Impact on Refineries of Upstream Additives in Crude Oil

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Agenda

- Introduction
- Problem additives
- Managing Contaminant Issues in Crude Oil
  - Refinery level
  - As an industry
Why are there additives in Crude Oil?

- Many reasons for crude oil additives
  - Production/Well performance (e.g. Silicon, phosphorous, hydrate inhibitors)
  - Safety & Performance of the transportation system (e.g. H2S scavengers and drag reducers)
  - Added during production, storage & transportation
- Cost of additives small relative to value of crude
  - If a perceived benefit to the producer then why not use?
  - “If a little is good, more is better” mentality
- Impact on refineries typically of little concern
- NACE Publication 21415 provides additional information on a number of different types of additives
Some Common Problem Additives

- Organic Chlorides
- **H2S Scavengers**
- Silicon Antifoams
- **Phosphate esters**
- Methanol/hydrate inhibitors
- Organic acids
H2S Scavengers Overview

• Used to reduce H2S in natural gas and to reduce H2S in head space of vessels (Truck, rail, ships) during transportation

• Primary sources
  • Synthetic crudes (H2S generated during processing)
  • Tight Oils
    • H2S levels too low to justify amine treating and sulfur plants
    • Souring of well from oxygen ingress with water injection
  • Refinery products such as ATB, VGO, HSFO etc.

• Chemistries used
  • Triazine – Amine (usually MEA) byproduct of scavenging reaction results in amine chloride salt formation in crude unit
  • Zinc – fouling issue
  • Other compounds available but less commonly used
Corrosion Manifestations – MEA Triazine

Low Velocity Naphtha Line Corrosion (CR of 3-7000 mpy in 6 O’clock position)

High turbulence TPA pump case

Aggressiveness of corrosion makes it difficult to manage with traditional inspection programs
More issues

Impacts high alloy trays like Alloy 600 and AL6XN

Salts and corrosion products cause fouling
Phosphorous

- Oil based well fracturing additive in Canadian gas operations
  - Contains volatile and non volatile P compounds
  - US fracturing primarily uses water based additives
- Found in light sweet Alberta crude oil and condensate
  - May now be in the heavy crude supply from use of condensate as diluent

**Symptoms**

- Fouling between kero and diesel draws in atmos tower
- Also seen in atmospheric heaters
  - Water carryover from desalter believed to promote hydrolysis and fouling in heater
- Suspect that non volatile P will foul coker heaters like other metals
- Some of the nap acid corrosion inhibitors use similar chemistry and may be an internal source of fouling
Problems reported to CCQTA

- 13% P in deposit
- 4% P in deposit
Phosphorus Fouling in a Crude Tower

This case may be nap acid corrosion inhibitor
Why additives continue to cause problems

- Lack of knowledge by refiners
  - Knowledge tends to be experience based
  - Difficulty in proactively detecting what is in the crude
  - Lack of transparency from suppliers

- Suppliers can get away with it
  - Strong incentives to use additives
  - Ignorance of problems caused
  - Often difficult to trace problems back to a specific producer (especially for onshore production)
More Additive Challenges

- Refining industry does not speak with one voice
  - Impacts not uniform
  - Depends on
    - Amount of crude and additive concentration
    - How refinery is operated
    - Design of refinery (configuration & metallurgy)
  - One refiners problem is another’s opportunity
  - No formal feedback loop to producers

- No common industry approach to proactively screen additives for potential impacts
Managing Refinery Additive Problems Today

- Reactive in nature
  - Wait until have a problem
  - Figure what it is and out how to manage
    - Eliminate problem crudes
    - Alter operating conditions
    - Do some sort of chemical treatment

- Troubleshooting challenges
  - Lack of expertise
  - Problems often sporadic
- Forced to rely on chemical supplier expertise
  - Same companies supplying additives to U/S
Traditional Industry Approach

- Do nothing
- If problem severe enough, eventually act
  - Apply pressure through industry organizations
  - Eventually get specs to address problems
  - Lengthy process to effect change
  - Lots of damage done in meantime
- Challenges with policing compliance
A More Proactive Industry Approach

- Require full disclosure from suppliers & transporters
  - Require disclosure of additives and range of concentrations used in their products
  - How to disclose useful info for refiner without giving away trade secrets
  - Producer may not know chemical composition
- Require harms testing for additives
  - Assessment protocol for potential refinery effects
  - Give refiners access to results so they can make informed decisions
Harms Testing – One way to ID potential impacts of new additives

- Harms testing – tests to mimic basic refinery operation to assess likely refinery impacts
- Key impacts to consider
  - Corrosion
  - Fouling
  - Waste Water System
  - Product Quality
- Key Inputs
  - Knowledge of the chemistry
  - Range of potential concentrations of additive
  - Standard set of tests to mimic refinery impacts
Understanding how additives may impact refinery

Key Factors
- Nature of the additive
- Concentration of additive
- Water vs. Oil partitioning in desalter
How a Harms Testing Protocol Might Work

- Checklist of questions about new additive
  - Used to ID required tests
    - Potential problems
    - Answers unknown
  - Eliminate wasteful tests (e.g. new emulsion breaker containing a variation of EO/PO polymer already known to be safe)

- Standard tests defined to allow consistent assessment of potential problems ID’d in checklist

- Results compiled into a standard report (incorporate into MSDS?)
Test Methods Exist Already

- Portable Electrostatic Desalter (PED) or bottle testing
  - Emulsion evaluation
  - Oil/water partitioning
- Hot Liquids Process Simulator (HLPS)
  - Fouling
- TGA – mass spec
  - ID thermal decomposition products to assess what happens D/S of crude heater
- Water Testing
  - BOD/COD
  - Toxicity
Challenges in Making Such a Program work

- Resistance by producers & chemical suppliers
  - Key: keep disclosures results based and avoiding disclosure of proprietary chemicals
- Do suppliers have skills to complete checklists and do testing?
  - especially small “mom & pop suppliers”
- How to address things like fracking additives that in theory stay underground?
Conclusions

- Keep doing things the same way....
- Need a more proactive approach
  - Allow informed decisions
  - Avoids overly proscriptive specs
  - Protects trades secrets of producers & chemical suppliers
- Additive disclosure with harms testing can fill that need for refiners without undue burden on U/S
  - NOT a guarantee that a refinery won’t have problems
  - MSDS system may provide a model to follow
QUESTIONS?
**Halides**

- Historically – issue was organic chlorides
- Recently
  - Highly publicized organic chloride events in Europe
  - Other halides like F & Br – both organic and inorganic forms
- Problems with corrosion mostly in downstream NHT units
  - Most will not hydrolyze in crude unit (but some can)
  - Concentrate in naphtha off crude tower
- Inorganic halides mostly removed at desalter
Challenges with Organic Halides

- Oil soluble
- Tend to concentrate in naphtha
- Form HCl, HF or HBr in NHT reactor
- Lack of N in NHT feed means little NH3 available to neutralize acids
- Lack of water wash to prevent salt formation
- Also used as chloriding agents in refinery
  - Problems can be self-inflicted
Severe HCl Corrosion in NHT Effluent Exchanger
Silicon - Antifoam

- Antifoam used to control foam in oil/gas production
  - Same product as cokers use (PDMS)
  - Polymer degrades in heater
  - Si concentrates mostly in naphtha, also in diesel and gas oil cuts

- Problem
  - Si blocks active sites on HDS catalyst
  - Most NHT's not designed for Si in virgin naphtha
  - Disproportionate effect on nitrogen removal
  - Breakthrough to reformer catalyst and increased N in feed

- Crudes more likely to contain Si
  - Associated gas production
    - Especially deep water and cold climates
  - Heavy crudes
  - Synthetic crudes using delayed coking technology
Impact depends on refinery operation

- Amount in crude charge
- Max process temperature
- Stream routing
- Capacity of reactors for Si
- Refinery A
  - Went from 6-7 yr NHT runs to <18 mo
  - Si found in main crude processed
  - Problem linked to rerouting of vac tower OH slop back to crude feed
- Refinery B – went to Lube HCK
A sample test program for a non-reactive additive

**Transportation**

- **Low Shear Mixing**
- **Low Temperature water settling**

**Tank Farm**

- **Generation of Desalted Samples for other testing**
- **Bottle Testing of Crude Oil**

**Desalting**

- **TGA – MS and metals testing**
- **HLPS fouling testing**
- **Water Testing**

**Rest of Refinery**

- **Results could trigger additional tests depending on byproducts**