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Study on Hop Extract as Environmentally Friendly Stabilizer for Starch and Guar Polymers Used in Drilling and Fracturing Fluids

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Abstract

Various hop products (a CO_2 extract, pure α acid, β acid, a blend of α+β acid and isomerized α+β acid) were tested for their anti-bacterial effect on commercial oilfield grade guar, HP guar, three potato starches, one corn and one wheat starch sample. Stability was defined as the ability of the hop product to retain viscosity of the polysaccharide solution over periods of up to seven weeks when stored at 26 °C (79 °F). For comparison, a commercial, highly effective chemical biocide was used as well.

It was found the commercial CO_2 extract stabilizes solutions of guar and HP guar very well, but is less effective on starch polymers. These polysaccharides are particularly well protected against bacterial attack by a blend of α+β acids. Whereas pure β acid which in literature is presented as the most potent bacteriostatic component in hop fails in almost all fluid systems tested.

The results obtained here signify that hop products might present an environmentally more friendly alternative to toxic chemical biocides, because the hop acids work by inhibiting bacterial growth resulting from their ability to function as an ionophore, while biocides kill bacteria.

Introduction

Fluids used in drilling and stimulation operations often rely on natural or semi-synthetic biopolymers to provide viscosity to those fluids [1]. Most common for this purpose are polysaccharides such as starches, guar gums (natural or modified), microbial biopolymers such as Xanthan gum or Welan gum, and cellulose ethers [2, 3]. Depending on the specific type of polysaccharide, fluids possessing exceptional shear-thinning behavior and – consequently – high carrying capacity, or fluids of high plastic viscosity and low yield point can be formulated. In drilling fluids, starch polymers obtained from corn, potato or wheat are often used in the top hole section where temperatures are still low. While in fracturing fluids, guar gum and – at higher temperature – hydroxypropyl guar are used to keep proppants well in suspension [4].

In spite of their overall high effectiveness, the polysaccharide-based viscosifiers unfortunately exhibit some disadvantages when compared with their counterparts based on synthetic copolymers such as those incorporating ATBS monomer. First, polysaccharides quickly decompose at elevated temperatures and second, they are prone to bacterial attack which leads to fragmentation of the polymer chain and a subsequent decrease or even total loss of fluid viscosity. In order to prevent such bacterial degradation, biocides are commonly added to those fluids. Some common examples include glutardialdehyde, 2,2-dibrom-2-cyan acetamide or N,N'-methylene bis[5-methyl oxazolidine]. The anti-bacterial effect of these biocides is based on their toxicity towards such microorganisms. N,N'-methylene bis[5-methyl oxazolidine], for example, releases formaldehyde over time and through this way prevents bacterial growth [5]. However, this toxicity causes serious concerns about the environmental impact of biocides, especially, as they are frequently used in the top hole section of a borehole where contamination of ground water easily is possible. Hence there is a desire to substitute those unwanted toxic compounds with environmentally friendly alternatives.

Hop (*Humulus lupulus*) is a natural crop which belongs to the order of *Rosales* and the overall family of *Cannabaceae* (hemp family, the same family to which *cannabis* belongs). Among *Humulus*, three different species are distinguished: *Humulus japonicus*, *Humulus lupulus* and *Humulus yunnanensis*.

Hop develops male and female blossoms, however, for beer brewing only the female umbels containing the yellow lupulin can be used (**Figure 1**). The umbels are dried after harvesting and their extract which contains aromatic oils and bitter substances is used in food preparations such as beer or in the recovery of sugar from sugar beets. Furthermore, hop presents a mild sedative and is used as such in organic sleeping aids. Still, the main application of hop relates to the beer brewing industry. There, hop controls bacterial growth during the alcoholic fermentation, introduces the characteristic bitter taste of beer (especially in Pilsner beer which is particularly rich in hop) and provides ample of stable foam.

Lupulin contains resins which are classified into soft and hard resins. The soft resins consist of humulone (also referred to as α acid), lupulone (= β acid) and non-specific resins (see **Figure 1**). Humulone in fact presents a mixture of five different, optically active hexa cyclic compounds which include humulone, cohumulone, adhumulone, prehumulone and posthumulone. Their chemical structures are displayed in **Figure 2**. Similarly, lupulone also contains five different molecular species which are exhibited in **Figure 2**.

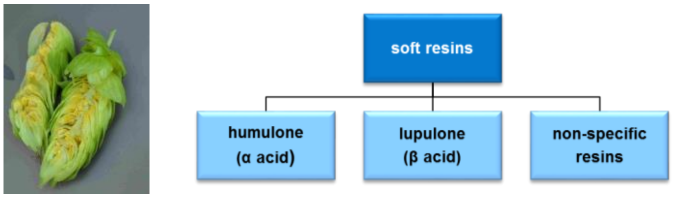
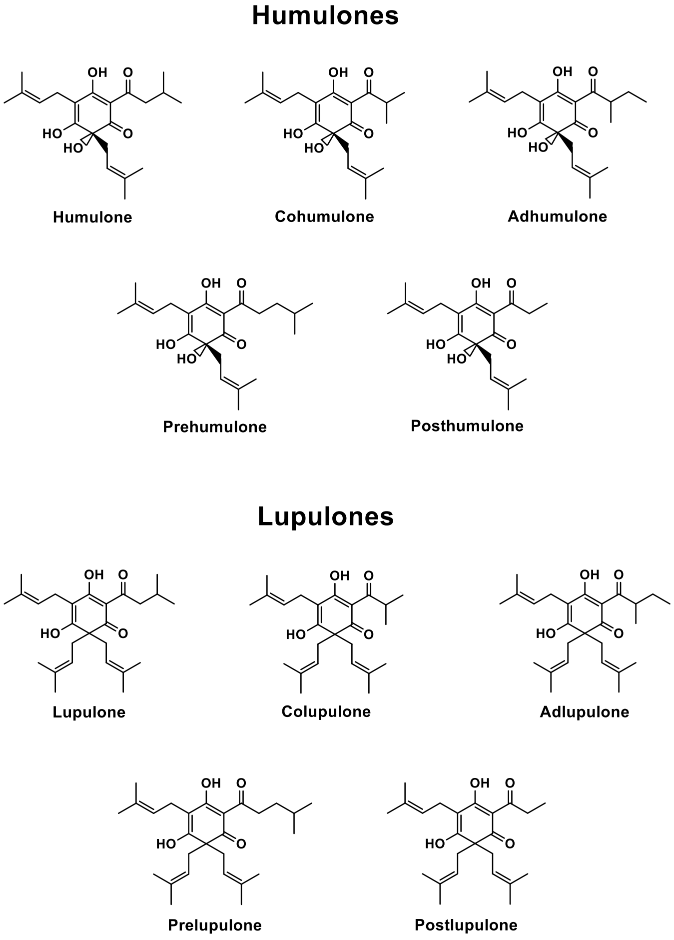


Figure 1: Female umbles [6] (left) and classification of hop soft resins (right).


Humulones

Lupulones

Figure 2: Chemical structures of humulones (= α acids) and lupulones (= β acids) contained in hop.

The bitter taste of beer is owed to an isomerized form of the α acid, the so-called iso α acid [7]. In the beer brewing process it forms at higher temperature, resulting in a mixture of *cis*- and *trans*-iso humulone, as is shown in **Figure 3**.

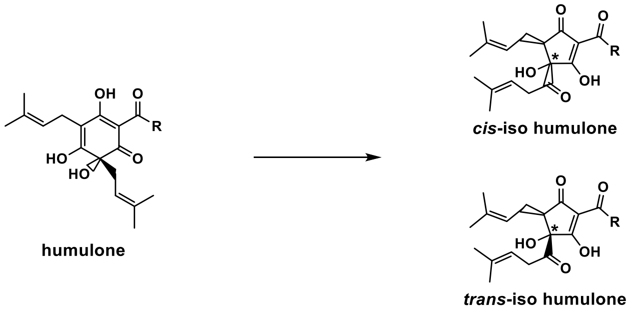


Figure 3: Conversion of humulone (α acid) into the *cis*- and *trans*-isomers during the brewing process.

The anti-bacterial effect of hop acids is already known since medieval times. More recent research has demonstrated that – contrary to common biocides – hop acids do not kill bacteria, but inhibit their growth. The mechanism behind is that hop acids function as so-called ionophores. Those are molecules which can transport inorganic ions through biological membranes by forming hydrophobic complexes with those ions. Hop acids present protonophors which disturb the proton gradient in the cell, resulting in a decreased intracellular pH value which hinders the uptake of nutrition by the cell and reduces or even completely prevents the growth of bacteria [8-10]. As such, hop acids present bacteriostatic additives with apparently no human toxicity whereas bactericides rely on a toxic effect on microorganisms and humans.

In consideration of the favorable environmental properties of hop acids, their effectiveness as viscosity stabilizer in aqueous solutions of guar gum, hydroxypropyl guar and five different starches (three potato starches, one corn and one wheat starch) was studied by tracking fluid viscosity at 26 °C (79 °F) over a period of six weeks. Viscosity was recorded at different shear rates from 3 to 600 rpm using a rotational *Couette*-type viscometer.

As hop acids, pure α and β acids, mixtures of α and β acids as well as of iso α and β acids, and a commercial CO_2 hop extract were tested.

From the experiments it was hoped to obtain information whether hop extracts can principally stabilize those polysaccharide solutions by inhibiting bacterial growth. Another goal of the study was to determine which kind of hop acid works best for individual polysaccharide samples and across the board for a variety of polysaccharides.

Materials

Polysaccharides

Guar gum (GG) and hydroxypropyl guar (HPG) were commercial products manufactured by a major chemical company for application in fracturing fluids.

The three potato starch samples (P Starch 1 to 3) were received from two different companies manufacturing starch products for the drilling fluid industry. The food-grade corn starch (C Starch) and wheat starch (W Starch) samples were provided by two companies supplying to the food industry.

For comparison, drilling grade Xanthan gum from a biotech company and technical grade carboxymethyl cellulose from a major drilling fluid service company were tested as well.

CO_2 hop extract

A commercially available hop extract produced *via* extraction with supercritical CO_2 was received from a local company catering to the brewing industry.

It was used as is or for the extraction of the pure hop acids (see below). The CO_2 extract presents a greenish oily liquid.

Hop acids

From the CO_2 hop extract, pure α acid, β acid and the mixture of α+β acid were extracted with hexane in our laboratory following a literature description [11]. The pure extracts presented viscous, yellowish-orange oils of characteristic odor and were stored in a refrigerator at +4 °C (39 °F).

The blend of iso α+β acids was obtained *via* extraction of a so-called isomerized Kettle extract. This extract is produced industrially for applications in the food industry. Isolation of the iso acids was performed in our laboratory using aqueous NaOH and hexane [11] yielding a yellowish-orange oil which after drying with anhydrous Na_2SO_4 was stored in the refrigerator.

Comparative biocide sample

For comparison, a commercial biocide (N,N'-methylene bis[5-methyl oxazolidine]) was purchased and used as is. This product presents a powerful biocide.

Experimental Procedures

Viscosity measurements

From all polysaccharides, aqueous solutions (500 mL) were prepared by dissolving the powders in tap water using a propeller-type mixer operating at 30 rpm. The individual concentrations varied, as is shown in **Table 1**.

To all solutions, each of the hop products (in total five) or the reference biocide were added separately, mixed for about 15 min. at low speed, transferred into a glass bottle, sealed and stored in a dry box at 26 °C (79 °F) over a period of ~ six weeks. The dosages of the hop acids & extract and of the biocide were constant for all stabilizers (hop products and biocide) at 0.15 wt. % relative to the aqueous solution.

Table 1: Concentrations of polysaccharide, hop product and biocide present in the aqueous solutions tested.

Polysaccharide	Concentration [wt. %]	Dosage of stabilizer [wt. %]
guar gum	0.7	0.15
HP guar	0.7	0.15
P Starch 1	4.0	0.15
P Starch 2	5.0	0.15
P Starch 3	4.0	0.15
C Starch	4.0	0.15
W Starch	5.0	0.15
Xanthan gum	0.6	0.15
CMC tech. grade	5.0	0.15

Viscosity measurements were taken approx. every third day or as needed by transferring a part of the polysaccharide solution into the cup of a rotational viscometer and taking the 3; 6; 100; 200; 300 and 600 rpm readings following the procedure set forth by the American Petroleum Institute (API) [12]. After each measurement, the test fluid was transferred back into the 500 mL container holding the remaining fluid, sealed and stored until the next measurement was taken. From the dial readings, following the *Bingham* model the key parameters Plastic Viscosity and Yield Point were calculated.

Experimental Results

In the following, the results obtained from the rheological measurements will be discussed for each polysaccharide, and the effectiveness of the individual stabilizers (CO_2 extract, hop acids and biocide) in retaining fluid viscosity will be compared.

Guar gum

At 0.7 wt. % concentration, this galactomannan biopolymer develops a shear-dependent rheology corresponding to the *Bingham* model (**Figure 4**), with values of 16 cP and 51 lbf/100ft^2 for Plastic Viscosity and Yield Point, respectively.

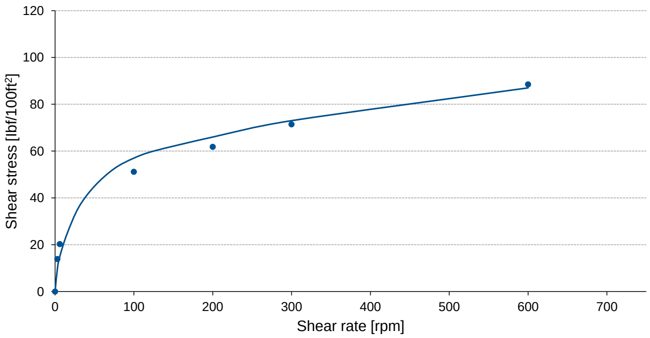


Figure 4: Flow curve of the aqueous guar gum solution as obtained from the rotational viscometer.

To probe into the stability of the GG solution over time, the 600 rpm readings from the rotational viscometer as well as the values at 3 rpm were taken and recorded over a period of seven weeks.

First, at 600 rpm shear (**Figure 5**) it was observed that the untreated, straight guar solution was stable only for ~ two days. Thereafter, its viscosity plummeted to almost zero within one day. This viscosity decrease came along with a characteristic rotten smell, indicating severe bacterial attack. Addition of any of the stabilizers had a very positive effect. The CO_2 extract could provide full viscosity retention over the entire test period of 50 days, thus matching the performance of the biocide. The mixture of α+β acids recorded only a very slight decrease, followed by pure β acid. The least effective were pure α acid and the mixture of iso α+β acid.

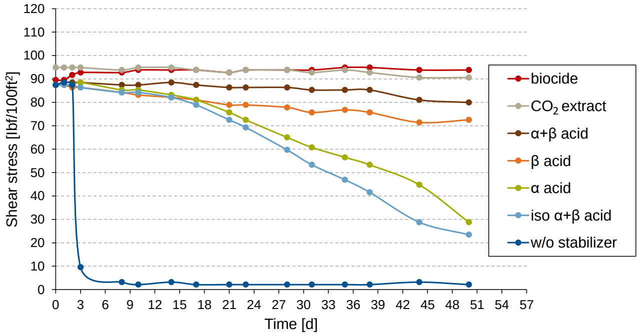


Figure 5: Shear stress values of the aqueous guar gum solution over time, measured at a shear rate of 600 rpm on a rotational viscometer. Concentration of the stabilizers was 0.15 wt. %.

Hence, it is demonstrated that specific hop products can stabilize guar gum similarly as a powerful commercial biocide.

As GG is mainly used for its suspending and carrying capacity of proppants which relates to low shear rheology, the time-dependent development of the viscosity at 3 rpm shear was also looked at.

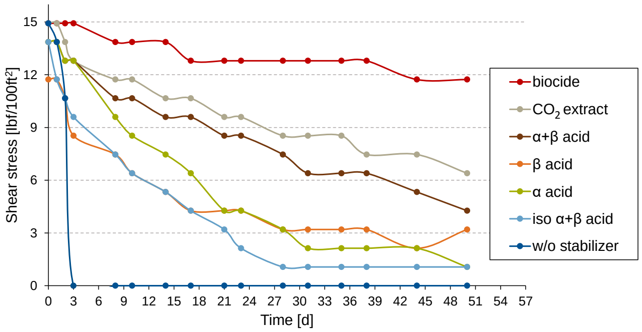


Figure 6: Time-dependent low shear viscosity measured at 3 rpm of the guar gum solution. Stabilizer concentrations were 0.15 wt. %.

Interestingly, the results displayed in **Figure 6** offer a more diverse picture than those obtained at 600 rpm shear. There, again the untreated guar solution experienced immediate and even faster viscosity degradation which begins already after one day of storage only. Different to the measurements at 600 rpm shear rate, here none of the stabilizers was able to provide complete viscosity stability to the fluid. The biocide performed best, but still produced a decline in viscosity of ~ 20 %. From the hop products, the CO_2 extract and the blend of α+β acids came next (viscosity reduction ~ 50 %) and the least effective were pure α acid and iso α+β acid.

Accordingly, at 3 rpm shear rate the same order of effectiveness was achieved for all hop products than at 600 rpm shear conditions. However, it became evident that under bacterial attack the low shear rheology of guar gum solutions became affected earlier and stronger than at high shear. This observation is significant, because as said above guar gum is mainly used for its ability to keep solid particles in suspension, and this is directly linked to its ability to maintain high low shear viscosity.

Hydroxypropyl Guar

The principle rheological behavior of a 0.7 wt. % aqueous HPG solution corresponds to a *Bingham* fluid (see **Figure 7**), similar to that of non-derivatized guar gum. Its rheological key parameters are 15 cP for Plastic Viscosity and 42 lbf/100ft^2 for the Yield Point, respectively.

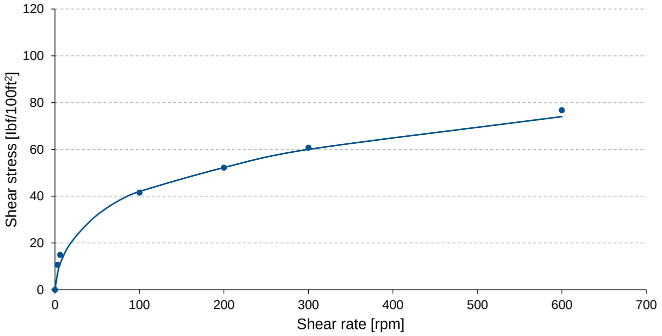


Figure 7: Flow curve of the aqueous HP guar solution, as obtained from the rotational viscometer.

Compared to guar gum, HPG exhibits a significantly higher stability towards bacterial attack, as is evidenced by the viscosity results at 600 rpm shear rate (see **Figure 8**). First, it is obvious that the non-treated HPG is stable over ~ four days before viscosity starts to decline, but less quickly than for GG. Furthermore, all stabilizers tested can well protect this polysaccharide from bacterial attack except for β acid and the iso α+β acid blend which encounter a viscosity reduction of ~ 37 % after 52 days.

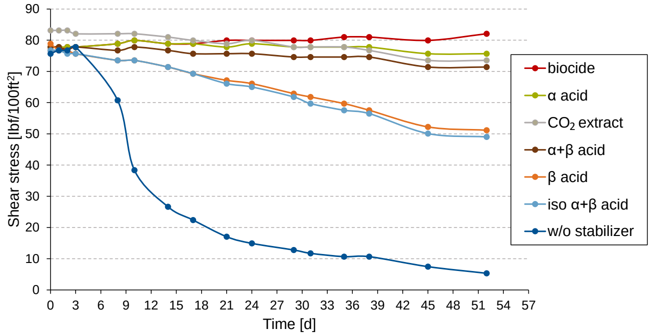


Figure 8: Shear stress values of the aqueous HP guar solution, measured at a shear rate of 600 rpm on a rotational viscometer.

Again, similar to GG, a different result is obtained at the low shear rate of 3 rpm (see **Figure 9**). There, only the biocide is able to stabilize the solution viscosity over the entire test period. The α acid, the CO_2 extract and the α+β acid blend experience viscosity declines of 50-70 % after 52 days, and the β acid and iso α+β acid blend exhibit even faster and more pronounced declines (reduction ~ 85 %).

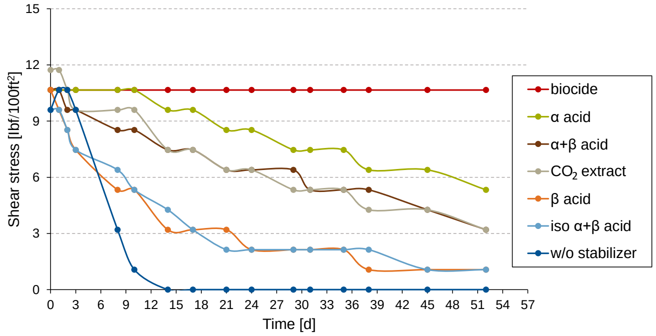


Figure 9: Time-dependent low shear viscosity of the HP guar solution, measured at a shear rate of 3 rpm.

The results allow to conclude that HP Guar generally is more robust against bacterial attack than guar gum, but hop products are unable to stabilize its low shear viscosity (carrying capacity) over more than ten days. Only the chemical biocide can accomplish this. Furthermore, the results suggest that under bacterial attack, the low shear viscosity of HPG is affected more quickly and stronger, compared to the high shear viscosity. This behavior is similar to that of guar gum.

Potato Starch 1

This polysaccharide produces an almost *Newtonian* fluid, as is shown in **Figure 10**. The characteristic rheological parameters are 22 cP for Plastic Viscosity and 10 lbf/100ft^2 for the Yield Point, respectively.

Analysis of the high shear rate viscosity at 600 rpm of the solution (starch concentration 4.0 wt. %) reveals that this biopolymer in the non-treated case is stable for ~ four days before its viscosity gradually declines (slower than for HPG).

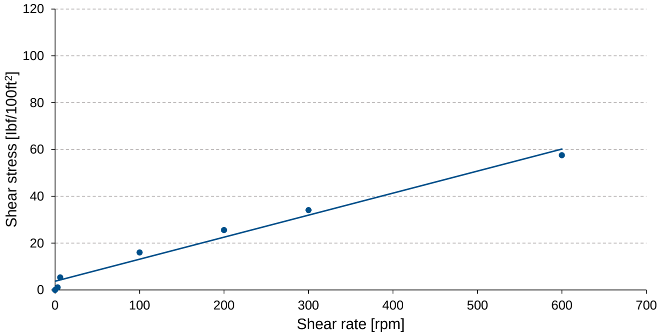


Figure 10: Flow curve of the aqueous solution of Potato Starch 1, as obtained from the rotational viscometer.

After 38 days it reaches only ~ 20 % of the initial viscosity (**Figure 11**). Again, the CO_2 extract and also the α+β acid blend can significantly stabilize this solution (viscosity reduction after 38 days ~ 15 %), and also the other hop products perform rather well. However, none of them can surpass the effect of the biocide which completely stabilizes this polymer over the entire test period.

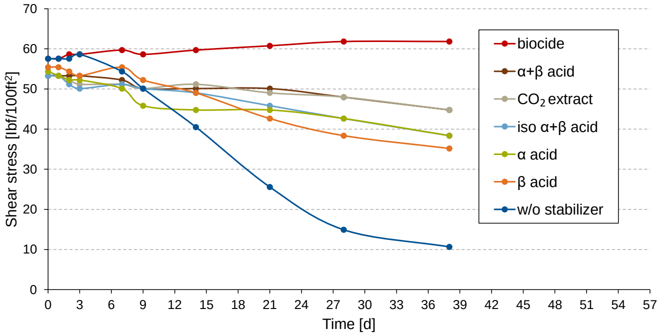


Figure 11: Shear stress values of the aqueous solution of Potato Starch 1, measured at a shear rate of 600 rpm on a rotational viscometer.

For this polymer, analysis of the effects at 3 rpm shear rate was not possible because of the very low dial readings (1-2 lbf/100ft^2) and the error margins being too large there.

The results allow to conclude that some hop products can stabilize this polysaccharide over a limited time period of ~ seven days, thereafter slow degradation occurs. The biocide, however, can fully protect this starch against bacterial attack, even after 38 days of storage.

Potato Starch 2

This derivatized starch product shows a nearly *Newtonian* flow behavior in aqueous solution (c = 5.0 wt. %), as is presented in **Figure 12**. Its characteristic parameters are 12 cP for Plastic Viscosity and 4 lbf/100ft^2 for the Yield Point, respectively.

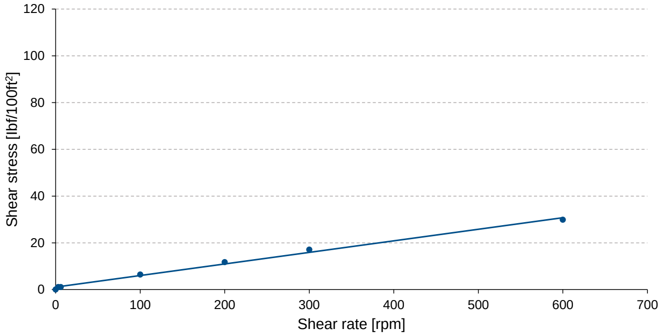


Figure 12: Flow curve of the aqueous solution of Potato Starch 2, as obtained from the rotational viscometer.

The high shear rheological measurements performed at 600 rpm reveal that the non-treated polymer solution is stable for four days before its viscosity quickly declines to ~ 10 % of the initial value, indicating severe degradation (**Figure 13**). However, most hop products are able to perfectly stabilize this polymer over six weeks, and comparable results as for the chemical biocide are achieved. Most interestingly, here the CO_2 extract does not perform well, contrary to all previously tested polysaccharides. Whereas the poor performance of β acid was consistently observed here and in the systems looked at before.

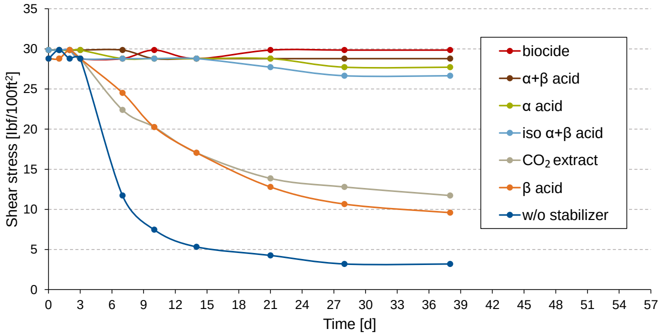


Figure 13: Shear stress values of the aqueous solution of Potato Starch 2, measured at a shear rate of 600 rpm on a rotational viscometer.

Potato Starch 3

This non-derivatized starch produces a fluid with extremely high Plastic Viscosity (53 cP) and no Yield Point (0 $lbf/100ft^2$), as is shown in **Figure 14**. Concentration of the biopolymer in this *Newtonian* fluid was 4.0 wt. %.

Measurements under high shear rate (600 rpm) first revealed that this biopolymer is immediately degraded by bacteria. After two days of storage only, viscosity dropped by ~ 10 %, and after three days a loss in viscosity of ~ 85 % was recorded (**Figure 15**).

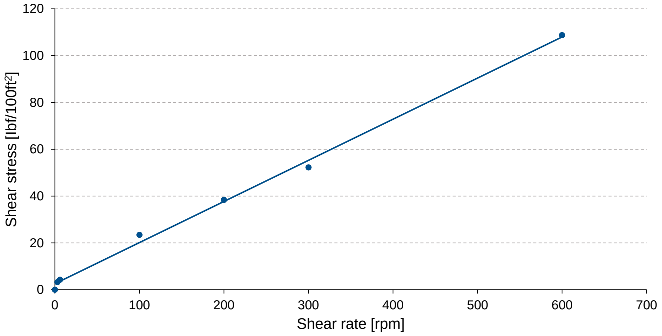


Figure 14: Flow curve of the aqueous solution of Potato Starch 3, as obtained from the rotational viscometer.

Most interestingly, addition of the hop products and the biocide reduced initial solution viscosity by 12-20 %. The reason for this effect remained unknown. Furthermore, only the chemical biocide was able to protect this starch polymer against bacterial degradation. Surprisingly, from the hop products here the α+β acid mixture (isomerized and non-isomerized) came out best although their stabilizing effect in total was rather weak. Also, the CO_2 extract which had performed so well in the guar, HP guar and Potato Starch 1 solutions showed a poor effect here, similar as in the Potato Starch 2 solution.

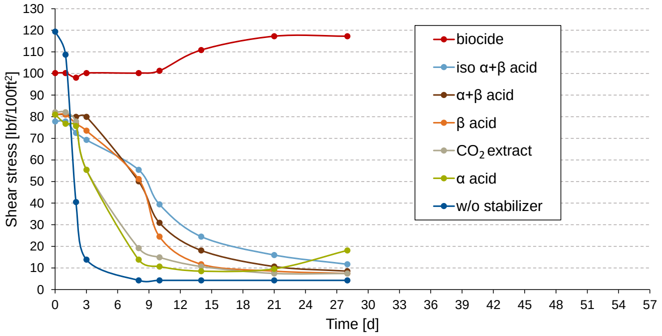


Figure 15: Shear stress values of the aqueous solution of Potato Starch 3, measured at a shear rate of 600 rpm on a rotational viscometer.

The results signify that specific hop products can protect this starch only for three to four days before massive degradation commences, and that the blend of α+β acids works best here.

Corn Starch

This starch polymer provides similar rheological parameters (PV = 11 cP, YP = 4 $lbf/100ft^2$) like the starch polymer P Starch 2 tested before (see **Figure 12**) and produces an almost *Newtonian* fluid (flow curve not shown here).

When tested at high shear rate (600 rpm), the non-treated solution remains stable over three days before its viscosity drops by ~ 85 % within the next five days (**Figure 16**). Whereas, all hop products succeed in stabilizing this solution over 28 days except for the CO_2 extract. Here again, this extract exhibits a surprisingly poor performance.

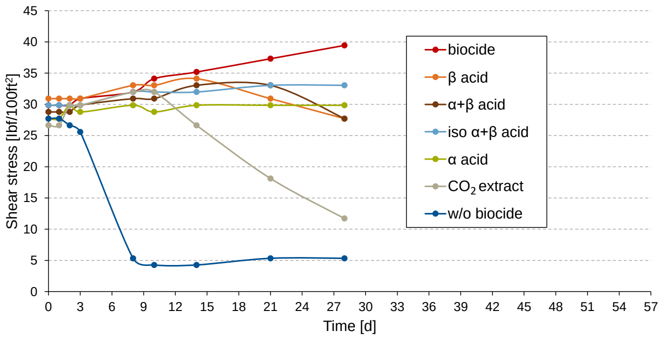


Figure 16: Shear stress values of the aqueous Corn Starch solution, measured at a shear rate of 600 rpm on a rotational viscometer.

Wheat Starch

This food grade polymer produces a solution (c = 5.0 wt. %) with a much lower Plastic Viscosity (PV = 17 cP) than the previously tested starches (**Figure 17**). The Yield Point of this fluid was 6 lbf/100ft^2.

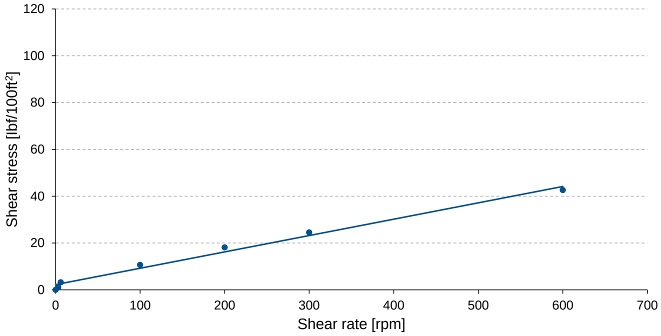


Figure 17: Flow curve of the aqueous solution of Wheat Starch, as obtained from the rotational viscometer.

Tests performed at a shear rate of 600 rpm evidenced limited stability of the pristine solution (**Figure 18**). Degradation started already after two days, and ~ 85 % of the viscosity were lost within one week of storage. Addition of any hop product stabilizes this polymer solution for at least three weeks. Thereafter, a slow decline of viscosity begins which is most pronounced for the CO_2 extract. Apparently, this extract does not work well for all starch products, with the exception of Potato Starch 1.

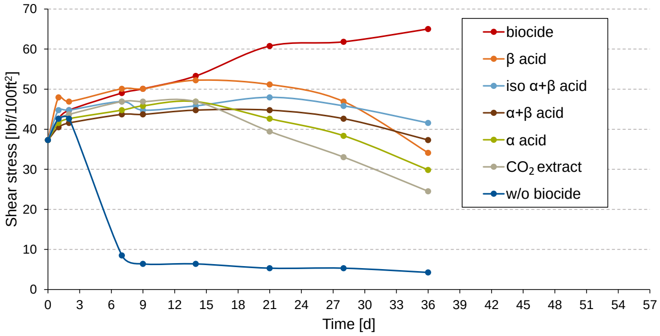


Figure 18: Shear stress values of the aqueous Wheat Starch solution, measured at a shear rate of 600 rpm on a rotational viscometer.

Xanthan gum and CMC

Comparative testing involving a 0.6 wt. % Xanthan gum solution revealed that under the storage conditions selected for our experiments, no noticeable decrease in viscosity occurred (graphs not shown here). Consequently, addition of a stabilizer to the solution did not show any improvement and is unnecessary here.

Similar observations were made for a 5.0 wt. % solution of carboxymethyl cellulose (graphs not shown here). The initial value for the reading at 600 rpm of 124 lbf/100ft^2 remained constant over four weeks, thus suggesting that a stabilizer could not benefit this fluid.

The experiments involving these two polymers instigate that under the storage conditions selected in our experiments, bacterial infection and growth appears to be less than in actual oilfield operations. There, it has been observed that after about one week of application, drilling fluids containing CMC and even more so Xanthan gum require a biocide to prevent polymer degradation and loss of performance. Consequently, this allows to conclude that the time periods shown in our tests for fluid stability may be considerably shorter in actual field use.

Discussion of Results

To gain a better overview of all data produced and to order the hop products based on their overall efficiency, all previous results were compiled in **Figures 19 – 24** which present the 600 rpm dial reading values for all polysaccharide samples treated with the individual hop products.

From there it is apparent that the blend of α+β acids performs best across all polysaccharides. Potato Starch 3 presents the only polymer where it fails to stabilize.

The CO_2 extract which is a readily available commercial product exhibits superior property in guar and HP guar solutions and one starch product, but is mediocre in all other fluids.

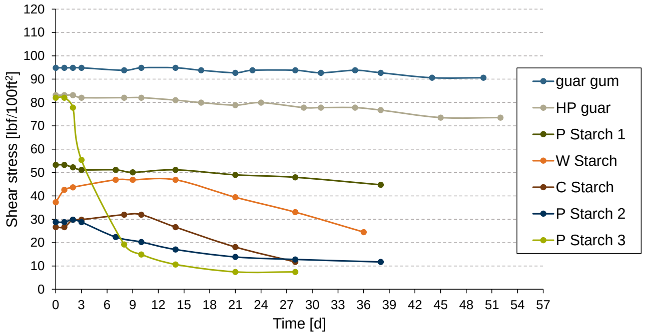


Figure 19: Effectiveness of **CO_2 extract** as stabilizer on all polysaccharide samples tested, as evidenced from measurements at a shear rate of 600 rpm.

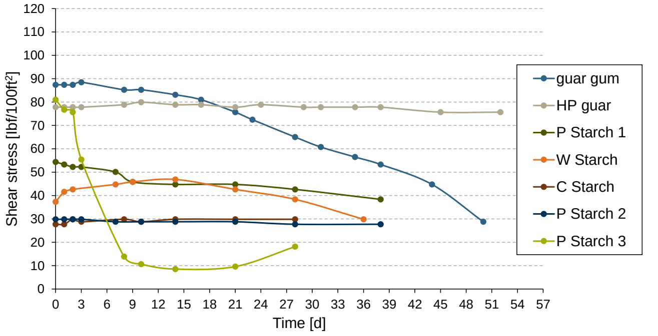


Figure 20: Effectiveness of **pure α acid** as stabilizer on all polysaccharide samples tested, as evidenced from measurements at a shear rate of 600 rpm.

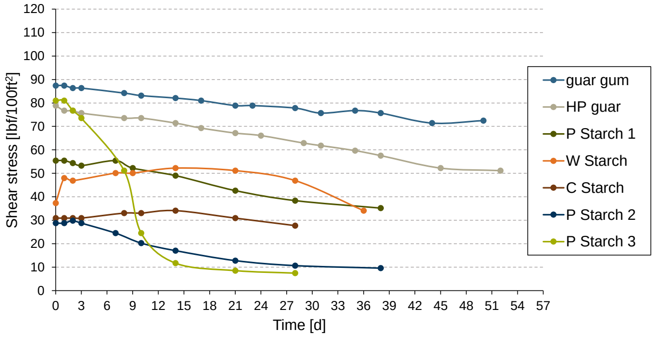


Figure 21: Effectiveness of **pure β acid** as stabilizer on all polysaccharide samples tested, as evidenced from measurements at a shear rate of 600 rpm.

The mixture of isomerized α+β acid is much inferior to the non-isomerized species. It is more expensive than the non-isomerized product anyway and therefore should not be considered any further.

The same applies to the β acid which is inferior to the α acid. Interestingly, both are inferior to the blend α+β acids.

The chemical biocide outperforms the blend of α+β acids only in one potato starch solution.

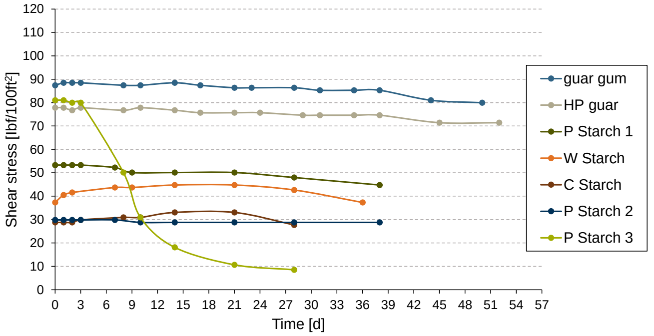


Figure 22: Effectiveness of **α+β acid** as stabilizer on all polysaccharide samples tested, as evidenced from measurements at a shear rate of 600 rpm.

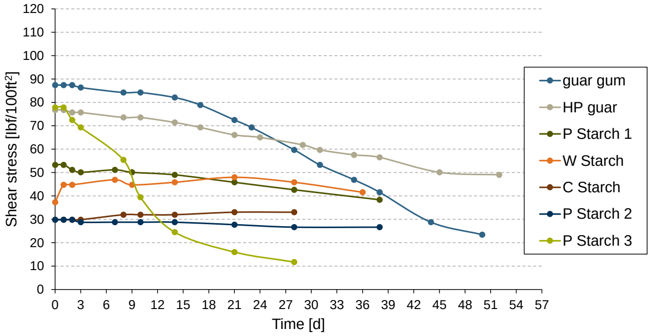


Figure 23: Effectiveness of **iso α+β acid** as stabilizer on all polysaccharide samples tested, as evidenced from measurements at a shear rate of 600 rpm.

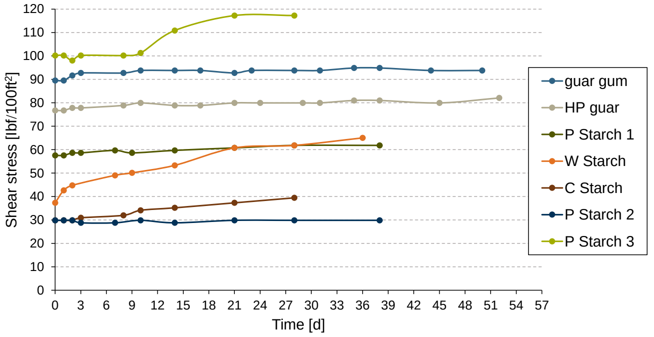


Figure 24: Effectiveness of the **biocide** as stabilizer on all polysaccharide samples tested, as evidenced from measurements at a shear rate of 600 rpm.

For a better overview, all results are compiled in **Table 2**.

Table 2: Comparison of the effectiveness of different stabilizers, based on viscosity data obtained at 600 rpm.

Poly-saccharide	**Stabilizer**					
	α acid	β acid	α+β acid	iso α+β acid	CO_2 extract	biocide
guar gum	□	▨	■	□	■	■
HP guar	■	□	■	□	■	□
P Starch 1	▨	□	■	▨	■	▨
P Starch 2	■	□	■	■	□	■
P Starch 3	□	□	□	□	□	□
C Starch	■	■	■	■	□	□
W Starch	▨	■	■	■	□	□

Legend:
Viscosity reduction < 20 % ■
Viscosity reduction 20-30 % ▨
Viscosity reduction > 30 % □

Conclusions

This preliminary study on the anti-bacterial effect of different hop products revealed that for controlling the bacterial growth in aqueous polysaccharide-based fluids they can present potential alternatives to toxic chemical biocides.

Effectiveness of the individual hop constituents (α, β acids, isomerized forms etc.) can vary with the kind of polysaccharide, however, a blend of α and β acids appears to work well for most guar and starch polymers.

An alternative to the blend of α+β acids (which have to be produced separately and require an additional extraction step) is a common, commercial CO_2 extract of hop. This product works particularly well with guar and its derivative HPG and might help to overcome the environmental concern on fracturing fluids as expressed in the media. It is however less effective with starch polymers.

Earlier literature presents that the β acid is particularly effective in bacterial control [13]. Their superior effect is assigned to their more hydrophobic character which enhances their ability to act as an ionophore. Interestingly, this effect could not be confirmed in our investigation. To the contrary, β acids often provided the least stabilization in our tests.

We consider the results obtained here as such encouraging to warrant a broader series of experiments whereby the effectiveness of hop products is studied dosage-dependent, at elevated temperatures and at different pH values on a greater variety of oilfield polysaccharides.

Furthermore, to minimize cost, a focus shall be made on different CO_2 extracts from several suppliers to optimize the economics of hop-based bacteriostatic additives.

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Nomenclature

°C = *degree Centigrade*
°F = *degree Fahrenheit*
CMC = *carboxymethyl cellulose*
CO_2 = *carbon dioxide*
$lbf/100ft^2$ = *pound force per 100 square feet*
mL = *milliliter*
rpm = *revolutions per minute*
wt. % = *concentration by weight percentage*

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