Anti-Agglomerant Low Dosage Hydrate Inhibitors (LDHI’s)

Lynn M. Frostman, PhD
Baker Petrolite

Courtesy of Cornell University
Types of Hydrate Inhibitors

No Inhibitor
- hydrates, possible plug

MeOH, Ethylene Glycol
- no hydrates

Kinetic Inhibitor
- short times: no hydrates
- long times: hydrates, possible plug

Anti-Agglomerant
- dispersed hydrates

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Baker Petrolite’s Anti-Agglomerant Inhibitors

General Characteristics

- Allow hydrates to form
- Hydrate particles remain small, well-dispersed, non-adherent
- Fluid viscosity remains low
- Require liquid hydrocarbon phase (condensate or oil)
- Inject continuously before fluid enters hydrate region
- No known limitation on severity of subcooling
- Effective even after prolonged (2 Week) shut-Ins
Anti-Agglomerants

Primary Advantages

- Low Dosage
  - Lower Capital Costs
  - Lower Chemical Costs
  - Lower Transportation Costs
  - Lower Storage Costs
  - Smaller Pumps
  - Less Maintenance

- Effective at Severe Conditions
- Effective During Extended Shut-ins
- Total System Approach to Ensure Products are Compatible with Production System
Limitations:

- Require liquid hydrocarbon phase and water cut < 50-75%
- Do not protect gas phase
- May not be effective at temperatures below 38 °F
Dosage is Independent of Subcooling

Minimum Effective Concentration (wt% of aqueous phase) vs. Subcooling (°F)
Currently available LDHI’s can:

- Cut treatment cost ($/bbl water) 50%
- Reduce umbilical diameters 35%
- Reduce number of umbilicals by combination with other production chemicals
- Reduce storage or increase time to resupply 2 orders of magnitude
- Reduce weight of stored chemicals 2 orders of magnitude
Previous and Existing Applications

- **Previous**
  - Deepwater Gulf of Mexico: 1.5 month subsea trial, continuous injection
  - North Sea: several brief trials, continuous subsea injection
  - New Zealand: 1 brief trial, continuous subsea injection

- **Existing**
  - Deepwater Gulf of Mexico: 2 platforms’ dry tree wells, intermittent use only
  - Canada: 2 continuous injection, onshore applications
Planned Applications

- **Early June**
  - continuous subsea injection in gas condensate line, ~500 gpd

- **July**
  - 2 new platforms’ dry tree wells, intermittent use only

- **Others**
  - 2 week field trial, continuous subsea injection
  - brief field trial, continuous topsides injection
Applications Under Consideration

- **Deepwater Gulf of Mexico**
  - 3 platforms’ dry tree wells, intermittent use
  - 2 subsea, intermittent use
  - 6 subsea, continuous applications

- **North Sea**
  - 4 subsea, continuous applications

- **Canada**
  - 2 subsea, continuous applications
Potential Concerns with LDHI’s

- Impact on desalter
- Impact on biotreater
- Corrosion in the overheads
- Ultimate fate of decomposition products
- Impact on jet fuel and diesel
Potential Concerns with LDHI’s

- Biggest unknown is the expected concentration due to dilution from other production
- Typical use concentration: 15,000 ppm basis water
- Water cut 1-50%
- Intermittent or continuous use
- Partitioning strongly depends on nature of oil, salinity of water, and water cut
  - high salinity, black oil systems: >95% tends to partition to oil
  - low salinity, condensate systems: ~50% tends to partition to oil
Well making 1000 bwpd, 45 mmscfd

Pumping 175 bpd MeOH - insufficient to control hydrates

Have well curtailed to 35 mmscfd

Plan to pump 500 gpd LDHI

Should be able to bring back to full production

Expected LDHI concentration at refinery = 40-50 ppm
No adverse effects are expected on emulsion tendencies in desalters.

Experimental test:
- shake oil and synthetic brine (20% water cut, 16 wt% salinity) with and without LDHI
- separate oil and water by gravity
- expect the majority of active ingredient to partition to oil phase (however, we did not specifically measure the partitioning in this sample)
- EDDA demulsification/dehydration test at 208 °F and 5% water cut
  - LDHI did not adversely affect ability to resolve emulsion
  - LDHI may have in fact helped break emulsion
Impact on Biotreater

- **Partitioning to desalter wash water**
  - under investigation; preliminary data suggests <10% of LDHI in oil will partition to water

- **Toxicity towards biotreater bugs**
  - used an actual sample of bugs from a refinery
  - exposed to different concentrations of RE 4136
  - 100 ppm RE 4136: there was no observed effect compared to a blank
  - at 1000 ppm RE 4136, we observed a significant drop in the bug population.
May be a possibility

Should be treatable
Ultimate Fate / Impact on Products

- LDHI is expected to decompose in crude distillation unit
- decomposition products have boiling point range overlapping with jet fuel and diesel (390-707 °F)
- impact on jet fuel and diesel under investigation
• Further partitioning studies under desalter conditions
• Bench scale distillation
  ➢ with and without LDHI’s
  ➢ analyze jet fuel and diesel cuts for standard specs
    ■ jet fuel 350-550 °F
    ■ diesel 550-700 °F
    ■ distillate specs as identified by David Bailey
  ➢ crude oil obtained from Equilon
• Pilot scale refinery test?
• Other suggestions?