcium carbonate minerals, *Phys. Chem. Chem. Phys.*, 16 (2014) 17634–17639.
- [35] G. Liu, M. Xue, Q. Liu, Y. Zhou, J. Huang, Carboxylate-terminated double-hydrophilic block copolymer as an effective inhibitor for carbonate and sulphate scales, *Tenside Surf. Det.*, 53 (2016) 235–242.
- [36] T. Kumar, S. Vishwanatham, S.S. Kundu, A laboratory study on pteroyl-L-glutamic acid as a scale prevention inhibitor of calcium carbonate in aqueous solution of synthetic produced water, *J. Pet. Sci. Eng.*, 71 (2010) 1–7.
- [37] X. Qiang, Z. Sheng, H. Zhang, Study on scale inhibition performances and interaction mechanism of modified collagen, *Desalination*, 309 (2013) 237–242.
- [38] M.M. Reddy, A.R. Hoch, Calcite crystal growth rate inhibition by polycarboxylic acids, *J. Colloid Interface Sci.*, 235 (2001) 365–370.
- [39] Suharso, Buhani, T. Suhartati, The role of C-methyl-4,10,16,22-tetramethoxy calix[4]arene as inhibitor of calcium carbonate (CaCO_3) scale formation, *Indo. J. Chem.*, 9 (2009) 206–210.
- [40] B.A. Miksic, M.A. Kharshan, A.Y. Furman, Vapor Corrosion and Scale Inhibitors Formulated from Biodegradable and Renewable Raw Materials, European Symposium on Corrosion Inhibitors (10 SEIC), Ferrara, Italy, 2005.
- [41] D. Liu, W. Dong, F. Li, F. Hui, J. Ledion, Comparative performance of polyepoxysuccinic acid and polyaspartic acid on scaling inhibition by static and rapid controlled precipitation methods, *Desalination*, 304 (2012) 1–10.
- [42] R. Fried, Y. Mastai, The effect of sulfated polysaccharides on the crystallization of calcite superstructures, *J. Cryst. Growth*, 338 (2012) 147–151.
- [43] Z. Shen, J. Li, K. Xu, L. Ding, H. Ren, The effect of synthesized hydrolyzed polymaleic anhydride (HPMA) on the crystal of calcium carbonate, *Desalination*, 284 (2012) 238–244.
- [44] X. Yang, G. Xu, The influence of xanthan on the crystallization of calcium carbonate, *J. Cryst. Growth*, 314 (2011) 231–238.
- [45] N.M. Kumar, S.K. Gupta, D. Jagadeesh, K. Kanny, F. Bux, Development of poly(aspartic acid-co-malic acid) composites for calcium carbonate and sulphate scale inhibition, *Environ. Technol.*, 36 (2014) 1281–1290.
- [46] M.K. Nayunigari, S.K. Gupta, V. Kokkarachedu, K. Kanny, F. Bux, Development of anti-scale poly(aspartic acid-citric acid) dual polymer systems for water treatment, *Environ. Technol.*, 35 (2014) 2903–2909.
- [47] F.H. Butt, F. Rahman, U. Baduruthamal, Evaluation of SHMP and advanced scale inhibitors for control of CaSO_4 , SrSO_4 and CaCO_3 scales in RO desalination, *Desalination*, 109 (1997) 323–332.
- [48] A. Kumar, Polyaspartic acid—a versatile green chemical, *Chem. Sci. Rev. Lett.*, 1 (2012) 162–167.
- [49] G.N. Mu, T.P. Zhao, M. Liu, T. Gu, Effect of metallic cations on corrosion inhibition of an anionic surfactant for mild steel, *Corrosion*, 52 (1996) 853–856.