



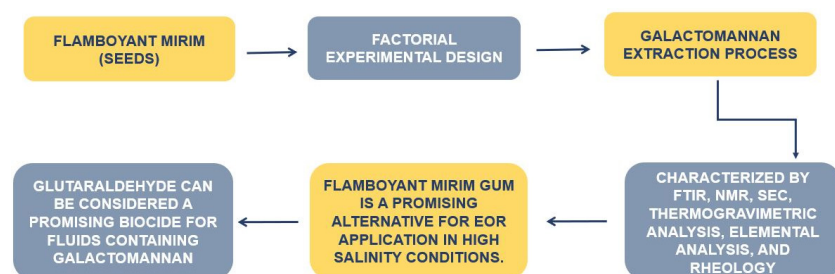
ARTICLE

Extraction and Evaluation of Flamboyant Mirim Gum as a Potential Viscosifying Agent for Enhanced Oil Recovery Fluids

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Flamboyant mirim gum is a galactomannan extracted from *Caesalpinia pulcherrima* seeds, a legume family shrub. The main objective of this work was to propose a factorial experimental design to optimize the galactomannan extraction process from its seeds and evaluate its potential as a viscosifying agent for

enhanced oil recovery (EOR). The galactomannan was characterized by FTIR, NMR, SEC, thermogravimetric analysis, elemental analysis, and rheology. Structural analyses confirmed the presence of the desired galactomannan content. The best yield obtained was 7.3% for initial seed mass and 24.6% for the endosperm. Rheological analysis showed that Flamboyant mirim gum is a promising alternative for EOR application in high salinity conditions. In addition, stability tests showed that glutaraldehyde can be considered a promising biocide for fluids containing galactomannan since it maintained the viscosity values of the systems for 42 days. Thus, the results confirmed the adequacy of the extraction procedure for obtaining galactomannan.

Keywords: Galactomannan, Flamboyant mirim, *Caesalpinia pulcherrima*, Enhanced oil recovery

INTRODUCTION

Chemical enhanced oil recovery (EOR) is a process in which an oil-immiscible fluid (such as water) is injected together with some chemical additives to increase the oil recovery factor. The application of polymers in EOR fluids increases the oil recovery factor by reducing the mobility ratio, which is a consequence of the increased viscosity the injection fluid. This effect increases the sweep efficiency in the reservoir, and depending on the type of polymer used, the increase in viscosity can also provide a reduction in the permeability of the medium to water.¹

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The most often used in EOR is partially hydrolyzed polyacrylamide (HPAM). However, under severe reservoir conditions (for example, high salinity and high temperature), HPAM loses the properties necessary to increase sweep efficiency. Other polyacrylamide-based copolymers have been developed to withstand thermal, chemical and mechanical degradation, but are expensive, and depending on the severity of the adverse condition, may have difficulty maintaining the properties necessary to improve oil recovery from reservoir.²⁻⁷

In this context, biopolymers are possible solutions for oil recovery operations, since they are resistant to high salinity and high temperatures. Some can maintain adequate viscosity under high salinity to improvement the sweep efficiency.^{8,9} With the exception of xanthan gum, the biopolymers schizophyllan and scleroglucan are not applied due to the high cost involved in their production, since this requires specific microorganisms, adequate environmental conditions and complex purification processes, and in some cases low yields are obtained. In addition, scleroglucan also has problems of low injectability.^{10,11}

In the case of xanthan gum, several articles have mentioned its application as a viscosifying agent for EOR fluids.^{8,12-15} However, due to the presence of carboxylate groups in the structure, its application can result in adsorption on the surface of carbonate rocks, due to its positive surface charge.⁶ This adsorption leads to loss of viscosity and reduction of sweep efficiency, thus reducing oil recovery. Because of this, galactomannans are a potential solution to the problems mentioned above, since they are nonionic and are inexpensive to produce.¹⁶ In particular, galactomannans can be extracted from the endosperm of seeds of different species and have wide applicability in the industrial sector, especially in the pharmaceutical and food segments, as well as in the production of films.¹⁷⁻¹⁹ In the food industry, they are generally used as stabilizers, thickeners and inedible coatings.²⁰ However, they have never been evaluated for enhanced oil recovery.

Galactomannans are neutral polysaccharides and compose the second-largest group of reserve polysaccharides available from plants. Besides plants, these polysaccharides can also be obtained from microbial sources, e.g., yeasts and fungi.²¹ The structure of galactomannans consists of repeated units of β -D-mannose, in the main chain, linked together by glycosidic bonds of type 1 \rightarrow 4 and α -D-galactose units, linked to the main chain by bonds of type 1 \rightarrow 6. The ratio and distribution of the D-galactose units depend on the origin and legume species, as well as on the extraction techniques.^{22,23} The mannose:galactose ratio (man:gal) plays an important role in the solubility of galactomannans, since the higher the proportion of D-galactose, the greater its solubility in water is.^{22,24}

The gum selected for analysis was extracted from the species *Caesalpinia pulcherrima*, a shrub belonging to the legume family (Fabaceae) that can reach 3 to 4 meters in height in adulthood. Its fruits appear in the autumn and are native to the Antilles but is widely cultivated in other countries, including Brazil, in parks and gardens as an ornamental plant. Because Brazilian conditions are extremely favorable for the development of fruits and seeds, they are produced abundantly throughout the year. Since the gum is obtained from a local renewable resource, it can be a good solution to the problems faced in the logistics and application of synthetic polymers for enhanced oil recovery, with the added advantage of low production cost.

The main focus of this study is to evaluate the extraction processes and the obtainment of fluids resistant to high salinity based on Flamboyant mirim gum as a potential viscosifying agent for enhanced oil recovery application. The Introduction should establish the general context and the background of the field the paper is about.

MATERIALS AND METHODS

Materials

Caesalpinia pulcherrima seeds (Flamboyant mirim) were purchased from the company Arbocenter S.A. (São Paulo, SP, Brazil). Ethyl alcohol 95%, used in the extraction of galactomannans, was purchased from Isofar (Rio de Janeiro, RJ, Brazil). The brine used in the preparation of polymeric fluids consisted of sodium chloride PA (NaCl), magnesium chloride hexahydrate PA ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), pure anhydrous calcium chloride (CaCl_2), strontium chloride hexahydrate PA ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4) and potassium

chloride PA (KCl), all from Sigma-Aldrich (São Paulo, SP, Brazil). Deuterium oxide (D_2O) was used as NMR solvent for galactomannan characterization, also purchased from Sigma-Aldrich (São Paulo, SP, Brazil).

Determination of galactomannan content in endosperms

According to the literature, the highest concentration of biopolymers with viscosifying power occurs in the endosperm of the seeds. Thus, because the focus here is on the extraction of this biopolymer, knowledge of the endosperm content is important. Although the endosperm is not composed of 100% biopolymer, it is the largest source of these biomolecules, so the polysaccharide extraction yield will always be lower than the endosperm content in the seed.^{25,26}

Hence, it was developed a method to determine the endosperm content, in which the Flamboyant mirim seeds were weighed and the respective mass values were recorded. Then, they were placed in an oven at 80 °C and weighed daily until constant weight. For each determination, the seeds were removed from the oven and placed in a desiccator for 15 minutes and then weighed at room temperature (dry seed mass).

Subsequently, the seeds were subjected to diversified procedures to facilitate the removal of the husks and isolation of their respective endosperms. After isolation, the endosperm material was dried to constant weight following the same procedure described above, to obtain the dry endosperm mass.²⁷

The experiment was carried out in duplicate and the determination of the endosperm content in the seeds was determined.

Extraction of biopolymer

The procedure for extracting Flamboyant mirim gum from the seeds was performed as described by the literature,²⁸ with minor modifications. Initially, 10 g of seeds was boiled at 100 °C for 30 minutes in order to inactivate the enzymes present in the seeds and facilitate the removal of the endosperm. After that, the seeds were washed and placed in a sieve to remove excess water and particles.

Subsequently, the seeds were manually removed and their endosperms were separated from the husks. Then, the endosperms were submitted to extraction with distilled water at a ratio of 1:50 (w/v) in a blender for 10 minutes until obtaining a viscous solution. The solution was centrifuged at 4000 rpm for 15 minutes. The supernatant was precipitated in ethyl alcohol in a proportion of 1:3 (v/v), with subsequent filtration through a standard sieve with 177 μ m mesh. Finally, the precipitate was dried in a lyophilizer for 48 hours, macerated, and the yield was determined.

Factorial experimental design of biopolymer extraction from Flamboyant mirim seeds

A 2³ factorial experimental design was used with 3 central points, totaling 11 experiments. The factorial planning matrix and the extraction process variables (temperature, extraction time and salt concentration) are reported in Table I.

Some extraction methods described in the literature were used as a basis for determining the conditions for construction of the planning matrix. In the case of temperature, the conditions used in the literature obtained maximum extraction under both cold and hot conditions.^{22,24} Given the possible favorable influence of the use of high temperature in the extraction, it was chosen 80 °C for hot extraction. On the other hand, it was used 4 °C for cold extraction. Due to the central point planning, the temperature of 42 °C was also evaluated, an intermediate value where there is less energy expenditure to maintain either the hot or cold temperature.

Regarding the addition of sodium chloride, it was reported that using a solution with concentration of 0.1 M of this salt increased the final yield in relation to the use of distilled water without its addition.²⁹ It was considered that a greater amount of salt could favor the yield even more, so 1.5 M concentration was used as the upper level of this variable.

The extraction time variables were fixed based on the literature, with 4 hours being considered optimal for hot extraction and 12 hours for cold extraction.³⁰

From here, all extractions of the Flamboyant mirim gum followed the factorial experimental design described in Table I.

Table I. 2³ factorial planning for Flamboyant mirim polymer extraction

Experiment	Coded					
	NaCl (Molar)	Temperature (°C)	Time (hours)	NaCl (Molar)	Temperature (°C)	Time (hours)
1	-1.0	-1.0	-1.0	0.1	4	4
2	1.0	-1.0	-1.0	1.5	4	4
3	-1.0	1.0	-1.0	0.1	80	4
4	1.0	1.0	-1.0	1.5	80	4
5	-1.0	-1.0	1.0	0.1	4	12
6	1.0	-1.0	1.0	1.5	4	12
7	-1.0	1.0	1.0	0.1	80	12
8	1.0	1.0	1.0	1.5	80	12
9	0.0	0.0	0.0	0.8	42	8
10	0.0	0.0	0.0	0.8	42	8
11	0.0	0.0	0.0	0.8	42	8

Initially, the seed husks were removed and the seeds were weighed to form samples of approximately 25 grams, which were boiled in distilled water [1:5 (w/v)] at 100 °C for 2 hours under stirring, for enzymatic inactivation. They were then kept immersed in water for 18 hours at 25 °C to facilitate husk removal. After this period, the husks were removed manually. However, some seeds remained hard, hindering the husk removal. For these, new heating under stirring was carried out for 2 hours, followed by 18 hours at rest in distilled water, enabling removal of the husks from more seeds. When hard seeds remained, they were weighed and placed in an oven at 40 °C for one day, weighed and then discarded.

After removing the husks, the endosperm material was ground using a blender (50 seconds) with a NaCl solution (1:10 w/v) with the concentration stipulated in the experimental design (Table I), at 25 °C. Then, the extraction was performed under stirring at 500 rpm, at the temperatures and for the times described in Table I.

After the extraction time, the solution was centrifuged (4000 rpm, 10 minutes), precipitated in 95% ethanol [1:3 (v/v)] and filtered through a 45 µm sieve. The precipitated material was lyophilized, ground, and weighed. The extraction yield was calculated based on the initial seed mass and also the initial dry endosperm mass.

Hydrogen magnetic resonance spectroscopy (¹H-NMR)

The Flamboyant mirim gum was characterized by ¹H-NMR to measure the mannose/galactose ratio, which is an important characteristic of galactomannans. The samples were solubilized in deuterated water at room temperature. After solubilization, the samples were placed in NMR tubes with diameter of 5 mm. The samples were characterized in a Varian VNMRSYS 500 (500 MHz) spectrometer, with deuterium oxide (D₂O) as solvent. The analyses were performed at room temperature. The analyses were performed using a 5 mm universal probe, spectral width of 4800 Hz, acquisition time of 2.5 s, pulse width calibration of 90 degrees, pulse interval of 10 s and transient number 80.

Fourier-transform infrared spectroscopy (FTIR)

The Flamboyant mirim gum was characterized by FTIR to observe and classify some bands related to functional vibrations. FTIR spectra were obtained using a Perkin-Elmer Frontier FTIR/FIR spectrometer using 20 scans and resolution of 4 cm^{-1} . The main peaks were highlighted using the Perkin-Elmer Spectrum software, version 10.4.2, and each sample was prepared by weighing 5 mg of the dry biopolymer, which was pressed to form KBr pellet (15 mg) and then analyzed at room temperature, using wavelengths from 4000 to 400 cm^{-1} .

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG)

The Flamboyant mirim gum was characterized by thermogravimetric analysis (TGA) to evaluate the temperatures of degradation of the samples. Therefore, known masses of gum were subjected to heating using a TA Instruments model Q500 analyzer, nitrogen atmosphere with flow rate of 60 mL/min, applying a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ to a maximum temperature of $800\text{ }^{\circ}\text{C}$.

Elemental analysis (CHN)

In this technique, the sample is subjected to high temperatures to convert the carbon present into carbon dioxide, hydrogen into water, and nitrogen into nitrogen gas. Flamboyant mirim gum was characterized by elemental analysis in order to confirm the presence of nitrogen compounds, which can be correlated with the presence or absence of proteins adhered to the extracted biopolymer, since there is no nitrogen in the gum's basic structure.

The equipment used was a Leco QQSC632 analyzer with limit of detection of 0.3%, where about 2 to 3 mg of the sample was burned to measure the percentages by mass of carbon, hydrogen, and nitrogen (CHN) present in the final product.

Size-exclusion chromatography (SEC)

The molar mass determination of the biopolymer was different from other characterizations, since the parameters used were highly dependent on its structure and solubility. To determine the molecular weight of the Flamboyant mirim gum, it was initially necessary to calculate the dn/dc value of each experiment. The dn/dc value is the variation of the refractive index divided by the variation in concentration before injection. This value is highly dependent on the solvent/polymer ratio, since polymers can have different conformations in different solvents, directly influencing the signal observed by the equipment. Thus, the calculation of dn/dc indicates the reliability of the results obtained.

The dn/dc value was determined through direct analysis with a Wyatt Technology Optilab T-rEX refractive index detector, performing sequential injections of the biopolymer solution with different concentration (0.2 to 1.0 mg mL^{-1}), which generated a biased linear curve, which with extrapolation corresponded to the desired value (dn/dc). The operational flow rate was maintained between 0.1 - 0.5 mL min^{-1} , varying according to the need and viscosity of each sample. From the data obtained, the dn/dc value was calculated and then inserted in the molar mass determination analysis.

For analysis of the biopolymer, an Agilent Technologies 1260 Infinity gel permeation chromatograph was used with Shodex LG-G 6B pre-column and two Shodex LB-806M columns, coupled to a Wyatt Technology DAWN8 light scattering detector and Optilab T-rEX refractive index detector. According to the manufacturer, the error limits for SEC analysis is 10%.

The mobile phase used in the determination of dn/dc and molar mass was based on an aqueous solution of sodium nitrate at a concentration of 0.1 M and sodium azide at a concentration of 250 mg L^{-1} . For injection, the samples were filtered with a $0.22\text{ }\mu\text{m}$ filter before storage in vials. The samples also needed to be within the proper reading range for detection, with a minimum of 0.05 mg mL^{-1} and a maximum of 2.5 mg mL^{-1} .

The conditions for analysis were adjusted to the temperature of $40\text{ }^{\circ}\text{C}$ in the columns and detectors and flow rate of $0.5\text{ mL}/\text{min}$. To guarantee accuracy of the results, the peaks with a low molar mass

poly (ethylene oxide) were normalized and aligned to a standard of the same mobile phase used for the biopolymer. Finally, the sample was injected and the data processed using the Astra 1.7.3 software, which performs the necessary calculations and provides the number-average molecular mass (M_n), weight-average molecular mass (M_w), and polydispersity values for the biopolymer when the dn/dc is supplied to the software.

Rheological analysis

The rheological analyses of the Flamboyant mirim gum were carried out in a TA Instruments Discovery Hybrid rotary rheometer (DHR3), with a 40 mm 2° cone plate accessory of titanium. For all experiments, flow curves were obtained with shear rates varying from 0.1 to 500 s⁻¹ and an analysis time of 45 minutes to acquire 5,400 points. These parameters were selected after an extensive previous study to determine the conditions of the rheological analyses necessary for better determination of viscosity values, by giving the necessary time for the polymer molecules to respond to the imposed shear. The analyses were performed at temperatures of 25, 60, and 80 °C. Viscosity values at the oil reservoir shear rate (7,37 s⁻¹) were used to evaluate the biopolymer viscosifying power for enhanced oil recovery application.

All samples were evaluated in injection brine (with compositions similar to those of desulfated brine), called Brine 1, and brine with a higher concentration of salts, simulating water from a typical mixture of injection water and formation water (Brine 2). Brine 1 was composed of NaCl, MgCl₂, KCl, CaCl₂ and Na₂SO₄, with a total concentration 29711 ppm of total dissolved solids (TDS). Brine 2 was composed by the same salts as Brine 1 with the addition of SrCl₂, a salt commonly present in reservoirs, and this brine also presented higher salinity, with a total of 68317 ppm total dissolved solids.

Initially, biopolymer solutions at a concentration of 2000 ppm were prepared in Brines 1 and 2. The solution containing 1000 ppm of biopolymer was obtained from dilution of this solution. To obtain the biopolymer solution with 3000 ppm, only Brine 1 was used as solvent, and only for the biopolymer that presented the best viscosifying power. The time it took the biopolymer to completely dissolve in these brines was about one day, at room temperature.

Stability of biopolymer solutions

This test was carried out to evaluate the stability of the most promising biopolymer (the one that presented the most appropriate viscosity for application as a viscosifying agent for EOR applications).

In this evaluation, the main objective was to verify the need to add a biocide to maintain the viscosity of the biopolymer solution under shelf conditions. The samples were observed regarding color, phase separation, appearance of a precipitate and presence of particulates. Viscosity measurements were performed during 42 days.

Initially, a stock solution of the selected biopolymer was prepared in Brine 1 at a concentration of 3000 ppm. After that, the initial solution was separated into 5 vials containing 20 mL of solution each and then the biocide: glutaraldehyde was added, which has already been applied in the oil industry.³¹ The concentrations of the biocide added to the systems were 50, 100, 200, 300, 1000, 2000, and 4000 ppm.

RESULTS AND DISCUSSION

Endosperm content in seeds

The determination of the endosperm content is essential to evaluate the viability of the seed as a source of biopolymer with viscosifying power, because the higher the endosperm content in the seeds is, the greater will be the yield of extractions.²⁷ The endosperm content in the Flamboyant mirim seeds was 33%.

Extraction yields of biopolymer

The yields of Flamboyant mirim gum were 3% when calculated from the initial seed mass, and 9% when calculated based on the endosperm mass. This seed yield (3%) was low in comparison with the amount of polymer used in enhanced oil recovery operations, making its application economically unfeasible.

Thus, it was concluded that the extraction of galactomannan still needed some adaptations to obtain satisfactory final yield. For this, it was necessary to use an experimental design to ascertain best extraction conditions.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG)

Initially, the thermal stability of the Flamboyant mirim gum was evaluated through thermogravimetric analyses. In addition to thermal stability, other information can be obtained through this technique, such as the percentage of organic and inorganic materials, moisture and presence of a residual solvent, which allow judging the efficiency of the extraction methods used, as well observing the dehydration of the polysaccharide.³²

The thermogravimetric curves obtained showed similar behavior in all experiments (Table II). All samples showed two mass loss events, as shown in Figure 1, using the thermogravimetric curves obtained in experiment 1.

Table II. Mass losses calculated in the three stages of degradation and the total mass loss of Flamboyant mirim gum extracted through experimental design

Experiment	Volatile solvents (%)	Organic compounds (%)	Inorganic compounds (%)	Total mass loss (%)
1	12	76	12	88
2	8	47	45	54
3	12	79	9	91
4	6	33	61	38
5	14	78	8	92
6	7	39	54	46
7	11	75	14	86
8	9	45	46	53
9	12	70	18	81
10	16	66	18	81
11	14	69	17	83

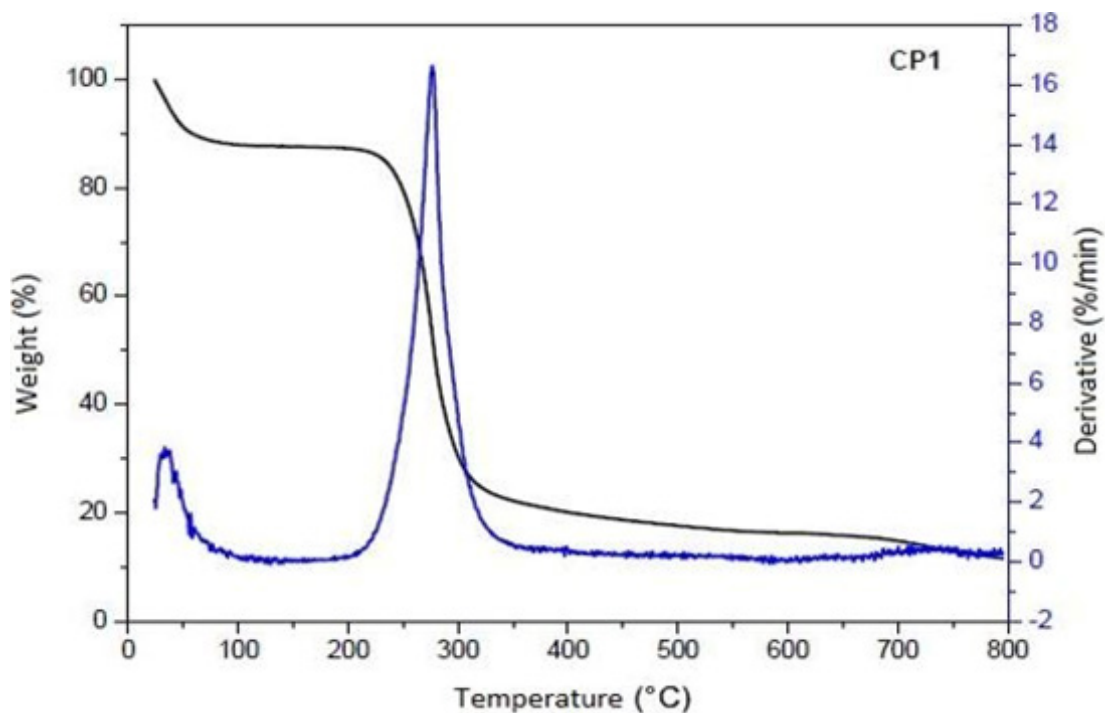


Figure 1. Thermogravimetric curves of the Flamboyant mirim gum (Experiment 1).

The first event is related to the highest volatile output temperatures, which are applied to the mixture of water and ethyl alcohol from the extraction processes. The second event, referring to the degradation of the biopolymer, showed maximum kinetics in the temperature range between 200 and 350 °C, with is the region related to the thermal degradation of polysaccharides.³³ Another important observation from the thermogravimetric curves regarding the extracted galactomannan was the loss of total mass. The residual mass obtained at the end of the analysis, at temperature of 800 °C, can be correlated with the subproducts of degradation or compounds contained in the raw material used in the extraction process. Therefore, higher mass loss is theoretically associated with greater biopolymer purity.

Based on the total mass loss of the galactomannan samples, the Flamboyant mirim gum extracted in experiment 5 presented the highest degree of purity, as shown in Table II. Still according to Table II, the values of volatile solvents lost from the products obtained through extractions from Flamboyant mirim seeds were between 5 and 16% w/w (first event), while the losses of organic compounds were between 32 and 79% w/w (second event) and of inorganic compounds were from 8 to 61% w/w (residue contents calculated using the percentage of the total mass in the samples).

Table II also shows that experiments 2, 4, 6, and 8 presented the highest levels of residual inorganic matter after the extraction processes. All these experiments were carried out with the addition of 1.5 M NaCl, which probably remained in the final product and was not degraded in the TGA analysis, since it has a boiling point of 1465 °C, higher than the maximum temperature employed in the thermogravimetric analysis.

The contents of inorganic matter and solvents were used to obtain the biopolymer masses for the calculation of extraction yields. It is worth mentioning that the results published in the literature do not consider adjustments in yield. Instead, these results pertain to the final biopolymer products, containing many residues from the extraction processes.³⁴⁻³⁸

Extraction yields obtained through factorial experimental design

The extraction yields for the Flamboyant mirim gum obtained from the factorial experimental design were satisfactory and are listed in Table III. There was an increase in the extraction yield compared to the result obtained by extraction method carried out before experimental design, since the previous maximum yield was 3% in relation to seed mass. After the factorial experimental design, it was possible to reach about 25% in Experiment 4, a yield similar to those found in the literature.³⁹⁻⁴¹

Table III. Yields obtained after factorial experimental design for the extraction of flamboyant mirim gum

Experiment ^(a)	Mass ^(b) (g)	Yield in relation to the endosperm (%)	Yield in relation to seed mass (%)	Yield in relation to endosperm mass (%)	Yield in relation to seed mass (%)
		In the presence of residual materials ^(c)		In the absence of residual materials ^(c)	
1	2.3	31	9	23	7
2	4.3	58	17	21	6
3	2.7	36	11	26	8
4	6.2	84	25	25	7
5	2.0	27	8	19	6
6	4.7	63	19	20	6
7	2.1	28	8	20	6
8	2.5	34	10	14	4
9	2.2	30	9	18	5
10	2.7	36	11	21	6
11	2.2	30	9	20	6

(a) Experimental design;

(b) Mass of biopolymer obtained after the lyophilization step;

(c) Residual materials (salt, water and solvent);

Average moisture content present in the seeds = 9.8%; percentage of endosperm calculated (%w/w) = 33%; mass of endosperm used in calculations = 7.5 g; average dry seed mass used in calculations = 22.7 g.

It should be noted that these higher yield values are related to the presence of biopolymer and also residual materials (RM) from biopolymer extraction, such as salt (NaCl), water, and solvent (ethyl alcohol) used in the extraction steps. The presence of these residues was observed in the thermogravimetric analyses. After the entire extraction process, these residues were not completely removed, resulting in an increase in the final mass of the product obtained.

To obtain the greatest accuracy of biopolymer mass measurement, the contents of organic and inorganic materials were used as well as moisture and solvent, obtained utilizing thermogravimetric analyses, to determine the content of salt, water, and residual alcohol in the final product. Through these analyses it was possible to arrive at the corrected yield of biopolymers.

Table III shows the final biopolymer yields related to the total dry seed mass (22.7 g) and the mass of endosperms present in the seeds (7.5 g). The results of yields obtained for seeds clearly show that the adjustments in the procedures used made their production feasible. There was an increase of 22% referring to seed mass.

Results of factorial experimental design

After processing the data generated with the 2^3 factorial design with the Design Ease 10[®] program, it was possible to obtain information regarding the effects of each experimental variable, as well as the relationships between them. This enabled assessment of which variables and interactions were statistically relevant and influenced the response variable (in this case, final yields of biopolymers obtained from the initial mass of Flamboyant mirim seeds), shown in Table IV, without considering the presence of salt, water, and solvent in this study, since their consideration relates to unlikely values.

Table IV. Estimated effects and significance of each factor and their respective interactions on the final yield response of Flamboyant mirim gum to the initial seed mass

Factor	Effect	Standard error	p-value
Average/interaction	6.09	0.11	0.0
(1) salt	-0.57	0.27	0.2
(2) temperature	0.08	0.27	0.8
(3) time	-1.58	0.27	0.0
1 x 2	-0.48	0.27	0.2
1 x 3	-0.23	0.27	0.5
2 x 3	-0.88	0.27	0.1

The statistical significance of each effect is measured by the p-values. Significant effects are those with p-values less than 0.05 in Table IV. Values less than 0.01 indicate the effect is very significant and values between 0.05 and 0.10 are classified as marginally significant, because although they are not in the stipulated range up to 0.05, they are close. Values greater than 0.10 indicate the effect is not significant.⁴¹

Based on this observation and the results in Table IV, it was possible to verify that of the three variables studied, only time was significant, with a statistically negative effect. The fact that the production of biopolymer in less time already allowed obtaining a high yield is a positive aspect, since it reduces the cost.

The analysis of variance results can be seen in Table V. The value of $F_{\text{calculated}}$ of the regression was not greater (3 to 4 times) than that of F_{tabled} ,⁴² so the model cannot be considered predictive, but it was still possible to verify the effects of variables normally by the p-values. Analysis of variance for experimental design is used to assess whether the model we are suggesting to describe our data is statistically significant or not. For the model to be statistically significant, a hypothesis test must be performed. There are two possibilities:

- The null hypothesis (H_0) is the hypothesis that will be tested, and it says that the model is not significant.
- The alternative hypothesis (H_a) says that the model is significant, and will be accepted as long as the null hypothesis is rejected.

To evaluate the hypotheses, the Fischer distribution table F is used. The $F_{\text{calculated}}$ is obtained by dividing the mean square of the regression by the mean square of the residuals. Subsequently, this calculated F value is compared with the Fischer distribution F_{tabled} , where the tabulated F (also called F_{critical}) is arranged according to the regression degrees of freedom ($DF = 6$) and the residuals degrees of freedom ($DF = 4$) (Table IV). For the null hypothesis to be rejected, the $F_{\text{calculated}}$ has to be greater than the F_{tabled} . Rejecting the null hypothesis, it can be said that the model is statistically significant.⁴³

Table V. Analysis of variance of the central composite rotational design of the Flamboyant mirim study

Source of variation	Quadratic sum	Degrees of freedom	Quadratic average	F _{calculated}	F _{tabled}
Regression	7.7	6	1.3	4.6	6.2
Residual	1.1	4	0.3		
Lack of adjustment	0.8	2	0.4	2.9	19
Pure error	0.3	2	0.1		
Total	8.8	10			
R ²	0.9				

The coefficient of determination (R^2) obtained in the experimental design of Flamboyant mirim was 0.87409, which means that a quadratic function explained 87.41% of the total variation of the responses. This shows that the proposed planning can affect the percentages of the experimental data.

However, to consider a model well adjusted, the $F_{\text{calculated}}$ value of the regression must be greater than F_{tabled} and that the $F_{\text{calculated}}$ of the lack of adjustment is smaller than the F_{tabled} . Besides, the $F_{\text{calculated}}$ of the regression is 3 to 4 times greater than the F_{tabled} .⁴¹ Thus, it can be concluded that the model is not well adjusted. Thus, the factorial experimental design still needs adjustments, but the yield values obtained were satisfactory based on those found in the literature.³⁹⁻⁴¹

Hydrogen magnetic resonance spectroscopy (¹H-NMR)

The chemical structure of galactomannan was determined by ¹H NMR analysis of the Flamboyant mirim gum. Based on the gum's chemical shifts, anomeric hydrogen signals were identified of α -D-galactose (5.44 ppm) and β -D-mannose (5.06 ppm) (Figure 2). In addition to the main hydrogens referring to the α -D-galactose and β -D-mannose the hydrogens of the rings of both units with chemical shifts between 3.6 and 4.25 ppm were also identified.⁴⁴ All extractions presented very similar NMR spectra (data not shown), regardless of the method used in the process. For this reason, only Experiment 2 is reported, since the others had similar spectra.

As mentioned earlier, the mannose/galactose ratio is an important parameter for the study of galactomannans. The D-mannose/D-galactose ratios found for all the experiments were around 3.1, similar to that found in literature.³⁸ These ratios were determined through the integration of peaks related to chemical shifts of α -D-galactose and β -D-mannose present in galactomannans. Some studies present different mannose/galactose ratios,^{41,45} but these divergences can probably be explained by differences in the galactomannan extraction and purification procedure. Also, the mannose/galactose ratio plays an important role in the solubility of galactomannans, since to have greater solubility in water, a higher D-galactose content is required.^{22,24}

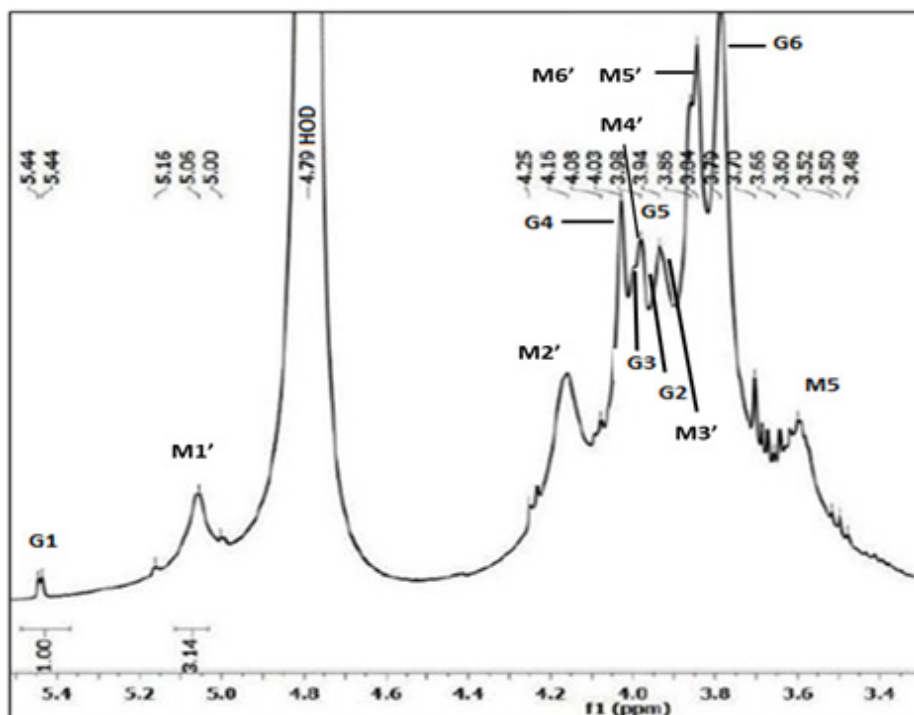
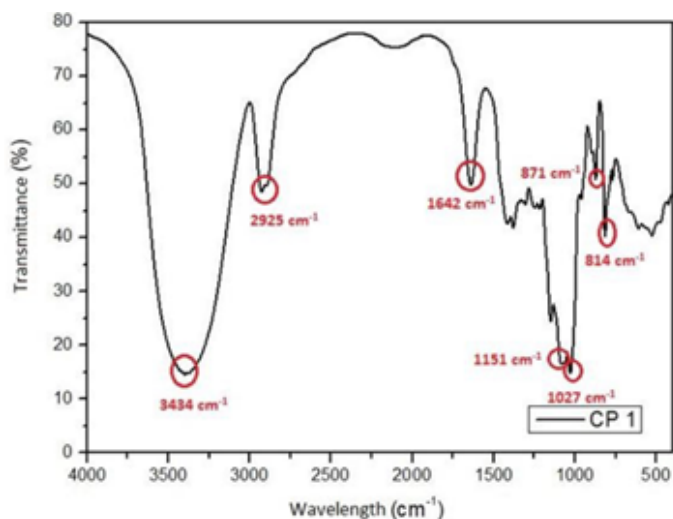


Figure 2. ^1H NMR spectrum of the Flamboyant mirim gum (Experiment 2).

Fourier-transform infrared spectroscopy (FTIR)

The analysis by FTIR allows observing and classifying some bands related to the vibrations of the functional groups present in organic compounds. The spectrum obtained and stretching vibrations presented in Figure 3 were similar in all the experiments carried out, as well as to those found in the literature, confirming the structure of galactomannan.^{22,33,46-51}



Wavelength (cm^{-1})	Group features
3434	Vibrational stretching of the O-H group
2925	Group stretching -CH ₂
1642	Stretching of the galactose ring and mannose
1151	Stretching vibrations of glycosidic linkages (C-O-C)
1027	Vibrational CH ₂ stretch
871	Stretching of the anomeric conformations of polysaccharides (α -D-galactopyranose)
814	Stretching of the anomeric conformations of polysaccharides (β -D-mannopyranose)

Figure 3. FTIR spectrum of the Flamboyant mirim gum and the galactomannan groups identification (Experiment 1).

Elemental analysis (CHN)

To evaluate the efficiency of the purification process, nitrogen microanalysis was also carried out to determine the presence or absence of proteins adhered to the Flamboyant mirim gum, since its structure

does not contain nitrogen, whose presence can hinder the solubilization process.^{51,52} According to the manufacturer, the detection limit of the equipment is 0.3%, with concentrations equal to or below this value being considered as absence of a determined chemical compound, and hence absence of proteins. Negligible concentrations of nitrogen were detected, ranging from 0.13 to 0.28% through samples CP 1 to CP 11, demonstrating that the process to separate this polysaccharide and proteins was highly effective. Consequently, the samples could be considered pure concerning the presence of remaining proteins.

Size-exclusion Chromatography (SEC)

The main objective of this analysis is to determine the molar mass of polymers and their distribution. Therefore, for all Flamboyant mirim gum samples the dn/dc values were calculated. These values were close to each other. The variations possibly occurred due to the different conditions for extraction of the biopolymer. However, a small variation in the dn/dc values often equals a large variation in the molar mass values. This determination is important according to the Zimm equation (Equation 1), because the dn/dc value is squared in the equation, making it the factor that most influences light scattering.

$$R_{\theta} = \left(\frac{dn}{dc} \right)^2 \cdot c \cdot M_w \quad \text{Equation 1}$$

Different mass recovery rates were observed for all tested samples. The reduction in the percentage of recovered mass can occur due to several factors: polymer content of the sample, impurities, insufficient solubilization, and sample loss due to adsorption in the column, among others. This data indicates the actual concentration of biopolymer analysed.⁵⁴ The mass recovered varied from each experiment performed, from 18.1% (CP 2) to 100% (CP5). This parameter can be influenced by the purity of the final material, showing that CP 5, one of the samples obtained with the lowest salt concentration salt (0.1M) exhibited greater purity in these analyses. Comparison with the results obtained by TGA (Table II) reveals that in both techniques, the purest biopolymer was obtained in Experiment 5 (CP5).

Regarding the number average molecular mass (M_n) and the weight average molar mass (M_w), Experiment 5 produced the best result, probably due to the low temperature used in the extraction process, which may have favoured less degradation of galactomannan.

The results obtained for all galactomannans extracted from seeds of *Caesalpinia pulcherrima* presented a range of average molar mass around $10^4 - 10^6 \text{ g mol}^{-1}$, similar to the range reported in literature, whereas the smallest molar mass was observed for CP 9 ($8.328 \times 10^4 \text{ g mol}^{-1}$) and CP 5 exhibited the highest molar mass recorded in this work (1.260×10^6). Apart from those, all galactomannans presented molar mass within 10^5 g mol^{-1} .³²

Rheological analysis

According to the results of the rheological analyses of the galactomannan samples extracted from Flamboyant mirim gum, the samples in general were soluble in water, which may be related to the low ratio between the mannose and galactose groups. The solubility of galactomannan decreased with decreasing galactose content, so the efficiency of aqueous extraction depends on the composition of galactomannan.^{22,24}

The brine solutions of galactomannan obtained in Experiments 1 (CP1) and 5 (CP5), prepared in Brine 1, showed pseudoplastic behavior and an increase in viscosity values with increasing concentration. Furthermore, Figure 4 shows that the pseudoplastic character declined with increasing concentration of galactomannan in the brine solution, because with the increase in the shear rate there was a lesser reduction in the viscosity values of the solutions. All galactomannan samples obtained in the factorial experimental design showed similar behavior when solubilized in brine.

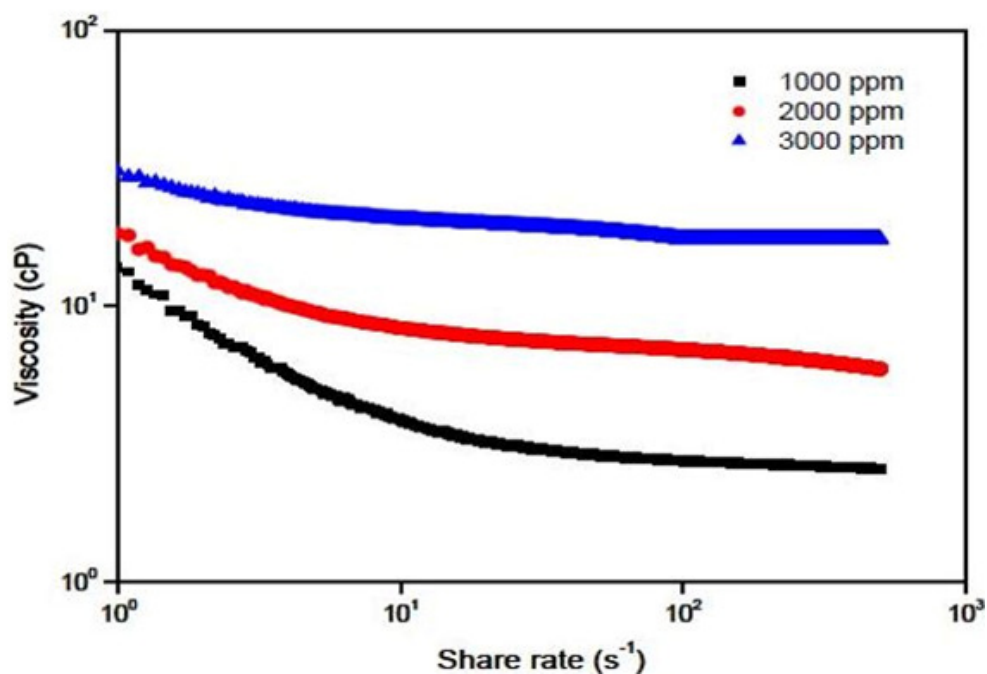


Figure 4. Flow curves of the galactomannan solutions obtained in Experiment 5 (CP5), at concentrations of 1000, 2000, and 3000 ppm in Brine 1, at 25 °C.

The brine solutions of the samples obtained in the 11 experiments were also analyzed by obtaining flow curves at different temperatures (25, 60, and 80 °C) and at concentrations of 1000 and 2000 ppm, to simulate application conditions closer to reality. These solutions were prepared in both brines used in this study (1 and 2).

For a more detailed analysis, viscosity values of the solutions at shear rate of $7.37 s^{-1}$ were evaluated, simulating the flow inside an oil reservoir.⁵⁵ The values were obtained with polymer concentrations of 1000 and 2000 ppm in the two different synthetic brines. The results are shown in Figure 5. It is possible to notice the brine solution prepared with galactomannan obtained in Experiment 5 presented a higher viscosity value, which was expected since it presented the highest molar mass values and TGA analyses indicated a higher organic content.

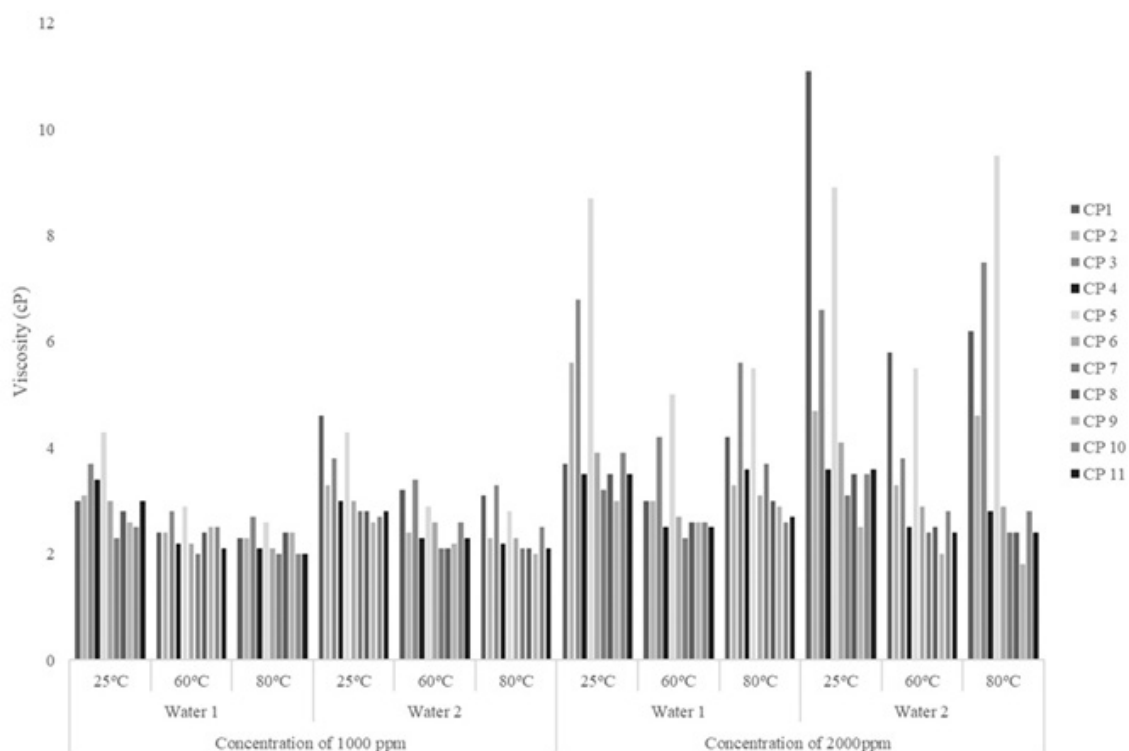


Figure 5. Viscosity values for Flamboyant mirim galactomannan at $7,37 \text{ s}^{-1}$ at 1000 ppm and 2000 ppm concentrations in Brines 1 and 2.

Another factor to be considered is that, in general, there were no significant variations in the viscosity values of the solutions prepared with Brine 2 (TDS = 68317 ppm) compared to the values obtained for solutions prepared with Brine 1 (TDS = 29711 ppm). This behavior is satisfactory because even with the increase in the TDS values and with the increase in the concentration of divalent cations in Brine 2, the viscosity values of the solutions did not significantly change. This behavior is not observed for the partially hydrolyzed polyacrylamide synthetic polymer (HPAM), which has been studied and is currently the most applied polymer in EOR fluids. The brine solutions of this polymer in the severe conditions of some oil reservoirs, such as high salinity, have lower viscosity values, caused mainly by the presence of divalent cations, whereas the galactomannan, a non-ionic biopolymer, does not suffer salinity effects.^{56,57} This is one more indication of how promising the use of biopolymers really is, when compared to HPAM, obtaining a more or equally viscous material without the use of synthetic polymers.^{57,58}

Calculations were also performed to determine the concentration of product extracted in each experiment for preparation of galactomannan brine solutions so that the concentration of this biopolymer in the solutions would be 2000 ppm. These calculations were performed based on the results obtained in the thermogravimetric analyses, with deduction of the percentage of mass of the volatiles (solvents used in the extractions) and the non-degraded material (inorganic matter, like NaCl), to obtain the real values of organic matter, which was considered to be galactomannan in its entirety. Thus, the calculation to obtain the corrected concentration was carried out by applying equation 2. The results are shown in Table VI.

$$\text{Corrected concentration} = \left(\frac{2000}{(\% \text{ decomposed until } 800 \text{ }^\circ\text{C} - \% \text{ decomposed in the } 1^{\text{st}} \text{ event})} \right) \cdot 100 \quad \text{Equation 2}$$

Table VI. Viscosity values at the shear rate of 7.37 s^{-1} of the galactomannan samples obtained in the experiments, solubilized in Brine 1 at $25 \text{ }^{\circ}\text{C}$

Experiment	Corrected concentration ^(a)	Viscosity (cP)
1	2753	23
2	5405	25
3	2803	12
4	6845	13
5	2839	18
6	6289	19
7	2836	4
8	4879	7
9	3258	6
10	3494	7
11	2926	7

(a) The concentration of the final formulation, to contain 2000 ppm of biopolymer.

The viscosity values obtained in the formulations based on Flamboyant mirim gum were promising for potential application, since they were high for the solutions prepared with the samples obtained through the experiments carried out at low temperature ($4 \text{ }^{\circ}\text{C}$) (Experiments 1, 2 5 and 6), as can be seen in Table VI. However, due to the higher salt concentration in Experiments 2 and 6 (1.5 M NaCl), the corrected concentration was very high, not feasible for application. According to the literature, the concentration considered optimal for injection of the final product is up to 3000 ppm ,⁵⁹ with a viscosity of around 20 cP , at a shear rate of 7.37 s^{-1} . Thus, the samples obtained in Experiments 1 and 5, in addition to presenting the highest molar mass results, also showed better viscosifying power, so they can be considered applicable fluids for enhanced oil recovery.

Stability of biopolymer solutions

The stability of the biopolymer was performed with the product of Experiment 5 (CP 5), which was the one with the most promising properties from all 11 tested in this study. Since it is a green material, i.e., environmentally friendly polymer, it is highly susceptible to biodegradation. So, it is commonly used with biocides to protect them from considered one the most promising biopolymers for EOR application due its good viscosifying power and high stability under high-salinity environments.

First, a solution of 3000 ppm of CP5 was formulated and divided into 5 flasks containing 20 mL each. After that, a 20% glutaraldehyde solution was prepared and added to the respective flasks in concentrations of 50 , 100 , 200 , 300 , 1000 , 2000 , and 4000 ppm .

The viscosity values of the solutions were monitored for 42 days, as reported in Figure 6, to verify the efficiency of the biocide in the prepared solutions. It is possible to observe that the control viscosity already decays by half just 7 days after the beginning of the experiment, followed by another strong decay in 14 days and seems to remain constant for the rest of the experiment. Only the 4000 ppm concentration was able to maintain the solution viscosity after 42 days.

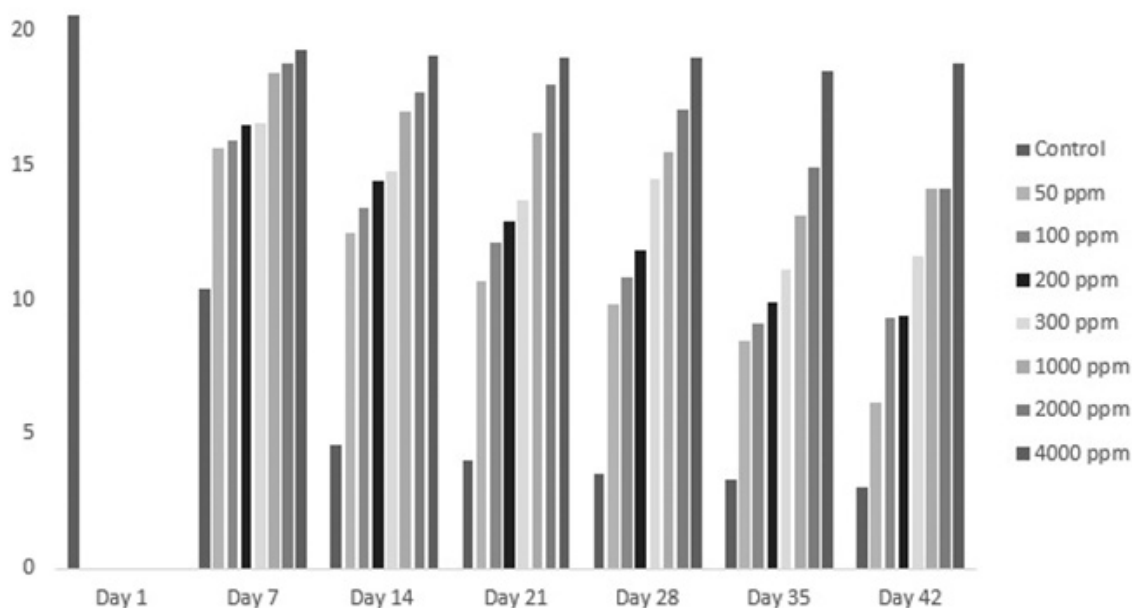


Figure 6. Viscosity of a 3000 ppm galactomannan solution with different biocide concentrations for 42 days.

These results reinforce those found in literature that suggests the optimal polymer: biocide ratio for biopolymers in EOR is 1:1.⁶⁰ Thus, as observed in Figure 6, the 4000 ppm concentration was capable of maintain the viscosity of a 3000 ppm biopolymer solution, since it is possible to observe a weekly decay in viscosity for biocides concentrations 50 to 2000 ppm. This result suggests that there is compatibility between the Flamboyant mirim galactomannan and glutaraldehyde, a established biocide in the petroleum industry.

CONCLUSIONS

Galactomannan extracted from Flamboyant mirim seeds can be obtained through simple and low-cost extraction processes, with the addition of inexpensive materials such as NaCl, water and alcohol. The experimental results showed that the most significant factor was time, but this was negative. This behavior suggests that the shortest extraction time was already sufficient to reach the maximum extraction of galactomannan, leading to a lower production cost. The best galactomannan yields obtained, disregarding the residual materials from the extraction processes, were 7.3%, calculated from the initial seed mass, and 24.6%, calculated from the endosperm content.

The galactomannan samples obtained through the experiments showed average molar mass values in the range of 10^4 to 10^6 g mol⁻¹. Also, the absence of protein linked to galactomannan chains was observed. The highest values of molar mass and purity degree of galactomannan were obtained through Experiment 5, which was carried out with the lowest temperature and least NaCl for extraction.

The rheological analysis revealed that the brine solutions of Flamboyant mirim gum with higher molar mass presented viscosity values around 20 cP, at the shear rate of 7.37 s⁻¹, using concentrations up to 3000 ppm in brine 1. These results are promising, considering they are in line with the requirements for fluids for application in EOR.

Finally, the stability tests carried out with the galactomannan solution in Brine 1 showed that the presence of the biocide (glutaraldehyde) resulted in the maintenance of the viscosity of these solutions.

Conflicts of interest

The authors declare no conflict of interest in this work.

Acknowledgements

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