Diesel Desulfurization Technologies

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2001 DEER Workshop, August 9, 2001.

What Should You Expect From This Presentation?

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- How to Design Desulfurization Units?

What Should You Expect From This Presentation?

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- How to discuss Desulfurization Economics?

What Should You Expect From This Presentation?

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- Feel Sympathy for Refinery Engineers!

Diesel Desulfurization Background

- 15 ppm cap (80%) ULSD needed by mid-2006. Average around 7 ppm depending on pipeline/testing experience
- Uncertainty of how to comply with diesel regulations
  - Credit Program
  - New Technology
- Non-road diesel rule affects investment decision
  - EPA will not define until mid-2003

Diesel Desulfurization Background (continued)

- Wide range of sulfur species in diesel – some are easy and some are difficult to remove
- Quality of fractionation is important for separation precision
- Typically, the impact of reducing sulfur from 500 ppm to 15 ppm is a 3-4 times increase in catalyst volume

Diesel Desulfurization Background (continued)

- Revamp vs. grass roots
- Making the most of the existing HydroDeSulfurizatrion (HDS) unit is key
  - Revamps
    - Have made previous highway diesel investment
    - Costs less than 50% of new grass roots units
    - Will be first units to be converted
    - Are limited to current capacity

Diesel Desulfurization Options

- HDS-High Pressure Hydrogen Removes sulfur compounds from combined distillate streams
- FCC Feed Pretreater
  - HDS for Gas Oil
  - Requires additional HDS unit to finish diesel
  - Also removes sulfur from FCC gasoline
- Hydrocracker
  - Extreme HDS-1200 psi or higher
  - Expensive
  - Converts some diesel to gasoline
- Most non-California refiners will use HDS

Impact of diesel sulfur species

Sulfur Species	Relative reaction rate	Boilint Point, F
Thiophene	100	185
Benzothiophene	30	430
Dibenzothiophene	30	590
Methyl dibenzothiophene	5	600-620
Dimethyl dibenzothiophene	1	630-650
Trimethyl dibenzothiophene	1	660-680

Diesel HDS Chemistry
Dimethyl Dibenzothiophene (DMDBT)

- ULSD production involves DMDBT chemistry
- DMDBT's have low reactivity
- DMDBT's are present in aromatic feedstocks such as Light Cycle Oil and Coker Gas Oil
- Sterically hindered molecules make the sulfur atoms difficult to reach and remove
- Light Cycle Oil from Catalytic Cracking Units is the most difficult to treat
  - May be more economic to undercut LCO than to treat

Diesel HDS Chemistry
Dimethyl Dibenzothiophene (DMDBT)

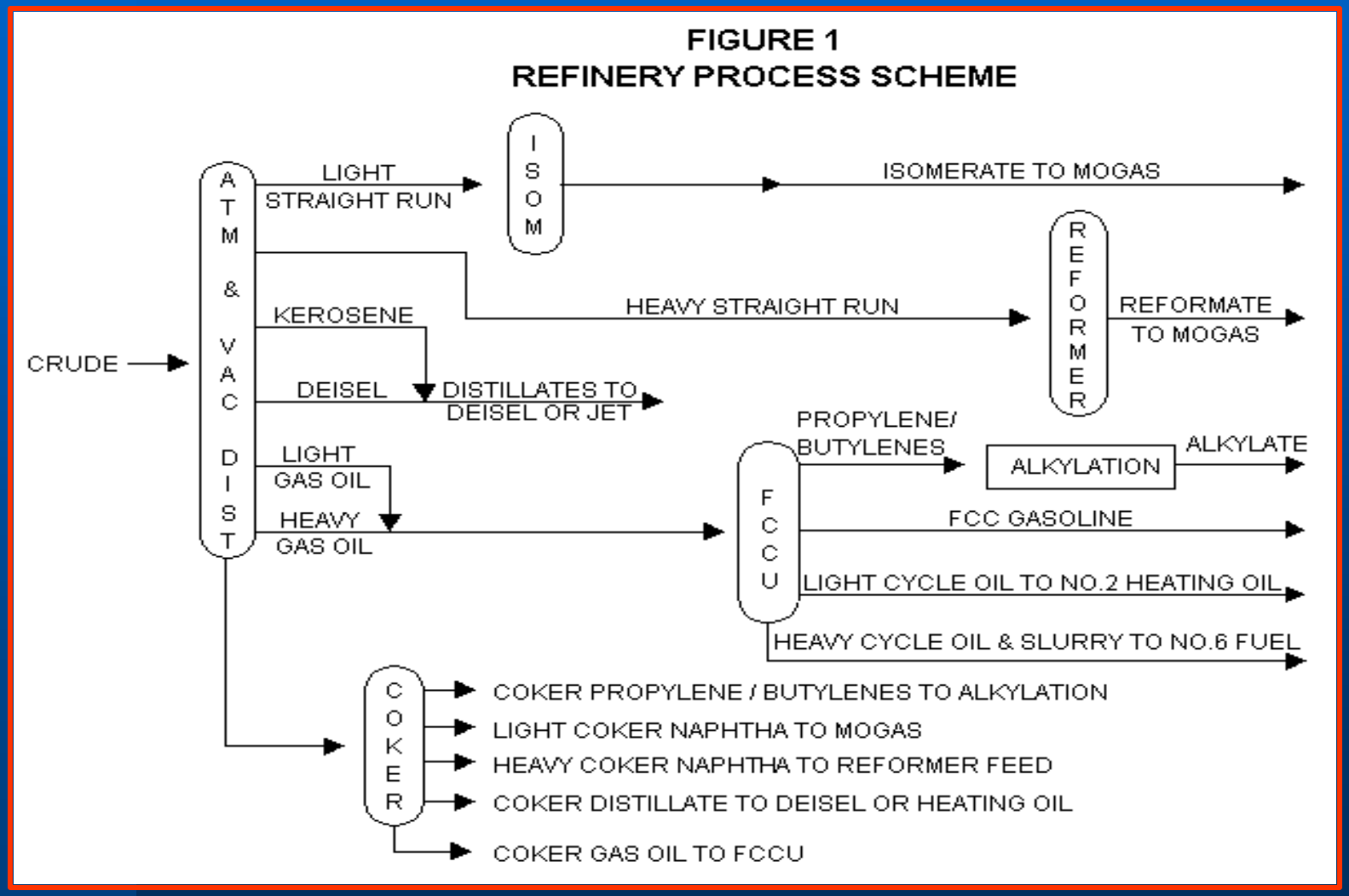
- Two reaction pathways for sulfur removal – direct extraction and hydrogenation
- Hydrogenation pathway is the key for ULSD production
- To complicate matters, a “floor” exists for sulfur removal, at which further increase in temperature has no effect on sulfur reduction
- If “floor” is too high, no option other than reducing end point or space velocity or increasing pressure

Options for improving HDS

For ULSD all the following must improve:

- Catalyst Factors
  - Activity and stability
  - Type (Co-Mo, Ni-Mo)
  - Loading
- Process Factors
  - LHSV
  - Hydrogen partial pressure
  - H2S scrubbing
  - G/O ratio
- Reactor Design
  - Contact optimization

Refinery Process Scheme



Diesel Desulfurization Technologies

- MAKFining
- Haldor Topsoe
- Criterion
- UOP
- IFP
- Emerging technologies

MAKFining Technology

- Uses STARS technology for catalyst improvement
- Very high intrinsic activity for HDN and HDS
- If cracked distillate streams are to be processed, two stage higher pressure reactors may be required
- <15 ppm diesel production still problematic for difficult feedstocks
- If LCO and LCGO are to be processed, End Point may have to be lowered to reduce DMDBT's

Haldor Topsoe Technology

- Uses either Co-Mo or Ni-Mo catalysts
- For ULSD, Ni-Mo is preferred
- Two stage HDS/HDA used for CARB diesel – low sulfur, aromatics and high cetane
- Moderate pressures – 1000 psig
- Commercial experience for producing ULSD

Criterion Catalysts & Technologies

- Uses CENTINEL Technology Catalysts
- HDS, SYNShift and SYNSAT technologies
- To lower sulfur to <15 ppm,
  - Hydrogenation of aromatic rings
  - C-S bond cleavage
  - addition of hydrogen for HDS
- To increase API gravity and cetane,
  - Hydrogenate aromatics rings
  - Open naphthenic rings
  - Isomerize selectively to branched chain
- Commercial experience for ULSD

UOP Technology

- MQD Unionfining technologies
- Heteroatom removal – HDS, HDN
- Aromatic saturation
- Hydrocracking
- Catalytic dewaxing or isomerization
- The processes are commercially proven

IFP Technology

- Prime – D process utilizes either Co-Mo or Ni-Mo catalysts
- Optimization of reactor internals – Equiflow
- A two stage process can be used for cracked distillate streams
- Commercial experience

Other Emerging Diesel Technologies

- Adsorption – Phillips S-Zorb
- Oxidation/extraction – Unipure ASR-2
- Ultrasonic Selective Oxidation – Sulphco
- Biodesulfurization – Enchira Biotechnology Corporation (EBC) BDS

Phillips S Zorb Technology

- Uses a proprietary adsorbent which removes the sulfur atom from the molecule
- Sulfur is retained on the adsorbent
- Originally developed for FCC gasoline and now applied to diesel
- Bench scale studies show diesel can be treated to below 5 ppm at 2 LHSV
- No net hydrogen consumption is reported

Unipure ASR – 2 Technology

- The sulfur species is oxidized to sulfones
- Near atmospheric pressures and mild temperatures
- Laboratory studies show residence time of 5 minutes for complete conversion to sulfones
- Separation of oil and aqueous phases may be problematic
- Pilot plant is being initiated
- Sulfones can be used as surfactants

Sulphco Ultrasound Selective Oxidation Technology

- Typically, DBT is oxidized to sulfoxide and then to sulfone
- Oxidation catalysts are relatively slow and low desulfurization rates
- Sulphco process uses ultrasound waves to produce bubbles known as cavitation
- The bubbles collapse causing vigorous micro-mixing and shock waves
- Bench scale studies show sulfur reduction to 10 ppm

Enchira Biotechnology BDS

- Process uses microbes to remove sulfur species
- Four distinct steps identified for sulfur removal
- Fourth step is slow leaving extractable polar intermediate
- Slow reaction means large volume
- Microbes live in water so large aqueous phase
- Several engineering concerns not addressed fully
- EBC is pursuing new areas

Summary

- Effective June 1, 2006, ULSD with 15 ppm max and about 7 to 8 ppm average will have to be made
- Reducing the sulfur content of diesel from 500 ppm to 15 ppm may be achieved by a combination of
  - Increasing catalyst activity using new generation catalyst
  - Installing state-of-the-art reactor internals
  - Increase in catalyst quantity by dense loading and adding a second reactor to decrease LHSV
  - Increasing hydrogen partial pressure and purity
  - Recycle gas scrubbing

Summary (continued)

- Several technologies are being offered by vendors
- No cookie cutter solutions. Wide variation in refinery configurations and feed stocks. Little margin for error.
- LCO processing does present a challenge. Undercutting and higher pressure processing are options
- Emerging technologies are not expected to play a major role in the 2006 time frame when ULSD is required

Acronyms

- ULSD = Ultra Low Sulfur Diesel
- HDS = Hydrodesulfurization
- DMDBT = DiMethylDiBenzoThiophene
- LCO = Life Cyle Oil
- CGO = Coker Gas Oil
- SHDMDBT = Sterically Hindered DiMethylDiBenzoThiophene
- LHSV = Liquid Hourly Space Velocity
- IFP = Institute Francais Du Petrole
- STARS = Super Type II Active Reaction Sites
- MAKFining = Mobil M.W. Kellogg Akzo Fina Technology
- UOP = Universal Oil Products
- HDN = Hydrodenitrogenation
- RVA = Relative Volume Activity
- EP = End Point
- LCGO = Light Coker Gas Oil
- HDA = HydrDeAromatization
- CARB = California Air Resources Board
- BDS = BioDesulfurization
- FCC = Fluid Catalytic Cracker
- MQD = Maximum Quality Diesel