

# Modification of Gambier Extracts as Green Inhibitor of Calcium Carbonate (CaCO<sub>3</sub>) scale formation

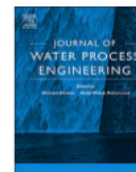
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## Modification of Gambier extracts as green inhibitor of calcium carbonate ( $\text{CaCO}_3$ ) scale formation



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### ABSTRACT

The addition of the Gambier extract (*Uncaria gambier* Roxb leaves) modification (Gambier:benzoic acid:citric acid/2:1:2) as a green inhibitor on the formation of  $\text{CaCO}_3$  scale at various concentrations was carried out using a seeded experiment method. The experiments were performed with observing the precipitation change of the  $\text{CaCO}_3$  crystals growth obtained. In order to prove the efficacy of the inhibitor in inhibiting the formation of the  $\text{CaCO}_3$  crystals, the changes of the crystal morphology were investigated by scanning electron microscopy (SEM) and the changes of the crystal size distribution were analyzed by particle size analyzer (PSA). The research results showed that the Gambier extract modification was able to inhibit the formation of the  $\text{CaCO}_3$  scale indicated with the morphology change of the  $\text{CaCO}_3$  crystals and smaller crystal size distribution after the addition of this inhibitor.

### 1. Introduction

Scale formation causes a serious issue encountered by many industries in Indonesia and other countries such as; the industry of oil or gas production, water transport, power generation, and batch precipitation [1–6]. Faced with this issue; PT Pertamina Geothermal Energy (PGE) which is one of subsidiary of Indonesian Oil Company (PT. Pertamina) has spent US\$ 6–7 million to rejuvenate the pipe installation of the Geothermal Energy Industry for 10 years. In order to solve this problem, several researchers studied many additives to prevent the scale formation or to modify the crystal morphology [7–12]. The addition of the additive in a growth solution of the scale formation is looked a cheaper method and an effective enough to inhibit the scale formation an inorganic material.

Gambier extract from *Uncaria gambier* Roxb leaves was reported as a green inhibitor of  $\text{CaCO}_3$  scale formation [13]. Nevertheless, the Gambier extract has several problems, such as; it is easily moldy and cannot be stored for a long time. In order to control these problems, the Gambier extract was mixed with citric and benzoic acid. Previous research reported that the citric and benzoic acid can play a role as an inhibitor also to inhibit the scale formation [14–16]. In addition, these mixtures are potential as a green inhibitor of the scale formation because they have some chemical compounds such as tannic acid, catechin, and quercetin [13] which are effective inhibitors of scale formation of  $\text{CaCO}_3$  beside the citric and benzoic acid. Other advantages of these mixtures are cheaper and they can be applied as a green inhibitor like other materials which have been used previously [17–27] to keep our environment.

The effects of the Gambier extract modification as the inhibitor  $\text{CaCO}_3$  scale formation at various concentrations from 0 to 300 ppm on the precipitation rate of calcium carbonate was observed at temperature of 80 °C and at a growth solution of 0.1, 0.3 and 0.6 M under seeded experiment. The seeded experiments were applied by previous researchers to investigate the inhibition of the calcite crystal growth with using phosphate additive and they monitored the rate of crystallization by measuring the concentration of calcium ion as a function of time [28]. In this experiment, the rate precipitation of the calcium carbonate seed crystals was monitored by weighing the amount of the calcium carbonate precipitated as function of time [13]. The precipitation obtained was characterized using scanning electron microscopy and particle size distribution to give an overview of its composition, size and morphology of the  $\text{CaCO}_3$  crystals was analyzed by particle size analyzer.

### 2. Experimental procedure

#### 2.1. Preparation of Gambier extract modification

Preparation of Gambier extract modification was made with the ratio of 2:1:2 (Gambier:benzoic acid:citric acid). The benzoic and citric

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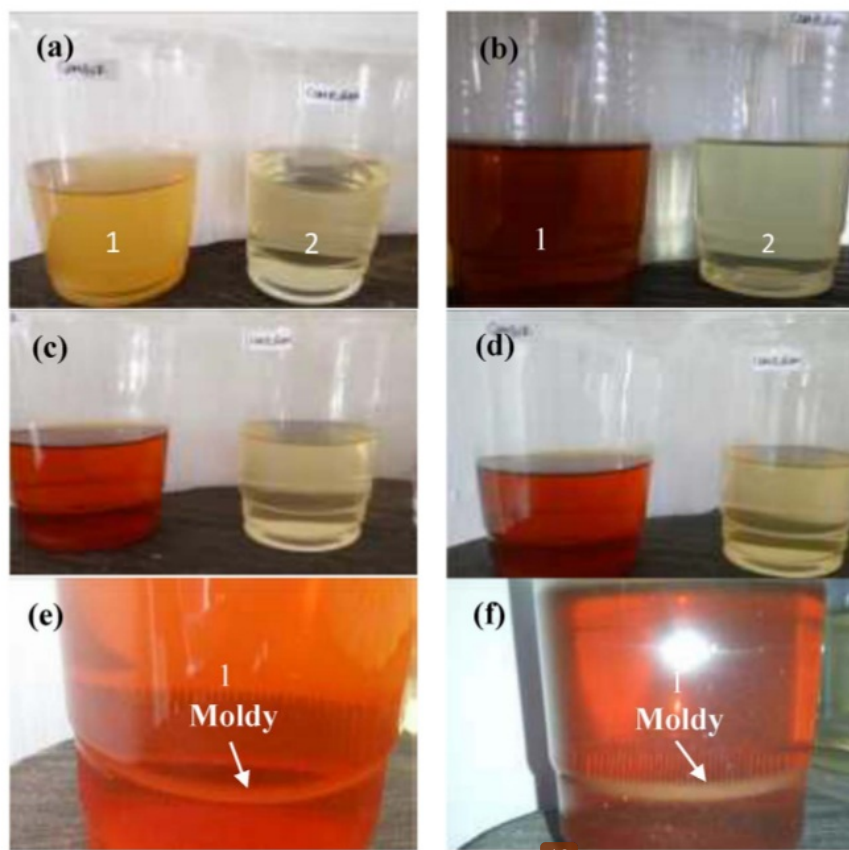


Fig. 1. The quality of Gambier extract (1) and modified Gambier (2) in the room temperature at (a) First day, (b) 7 days, (c) 14 days, (d) 25 days, (e) 14 days (drawn closer), and (f) 25 days (drawn closer).

acid used was produced by commercial products of Merck, Germany. Gambier was prepared from dry leaves of *Uncaria Gambir* Roxb fr. 4. West Sumatra, Indonesia. The amount of 2 g powdered Gambier, 1 g benzoic acid, and 2 g citric acid was placed into a 1 L volume glass 4. Fed water up to 1 L. The mixtures were heated at temperature of 80 °C for 1 h and left for 1 night. Then, the mixtures were filtered and the filtrate was used as an inhibitor of  $\text{CaCO}_3$  scale formation. Similar with previous research, the Gambier extracts was identified containing 40% of tannic acid, 25% of catechin, and 12% of quercetin [13].

## 2.2. Seed crystal production

The crystal seeds of  $\text{CaCO}_3$  were made with mixing each  $\text{CaCl}_2$  anhydrate solution (1 M) and  $\text{Na}_2\text{CO}_3$  solution (1 M) in 50 mL of water. The  $\text{CaCl}_2$  anhydrate and  $\text{Na}_2\text{CO}_3$  used was purchased by commercial products of Merck, Germany. The mixture was stirred by magnetic stirrer and it was left for 2 h to produce seed crystals containing 36. With separating the seed crystals from the liquor by filtration through a 13  $\mu\text{m}$  Millipore filter. The seed crystals obtained were cleaned thoroughly with water and dried at room temperature for at least two days. This work was replicated a bunch of times to produce the required amount of the  $\text{CaCO}_3$  seed crystals for the work.

## 2.3. Experiments of crystallization

An amount of 200 mL of  $\text{CaCl}_2$  anhydrate solution (0.2 M) was mixed into 200 mL of  $\text{Na}_2\text{CO}_3$  solution (0.2 M) in 500 mL Nalgene polypropylene bottles followed by shaking to produce a homogeneous

solution. This procedure was to prepare the growth solution of 0.1 M  $\text{CaCO}_3$ . The homogeneous solution produced was separated through a 0.45  $\mu\text{m}$  Millipore filter. The solution was fed into 250 mL Nalgene polypropylene bottles, each containing 50 mL consisted of 7 bottles. The bottles were fed back to the bottle-roller bath adjusted the temperature at 80 °C and the rotating at 40 rev min<sup>-1</sup> continued with adding together 100 mg of the  $\text{CaCO}_3$  seed crystals into each bottle. Over the 90 min the experiment run, each bottle was picked up for every 15 min. The crystals obtained were cleaned thoroughly with water and placed in oven at temperature of 105 °C for one day. The weight of the  $\text{CaCO}_3$  crystals obtained from each bottle was measured and the amount precipitated of  $\text{CaCO}_3$  crystals was calculated.

For each crystallization experiment, a blank containing no inhibitor was performed in conjunction with the presence of inhibitor. The similar experiments were carried out for concentration variety of  $\text{CaCO}_3$  growth solutions for each 0.3 and 0.6 M. Following the similar experiment applied for the 0.1 M  $\text{CaCO}_3$  growth solution concentration, a growth solution concentration of 0.3 M  $\text{CaCO}_3$  was made with mixing 200 mL of  $\text{CaCl}_2$  anhydrate solution (0.6 M) and 200 mL of  $\text{Na}_2\text{CO}_3$  solution (0.6 M), and a growth solution of 0.6 M  $\text{CaCO}_3$  was made with mixing 200 mL of 1.2 M  $\text{CaCl}_2$  anhydrate solution and 200 mL of 1.2 M  $\text{Na}_2\text{CO}_3$  solution.

## 2.4. Presence of additives

The influence of various additive concentrations was observed by adding different amount of the additive (0, 50, 100, 200 and 300 ppm) in the similar treatment. The weight of the crystals was measured and

the amount precipitated was calculated.

### 2.5. Data analysis

The data produced as amount of precipitate versus time at various concentrations of growth solution and in the presence of additive, each was plotted as an amount of precipitate versus time using MS Excel 2010. The effectiveness of the additive in inhibiting the rate of the  $\text{CaCO}_3$  scale formation were able to be identified from the mass of precipitate obtained and the morphology of the  $\text{CaCO}_3$  observed by SEM (JSM 6360 LA, Made in Japan). The distribution of particle size from the  $\text{CaCO}_3$  crystal precipitate resulted was also investigated by particle size analyzer (Sedigraph III 5120-Micrometrics).

## 3. Results and discussion

The quality of the Gambier extract and modified Gambier (Gambier extract:benzoic acid:citric acid) with the composition ratio of 2:1:2 in 1 L of water solution can be observed in Fig. 1. In this figure, it can be seen that the quality of the Gambier extract decreased after 14 days left in the room temperature. On the day of 14, the Gambier extract become moldy and on the day 25, the number of fungus contained in the Gambier extract was increased. The existence of the fungus in the Gambier extract may cause the chemical compounds as main component playing a role in inhibiting of the  $\text{CaCO}_3$  scale formation having damaged. While the quality of the modified Gambier in the addition of benzoic and citric acid after 25 days was still good enough. This modified Gambier added benzoic and citric acid with the composition ratio of 2:1:2 was used in this experiment as a green inhibitor of the formation of  $\text{CaCO}_3$  crystals.

The observations of the  $\text{CaCO}_3$  formation rate at different concentrations were displayed in Fig. 2. These observations were performed at temperature of  $80^\circ\text{C}$  and the growth solution concentration of 0.1, 0.3, and 0.6 M with adding 2 g crystal seeds in 1 L growth solution. The results showed that the growth rates of the  $\text{CaCO}_3$  crystals were linear with the growth solution concentrations. The bigger the growth solution concentration was the bigger the precipitation formatted. The biggest precipitation change occurred at growth solution concentration of 0.6 M with the precipitation amount increasing was approximately 0.6 g. The raising of the precipitation amount indicated the increasing of the  $\text{CaCO}_3$  crystal formation as a crystal deposit. The increasing change of precipitation amount from the concentration of 0.1, 0.3, and 0.6 M can be seen in Fig. 2.

Effect of the inhibitor mixture addition (Gambier:benzoic acid:citric acid/2:1:2) on the formation of the  $\text{CaCO}_3$  crystal at various growth solution concentrations can be observed clearly in Figs. 3–5. From these figures, it can be seen that the inhibitor mixture was able to inhibit the formation of the  $\text{CaCO}_3$  crystal based on the concentration of growth solution and the amount of the inhibitor added. The data show that at the concentration of 0.1 M, inhibitor ability inhibits the formation of

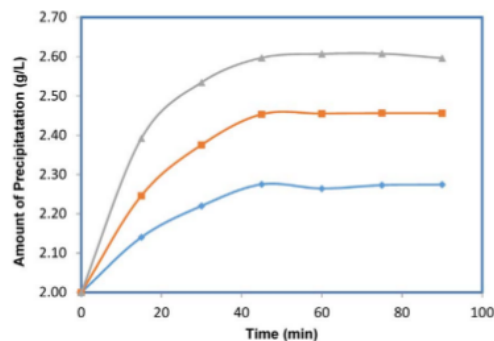


Fig. 2. The growth rate of  $\text{CaCO}_3$  precipitation at various growth solution concentration.

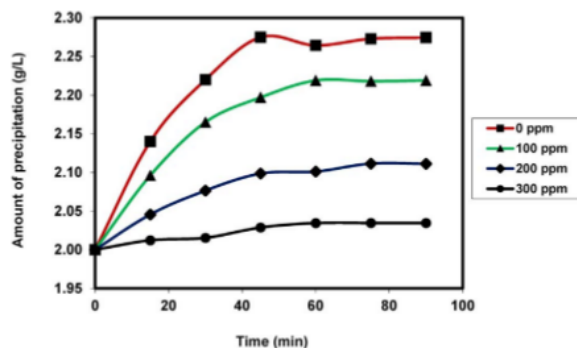


Fig. 3. Effect of inhibitor added on the formation of  $\text{CaCO}_3$  precipitation at the growth solution concentration of 0.1 M.

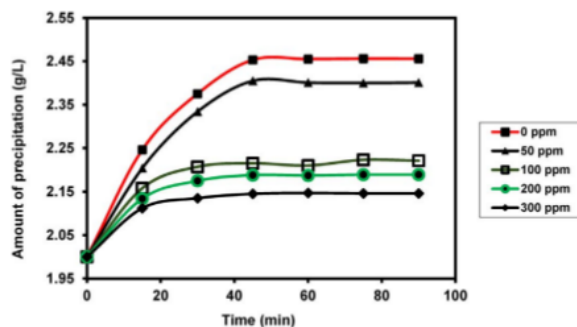


Fig. 4. Effect of inhibitor added on the formation of  $\text{CaCO}_3$  precipitation at the growth solution concentration of 0.3 M.

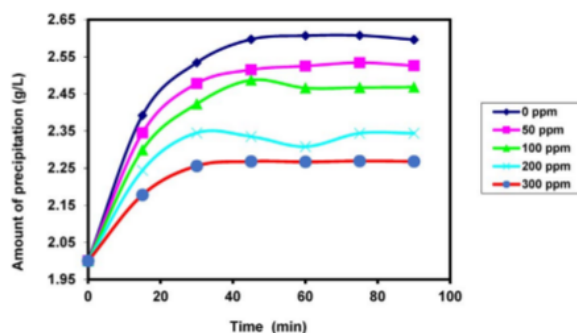


Fig. 5. Effect of inhibitor added on the formation of  $\text{CaCO}_3$  precipitation at the growth solution concentration of 0.6 M.

the  $\text{CaCO}_3$  higher than at the concentration of 0.3 and 0.6 M.

In order to investigate the inhibitor efficiency in inhibiting the rate of  $\text{CaCO}_3$  scale formation may use equation reported by previous research [29] as this below;

$$\text{Percentage of Inhibitor Efficiency (\% IE)} = 100 \times \frac{(C_a - C_b)}{(C_c - C_b)} \quad (1)$$

Where:

$C_a$  = Precipitation amount of  $\text{CaCO}_3$  after added inhibitor at equilibrium (g/L).

$C_b$  = Precipitation amount of  $\text{CaCO}_3$  without inhibitor at equilibrium (g/L).

$C_c$  = Initial precipitation amount of  $\text{CaCO}_3$  (g/L).

From the calculations using Eq. (1) were obtained % IE from variety of the growth solution concentrations and the amount of inhibitor added as listed in Tables 1–3. From these tables, it can be stated that the



**Table 1**  
Inhibitor efficiency in inhibiting the scale formation of  $\text{CaCO}_3$  at the growth solution concentration of 0.1 M.

Inhibitor Concentrations (ppm)	Percentage Inhibitor Efficiency (% IE)
0	0.00
100	20.22
200	71.34
300	91.46

**Table 2**  
Inhibitor efficiency in inhibiting the scale formation of  $\text{CaCO}_3$  at the growth solution concentration of 0.3 M.

Inhibitor Concentrations (ppm)	Percentage Inhibitor Efficiency (% IE)
0	0.00
50	12.08
100	51.55
200	58.56
300	67.99

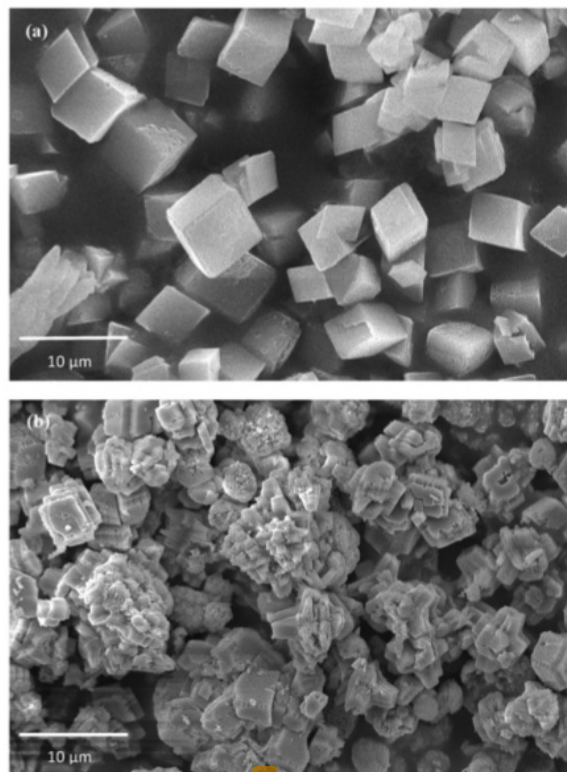
**Table 3**  
Inhibitor efficiency in inhibiting the scale formation of  $\text{CaCO}_3$  at the growth solution concentration of 0.6 M.

Inhibitor Concentrations (ppm)	Percentage Inhibitor Efficiency (% IE)
0	0.00
50	11.75
100	21.48
200	42.28
300	55.03

**Table 4**  
Inhibitor Efficiency in inhibiting  $\text{CaCO}_3$  crystal of different inhibitors, experiment methods, and growth solution concentrations.

Name of Inhibitors	Inhibitor Concentration (ppm)	Inhibitor Efficiency (% IE)	References
Modified Gambier	50–300	12–92	This work
Gambier extracts	50–250	60–100	[13]
Polymaleic acid	1–4	20–100	[18]
Homopolymer of polymaleic acid	4	67	[29]
Terpolymer of polymaleic acid	4	73	[29]
Copolymer of polymaleic acid	4	18	[29]
Polycarboxylic acid	4	70	[29]
5-allocene complexes	10	27–66	[30]
C-methyl-4,10,16,22-tetrametoxycalix[4]arene	10–100	34–100	[31]

inhibitor can inhibit the formation of the  $\text{CaCO}_3$  crystals with% IE of 11.75–91.46% depending on the growth solution concentration and the amount of inhibitor added. The highest% IE of 91.46% occurred at the growth solution concentration of 0.1 M with the amount of the inhibitor added 300 ppm. While, the lowest% IE of 11.75% occurred at the growth solution concentration of 0.6 M with the presence of the inhibitor 50 ppm. In addition, the inhibitor ability in inhibiting the formation of the  $\text{CaCO}_3$  scale formation is still strong enough at the amount of inhibitor added 300 ppm and the growth solution concentration of 0.6 M with the% IE of 55%. Therefore, it can be concluded that the inhibitor can still work at the higher growth solution concentration of 0.6 M. The Inhibitor Efficiency (% IE) from this experiment and other inhibitors from the previous research results in inhibiting the calcium carbonate crystal growth with the addition of



**Fig. 6.** Morphology of  $\text{CaCO}_3$  crystals (a) in the absence of inhibitor (b) in the presence of inhibitor 300 ppm at the concentration of growth solution of 0.1 M (Magnification 2500 $\times$ ).

homopolymer of polymaleic acid (PMA-1), terpolymer of polymaleic acid (PMA-2), copolymer of polymaleic acid (PMA-3), polycarboxylic acid (EM), polyacrylate (PAA), and phosphonate can be seen in Table 4 [18,29–31]. The Inhibitor Efficiency (% IE) from the inhibitors derived from the polymaleic acid, polycarboxylic acid, polyacrylate, and phosphonate groups in inhibiting the formation of calcium carbonate crystals was around 20–100% [18,29,30].

For further identification of the inhibitor effect on the  $\text{CaCO}_3$  crystal growth, SEM analysis was performed toward morphology and crystal surface of the crystal resulted. SEM analysis results toward morphology and crystal surface of the  $\text{CaCO}_3$  crystals with and without inhibitor displayed in Figs. 6 and 7. From these figures, it can be observed that the presence of the inhibitor not only changes the morphology of  $\text{CaCO}_3$  crystals but also inhibits the growth of the  $\text{CaCO}_3$  crystal. The size of  $\text{CaCO}_3$  crystal in the presence of inhibitor (Figs. 6 and 7) was smaller compared with in the absence of inhibitor. Thus, Figs. 6 and 7 are visual evidences of the effect of adding the inhibitor on the  $\text{CaCO}_3$  scale formation. The morphology change of  $\text{CaCO}_3$  crystal was because of crystal distortion. In the crystal distortion mechanism, the inhibitor added into the  $\text{CaCO}_3$  growth solution affected the ordering and growth reaction of crystals and induced an irregular, noncrystalline shape. The inhibitor also delayed the crystal growth of the usually highly ordered  $\text{CaCO}_3$  crystal. The inhibitor molecules especially tannin from the Gambir extract adsorbed onto the active growth sites of the  $\text{CaCO}_3$  seed crystals, resulting in the blockage and inhibition of further growth [32]. This inhibitor effect can be seen in Figs. 6 and 7.

Further evidence of the inhibitor efficiency can be observed with analyzing the particle size distribution of the  $\text{CaCO}_3$  crystal produced with and without inhibitor added into the growth solution of the  $\text{CaCO}_3$  crystals (Figs. 8 and 9). The observation results from Figs. 8 and 9 show

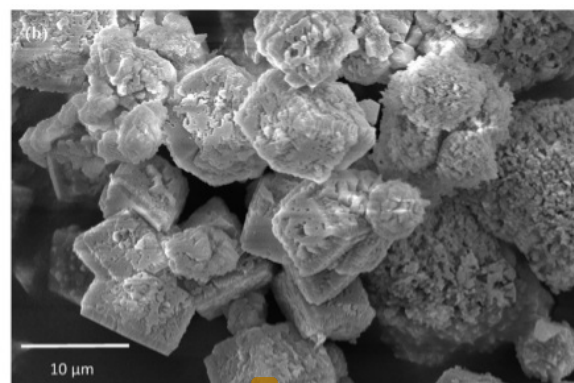
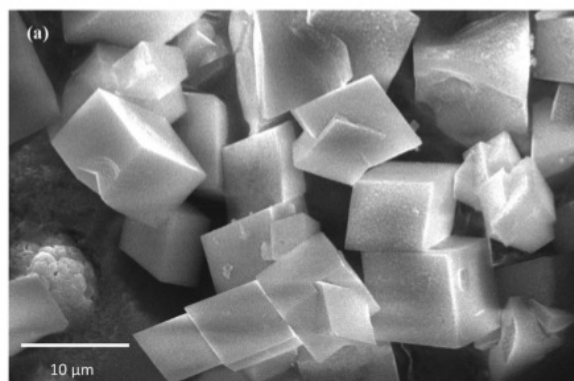


Fig. 7. Morphology of  $\text{CaCO}_3$  crystals (a) in the absence of inhibitor (b) in the presence of inhibitor 300 ppm at the concentration of growth solution of 0.6 M (Magnification 2500 $\times$ ).

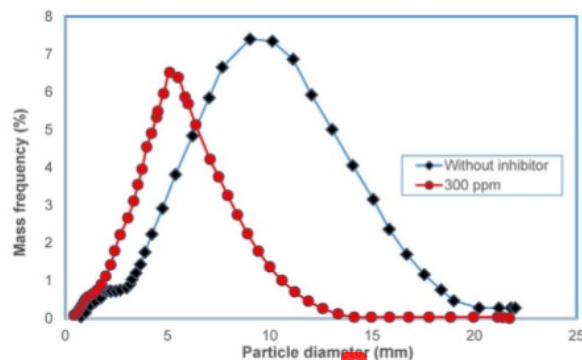


Fig. 8. Particle size distribution of  $\text{CaCO}_3$  crystals in the absence of inhibitor and in the presence of 300 ppm of inhibitor at the growth solution concentration of 0.1 M.

that the average of the particle size distribution of the  $\text{CaCO}_3$  crystals in the presence of inhibitor increased dramatically. In the growth solution of 0.1 M, the average of particle size distribution of  $\text{CaCO}_3$  crystals in the absence of inhibitor was around 10.6  $\mu\text{m}$ . After the inhibitor added into the growth solution of  $\text{CaCO}_3$  crystal, the average of particle size distribution of the  $\text{CaCO}_3$  crystal was 5.01  $\mu\text{m}$ . While, in the growth solution of 0.6 M, the average of particle size distribution of the  $\text{CaCO}_3$  crystals in the absence of inhibitor was 17.3  $\mu\text{m}$ . When the inhibitor added into the growth solution of the  $\text{CaCO}_3$  crystal, the average particle size distribution of  $\text{CaCO}_3$  crystals dropped to 8.5  $\mu\text{m}$ . Thus, it can be concluded that generally the addition of inhibitor into the growth solution of the  $\text{CaCO}_3$  crystal can inhibit the  $\text{CaCO}_3$  scale formation. The particle size distribution data produced from the  $\text{CaCO}_3$

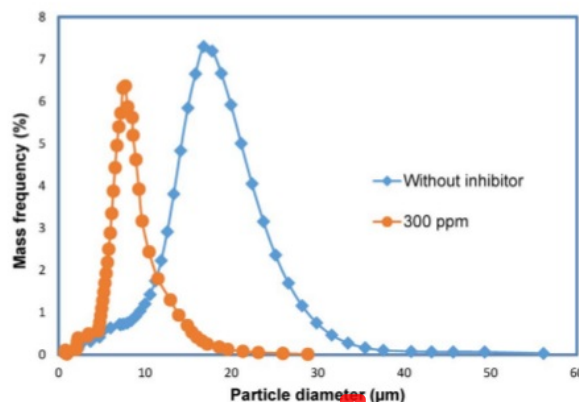


Fig. 9. Particle size distribution of  $\text{CaCO}_3$  crystals in the absence of inhibitor and in the presence of 300 ppm of inhibitor at the growth solution concentration of 0.6 M.

crystal formation were accordance with the previous result using Gambier extract as inhibitor of the  $\text{CaCO}_3$  scale formation [13].

As seen in Tables 1–3 and Figs. 3–5, the inhibition on  $\text{CaCO}_3$  scale formation substantially increased when the inhibitor concentration increased. This case can be interpreted that after the scale inhibitor was added into the solution, chelating reaction among the carboxyl from citric and benzoic acid, and  $\text{Ca}^{2+}$  ions occurred in aqueous solution. And also, chelating reaction can be occurred between the hydroxyl from tannic acid, catechin, and quercetin (from the Gambier extracts as the main chemical compounds) and  $\text{Ca}^{2+}$  ions, as well as scale inhibitor- $\text{Ca}$  was adsorbed on the surface of  $\text{CaCO}_3$  crystal. The microcrystalline of  $\text{CaCO}_3$  with the similar charges repelled each other, prevented the formation of crystal nucleus, and reduced the  $\text{CaCO}_3$  crystal growth rate. The similar case occurred in the presence of curcumin-malic acid in controlling of scale in industrial cooling water treatment [4]. In addition, the  $\text{CaCO}_3$  crystal growth in the presence of inhibitor did not form the regular crystal as seen in Figs. 6 and 7, therefore inhibiting the formation of the  $\text{CaCO}_3$  scale. Thus, the percentage inhibitor efficiency increased as the inhibitor concentration level raised from 50 to 300 ppm. At the  $\text{CaCO}_3$  growth concentration of 0.1 M, the percentage of inhibitor efficiency in the inhibitor presence of 100 ppm was around 20% and it increased to be 71 and 92% when the inhibitor presence was increased to be 200 and 300 ppm respectively. The similar cases were also occurred at the  $\text{CaCO}_3$  growth concentration of 0.3 and 0.6 M. However, the percentage of inhibitor efficiency in the  $\text{CaCO}_3$  growth concentration of 0.3 and 0.6 M is lower than at the  $\text{CaCO}_3$  growth concentration of 0.1 M at all inhibitor concentration levels added (Tables 2 and 3). The differences of the percentage of inhibitor efficiency at the same concentration level were due to different concentrations of the  $\text{CaCO}_3$  growth concentration. The higher the concentration of the  $\text{CaCO}_3$  growth solution is the higher the growth rate of  $\text{CaCO}_3$  crystal. At the  $\text{CaCO}_3$  growth concentration of 0.3 and 0.6 M, the ability of the inhibitor to inhibit the formation of  $\text{CaCO}_3$  crystals will be slower compared at the  $\text{CaCO}_3$  growth concentration of 0.1 M. The percentage of inhibitor efficiency decreased with the increasing of the  $\text{CaCO}_3$  growth solution concentration because the increase of  $\text{CaCO}_3$  growth solution concentration facilitated the formation of the  $\text{CaCO}_3$  scale crystal, accelerated the crystallization process, and reduced the ability of inhibitor to inhibit the formation of the  $\text{CaCO}_3$  scale. Therefore, the inhibition of inhibitor at the addition of 300 ppm in the  $\text{CaCO}_3$  growth solution concentration of 0.1, 0.3, and 0.6 is 92, 68 and 55%, respectively. These experiment results are also comparable to those studied for the calcium carbonate crystallization in the presence of green inhibitor of polymaleic acid [18], green inhibitors of thiamine and pyridoxine [33], several commercial inhibitors produced by industry [34], and calix [4] resorcinarene [35].



The inhibitor efficiency depends on the concentration of the growth solution, in general the higher the concentration of the growth solution is the higher the inhibitor added. In this experiment, the growth solution concentrations of  $\text{CaCO}_3$  were 0.1–0.6 M with the percentage inhibitor efficiency of 12–92% and the inhibitor added up to 300 ppm. These results are still comparable with in the case of calcium carbonate crystal growth inhibition test at the calcium ion concentration (as growth solution) of 125 mg/L (0.003 M) and the inhibitor of polycarboxylic or polymaleic acid compounds added of 4 ppm [29]. Previous researchers reported also the use of citric acid as inhibitor of calcium carbonate at the concentration of calcium ion 0.0019 M with the citric acid added 1–10 ppm and the inhibitor efficiency of around 25–30% [36]. If it is compared these experiments, the doses of inhibitor added is still reasonable. Similar results with similar experiment condition were shown in Table 4 with the addition of Gambier extract [13] and C-methyl-4,10,16,22-tetramethoxy calix[4]arene [31].

#### 4. Conclusion

The modification of the Gambier extracts with the addition of benzoic and citric acid with the composition ratio of Gambier extract:benzoic acid:citric acid/2:1:2 in 1 L of water solution as green inhibitor increased the quality of this mixture. This mixture was able to inhibit the formation of  $\text{CaCO}_3$  scale at various inhibitor concentrations of 50–300 ppm and growth solution concentrations of 0.1–0.6 M using seeded experiment method with the Inhibitor Efficiency (% IE) of 12–92%. The inhibitor used also changed the morphology of  $\text{CaCO}_3$  crystals and it made the crystal size of  $\text{CaCO}_3$  crystals to be smaller in their crystal size distribution after addition of this inhibitor.

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