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New readily biodegradable and cost-effective Anti-Agglomerant for O&G industry

Davide Parravicini[1*], Hannah Davies[1], Juliana Lessa[1]
[1]Italmatch Chemicals
[*]d.parravicini@italmatch.com

Abstract

Eco Inhibitors was a start-up that developed an innovative portfolio that includes green and cost-effective LDHI[1]. These technologies have been proven to provide good performance over a wide range of conditions and could represent a valid solution for O&G industry, especially in regions where the environmental profile of the chemicals used is a concern. Italmatch Chemicals acquired this company in 2019 with the aim of scaling up and industrializing the technologies included in the Eco Inhibitors portfolio. This paper is focused on the Anti-Agglomerant solution (ECO GAA007 B), presenting some of the lab performance tests done.

RC20 tests are commonly used for assessing hydrates inhibition performance of AAs and new tests have been done in order to determine the effect of solvent, dosage, water cut and salinity on performance. Furthermore, data collected for this new AA has been compared to the performance of a relevant industry benchmark chemistry.

The environmental profile of this AA was also checked, confirming good and promising results.

This work contains in detail the test protocols and the obtained results proving that this new AA can work well in several conditions with performance comparable to benchmark but with better biodegradability.

Keywords

Hydrates; Green; Anti-Agglomerant

Introduction

Hydrates is one of the biggest issues for the O&G industry. Formation of these particles can lead to unexpected shut-downs, risks for operator safety and potential integrity problems. One of the most effective ways to prevent hydrate formation involves the use of chemicals. Basically, there are three types of hydrates inhibitors: thermodynamic inhibitors (THIs), anti-agglomerant (AAs) and kinetic inhibitors (KHIs)[2]. Examples of THI are methanol and glycols and, although they are very effective, they need to be dosed at very high dosage (20-30%) to achieve performance, leading to potential logistic and storage issues. The dosage required for AA and KHI is much lower but they are typically more expensive. They typically aren't biodegradable and, especially AA, quite toxic so their use in region where the environmental profile is a concern (for example North Sea) is limited or forbidden. In order to fill this technology gap, Eco Inhibitors developed a portfolio of innovative and green LDHI technologies that includes:

- ECO GAA007 B (AA)
- ECO K530 (KHI)
- ECO KS6 (KHI synergist)

Scaling up and industrialization for ECO K530 and ECO KS6 is currently ongoing while a lot of work has been already done on ECO GAA007 B.

Methodology

Sapphire Rocking cell test

A rocking cell device RCS (PSL Systemtechnik, Germany) has been used for assessing the performance of ECO GAA007 B in controlling hydrates. It offers the opportunity to simultaneously investigate rheological properties of several test samples. Tests can be conducted at a pressure up to 2.900 psi (200 bar) and an attached chiller bath is able to control the bath temperature in a range between 2 – 60°C (35.6 – 140°F). The measuring principle of the rocking cell is based on the constant tilting (rocking) of temperature and pressure controlled sapphire test cells, which enables the determination and visual observation of the gas hydrate formation under live conditions. Each cell contains a metal ball which can move through the pressurized liquids. Proximity sensors are used to monitor ball movements within the cells, with one sensor placed near each end of the cell, a top sensor and a bottom sensor. The times for the ball to travel from one end of the tube to the other, passing the top sensor and the bottom sensor are recorded. A decrease in temperature will first cause a linear increase in travel time for the ball, as the viscosity of the liquids increases. On the onset of crystallization of hydrates or paraffins, the viscosity will increase as the dispersed crystals are impacting the apparent viscosity. Subsequent growth of hydrate (or paraffin) crystals will result in additional viscosity increases until the crystals potentially start to agglomerate and form a plug, preventing the ball to reach the opposite sensor. The following parameters are recorded during the Rocking Cell tests:

- System Temperature
- Individual cell pressure
- Ball travel time
- Visual observations / photo & video imaging

Hydrate formation or blockage is indicated by:

- Pressure drop in constant volume test
- Increase of ball travel time and/or varying travel times
- Visual observation of hydrate particles in the cells

Test is considered as a "fail" in case the hydrate particles block ball movement from one sensor to the other. In all the other cases, the test is considered as "pass".

Different steps are involved during a Rocking cell test and the most relevant are:

- 1. Start preparation, pre-pressurize and release pressure to remove air (< 0.1%)
- 2. Heat up the system to the starting test temperature
- 3. After start temperature has been reached, pressurize cells to the desired pressure
- 4. Wait for pressure and temperature equilibrium for at least one hour, while rocking
- 5. Re-adjust pressure, start test, cool down to target temperature
- 7. Shut-in
- 8. Restart rocking and continue rocking at target temperature
- 9. Heat up the system to the start temperature and remain at start temperature
- 10. End test

ECO GAA007 B has been tested against a benchmark, being one of the most effective, non-biodegradable AA currently used by the O&G industry, considering same dosages and conditions for both products:

- Pressure: 175bar
- End T: 3-4°C (Subcooling 13°C)
- Water phase: artificial brine containing 4.88% NaCl and 0.35% $CaCl_2$
- Organic phase: White Spirit (amount adjusted to maintain same subcooling for each water cut considered)
- Gas phase: 93,3% CH_4, 4.4% CO_2, 1.8% N_2, Ethane 0.5%
- Water cut: 15%, 25%, 35%, 65% and 85%

The testing protocol has been selected in order to mimic what could happen in a real oil pipeline. Duration and rocking rate (if any) are listed in Table 1:

Step	Rocking rate	Duration	Test time
Start-Up / Pre-Saturation	10 RPM	2h	0-2h
Saturation / Equilibrium	10 RPM	2h	2-4h
Cooldown	10 RPM	4h	4-8h
Steady State	10 RPM	8h	8-16h
Shut-In	0 RPM	6h	16-22h
Constant Temp (Restart)	10 RPM	4h	22-26h
Warmup	10 RPM	4h	26-30h
Constant Temp (Pressure Check)	10 RPM	2h	30-32h

Table 1: testing protocol

Biodegradation

This step has been executed by following the OSPAR guidelines[3] and the test has been performed at independent GLP certified laboratories on the isolated active substance, without the presence of any organic solvent, according to OECD306 protocol[4]. 60% biodegradation after 28 days is the target to consider a chemistry as readily biodegradable in seawater.

Results and Discussion

Results of the RC20 test described in the previous section are summarized in Table 3:

Water cut	Dosage (%)	ECO GAA007 B	Reference sample
15%	1.0	PASS	PASS
	1.5	PASS	PASS
	2.5	PASS	PASS
25%	1.5	PASS	PASS
	2.5	PASS	PASS
35%	1.5	FAIL	PASS
	2.5	PASS	PASS
65%	2.5	FAIL	FAIL
85%	2.5	FAIL	FAIL

Table 2: performance results

ECO GAA007 B performance profile is in line with those of benchmark. The only difference can be found at 35% WC for the lower dosage where ECO GAA007 B failed while benchmark passed the test. It can be clearly seen an effect relative to the water cut for both the product. As expected, it will be more difficult for AAs to provide satisfactory results when the water cut is high.

The OECD306 test provided the biodegradation profile that can be seen in Figure 1. This chemistry reached the target biodegradation after about 21 days, with the final results after 28 days being close to 70%. This confirms the technology is readily biodegradable in seawater and suitable for regions where the environmental profile is a crucial parameter.

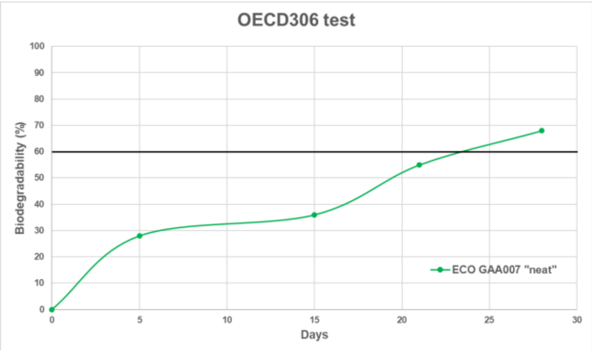

Figure 1. Biodegradation profile

Conclusions

Results presented in this paper confirmed ECO GAA007 B can be successfully used for preventing hydrates deposition is O&G pipelines. It provides good performance in line with those of currently available technologies, with the important advantage that it is readily biodegradable in seawater and for this reason applicable also in regions where environmentally acceptable solutions are requested.
More work will be done to further investigate performance (for example, against hydrate type II) and properties of this technology.

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Responsibility Notice

The authors are the only responsible for the paper content.

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