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Study of Carboxymethylated Modified Polysaccharides as Scale Inhibitors in Petroleum Production

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Abstract
Research on 'green' scale inhibitors is fundamental for the petroleum industry. This work studied the potential of two modified polysaccharide as scale inhibitors. Soluble starch and maltodextrin, biodegradable water-soluble polymers of glucose, were modified by carboxymethylation of one of the monomer's hydroxyl groups to improve their scale inhibition performance. The modified polysaccharides were obtained through the reaction of soluble starch and maltodextrin with chloroacetic acid in the presence of sodium hydroxide using ethanol as a solvent. The reactions were conducted in an automated reactor at 50 ºC with magnetic stirring for 4 h. At the end of the experiment, the pH was neutralized and the reaction product was vacuum-filtered and dried at 60 ºC for 48 h. The performance of the modified polysaccharides in calcium carbonate scale inhibition was evaluated through a tube-blocking test in a dynamic scale loop system. A concentration of 150 mg L^{-1} of carboxymethyl soluble starch inhibited scale formation, improving the performance of soluble starch by increasing the scaling time from 40 to 80 min. This improved behavior was also observed with the carboxymethyl maltodextrin. Therefore, the carboxymethylation of biodegradable polysaccharides showed a promising path to develop scale inhibitors based on these types of molecules.

Keywords
Carboxymethylation; biopolymers; green scale inhibitor

Introduction

Scale is a significant flow assurance challenge for the petroleum industry, reducing or even halting production. The primary approach to tackle this issue is the use of scale inhibitors, which act through various mechanisms to prevent or retard the scale formation [1]. However, a drawback of commercially available scale inhibitors is their potential to enrich aquatic ecosystems with phosphorous and nitrogen, leading to eutrophication. Consequently, recent research efforts have been directed toward the development of 'green' scale inhibitors [2].
Previous studies have demonstrated the influence of biodegradable polysaccharides like maltodextrin and soluble starch on the calcium carbonate precipitation process and scale formation [3]. Moreover, starchy food effluents have shown promise as scale inhibitors, notably the aqueous extract of sweet potato. The efficacy of sweet potato aqueous extract was attributed not only to its starch content but also to the presence of phenolic acids. This suggests that the presence of carboxyl groups improves the performance of a scale inhibitor [4].
The present study evaluated the modification of soluble starch and maltodextrin to improve their performance through carboxymethylation reaction, involving the substitution of a hydroxyl group with a carboxymethyl group in the monomer structure. The efficiency of the modification was evaluated using a tube-blocking test.

Methodology
Materials

Soluble starch and maltodextrin were purchased from ACS Cientifica (Sumaré, Brazil). Chloroacetic acid, sodium hydroxide, hydrochloric acid, ethanol, calcium chloride, sodium bicarbonate, and sodium chloride were purchased from Isofar (Rio de Janeiro, Brazil). All reagents were of analytical grade and used as received. Carbon dioxide was supplied by Air Products (Rio de Janeiro, Brazil). Ultrapure water was used for the preparation of aqueous solutions.

Modified polysaccharides preparation

The reactions to produce the modified polysaccharides were conducted in an automated reactor equipped with temperature and stirring control. 8,0 g of soluble or 11,6 g of maltodextrin and 4,0 g of sodium hydroxide were added to 100 mL of ethanol and allowed to dissolve for 1 h at 50 ºC with stirring. Subsequently, 4,33 g of monochloroacetic acid were added to start the carboxymethylation reaction, which continued for 4 h. Following completion, the pH of the reaction medium was neutralized, and the product was vacuum filtered and dried at 60 ºC for 48 h. The modified polysaccharides were then stored at room temperature in a desiccator, to protect it from moisture. Figure 1 represents the carboxymethylation reaction of the soluble starch and maltodextrin. The difference between the two polysaccharides is the lenght of the polymeric chain. The chain (n value in the Figure 1) is greater for the starch.

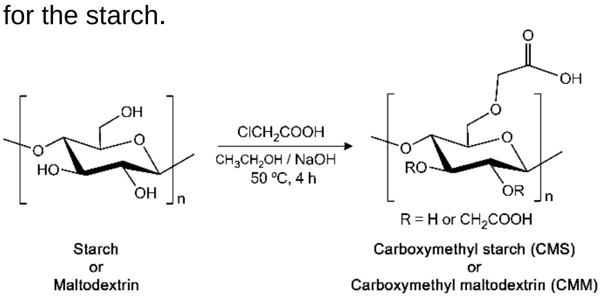

Figure 1. Schematic reaction showing the carboxymethylation of the starch and the maltodextrin.

Tube-blocking test

The performance of the modified polysaccharides in inhibiting calcium carbonate scale formation was evaluated using a tube-blocking test protocol conducted in a dynamic scale loop (DSL) system. The DSL system operated by pumping two aqueous solutions of calcium chloride and sodium bicarbonate through a test coil. Scale formation was monitored by detecting a pressure increase of more than 0.5 psi between the inlet and outlet of the test coil, measured by a pressure transducer. The concentrations of the aqueous solutions were 1495 mg L^{-1} of calcium chloride and 1500 mg L^{-1} of sodium bicarbonate, with 17500 mg L^{-1} of sodium chloride in both solutions. Various concentrations of the modified polysaccharides were tested by adding the desired amount to the sodium bicarbonate solution. The experimental conditions for the tube-blocking tests used a flow rate of 5 mL min^{-1} for each solution, pH 7, 80 ºC, and 10 bar.

Results and Discussion

Figure 2 illustrates the tube-blocking test results for carboxymethyl soluble starch (CMS). It is evident that the presence of this modified polysaccharide prolonged the scaling time compared to the control test (without inhibitor), demonstrating its inhibitory effect. Moreover, scaling time increased with higher concentrations of carboxymethyl soluble starch, revealing a minimum inhibitory concentration (MIC) of 150 mg L^{-1}.

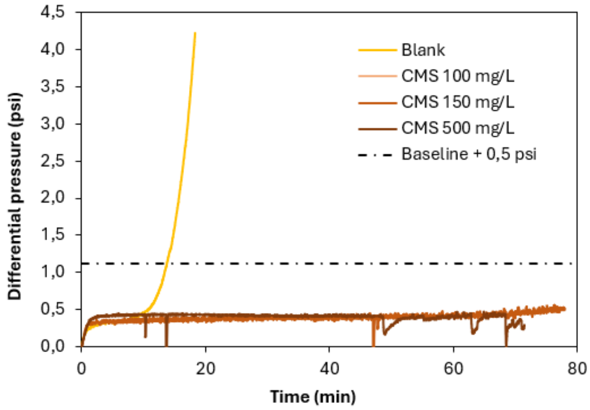

Figure 2. Tube-blocking test results for different concentrations of CMS.

Figure 3 provides a comparative evaluation of the scale inhibition performance between unmodified soluble starch and CMS at equal concentrations (150 mg L^{-1}). At this concentration, unmodified soluble starch exhibited a scaling time of 40 min. Conversely, CMS exhibited a scaling time twice as long that of the unmodified starch. This suggests that the substitution of a hydroxyl group with a carboxymethyl group in the monomer (glucose) structure improves the performance of the polysaccharide as a scale inhibitor.

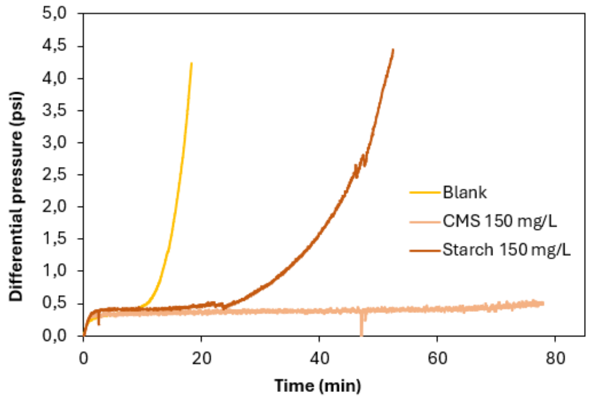

Figure 3. Comparative evaluation of the scale inhibition performance between soluble starch and CMS.

Figure 4 displays the results for maltodextrin, showing that its MIC is of 300 mg L^{-1}, which is higher than that of CMM. This discrepancy may be attributed to the polymer chain length, which is approximately 20 glucose units for maltodextrin compared to more than 300 for soluble starch [5]. A study conducted previously by our group already showed a strong relationship between the chain length of the polysaccharide and their efficiency as scale inhibitor. Also, due to its length, soluble starch has more hydroxyl groups available for substitution with carboxymethyl groups, resulting in an improved performance as scale inhibitor.

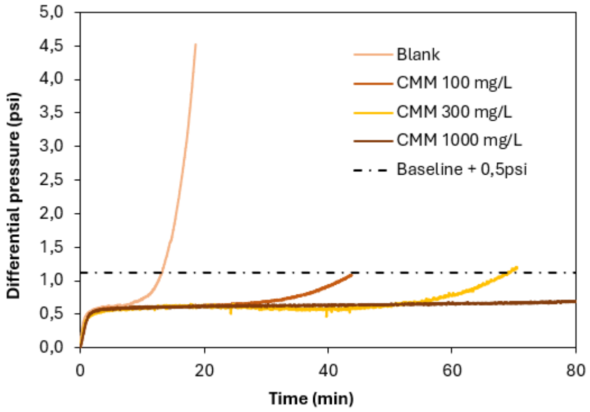

Figure 4. Tube-blocking test results for different concentrations of CMM.

Although the MIC of CMM was higher than that of CMS, as depicted in Figure 4, the effect of carboxymethylation was still notably significant. As shown in Figure 5, at a concentration of 1000 mg L^{-1}, unmodified maltodextrin exhibited a scaling time of 50 min. In contrast, CMM, even at a lower concentration of 100 mg L^{-1}, resulted in an almost equal scaling time as its unmodified version. This means that, with only one step modification of the carbohydrate, there was a reduction of 10x in its concentration to achieve a similar efficiency. While even at a high concentration of 1000 mg L^{-1} maltodextrin was not competitive to be used as inhibitor, modifying it made this molecule be interesting to be used as a 'green' inhibitor.

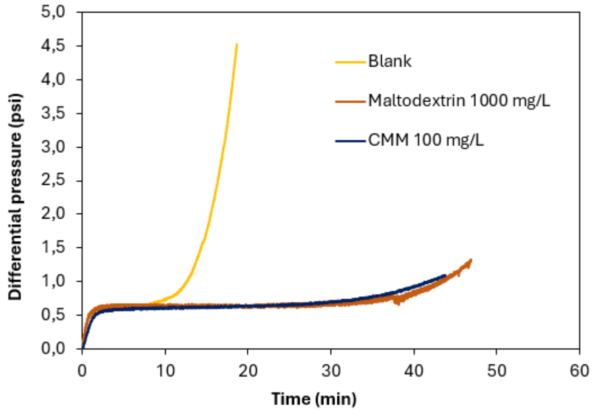

Figure 5. Comparative evaluation of the scale inhibition performance between maltodextrin and carboxymethyl maltodextrin.

Conclusions

The modified polysaccharides, CMS and CMM, showed a significant better performance in the inhibition of calcium carbonate scale compared to their unmodified counterparts. These results suggests that the carboxymethylation of biodegradable polysaccharides is a promising path to develop scale inhibitors for petroleum production.

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Responsibility Notice

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