Natural Plant-derived Antibacterials in Drilling Fluids – Applications for Geothermal Energy Production

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Abstract

Different microorganisms located in earth crust and soil can disrupt geothermal drilling processes by polymer destruction in drilling fluids and formation of unpleasant smell. In addition, microbial activity may lead to corrosion of metallic equipment by their metabolites. For prevention, environmentally problematic biocides such as glutaraldehyde, triazine derivatives or formaldehyde-releasing substances are used in process fluids. As an alternative to these potentially harmful products to human health and environment, plant-derived ingredients, such as hop acids and rosin acids were tested in laboratory as well as in industrial scale. These so called "natural antibacterials", e.g. hop acids, rosin acids and fatty acids have been introduced in the sugar industry in the 1990ies and since then have become the second most important group of antimicrobial control agents in the global conventional sugar production and will also become available for organic sugar production soon.
In laboratory trials, natural antibacterials could inhibit the growth of bacteria isolated from drilling fluids such as *Haloanaerobium congolense* (DSM 11287), *Halolactibacillus miurensis* (DSM 17074) and *Halolactibacillus halophilus* (DSM 17073). The needed amount was comparable or even lower than the reference product "Grotan OX". Natural antibacterials were also effective in industrial scale applications, significantly reducing microbial contamination and therefore avoiding development of unpleasant smell as well as problematic property changes of drilling fluids.
Consequently, natural antibacterials are promising alternatives to conventional chemicals to combat microbial activity in drilling fluids and ensure their properties and stability. The advantage of these plant-based substances is their natural origin and harmlessness for humans and environment (GRAS status), which is particularly demonstrated by water hazard class 1 rating for hop acids ("Wassergefährdungsklasse 1", based on German regulation).

1. Introduction

For drilling processes, drilling fluids – beside other functions – are used to stabilize the borehole and transport the drill cuttings from the borehole to the surface. Therefore, the drilling fluid needs to have a certain composition, usually containing bentonite, polymers and different other additives for example biocides to prevent the growth of microorganisms. Different microorganisms such as mesophilic, thermophilic and hyperthermophilic bacteria are located in earth crust and soil. Furthermore, halo-tolerant or halophilic bacteria can exist depending on local conditions. These different bacteria can disturb or even disrupt geothermal drilling processes by polymer destruction in drilling fluids and formation of unpleasant smell. The undesired bacteria belong to the phylum of Firmicutes, Bacteroidetes, Actinobacteria or Proteobacteria. The genera *Pseudomonas, Shewanella, Halolactibacillus* and *Burkholderia* belong to the phylum Firmicutes (Emerstorfer, Omann et al. 2016). For prevention, environmentally problematic biocides such as glutaraldehyde, triazine derivatives or formaldehyde-releasing substances are used in process fluids (Ashraf, Ullah et al. 2014). Due to the continuing development of geothermal industry, an increasing amount of drilling fluids is necessary. For the deep geothermal drilling with well depth of >3000 m, drilling fluids of 300 – 800 m^3 are needed

(Liu, Wang et al. 2019). The waste management for the drilling fluids is getting more and more regulated because of the biocides used in these drilling fluids, which can be harmful to human health and environment. According to our responsibility for the environment and occupational safety, it is imperative to work on developing less harmful products. An alternative to these biocides are plant-derived natural ingredients (Emerstorfer, Omann et al. 2016). These so called "natural antibacterials", such as hop acids, rosin acids and fatty acids have been introduced in the sugar industry in the 1990ies and since then have become the second most important group of antimicrobial control agents in the global conventional sugar production. After undergoing a thorough registration process in 2018, these substances will now also become available for organic sugar production (Expert Group for Technical Advice on Organic Production 2018). We tested these natural antibacterials in laboratory and industrial trials during our study.

2. Material and methods

2.1. Minimal inhibitory concentration

The genera *Halolactobacillus* and *Haloanerobium congolense* (DSM 11287), *Halolactobacillus miurensis* (DSM 17074) and *Halolactobacillus halophilus* (DSM 17073) were cultivated in culture media recommended by DSMZ (Table 1).

Table 1: Incubation conditions for different bacteria species

Bacteria species	Media	Incubation time	Incubation condition
H. congolense	DSMZ-Media 933	120 h	anaerobic, 42 °C
H. miurensis	DSMZ-Media 785	24 – 48 h	microaerophilic, 30 °C
H. halophilus	DSMZ-Media 785	24 – 48 h	microaerophilic, 30 °C

Each species was transferred to 0.9% NaCl solution to reach the McFarland Standard (OD_{600} 0.16 – 0.2) and added to media in duplicate to Honeycomb format plates (Bartelt GmbH, Graz, Austria). Natural antibacterials (hop beta acids) were added to the bacteria solution in the concentrations of 0.25, 0.5, 10, 20, 50, 100 and 200 ppm based on active ingredient. Rosin based product was added in the concentrations of 10, 20, 100 and 250 ppm based on active ingredient. Furthermore, Grotan OX was also tested in the concentration range 50, 100, 1000, 2000 and 5000 ppm. To ensure anaerobic conditions for *H. congolense* the enzyme oxyrase was added to the culture media. All wells were covered with silicone oil to ensure oxygen exclusion. The OD measurement was done every 15 minutes after shaking for 5 seconds with Bioscreen C analyser (Oy Growth Curves Ab Ltd., Helsinki, Finland) at a wavelength of 600 nm.

2.2. Temperature stability

Temperature stability tests for products based on hop beta acids and rosin acids were carried out in so-called mini fermenter trials. This trial set up was developed in sugar industry for testing the effectiveness of different antimicrobial products (Hein, Pollach et al. 2006). Media (Table 2) was incubated with 20 mL raw juice from a sugar factory at 65 °C. pH and temperature were measured online. After pH reduction to 5.7, caused by microbial activity and formation of organic acids, the antibacterial was added in a concentration of 1 ppm (hop beta acids) or 8 ppm (rosin acids) based on active ingredient in the product. The natural antibacterial products were heat treated at 121 °C for 20 minutes at 1 bar and cooled to room temperature prior to addition. The trial period was 24 hours.

Table 2: Composition of media in mini fermenter trials

Component	Amount [g]
Peptone	10.00
Meat extract	5.00
Yeast extract	5.00
$K_2HPO_4(3*H_2O)$	1.31
$MgSO_4*7H_2O$	0.10
$FeSO_4*7H_2O$	0.01
Distilled water	1000

2.3. Industrial trials

Hop beta acids were added to drilling fluids based on biopolymers in different concentrations at drilling sites in Austria and Germany (Table 3).

Table 3: Use of hop beta acids at different drilling sites

Drilling site		Bore hole depth [m]	Concentration of hop beta acids [ppm]
Country	City		
Austria	Bernhardsthal	>2000	5.1
	Linenberg	>1000	13.0
	Prottes	>3000	4.6
	Bockfließ	>1500	12.1
Germany	Bruck 1	>5000	3.4
	Freiham / Munich	>3000	8.3
	Holzkirchen	>5000	10.3

In Bruck, Germany, 3.4 ppm hop beta acids were added to the drilling fluid and stored for two months. The composition and pH of the drilling fluid was measured before and after the storage time.

2.4. Microbiological analyses

Determination of bacterial contamination level

Samples from the drilling site in Holzkirchen, Germany were collected and stored under cooled conditions before determining the viable cell count. Samples were spread on plate count agar plates, incubated at 37 °C under aerobic conditions for 48 hours.

Microbial rapid test system

Drilling fluid samples were analyzed on-site for determination of microbial contamination by using the microbial quick test “Cult-Dip combi” (Merck Millipore, Darmstadt, Germany) following the manufacturer’s handbook. Optical quantification of cell count was carried out as described in the manufacturer’s handbook.

3. Results and discussion

Natural antibacterials such as hop acids and rosin acids can inhibit growth of *Halanaerobium* and *Halolactobacillus*, which are problematic genera for geothermal industry (Emerstorfer, Omann et al. 2016). The hop acids were effective in lower concentrations compared to rosin acids and Grotan OX (Table 4). Grotan OX is a commonly used biocide in drilling fluids.

Table 4: Minimal inhibitory concentration of products based on hop acids and rosin acids and Grotan OX for different bacteria species (Emerstorfer, Omann et al. 2016)

Strain	Hop acid based product [ppm]	Rosin acid based product [ppm]	Grotan OX
H. congolense (DSM 11287)	10	100	100
H. miurensis (DSM 17074)	50	10	100
H. halophilus (DSM 17073)	1	250	50

The temperature increase is approx. 25 – 30 °C with every kilometer of drilling. In deep geothermal energy projects, boreholes have a depth of > 3000 m (Liu, Wang et al. 2019). This implicates temperatures of more than 100 °C (Emerstorfer, Omann et al. 2016), which is a challenging environment for natural substances. In our tests, we determined the temperature stability of products based on hop beta acids and rosin acids (Figure 1). Both products were still effective after heat treatment (20 min, 121 °C).

A **B**

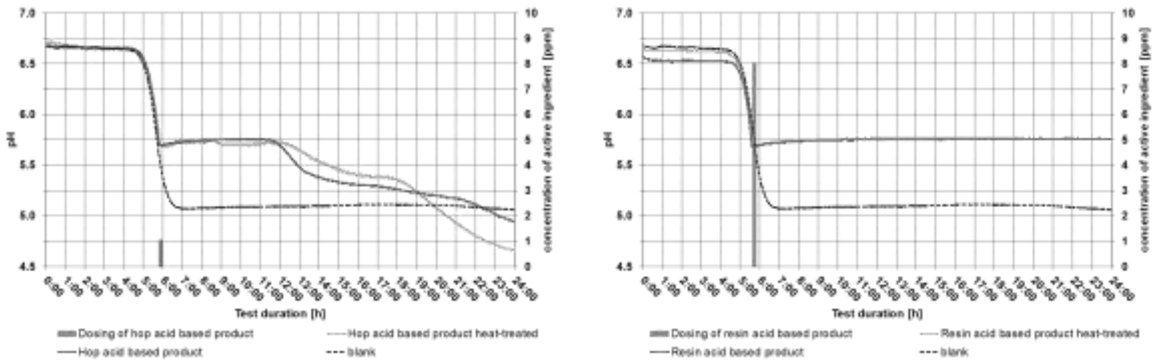

Figure 1: Mini fermenter trials for determination of temperature stability of hop beta acids (A) and rosin acids (B)

The hop-based product was tested at different drilling sites. Upon addition, microbial contamination of the drilling fluid could be reduced significantly. This could be demonstrated by analyzing microbial counts with rapid test systems used on-site (Figure 2) and by determining the viable cell count. By adding hop beta acids to the drilling fluid used in Holzkirchen (Germany) the mesophilic aerobic cell count could be reduced significantly from > 3000 CFU/mL to < 20 CFU/mL. This low level could be kept for more than 30 days.

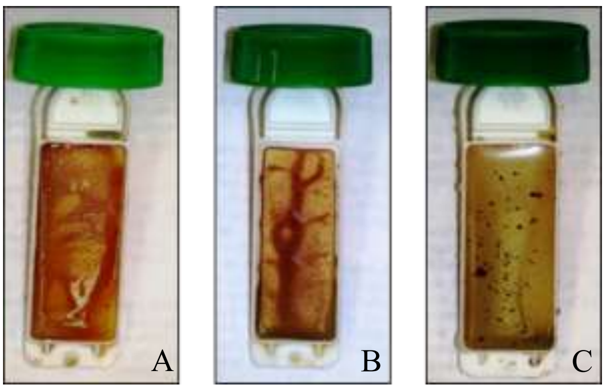

Figure 2: Microbial quick tests without (A & B) & with (C) hop beta acid addition in the drilling fluid

Property changes of drilling fluid could be avoided during two months of storage by addition of hop beta acids (Table 5). Only Yield Point and Low Shear rate viscosity (10 sec gel strength) decreased, and

API fluid loss slightly increased. The pH is often used as a parameter for microbiological growth. A decrease may suggest microbial growth because of formation of microbial metabolites such as organic acids. In our study, no decrease of the pH could be observed. The drilling fluid was re-used after the described storage period at another drilling site.

Table 5: Composition of drilling fluid with addition of 3.4 ppm hop beta acids before and after storage period of two month

	before storage	after storage
Yield Point lb/100 ft²	30	18
10" Gel	6	3
10' Gel	9	7
API-Fluid Loss (ml /30 min)	2,6	3,9

4. Conclusion

Plant-derived ingredients such as hop acids, rosin acids and fatty acids are well-known antimicrobial control agents in the sugar industry. The hop acid-based products have already been tested at various drilling sites. Conclusively, they are promising alternatives to conventional biocides to combat microbial activity in drilling fluids as they are well known from food industry, possess GRAS (generally recognized as safe) status and are non-hazardous to human health or environment. Bacterial contamination in drilling fluids could be reduced significantly, thus ensuring their stability and viscosity. Furthermore, our tests demonstrated that the drilling fluids can be stored and reused, which is a significant advantage with regards to cost effectiveness, sustainability and conscious approach with the use of processing aids.

Literature:

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