

Removing Acid from Crude Oil

Crude Oil Quality Group

New Orleans Meeting

February, 2006

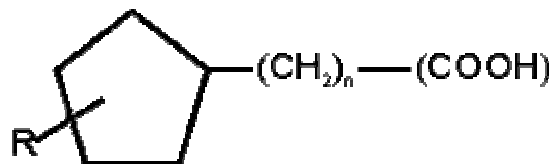
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Presentation Overview

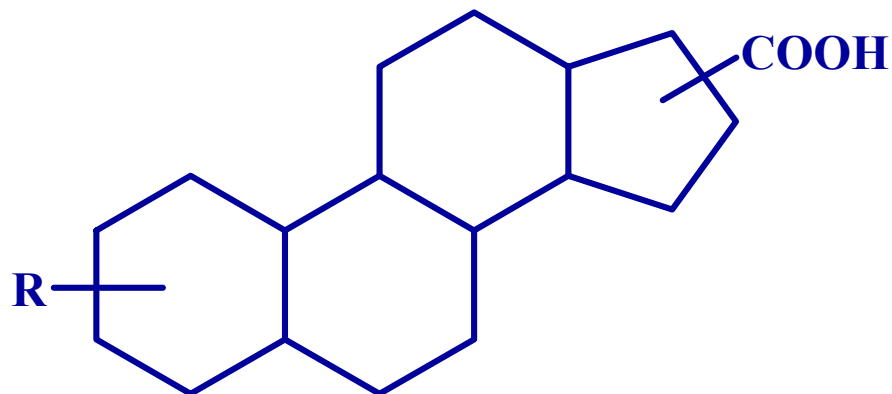
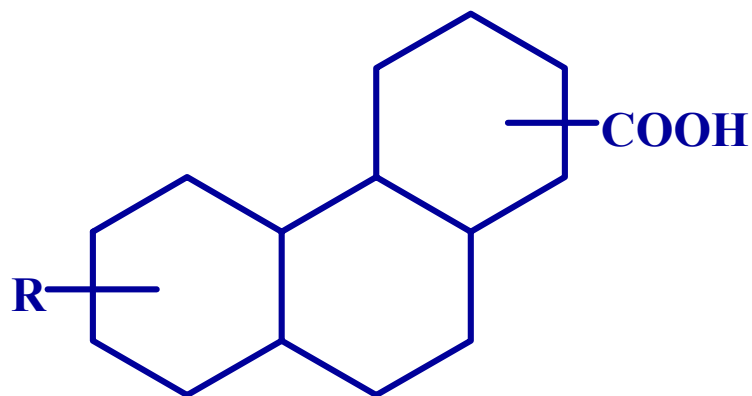
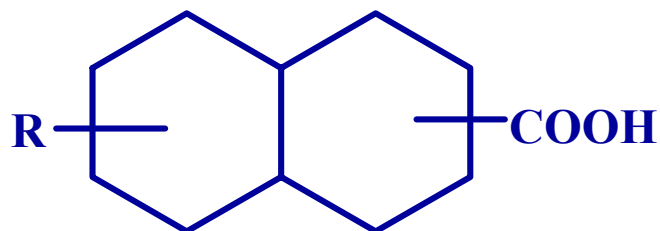
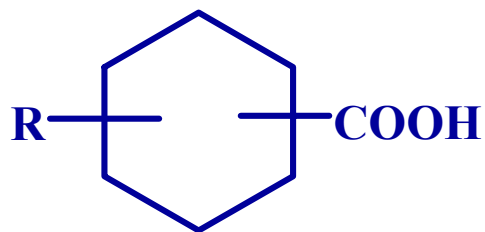
- HAC Definitions
- Problems with HAC
- Refinery Solutions
- Solution at Source – Removal of Acids from Crudes
- HAC Discount
- Questions from and for audience

- 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



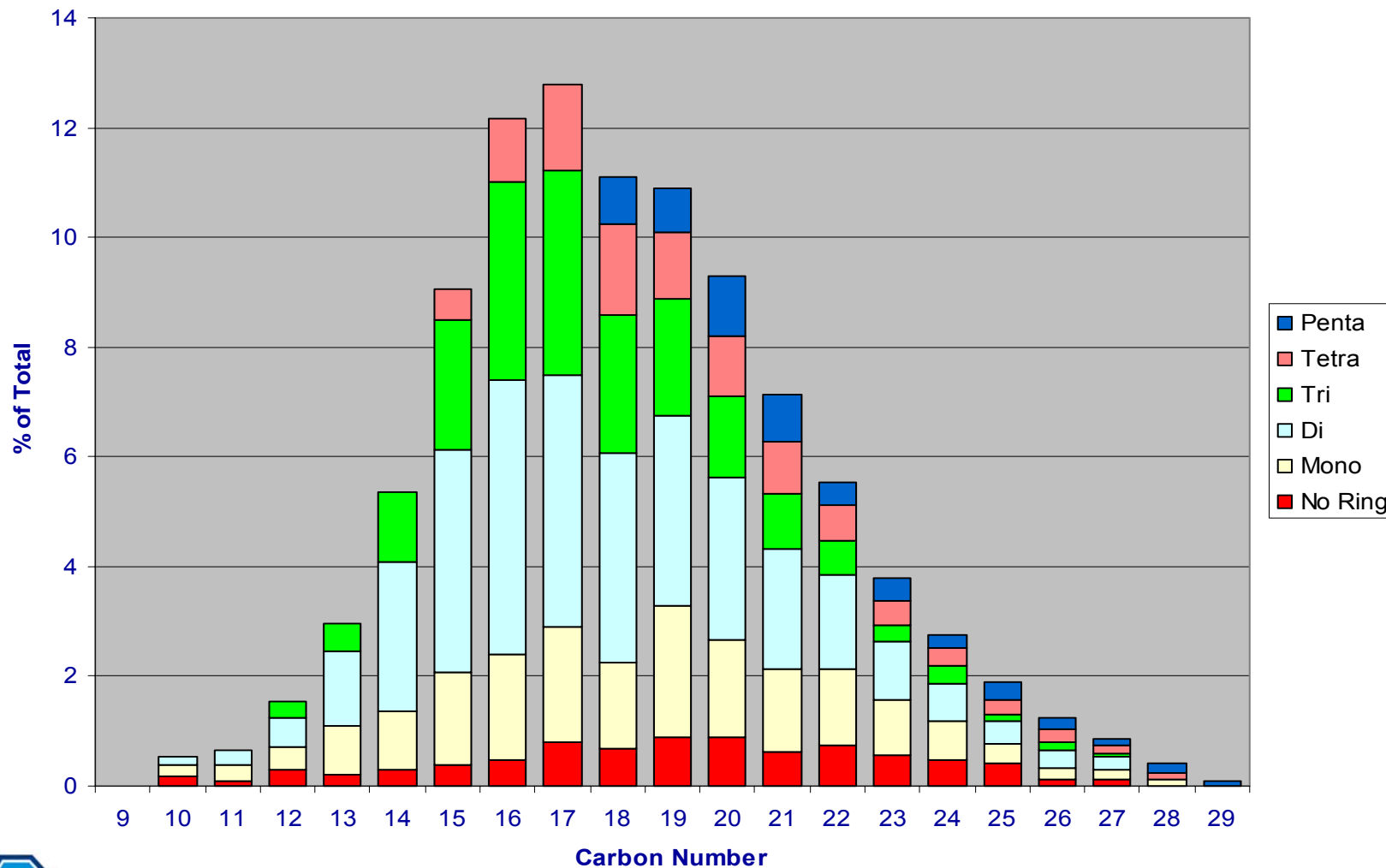
- TAN is the industry measurement standard but of limited use in predicting problems in refineries
- Hundreds of Different Naphthenic Acids with different boiling points

Typical Naphthenic Acid Structures



Mass Spectrometry Analyses

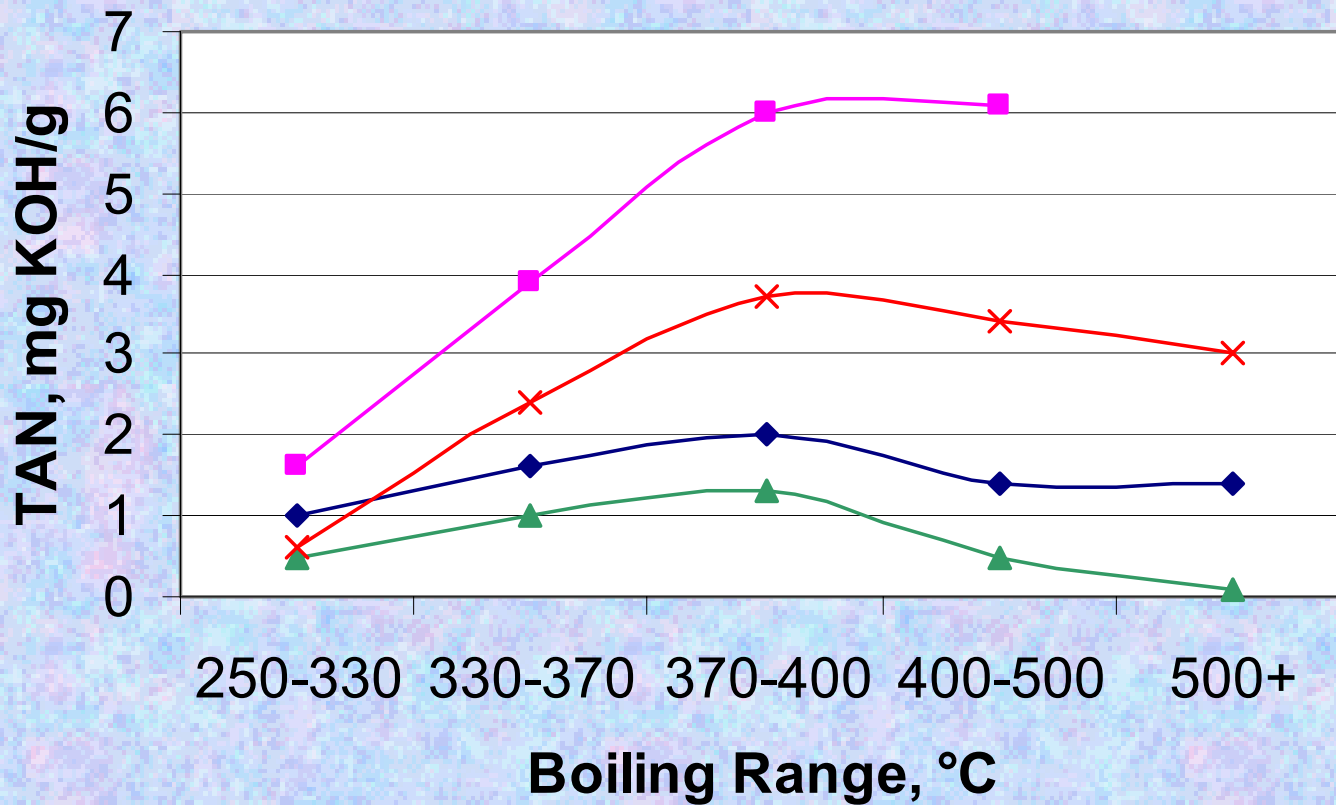
Sample CJ



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



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 (NapfiningSM).
- 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).