Preliminary Evaluation of a Barley-Based Polyaspartic Acid Formulation for Calcium Carbonate Scale Control

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Calcium carbonate ($CaCO_3$) scale deposition remains one of the major flow assurance challenges in oil and gas production systems, leading to reduced productivity, equipment damage, and increased operational costs. Conventional scale inhibitors are generally effective; however, concerns regarding environmental toxicity have motivated the search for sustainable alternatives. In this study, a green scale inhibitor formulation comprising barley powder and polyaspartic acid (PASP) was developed and evaluated for its potential to mitigate $CaCO_3$ scale deposition. Barley powder was prepared through drying, milling, and particle-size classification, followed by formulation with PASP at different concentrations. The scale inhibition performance of the formulations was assessed using a static jar test, and the remaining $CaCO_3$ was quantified gravimetrically. Among the tested formulations, the combination of 7 wt.% barley and 1 wt.% PASP exhibited the highest scale inhibition efficiency (42.6%), suggesting the presence of an optimum formulation composition. Chemical characterization of barley using Triple Quadrupole Gas Chromatography–Mass Spectrometry (TQ GC–MS) identified several organic compounds, including 9-octadecanamide, octadecanamide, 5-nonylamine, and fatty acid derivatives, which may contribute to scale inhibition through calcium-ion complexation and crystal growth modification. These findings highlight the potential of barley–PASP formulations as environmentally friendly alternatives for calcium carbonate scale control and provide a foundation for future optimization and mechanistic studies.

Keywords: Calcium carbonate scale, green inhibitor, barley, polyaspartic acid, scale inhibition efficiency

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Flow assurance remains one of the major operational challenges in oil and gas production systems. The uninterrupted transportation of hydrocarbons from the reservoir to processing facilities can be significantly affected by various deposition-related problems, including corrosion, wax deposition, hydrate formation, and mineral scale precipitation. Among these challenges, inorganic scale deposition is particularly problematic because it restricts fluid flow, reduces production efficiency, increases maintenance costs, and shortens the operational lifespan of production equipment [1, 2].

Scale formation can occur throughout the production system, including the reservoir, wellbore, production tubing, flowlines, and surface facilities such as pumps, separators, and valves. The deposition of scale is commonly associated with changes in pressure, temperature, fluid composition, and the mixing of incompatible waters, which alter the chemical equilibrium of produced fluids and promote mineral precipitation [1]. Figure 1 illustrates a typical example of scale deposition in production tubing, where the accumulation of mineral deposits restricts fluid flow and adversely affects production performance.

Calcium carbonate ($CaCO_3$) is one of the most frequently encountered inorganic scales in oil and gas operations. The formation of $CaCO_3$ scale generally involves a series of processes, including ion pairing, nucleation, crystal growth, agglomeration, and deposition [4, 5]. As illustrated in Figure 2, dissolved calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}) initially combine to form ion pairs, which subsequently aggregate and develop into stable nuclei. These nuclei continue to grow through the incorporation of additional ions, forming microcrystals and eventually larger macrocrystals.

Figure 1. Scale Formation in the Tubing [3].

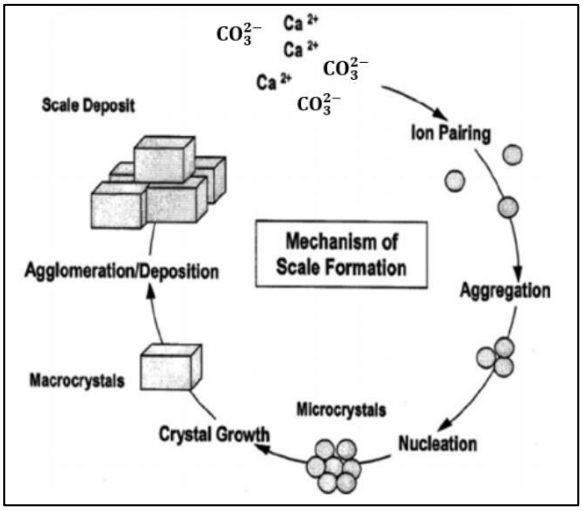

Figure 2. Mechanism of Scale Formation [4].

The accumulation and deposition of these crystals on equipment surfaces result in scale formation, causing flow restrictions and operational difficulties [4].

Chemical scale inhibitors are widely employed in the petroleum industry to mitigate scale formation and maintain production efficiency. Conventional inhibitors, particularly phosphonate and polymer-based formulations, are generally effective in preventing mineral precipitation. However, increasing environmental concerns regarding toxicity, persistence, and potential ecological impacts have stimulated interest in the development of environmentally friendly alternatives [2, 6]. Consequently, significant research efforts have been directed toward the investigation of green inhibitors derived from renewable and biodegradable materials.

Polyaspartic acid (PASP) has emerged as a promising biodegradable scale inhibitor due to its excellent calcium-chelating capability and low environmental impact. The presence of multiple carboxyl functional groups enables PASP to interact with calcium ions, thereby reducing their participation in scale formation processes [7, 8]. Nevertheless, the inhibition performance of PASP may be influenced by operating conditions and inhibitor dosage, creating opportunities for further enhancement through formulation with natural materials.

Plant-derived biomaterials have recently attracted considerable attention as sustainable alternatives for industrial water treatment and scale control applications. Natural materials rich in polysaccharides, fatty acids, amides, and nitrogen-containing compounds have demonstrated potential in modifying crystal growth behaviour and reducing mineral deposition [9, 10]. Barley is an abundant agricultural material containing carbohydrates, proteins, fatty acid derivatives, and other bioactive compounds that may contribute to scale inhibition through crystal growth modification and calcium-ion interaction mechanisms.

Despite extensive studies on biodegradable scale inhibitors, limited information is available regarding the application of barley-derived materials for calcium carbonate scale control, particularly in

combination with biodegradable polymers such as PASP. Therefore, the development of a barley–PASP formulation represents a potentially sustainable approach for mitigating calcium carbonate scale formation while reducing environmental impact.

The objectives of this study were: (i) to develop a barley–PASP formulation as a potential green inhibitor for calcium carbonate scale mitigation, (ii) to evaluate the scale inhibition performance of the formulation at different concentrations using a static jar test, and (iii) to identify the major chemical compounds present in barley using Triple Quadrupole Gas Chromatography–Mass Spectrometry (TQ GC–MS) and assess their potential contribution to scale inhibition.

EXPERIMENTAL

Chemicals and Materials

Barley grains were purchased from a local commercial supplier in Johor, Malaysia. Polyaspartic acid (PASP), calcium chloride ($CaCl_2$), sodium carbonate (Na_2CO_3), and distilled water were used throughout this study. All chemicals were of analytical grade and used without further purification. Distilled water was employed for the preparation of all solutions.

Preparation of Barley Powder

Barley grains were thoroughly washed with distilled water to remove dust and surface impurities prior to drying. The cleaned grains were dried in a roller oven at 60 °C for 2 h to reduce moisture content. Subsequently, the dried grains were ground using an electric blender to obtain barley powder. Figure 3 shows the experimental workflow for barley powder preparation. The resulting powder was sieved using a mechanical sieve shaker to obtain particle size fractions of 355, 250, and 150 µm. Based on preliminary observations, the 250 µm particle size fraction was selected for subsequent formulation studies due to its good dispersibility and ease of preparation.

Preparation of Barley-PASP Formulations

Barley–PASP formulations were prepared by dispersing barley powder in distilled water under continuous stirring. The suspension was filtered through filter paper to remove insoluble particles. Subsequently, polyaspartic acid (PASP) was added to the filtrate and stirred until a homogeneous solution was obtained.

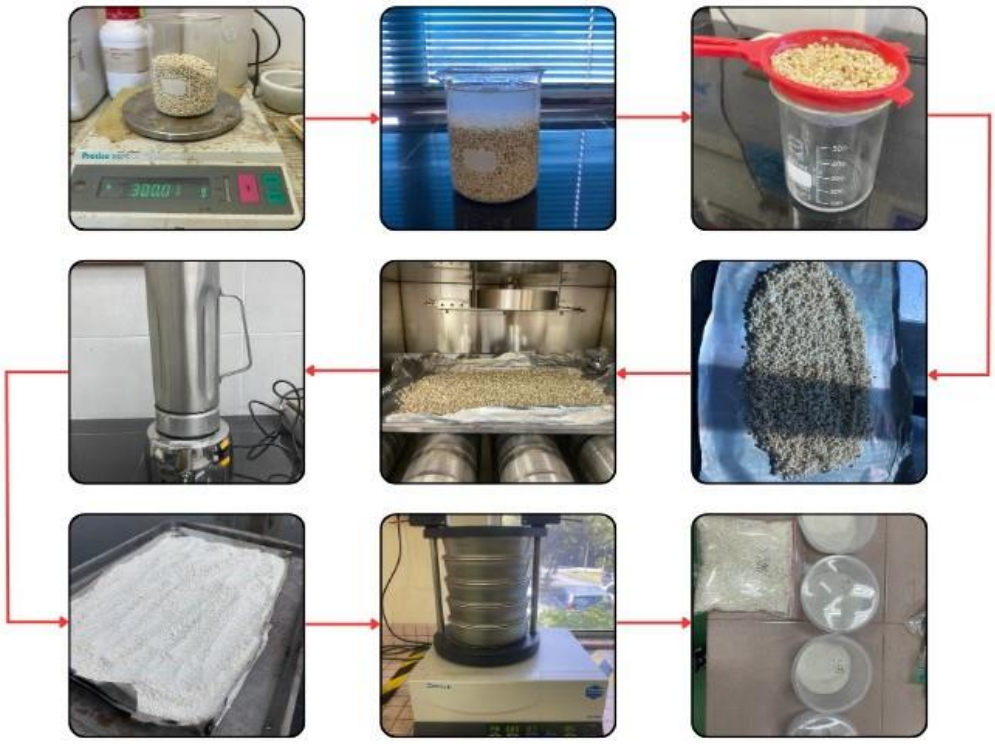

Figure 3. Experimental workflow for barley powder preparation.

Table 1. Composition of barley-PASP formulations.

Formulation	Barley (wt.%)	PASP (wt.%)
B5	5	0
BP5	5	1
BP7	7	1
BP10	10	1

Four formulations were investigated, namely B5 (5 wt.% barley), BP5 (5 wt.% barley + 1 wt.% PASP), BP7 (7 wt.% barley + 1 wt.% PASP), and BP10 (10 wt.% barley + 1 wt.% PASP) as shown in Table 1. For each formulation, the required amount of barley powder was dispersed in 100 mL of distilled water prior to PASP addition. The prepared formulations were used immediately for scale inhibition evaluation.

Scale Inhibition Test

Calcium carbonate ($CaCO_3$) was synthesized via a precipitation method using calcium chloride and sodium carbonate solutions according to Equation (1):

$$CaCl_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaCl(aq) \quad (1)$$

Briefly, calcium chloride and sodium carbonate were dissolved separately in distilled water. The sodium carbonate solution was gradually introduced into the calcium chloride solution under continuous stirring, resulting in the formation of a white $CaCO_3$ precipitate. The precipitate was filtered, washed with distilled water to remove residual sodium chloride, and dried at 60 °C for 45 min. The scale inhibition performance of the prepared formulations was evaluated using a modified static jar test adapted from commonly reported scale inhibition methodologies [2]. An initial mass of 10 g of synthesized $CaCO_3$ was introduced into each inhibitor formulation and mixed under identical experimental conditions. Following the treatment period, the remaining solid $CaCO_3$ was separated by filtration and dried in an oven at 60 °C for 1 h. The dried solids were weighed using an analytical balance. The effectiveness of each formulation was expressed as Scale Inhibition Efficiency (SIE), calculated using Equation (2), which is commonly employed for evaluating inhibitor performance in laboratory-scale studies [4].

$$SIE\ (\%) = [(W_0 - W_i)/W_0] \times 100 \quad (2)$$

where W_0 is the initial mass of $CaCO_3$ (g) and W_i is the mass of $CaCO_3$ recovered after treatment (g). The formulation exhibiting the highest SIE value was considered the optimum inhibitor formulation. All experiments were conducted in triplicate and the average values were reported. Figure 4 shows the experimental procedure for the scale inhibition test.

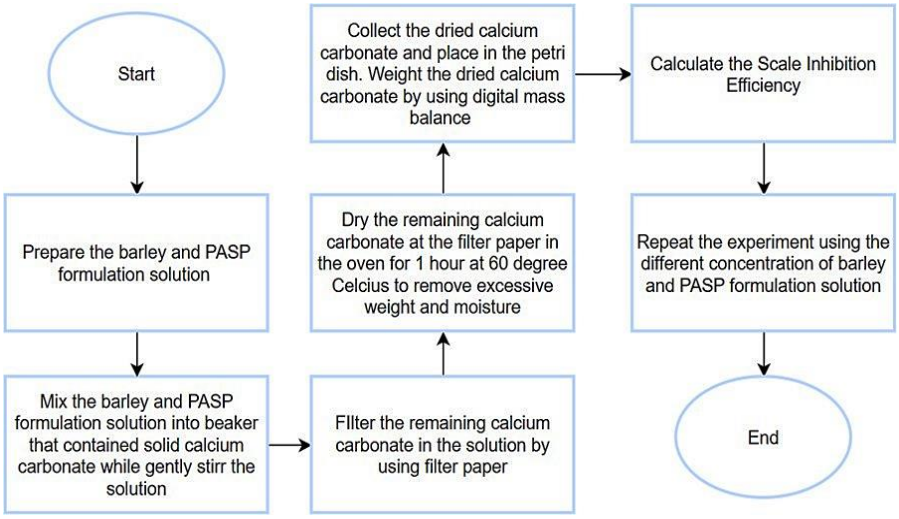

Figure 4. Experimental procedure for scale inhibition evaluation.

Figure 5. Barley powder fractions at different particle sizes.

Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The chemical composition of the barley solution was characterized using Triple Quadrupole Gas Chromatography–Mass Spectrometry (TQ GC–MS). Prior to analysis, the barley extract was filtered to remove suspended particles. The GC–MS analysis was conducted to identify the major organic compounds potentially associated with scale inhibition performance. The resulting chromatograms were analysed by comparing the obtained mass spectra with those available in the instrument library database. Compound identification was based on retention time, peak abundance, and spectral matching. The major compounds identified from the barley solution were subsequently evaluated and discussed in relation to their potential roles in calcium carbonate scale mitigation.

Data Analysis

The inhibition performance of each formulation was evaluated based on the calculated Scale Inhibition Efficiency (SIE). The influence of barley concentration on inhibition performance was assessed by comparing the SIE values obtained for different formulations. GC–MS results were interpreted to identify chemical constituents that may contribute to scale inhibition through potential mechanisms such as calcium-ion complexation, crystal growth modification, and particle dispersion. The optimum formulation was determined based on the highest observed inhibition efficiency.

RESULTS AND DISCUSSION

Particle Size Selection of Barley Powder

The barley grains were ground and sieved into particle size fractions of 355, 250, and 150 µm prior to formulation with PASP as shown in Figure 5. Particle size plays an important role in determining the dispersibility and dissolution behaviour of natural materials in aqueous systems [11]. Smaller particles generally possess a larger surface-area-to-volume ratio, facilitating greater interaction between active compounds and the surrounding medium.

Based on visual observation, the 150 µm fraction exhibited the finest texture, whereas the 355 µm fraction appeared relatively coarse. Although finer particles may provide enhanced dissolution characteristics, excessively small particles may increase filtration difficulty and handling complexity. Therefore, the 250 µm fraction was selected for subsequent experiments as it provided a balance between particle dispersion and operational practicality.

According to the Ostwald–Freundlich relationship, the apparent solubility of solid particles increases with decreasing particle size due to increased surface energy [11]. The improved dispersibility of the 250 µm barley powder is expected to facilitate the release of bioactive compounds that may contribute to calcium carbonate scale inhibition.

Scale Inhibition Performance of Barley-PASP Formulations

The scale inhibition performance of the barley–PASP formulations was evaluated based on the remaining calcium carbonate mass after treatment. Figure 6 summarizes the corresponding Scale Inhibition Efficiency (SIE) values.

The barley-only formulation (B5) reduced the calcium carbonate mass from the initial 10 g to 8.78 g, corresponding to an inhibition efficiency of 12.2%. The relatively low inhibition efficiency indicates that barley alone possesses limited ability to mitigate calcium carbonate scale formation under the investigated conditions.

The incorporation of PASP significantly improved the inhibition performance. The BP5 formulation (5 wt.% barley + 1 wt.% PASP) achieved an SIE of 30.5%, demonstrating that PASP contributed additional scale inhibition capability

through its calcium-binding functionality. Polyaspartic acid contains multiple carboxyl groups capable of interacting with calcium ions, thereby reducing their participation in calcium carbonate precipitation [7,8].

Among the tested formulations, BP7 (7 wt.% barley + 1 wt.% PASP) exhibited the highest inhibition efficiency of 42.6%. This result suggests the existence of an optimum concentration range where sufficient active compounds are available to interfere with crystal nucleation and growth processes. The improved performance may also indicate a complementary interaction between the naturally occurring compounds present in barley and the chelating properties of PASP.

Interestingly, a further increase in barley concentration to 10 wt.% (BP10) resulted in a decline in inhibition efficiency to 17.9%. Excessive concentrations of organic material may promote molecular aggregation, thereby reducing the availability of active functional groups responsible for inhibiting scale formation. Similar behaviour has been reported for various bio-based inhibitors, where inhibition performance increases up to an optimum concentration before declining at higher dosages [2, 6].

Although the maximum inhibition efficiency obtained in this study was moderate compared with some commercial scale inhibitors reported in the literature [6,8], the results demonstrate the feasibility of utilizing barley-derived materials as environmentally benign additives for scale mitigation. The findings provide preliminary evidence supporting further optimization of barley–PASP formulations for sustainable flow assurance applications.

GC-MS Characterization and Proposed Inhibition Mechanism

The chemical composition of the barley solution was investigated using TQ GC–MS analysis. A total of 26 chromatographic peaks were detected, indicating the presence of various organic compounds within the barley extract. The five most abundant compounds identified are shown in Figure 7.

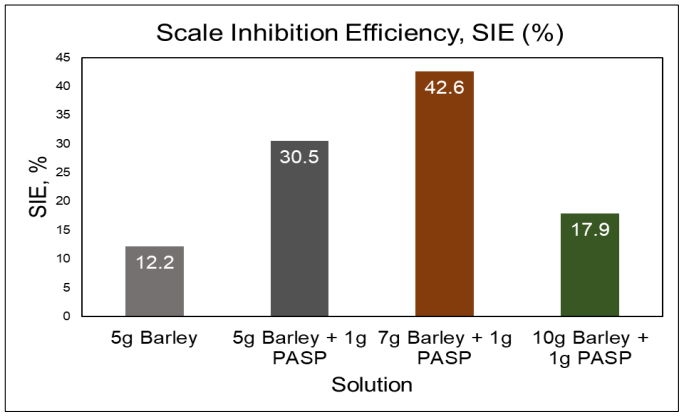

Figure 6. Scale inhibition efficiency of barley-PASP formulations.

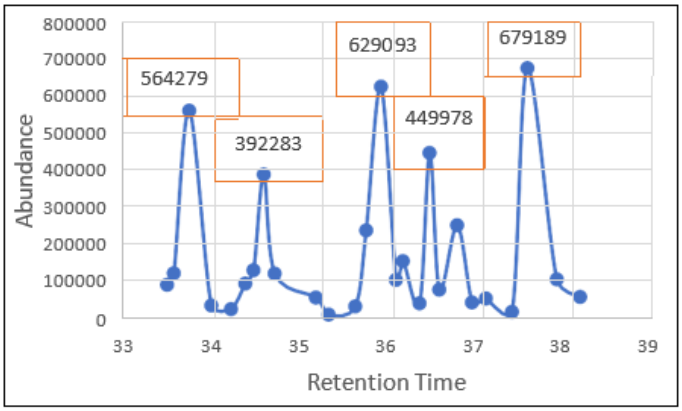

Figure 7. TQ GC-MS chromatogram of barley extract.

Among the identified compounds, 9-octadecanamide (Z)- exhibited the highest abundance, followed by 9-octadecenoic acid methyl ester, 5-nonylamine, octadecanamide, and hexadecanoic acid methyl ester. These compounds belong primarily to the amide, amine, and fatty acid derivative groups.

The presence of amine-containing compounds such as 5-nonylamine suggests the potential for interaction with calcium ions through electron-donating functional groups [2, 6]. Such interactions may reduce the availability of free calcium ions required for calcium carbonate precipitation. In addition, fatty acid derivatives and amides may adsorb onto developing crystal surfaces, thereby interfering with crystal growth and aggregation processes [9].

Previous studies have reported that organic compounds containing nitrogen and oxygen-bearing functional groups may contribute to scale mitigation through calcium-ion complexation, crystal growth modification, and particle dispersion mechanisms [9]. Therefore, the compounds identified in the present study may contribute to the observed inhibition performance of the barley–PASP formulations.

Nevertheless, the exact inhibition mechanism cannot be conclusively established based solely on GC–MS analysis. Additional characterization techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD) would be beneficial for confirming the interaction between the inhibitor formulation and calcium carbonate crystals.

CONCLUSION

A barley–polyaspartic acid (PASP) formulation was successfully developed and evaluated as a potential green inhibitor for calcium carbonate ($CaCO_3$) scale control. The inhibition performance was influenced by the formulation composition, with the BP7 formulation (7 wt.% barley and 1 wt.% PASP) exhibiting the highest Scale Inhibition Efficiency (SIE) of 42.6%. The results demonstrate the feasibility of combining naturally derived biomaterials with biodegradable polymers to develop environmentally friendly alternatives for scale management.

GC–MS analysis identified the presence of amides, fatty acid derivatives, and amine-containing compounds in the barley extract. These compounds may contribute to the observed inhibition performance through mechanisms involving calcium-ion interaction, crystal growth modification, and particle dispersion. The findings provide preliminary evidence that barley-derived compounds can function as sustainable additives for mitigating calcium carbonate deposition.

Although the inhibition efficiency obtained in this study remains lower than that reported for some commercial inhibitors, the renewable nature and biodegradability of the barley–PASP formulation highlight its potential for sustainable flow assurance applications. Future work should focus on optimizing the formulation composition and elucidating the inhibition mechanism through advanced characterization techniques, including Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD).

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