Removing Acid from Crude Oil

Crude Oil Quality Group

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Presentation Overview

- HAC Definitions
- Problems with HAC
- Refinery Solutions
- Solution at Source – Removal of Acids from Crudes
- HAC Discount
- Questions from and for audience
• High Acid Crudes (HAC) have a TAN > 1.0

• TAN is the total acid number defined as milligrams (mg) of potassium hydroxide needed to neutralize the acid in one gram of crude

• Naphthenic Acids are the acids of most concern
• TAN is the industry measurement standard but of limited use in predicting problems in refineries

• Hundreds of Different Naphthenic Acids with different boiling points
Typical Naphthenic Acid Structures

\[ C_nH_{2n-z}O_2, \text{ where } z = 0 - 12 \]
Mass Spectrometry Analyses

Sample CJ

Carbon Number

% of Total

Penta
Tetra
Tri
Di
Mono
No Ring
Problems with HAC

• Corrosion due to naphthenic acids
  – Less than 200 °C not a problem since naphthenic acids are heavier compounds
  – Greater than 420 °C not a problem because naphthenic acids break down to lighter acids
  – Can be problem for streams in the 200 °C to 420 °C range

• Naphthenic acids can be a problem in jet fuel and kerosene (which have a TAN specification) and in diesels.

• Desalting concerns – Naphthenic acids can form stable emulsions and lead to foaming problems. Calcium naphthenates are particularly bad actors.
Distillation Cut Acidities

TAN, mg KOH/g

Boiling Range, °C

- 250-330
- 330-370
- 370-400
- 400-500
- 500+
HAC Amounts are Increasing

• HAC crudes are projected to increase from 7.5% of total supply in 2000 to 10% in 2010 (to around 9 million barrels/day).

• HAC crudes are found all over the world.
  – Gryphon (North Sea) – 4.2 TAN
  – Doba (Chad) – 4.7 TAN
  – Some Syncrudes (Canada oil shale) – 2 to 3 TAN
Current Solutions

• Blending to bring average TAN to < 1

• Continuous injection of corrosion inhibitors
  – Nalco’s SCORPION

• Upgrade material of construction to a higher chrome and/or molybdenum in severely corroded areas of plant
Removal Of Acids from Crude

• Solve the problem at the source by removing acids from the crude.

• Methods in the literature
  – Destruction
  – Adsorption
  – Extraction
Destruction

• Decarboxylation
  – Carboxyl group reacted to carbon dioxide.
  – DOE/California Institute of Technology
    • Catalyst – CaO (2 to 5 wt% of oil)
    • 300 C for four hours
    • 70% conversion of acids
    • Deactivation due to impurities was a concern

• Statoil’s NAR process – Removes naphthenic acid under mild catalytic hydrotreating conditions.
Destruction - Continued

• Exxon (1998 US Patent) – Destroyed 57 to 88% of the naphthenic acids by heating to 750 F for one hour.
  – Sweep gas was critical because water in the feed and reaction water needed to be removed.

• Unipure (1999 US Patent) – Mix with lime (CaO), heat to 500 F, and separate from reacted lime.
Adsorption

• UOP (1995 US patent) – Adsorption on a nickel oxide for a kerosene stream, no data on regeneration.

• ExxonMobil (2001 US patent) – Adsorption on a strong base ion exchange resin. Patent was only for lube oils and naphthenic acid removal was about 50% in the example.
Extraction

- Simple caustic wash does not work. The naphthenate salts are too soluble in the crude oil.

- BP (WO 2000 patent) – Extraction with polar solvent like methanol. Five stages required to lower TAN from 2.77 to less than 1. Methanol/Crude ratio of 1.0
Cost Discount for HAC

• World Bank correlated discount price as a function of TAN
  – Less than 0.5 TAN no discount
  – Above this each point of excess TAN lowers the price of crude by $0.051 per dollar of Brent
  – Excess defined as TAN of crude oil minus TAN of Brent (0.07)

• World Bank correlates discount as function of API gravity, sulfur content, and TAN
Cost Discount Example

- Doba Crude – 4.7 TAN
- Brent Price – US$50 per barrel
- Discount = (4.7 - 0.07) * 0.051 * 50 = $11.81/bbl
Merichem Interest

• Merichem sells technology to remove naphthenic acid from jet fuels/diesel streams by caustic washing (Napfining\textsuperscript{SM}).

• Merichem is the world largest producer of refined naphthenic acids (plant is located in Tuscaloosa, Alabama).

• Merichem has developed proprietary technology to remove naphthenic acid from crude oil.
Audience Discussion

• How important is lowering the acid content of a crudes to a production company
  – Is the Work Bank discount in the right ball park?
  – What would be a good TAN spec?
    • Any particular acids more important (such as those that boil in the jet fuel range)?
  – How much could a production company afford to spend to have a low acid crude (i.e. if technology’s operating and capital charge was less than $0.50, 1.00, etc/bbl then there would be a definite interest).