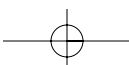Phoenix, Arizona

2006 NPRA Q&A and Technology Forum:
Answer Book

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NPRA

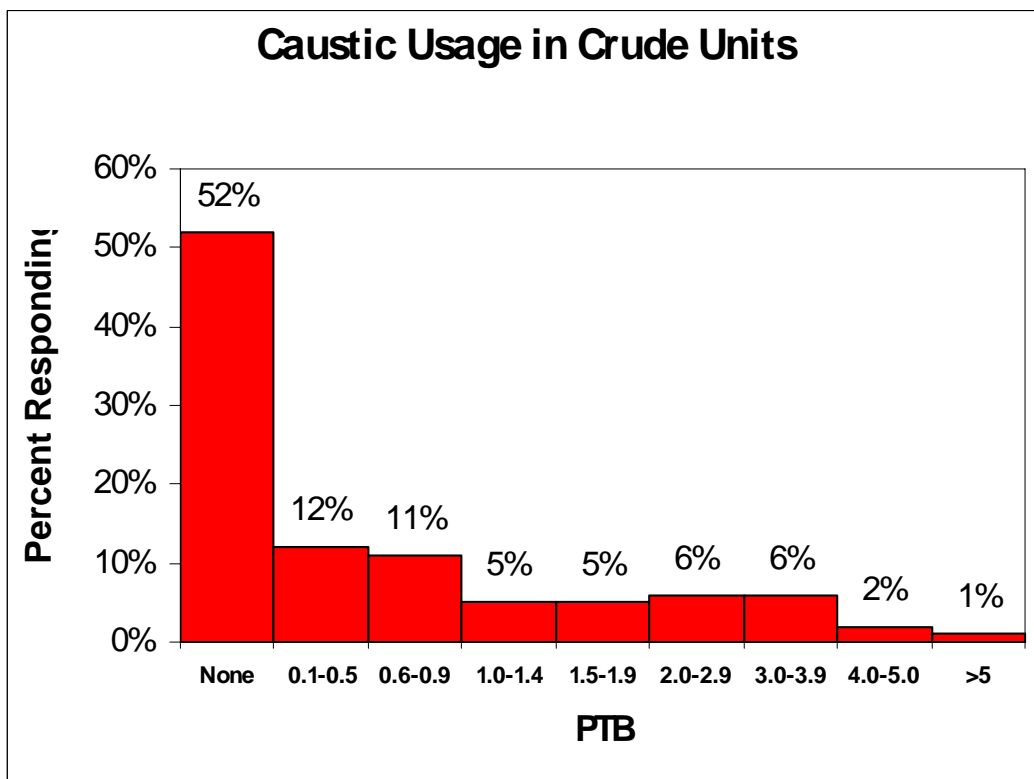**CRUDE/VACUUM DISTILLATION AND COKING**

Crude Preheat and Desalting

Question 1
Have you experienced fouling on the crude side of preheat exchangers in desalted crude service as a result of caustic injection for chloride control? Please discuss your experiences.

Harold Eggert (GE Water & Process Technologies)
A comprehensive desalter benchmarking survey of several hundred global refineries resulted in the summary of caustic addition practice shown in the plot below. Approximately half of the refiners did not add caustic ahead of the hot train or crude furnace for overhead chloride control.

Caustic Usage in Crude Units

Percent Responding (y-axis, 0% to 60%)

PTB	Percent
None	52%
0.1-0.5	12%
0.6-0.9	11%
1.0-1.4	5%
1.5-1.9	5%
2.0-2.9	6%
3.0-3.9	6%
4.0-5.0	2%
>5	1%

Question 3
What methods are used to remove solids from desalter effluent water? Can you provide design criteria for these applications?

Peter Norman (GE Water & Process Technologies)
Best practice is still API gravity separation, followed by flotation. Larger solid particles settle out in the API unit. Free oil and oiled solids float and go to oil recovery (e.g., slop oil system). The API separator is typically not chemically treated, but in some refineries it is found to improve separation. Others have found chemical treatment to reduce the quality of recovered oil.

Emulsified oil and smaller solid particles go through to second stage treatment, which is typically a flotation unit, such as a dissolved gas unit, using nitrogen. These units are treated with coagulants working as emulsion breakers and polymeric flocculants. Some installations have successfully used only one chemical, such as GE Water & Process Technologies Novus® flocculants.

Solids from API and float from DGF should be sent to the coker. If a coker not available, then they are typically dewatered, followed by incineration, or off-site disposal.

A good treatment system must have a strategy of both harvesting and disposing of solids from the waste stream. The emulsion layer from final slop tank should not be recycled to the unit or the front end of the waste treatment plant. This creates a vicious cycle. Never try to reprocess DAF/IAF/DGF skimmings, as unresolved emulsion and solids concentrated in these skimmings must be removed from the "slop to crude" circuit.

Best practices for removing/processing these streams are:

  i.   Centrifugation with the oil returned to the slop system, water sent to wastewater, and solids sent to disposal.
  ii.   Processed at the coker either with the coker feed or by introduction into the quench water during the early part of the quench cycle.
  iii. Processed in a cement kiln (their fuel value makes this attractive).
  iv.   Disposal wells.
  v.   Other thermal processes that can tolerate these materials

Typical Refinery Wastewater Treatment Plant
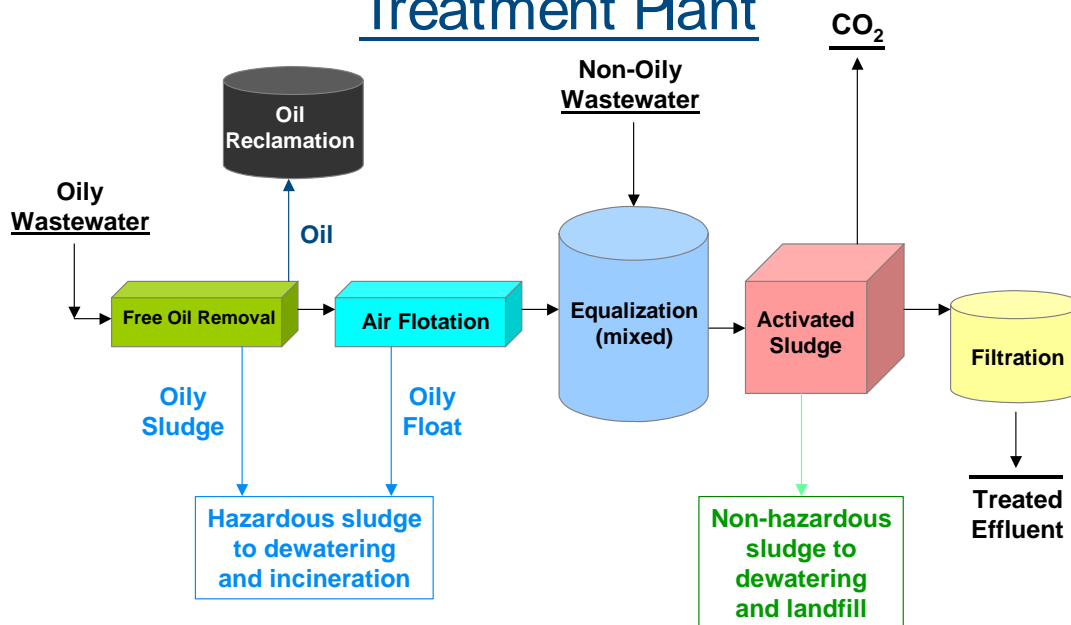
Opportunity Crudes

Question 7
What problems have you experienced processing crudes with high levels of amine-based H2S scavengers?

Alan Goliaszewski (GE Water & Process Technologies)
Amine-based H_2S scavengers are predominantly N-substituted hexahydro-triazines (known as "triazines"), along with dialkylamine/formaldehyde condensation products (non-triazine). The triazines are generally based on monoethanolamine (MEA) or methylamine, while the formaldehyde condensate has traditionally been based on dibutyl amine. These compounds react with H_2S to form generally benign S-containing ringed molecules along with free amine (see general reaction below). The ratio of product dithiazine to trithiane depends on reaction conditions.

Triazine   **Dithiazine**   **Trithiane**   **Amine**

3
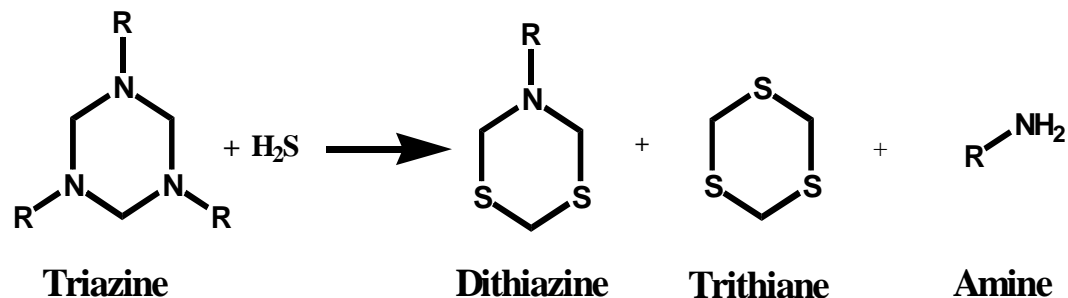
The free amine resulting from the scavenging process enters the desalter with the crude oil. Although a portion of the amine partitions to the wash water (i.e., 92-94% of MEA goes with water; only 40% of dibutylamine goes to the water), significant amounts of the amine enter the crude unit. In addition, unreacted triazine in the crude partitions between the water and oil (for MEA-triazine, ~40% to oil) and any triazine in the oil will thermally decompose quantitatively to liberate amine.

The main problem with volatile amines relates to the formation of hydrochloride salts that, with the right salt point, can deposit in crude unit towers and draws, resulting in pluggage and especially underdeposit corrosion. The corrosion can be very aggressive (>1000 mpy) and the molten amine hydrochloride salts have demonstrated the ability to etch through the bottom of a draw line. The salt deposition is dependent on column temperatures and species concentrations. The MEA hydrochloride salt is particularly problematic. Such salt properties, of course, led to the use of LoSalt® amines as crude overhead neutralizers. One must also note that not all the problematic amines can find their source in the H_2S scavengers (i.e., recycle from amine units). Significant levels of free amines can also negatively impact water separation in the desalter.

Strategies to improve this situation can involve amine extraction aids, typically fed to the wash water. GE Water & Process Technologies provides a unique Embreak® product that has demonstrated significant improvements in the extraction of "tramp amines" in the desalter. Up to a 70% increase in removal rates of polar amines is obtained. Use of this product causes no increase in overhead neutralizer demand, and improves overall desalter operation.

Hydrogen sulfide scavengers that do not generate free amine in the process have been developed by GE Water & Process Technologies. ProSweet® S1749 has been introduced with scavenging kinetics comparable to triazines, but with no release of amines in the scavenging reaction.

Question 8
What is your experience with processing high calcium content crudes (such as Doba)?   What problems do high calcium levels cause and what levels of calcium can be tolerated without operating problems? What mitigation strategies have been attempted (both successful and unsuccessful)?

Alan Goliaszewski (GE Water & Process Technologies)
Most Doba crude being sold globally contains almost 400 ppm calcium. This is extremely high. The calcium is believed to be associated (chelated) with the high levels of naphthenic acids in the Doba, and only approximately 15% of the calcium can be extracted under standard desalter conditions. Other new crude fields are reported to have similar properties.

Problems associated with the calcium naphthenates include:
- Quality issues with residual fuel oil (off spec for metals)
- Increased metal loading to coke (result in lower grade)
- Catalyst poisoning on FCC feeds
- Crude preheat and tower fouling
- Activation of coker furnace fouling
- Negatively impact desalting operations (especially oil undercarry)

4

In order to reduce the impact of the calcium, most refiners processing Doba blend this crude so that it constitutes only 10-30% of the crude feedstock.

If the calcium cannot be tolerated, successful extraction mitigation strategies have been successfully implemented globally by GE Water & Process Technologies. The GE process involves feeding a selective acidic extractant to the wash water or crude that exchanges the calcium ion to a water-soluble species.

RCOOH + CaNAP   **RCOOCa + NAP Acid**
         Oil soluble Ca   Water soluble Ca

Up to 80% of the calcium has been extracted by use of Embreak® MR2500 as a desalter aid. Furthermore, this treatment results in only positive impact on desalter performance, and no increase in crude overhead neutralizer demand. GE will include a scale control agent for the effluent brine circuit if very high levels of calcium are extracted. Doba crude processing has proven profitable for the numerous refiners in North America, Asia and Europe that have employed the GE calcium removal strategy.

Scott Bieber (Baker Petrolite Corporation)
Crude oils containing high levels of calcium, in the form of calcium naphthenates, can create stable emulsions in desalters, which can cause water carryover and oil carry under problems. If the calcium is not removed, higher levels of calcium in reduced crude streams can cause FCCU catalyst deactivation, and can also result in the production of lower quality heavy fuel oils and coke.

Baker Petrolite's EXCALIBUR™ Metals Removal Technology has been used successfully since 2004 to help refiners in Europe, Asia and North America remove calcium from crude blends high in calcium naphthenate content. The process involves injection of EXCALIBUR™ complexing agent into the crude unit desalter wash water to increase the solubility of metals in the aqueous phase. Dissolved metals are removed from the desalter with the effluent water drained from the bottom of the vessel. The complexing agent formulation contains corrosion inhibitors that allow its safe use in crude unit desalting equipment. Specially formulated Baker Petrolite emulsion breaking chemicals are also used to break naphthenate-stabilized emulsions and to maximize crude oil dehydration, thereby minimizing carry over of dissolved metals into the desalted crude oil stream. A Baker Petrolite calcium scale inhibitor can also be applied to prevent deposition of calcium carbonates and sulfates in the desalter effluent water removal system. A key success factor is to ensure use of desalting Best Practices, including using proper wash water rates, correct water and chemical injection locations, optimal mixing energy and the effective management of any slop oil reprocessing in the crude unit.

Use of this technology has allowed refiners to increase the proportion of high calcium naphthenate crude oils in their crude blends, with minimal impact on desalter and WWTP performance. Use of EXCALIBUR technology minimizes desalter grid amperage draw, minimizes water carryover, and provides excellent control of effluent water quality. Calcium removal efficiencies of 95% have been achieved in commercial applications of this technology.

This level of calcium removal has allowed refiners to maintain target charge rates of atmospheric bottoms to FCCUs, and to continue the manufacture of low calcium content heavy fuel oils and anode grade coke while processing high calcium crude blends.

Laboratory pre-screening tests and thorough unit surveys can be performed to develop an effective metals removal program for specific crude oil blends and desalter operating environments.

Several references regarding successful strategies for calcium removal from crude oils are given below.

1. Weers, J., "*New Process Removes Crude Oil Contaminants*," Paper AM-06-31, NPRA Annual Meeting, March 19 – 21, 2006, Salt Lake City, Utah.

2. Bieber, S., Fahey, B., Jiang, R.B., Tian, H.B., Liu, T.H., "*Successful Strategies for Processing High Calcium, High TAN Crude Oils*," 9th Annual Asian Refining Technology Conference, March 7-9, (2006).

3. Weers, J., Bieber, S., "*Calcium Removal from High TAN Crudes*," Petroleum Technology Quarterly, Q3 2005.

4. Weers, J., Nguyen, J, "*A New Metals Removal Process for Doba Crude Oil*," ERTC 9th Annual Meeting, Prague, Czech Republic, February 15, 2004.

5. Kremer, L., Nguyen, J., Weers, J., *"Removal of Calcium and other Metal Species from Crude Oil in the Desalting Process",* Presented at the AIChE Spring National Meeting 2004, New Orleans Louisiana.

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Coker Operations

Question 17
Have you closed a water balance around the coker furnace, drum and fractionator? What fraction of the water comes from steam purges? What has been done to reduce steam purges? What are typical values for sour water production per barrel of coker feed? To what coking cycle time does this correspond?

Richard Conticello (Foster Wheeler USA Corporation)
Yes, a water balance can be performed around the coker unit. It is recommended by FW that a water balance be performed on the coker unit after the unit is started up and then periodically to ensure there is sufficient steam purging of the coke structure valves and not excess purging. The design theoretical sour water balance around the coker unit provided by the coker licensor should be used as the starting point.

Sour water production is based on several factors including unit capacity; number of coke drums; size of coke drums; and coke drum quench time. Sour water flowrate from the fractionator overhead drum is somewhat predictable due to the steam injection flowrates known at the coker heater and side strippers. The unknown is the amount of purge steam used by the steam purge valves on the coker structure. Bypass lines around restriction orifices to steam purges in the coker structure have been found to be open on occasion and have contributed to higher than expected sour water production from the units. In order to more closely control the purge steam flowrates and get a better handle on the steam purge valve flowrates, a rotameter flow device could be used instead of the restriction orifices.

Sour water flowrate from the blowdown section is mainly based on the coke drum quench period. Shorter than design quench periods will result in an increase of sour water instantaneous flowrate to handle. However, the overall amount of sour water produced should be constant with the licensor design flowrate. Total sour water production from the coker unit can be monitored if there is a sour water surge tank upstream of the sour water stripper unit.

For an 18 hour coking cycle with 8 coke drums, the sour water production was found to be approximately 10% of the unit charge flowrate. The amount of sour water production is strongly influenced by the size of the unit and coke make. Therefore, the sour water production can vary plus or minus from 10% of the unit charge flowrate.

Question 21
In your experience, are coke drum hot spots (blowouts) related to feed properties and/or coke drum operating conditions? What indicators do you use to predict hot spots? What steps do you take to reduce the impacts of hot spots?

John Elliott (Foster Wheeler USA Corporation)
In contrast to shot coke, which is prone to hot spot formation, certain feedstocks or combination of feedstocks will make dense shot coke or bonded shot coke which has low pore diameter/volume and can result in increased incidents of hot spot formation. Operating conditions and procedures can also have a large impact on hot spot formation.
Predicting a hot spot is difficult. Methods used include checking total amount of quench water used against recommended quantity, unusual drum "banana" lean and high drum skin temperatures, if available.

There are a number of ways to mitigate hot spot incidents and their frequency of occurrence. Among these are:

1. Check predictive methods. If needed take remedial action.
2. Provide design details to limit the impact. For example cutting operators should be remote and protected in shelters and non-essential, non-protected personnel should be kept clear of drums being unheaded and cut; special designs for top head drill collars are being used and some refiners have increased pit wall heights. Sometimes drilling operators can anticipate a hot spot during drilling from the size of steam releases or drum rumbling. When this is the case, procedures for limiting water into the drum can be applied.

3. Operations: Hot spots occur when coke in one part of the drum doesn't get completely quenched. Quenching is a rate limited procedure. Improved procedures include:
   a. Keep a forward flow into the drum during switch; use enough steam.
   b. Provide longer quench time by rearranging the drum schedule
   c. Provide a large head of quench water above the coke bed and confirm it is above the bed.
   d. Provide a soak period after the drum is filled with quench water.
   e. Use a flow controlled quench schedule with the drum being quenched under pressure.
   f. Raise heater outlet temperatures to increase coke porosity.
   g. Consider an overflow quench system for very short cycles.

Question 22
Have you observed post-switch coke drum foaming while initially steaming the coke drums to blowdown? What can cause this to occur, and how do you minimize foaming?

John Elliott (Foster Wheeler USA Corporation)
Commonly, foaming during this operation is caused by depressuring the coke drum too quickly. High steam rates would also be hurtful and are not recommended. FW normally suggest that antifoam be left on through the depressuring step.

Question 24
What is the most effective way to inject coke drum overhead quench? Should the injection be in the horizontal or vertical run of the vapor line? Are spray nozzles effective? What is your typical frequency for cleaning vapor lines? Where is most of the plugging occurring in your system?

Jack Buckley (Foster Wheeler USA Corporation)
Foster Wheeler Delayed Cokers employ spray nozzles pointed in the direction of flow on a horizontal section of pipe. Foster Wheeler has found this an effective method of keeping the line clean. Some of our clients have experienced buildup of coke in the overhead vapor line. The two most common places for the buildup are at the Coke Drum outlet nozzle and at the Fractionator inlet. Our clients have been able to run 4 or more years between line cleaning when appropriate amounts of quench are used.

The coke drum outlet nozzle can be cleaned when the drum is finished being cut and should be checked monthly. If no coke is found, then the interval can be increased. One of our clients goes three months between cleaning this section of the line. The plugging at the Fractionator is thought to be because the line may become dry when insufficient quench is injected.

Coker Equipment

Question 25
What are your maximum allowed coker heater tube metal temperatures and how do you measure tube temperatures?   How does metallurgy (5 or 9% chrome, stainless steel or high nickel alloy) affect this limit?   Have you used ceramic-coated radiant tubes, and if so, has this extended heater run length?

Patrick Bernhagen (Foster Wheeler USA Corporation)
Foster Wheeler uses 9Cr -1Mo tubes and in many cases has the maximum TMT of 1300°F.

On revamped heaters SS tubes have a higher maximum TMT. The companies we have seen use this metallurgy have not changed their decoke temperatures significantly from our 9Cr 1Mo figures. This is because if you thin your tubes for the higher allowable stress you have done nothing. Leave the wall the same and you get between 100 and 150 degrees higher allowable TMT. That translates to another month or two of run length.

Foster Wheeler has not used the ceramic coating on coker heaters. Our opinion is the coating can be used to prevent external oxidation but we are not convinced of any other benefits for coker heater operation.

Question 26
Do you have a split feed/dual entry into your coke drums? Have there been problems with feed line plugging and keeping both flow paths open?

Richard Conticello (Foster Wheeler USA Corporation)
Foster Wheeler's current practice is to design with a single entry coke drum inlet. Having said that, Foster Wheeler has designs that have used multiple entry points and have one recent design that will use a dual entry inlet. Both applications were requested by our clients. Both applications incorporate additional valving and purging to avoid blockages. We do not have evidence of good or bad distribution with these applications even though the intention is to obtain a more uniform distribution in hope of avoiding potential hot spots in the coke drum.

Question 27
What has been your experience with coke drum switch valves (feed and vapor)? What are the pros and cons of ball valves vs. Wilson-Snyder switch valves?

Richard Conticello (Foster Wheeler USA Corporation)
The current industry standard is to use a motorized 4 way ball valve for the switch valve. The motorized 4 way ball valve has replaced the manually operated Wilson-Snyder switch valve, which is a tapered wedge plug valve. The Wilson-Snyder switch valve requires unseating of the valve before it rotates. In the past, the Wilson-Snyder switch valve was manually operated. Users have reported that they experienced at times reductions in plug movement, which in time, resulted in valve seizure causing a unit shutdown to repair. Additionally, reseating of the wedge plug back into its original position without experiencing leaking has also been a reported problem.

The 4 way ball valve has its advantages over the Wilson-Snyder valve. The speed of switching the valve is quicker with the ball valve, seconds versus minutes, and there is a reduction of manpower required to operate the ball valve over the plug valve (1 operator versus 2 operators). The 4 way ball valve switch valve has had issues in operation. Steam purges must be properly maintained at the vendor's recommended purge flowrates or the valve may stick. Too much steam consumption can also lead to cooling of the heater effluent which in turn can lead to increased volatile content matter in the coke. Another issue is too quick of switch could lead to a foamover if there is a loss in pressure if the operators are not closely watching this operation sequence. A controlled "slow" switch is recommended.

GASOLINE PROCESSES

Alkylation

Question 31
What is the current status of solid bed alkylation technology? For those working on this
technology, how does it compare in yield, octane, capital and operating costs with current
alkylation processes?

John Gieseman (ABB Lummus Global)
ABB Lummus Global, Albemarle Catalysts, and Neste Oil have successfully operated a
demonstration unit for nearly three years.   The yield, octane and other key parameters are all at
or better than the conventional liquid technologies. The ISBL capital to build these units is on
par with HF units and significantly lower than Sulfuric units.   Recent improvements to the
catalyst have reduced operating costs to levels lower than the liquid technologies.   Because of
the inherent advantages of the solid catalyst, reliability is expected to be better than the existing
acid technologies as well.

Question 33
API Recommended Practice 751 calls for all joints in HF acid service to be inspected at least
once every ten years. How do you comply with this recommended practice? Have you used non-
destructive testing techniques to avoid breaking and re-making flanges?

Kurt A. Detrick and Robert Dolejs (UOP LLC)
To start, "A ll joints" could refer to flanged, threaded, and welded joints, but the question is
specific to flanged joints.

Flanged joint inspections are covered in paragraph 3.4.3.4 in Section 3.4 Inspection of
Commissioned HF Unit Equipment in API-751.   It states that "the inspection frequency of
flanged joints should consider the respective corrosion rate in conjunction with the calculated
sealing surface requirements. In the absence of inspection data, *all flanges* in *Main Acid service*
should be inspected *every ten years*, and all flanges in *Trace Acid service every fifteen years*.
For flanges in the same process circuit, the findings from one flange inspection may be applied
to other flanges of equal size and age."

With that said, compliance is maintained through a proactive flange inspection program that
completes scheduled inspection on time. This program identifies all piping circuits and pressure
vessels in main and trace acid service. Each flange is given an identifier in the program. The
inspection planning process creates a schedule for mandated inspections and identifies
preparation and access requirements. This information is used in turnaround scope development
and maintenance planning. Cost of the program can then be tracked. Program compliance is
demonstrated by tracking and documenting inspections.   Updating inspection plans is also
critical to the success of the program to maintain compliance with API-751 and adjusting
frequency as needed.

With the frequency of inspection established the task of scheduling needs to be addressed. For example, if turnarounds are typically scheduled every 3 years, then one-third (1/3) of the Main Acid service flanges would be inspected every turnaround along with one-fifth (1/5) of the Trace Acid service flanges.

As far as using nondestructive testing to avoid breaking flanges we have heard that there is an ultrasonic based technology commercially available to detect flange corrosion while a unit is on-stream, but we have no actual experience with this technology. At this time, visual inspection of the opened flange is the only technique we have experience with for inspection of the seating surfaces of the flanged joint.

Although not addressed in the question, but something we feel that needs to be discussed here is the inspection of small bore non-butt welded piping. This is specifically covered in paragraph 3.4.3.2 in API-751.   It states that "threaded joint fatigue as well as corrosion product accumulation in inactive branch connections require more frequent assessment. Inspection programs should also include NDT provisions to examine and ensure the integrity of these small bore non-butt welded piping circuits. A representative sampling of these joints should be radiographically examined every 5 years. Owner-operator data should be used to increase or decrease the inspection interval within the limits of the applicable standards. Profile radiographs can be used to determine the condition of threaded joints including thread engagement and seal weld coverage of exposed threads in seal-welded joints. Disassembly of non-seal welded joints is an alternative to radiography."

Ethanol

Question 37
Discuss how ethanol blending requirements have impacted refining operations including: 1) blend formulations; 2) octane balance; 3) driveability specifications; 4) lab testing and procedures; and 5) reformer severities.

William H. Keesom (UOP LLC)
For those directly involved in ethanol blending, the following is well known, but as a general overview of approaches being taken, the following information is offered:

The question of ethanol blending should be considered for two different situations: as a replacement for MTBE in RFG; as a new blendstock in conventional gasoline. When ethanol replaces MTBE in RFG there is less impact on gasoline and refinery operations than when ethanol is a new blendstock in conventional gasoline.

The Energy Act of 2005 requires an increase in biofuel use. The act requires a gradual increase in biofuel use from 4 billion gallons in 2006 to over 7 billion gallons in 2012. These numbers translate to around 260 MBPD of biofuel in 2006 and 470 MBPD of biofuel in 2012. Most of this biofuel will be ethanol.

MTBE is being phased out of US gasoline because of bans on using MTBE and product liability concerns from blending MTBE in gasoline. Most MTBE is used in RFG, which comprises

around 30-35% of the gasoline consumed in the US. The amount of ethanol needed to replace MTBE in RFG is around 300 MBPD. With the removal of the oxygen requirement in RFG as a result of the Energy Act, ethanol is not required for RFG. However, ethanol is a logical replacement for MTBE. It has similar properties to MTBE and using ethanol in RFG avoids major change in RFG blending when MTBE is removed. While the major outlet for ethanol is currently RFG, the provisions of the Energy Act call for increased biofuel (ethanol) use which will require blending more ethanol into conventional gasoline. Market size and logistical costs will likely determine which conventional gasoline areas will blend the additional ethanol needed to meet the requirements of the Energy Act.

Ethanol containing gasoline cannot be shipped in conventional gasoline distribution systems because these systems often contain water and cause separation of ethanol from gasoline. As a result, ethanol is generally blended into gasoline at the final terminal before transport to the service stations and is not blended into gasoline at the refinery. Terminal blending of ethanol requires investment in ethanol unloading, storage, and blending facilities.

The impact of ethanol blending should be considered in two situations:

Ethanol as a replacement for MTBE in RFG:
- Blend formulation: There will be a small impact on volume – MTBE typically is used at around 11 vol% and ethanol at 10 vol%. Because ethanol adds around 1 – 1.3 psi to a gasoline blend it may be necessary to remove some light components to meet RFG VOC limits. There is no RVP waiver for ethanol in RFG.
- Octane: Ethanol has slightly higher octane than MTBE but the impact on gasoline octane from replacing MTBE with ethanol is small.
- Reformer severity: Because ethanol and MTBE have similar octanes, expect a small impact on reformer severity when ethanol replaces MTBE in RFG. Driveability: ethanol is reported to somewhat worsen the driveability of gasoline. A new driveability formula under consideration by ASTM includes a calculation of the impact of ethanol on driveability.

Ethanol as a new blendstock in conventional gasoline:
- Blend formulation: Ethanol will likely be blended at 10 vol%. If it is a new blendstock in conventional gasoline, this level of ethanol use will have significant impact on gasoline blending. Gasoline volume will increase. As a result of its higher octane and different distillation profile there will be some change in gasoline blend recipes when ethanol is used. Because conventional gasoline is allowed a 1 psi waiver when blending ethanol, there will be little or no need to blend around the RVP added by ethanol.
- Octane: Ethanol will add around 2 to 3 more octane numbers which will allow refiners to blend lower octane streams.
- Reformer severity: Refiners will be able to reduce reformer severity by a few numbers when ethanol is a new blendstock in gasoline. Expect reformate yield to increase but hydrogen yield to decrease.
- With the RVP waiver and less stringent RVP specs, this may be the more attractive place to blend ethanol.

HYDROPROCESSING

Hydrogen

Question 55
Regarding hydrogen recovery, please describe: 1) best practices for increasing hydrogen recovery; 2) current state-of-the-art in hydrogen recovery; and 3) your benchmark for percent hydrogen lost to fuel gas or mass balance closure.

Paul Zimmerman (UOP)
Best practices for increasing hydrogen recovery may include the following steps:

a. Identify and quantify all the sources of hydrogen currently going to fuel gas. Hydrogen accounting is not a trivial exercise.

b. Often, off gas streams are mixed together before scrubbing. Consider recovering high purity or higher pressure streams before they are diluted with other streams. This may make recovery more economic.

c. Make sure that new or revamped hydroprocessing units are designed where practical for low or medium pressure separators at high enough pressure to recover flash gases without compression.

d. Consider sending moderate purity streams as hydrogen plant feed and evaluate reduction in hydrogen plant operating cost with additional compression costs

To increase Hydrogen production, a refiner can take advantage of state-of art advancements in the PSA area. UOP continues to make advancements in adsorbents allowing increased recovery and higher throughputs to maximize hydrogen production. These advancements include adsorbents better able to withstand higher flows, and with higher impurity removal capacity. Also, UOP continues to work with our hardware suppliers to improve valve internal components and accessories that enable the PSA to cycle more quickly and maintain reliability of the hardware. In many cases an existing PSA can be revamped utilizing these advancements, to increase the hydrogen recovery or capacity.

Hydrogen recovery from a PSA will depend on the size of the unit and feed and tail gas pressures. A large PSA may typically have 85 to 90% hydrogen recovery. A small PSA may have a hydrogen recovery of 70 to 75%.

There have also been advancements for membrane fiber materials. These new fibers allow improved separation of impurities, greater hydrogen recovery or purity, and lower membrane surface area.

Hydrogen recovery from a membrane system is greatly dependent on the product hydrogen purity and the pressure difference between the feed and permeate. For example, a membrane operating with a product purity of 94% hydrogen may have a hydrogen recovery of about 90%. Hydrogen recovery will decrease sharply with higher hydrogen purity. If higher hydrogen purity is necessary, then recovery can be improved with a two-stage membrane system.

James Turner (Fluor)
The economics of hydrogen recovery can vary significantly from one refinery to the next, based on the following factors:

- Refinery hydrogen balance
- Presence of import hydrogen sources (such as a nearby pipeline)
- Number and operating conditions of the hydroprocessing units
- Make-up hydrogen compression scheme
- Refinery fuel gas balance.

Historically, many refineries produced all the hydrogen they needed as a product in naphtha catalytic reformer units, so there was little value for recovering hydrogen.

With the recently enacted Clean Fuels specifications, and the trend to process more heavy sour crudes, most U.S. refineries today cannot meet all their hydrogen needs with naphtha reformer units. The additional demand is met with hydrogen produced in steam methane reformers, either in their own hydrogen plants or imported from a third party supplier. In this case, there is normally good value in recovering hydrogen.

Hydrogen can be recovered off of hydroprocessing units in two streams: 1) high pressure reactor loop purges, or 2) low pressure off gas streams.

In many cases, hydrogen in high pressure purges can be used directly as make-up in lower pressure hydrotreaters. In other cases, the high pressure of these streams can be used as a driving force to recover hydrogen in a membrane skid at a lower pressure, either as make-up hydrogen to low pressure hydrotreaters, or as feed to make-up hydrogen compressors. Using a membrane scheme can be an effective, low cost way to recover hydrogen, particularly if the required make-up compression already exists. The decision on installation of a membrane scheme is normally made based on economics. The reduction in hydrogen production or improved catalytic performance in hydrotreaters (due to higher unit hydrogen partial pressures) should have an economic payout compared to the cost of the membrane skid and recovered hydrogen compression. The benefits of higher unit hydrogen partial pressure may be particularly significant for modest pressure ULSD units.

Hydrogen losses in the membrane tail gas are typically 5-15% of the feed stream hydrogen. The tail gas can be recovered at high pressure, so this stream may be a candidate for feed to an LPG recovery plant if it is rich in propane and butanes.

In high pressure hydrotreaters, medium pressure separator gas may be a good make-up hydrogen source. Recovered hydrogen from this source can often exceed 80% hydrogen purity. In some cases, it can be supplied direct to low pressure hydrotreaters. In other cases, purification by amine scrubbing or amine scrubbing followed by a PSA is justified. PSA Units typically recover hydrogen at 99.9% purity, with tail gas losses of 10-20%, depending on feed composition and tail gas pressure. The separator pressure should be specified so that the recovered hydrogen can get into the make-up system without separate compressors.

Cold boxes can also be used for hydrogen recovery, and has been proven to be economical in some cases, particularly if the refinery is integrated with a chemical plant.

Hydrogen may also exist in relatively low purity (less than 40% hydrogen purity) in stripper off-gas and FCC off-gas streams. While these streams can be purified with amine scrubbing followed by a PSA unit, or by compression followed by a membrane, historically it has rarely proven economical to recover hydrogen from these streams.

In refineries that have a tight hydrogen availability, or a high cost for hydrogen, the goal is often to recover 100% of the hydrogen from high pressure purges and high purity low pressure separator vapors for re-use. If these streams are purified in a membrane or PSA scheme, then recover of 90 – 95% of this hydrogen is possible.

James Fleshman (Foster Wheeler USA Corporation)
The main methods to purify or recover hydrogen are membranes and PSA units. Membranes are useful for pretreatment or bulk separation, while PSA units will provide the high purity needed for many hydrotreating or hydrocracking processes.

Current hydrogen recoveries are in the range of 88%-90% in a PSA system with up to five equalizations in the larger units. Feed pressures are in the 350-400 psi range with a tail gas pressure of 5 psig.

Once a PSA unit is built the main route to improving efficiency is changing of the adsorbent. Another option is to reduce the tail gas pressure by piping or burner changes, or by adding a tail gas compressor. Pre-treatment such as feed chilling to remove heavy hydrocarbons or adding low temperature shift in a steam reforming plant can be economic in some cases.

In the design phase, multiple stages in a membrane system or more equalization steps in a PSA unit will increase recovery.

Question 56
What is your hierarchy for managing hydrogen sources for different hydroprocessing units?
What adjustments do you make when the hydrogen demand is greater than hydrogen supply?

Paul Zimmerman (UOP)
Managing hydrogen sources requires an understanding of the minimum hydrogen partial pressure for each unit. In general, higher pressure process units benefit most from higher purity makeup. We can also consider the purge gas that can allow operation at the same hydrogen partial pressure with lower purity makeup. This is practical only if the purge gas is cascaded to another unit or recovered in a purification unit. Optimization of the whole network, pushing units to hydraulic, compression, and minimum hydrogen partial pressure constraints will produce the optimum configuration.

Ultimately, allocation of hydrogen should be based on refinery economics. If one or more hydrogen consuming units constrains refinery throughput, this should be factored into the unit economics. For example, one refinery used the short term planning LP to periodically update the

upgrade value in each unit per amount of hydrogen consumed. It was then obvious to everyone what units needed to shed rate to stay within the hydrogen supply constraint.

Bill Cotton (Johnson Matthey Catalysts)
The first stage in managing any refinery hydrogen balance is to determine the available supply capacity and purity levels against the size of demand and purity level requirements. Such study will provide a base line for the management of hydrogen around the refinery, and in some cases will enable changes to be made such that hydrogen is utilized more efficiently. There are a number of companies that offer this type of study, commonly known as a "hydrogen pinch study" around the world.

Once such a study has defined that there is a present or even a potential future hydrogen shortfall, additional hydrogen capacity will be required. Modifications within the refinery can be performed, but these can be costly and may require significant down time. One other option is to revamp any hydrogen plants associated with the refinery to increase production and or be converted to utilize different feedstocks. Traditionally, such changes have always shown that hydrogen plant capacity changes of between 10-20% are achievable. Recent studies by Johnson Matthey have found that this is a glass ceiling and can be easily broken through by the selection of appropriate technology enablers with capacity increases of up to 60% being achievable in a cost effective manner.

Question 57
What are the mechanisms for steam-methane reformer catalyst deactivation? Are you more likely to see deactivation in the top, middle or bottom of the reformer tube? What are the indications of this deactivation? How can conditions be optimized to prevent these localized problems?

**Tom Kiliany (ExxonMobil R & S)**
Several mechanisms can deactivate steam-methane reforming catalysts, including catalyst poisons, operation with low steam to carbon ratio and high aromatic content in the feed gas.

If the deactivation is due to a reforming catalyst poison (typically sulfur), then deactivation will start at the top of the catalyst tube, but can rapidly proceed throughout the tube. The deactivation will manifest itself by the tube getting hotter than the surrounding tubes, or if the poisoning is widespread, then nearly all the catalyst tubes will get hotter. Periodic analysis of the feed gas can reduce the potential of catalyst poisons.

If the reformer is operated at a low (<3 mole steam/ mole carbon) steam to carbon ratio, then carbon will form and deactivate the catalyst. The deactivation will first be apparent at the location of maximum heat flux on the tube. Heat flux is furnace design dependant, including bottom, top and side fired furnaces along with terrace wall fired. The figure below illustrates a proposed mechanism of whisker carbon formation during low steam to carbon operation.

CARBON FORMATION ON NICKEL CATALYSTS

TRANSMISSION ELECTRON MICROGRAPH OF METHANE DECOMPOSITION ON NICKEL*
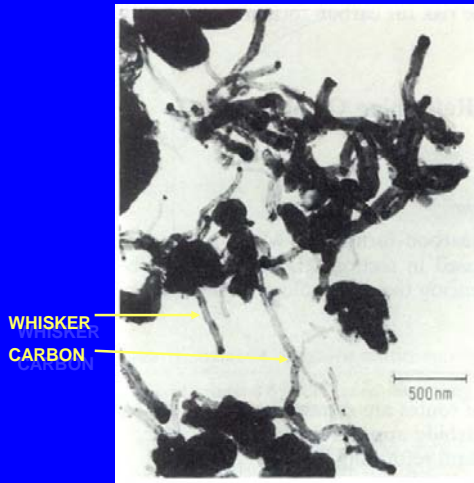
MECHANISM OF CARBON FILAMENT FORMATION**
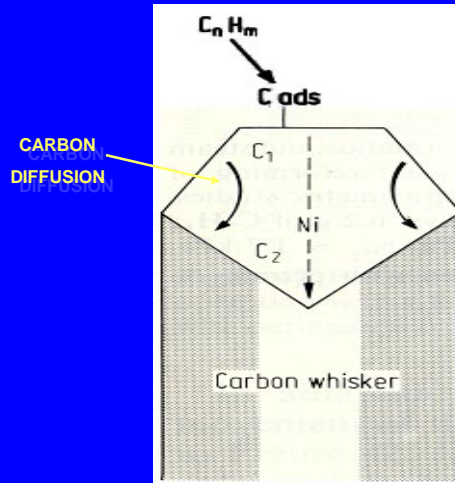
*Rostrup-Nielson, J. R., J. Catal ,**27,** 343 (1972)

Baker, R. T. K., Barber, M., Harris, P., Feates, F., Waite, R., J. Catal., **26, 51 (1972)

Careful control of the steam to carbon ratio will eliminate the concern of carbon formation. Another concern for catalyst deactivation is aromatic content of the feed while steam reforming naphtha. Operators that steam reform naphtha are usually located in regions where natural gas is in short supply. At high aromatic content in the naphtha, carbon formation occurs on the steam reforming catalyst resulting in hot tubes and shorter cycles. The upper limit of aromatics in naphtha feed is controlled by a number of variables including steam to carbon ratio, catalyst activity and furnace design. Steam reforming catalyst manufacturers recommend a naphtha content upper limit of 20-25 vol% aromatics.

James Fleshman (Foster Wheeler USA Corporation)
Reforming catalyst deactivation can occur by:
- Poisoning, primarily from sulfur.
- Fouling from boiler solids carryover.
- Carbon formation due to inactive catalyst, insufficient steam, heavy hydrocarbons or polymerization from olefins in the feed.

Catalyst breakup, usually due to thermal cycling, is as big a problem as actual deactivation. This can restrict flow and cause hot tubes.

Poisoning and fouling is more likely to occur at the process inlet to the reformer tubes. Carbon formation tends to occur about one-third the way down the tube. Crushing primarily occurs at the bottom.

Monitoring of the catalyst tubes by visual inspection and optical pyrometer survey is the most effective method to spot catalyst problems, but they can also be detected by an increase in methane slip or pressure drop.

The risk of catalyst poisoning can be significantly reduced if the feed is properly pretreated. Performance of the hydrogenator and sulfur adsorbers should be monitored, and the steam system checked to ensure that carryover is not a problem. Boiler chemicals should not contain sulfur.

It is important to have the correct catalyst, and enough steam in the reformer feed to avoid carbon formation. If the hydrocarbon feed is heavier than usual, increasing the steam-to-carbon ratio can help to reduce the risk of carbon formation.

The Foster Wheeler Terrace Wall™ Reformer has a lower heat flux at the inlet to avoid coke formation, and the firing and flux profile can be adjusted in case of poisoned catalyst.

Crushing of the catalyst can be avoided by keeping the reformer in a hot stand by mode rather than shutting down, for example in case of failure of an ID fan. A Terrace Wall™ reformer can be designed to switch from combustion air preheat to natural draft to stay on-line in case of fan failure, or drop back to minimum firing to keep the furnace hot.

Steve Catchpole (Johnson Matthey Catalysts)
Deactivation of steam reforming catalysts occurs for a variety of different causes but there are primarily three that are more often observed: (1) Sulfur poisoning (2) Sintering & (3) Carbon deposition.

Sulfur reacts with the active nickel metal on the catalyst ceramic support to form nickel sulfide. The sulfided form of nickel has a very low steam reforming activity. To prevent this, it is important that the feedstock desulfurization system purifies the hydrocarbon feedstock to sub 0.1ppmv levels. In fact a well-designed system should purify down to <0.05ppmv sulphur in the feed. Daily monitoring the performance of the desulfurisation system is recommended. Sulfur will mostly deactivate the steam reforming catalyst in the inlet to around 50% (sometimes more) along the tube. The visual observation will be an increase in reformer tube temperature associated with loss of steam reforming activity. The dull red coloration of the tubes could brighten and also appear patchy as the poisoning becomes more severe. For robust catalyst, it is possible to strip-off some of the sulfur by bringing the plant off-line and steaming the catalyst, though full activity is not readily achieved.

Sintering is an irreversible thermal effect and is the result of tiny nickel crystallites on the ceramic catalyst support combining to form crystallites of a larger size. As the steam reforming activity is heavily dependant on nickel crystallite surface area, the sintering will result in a loss of activity. Sintering is more significant where the temperature is hotter and so occurs faster in the bottom (exit) portion of the tube. Though the process of sintering is largely unavoidable, most steam reforming designs and catalyst performance predictions take into account this loss of

activity in the design life. Sintering normally results in the tubes increasing in temperature through most of the length.

Carbon deposition on the catalyst not only impedes access of the reactants to the active nickel metal, but also in some cases can result in weakening the catalyst when carbon deposition occurs deep in the catalyst pore structure. Assuming stable plant operation, carbon formation can occur after the catalyst is aged and some degree of poisoning has already taken place. More common though on refineries is when feedstock changes resulting in poorer control of the steam to feed ratio. For heavier feeds there is a far greater tendency for carbon deposition to occur and the steam to feed ratio needs increasing as per the recommendation of the catalyst vendor. Promoted catalyst (e.g. potash promoted) can help limit the amount of increase in steam addition. Carbon formation usually occurs in the inlet third of the steam reforming tube. Tubes can become very hot, not just due to the loss of catalyst activity, but also due to carbon deposition on the inside tube wall. So-called "hot-bands" may appear. In very severe situations, mottling and hot-banding can dramatically increase tube temperatures reducing tube creep life. It may be possible to gasify the carbon by bringing the plant off-line and steaming the catalyst.

Other poisons may include chlorides (e.g off gas feeds from catalytic reforming units), silicas say from upstream refractory linings or support balls, and phosphates from poorly managed steam systems. Most heavy metals (Pb, As, Hg) will poison the nickel steam reforming catalyst though are not common.

Ted Hallen (Haldor Topsoe)
The primary mechanisms for steam-methane reformer catalyst aging are:
- Poisoning, and
- Sintering

Sulfur Poisoning:
Poisoning is most commonly caused by sulfur entering the reformer. The sulfur is typically present due to inadequate performance of the desulfurization system immediately upstream of the reformer. Sulfur may also be present in steam that is added to the system (sulfur compounds in boiler feedwater chemicals). Total sulfur in the feed should be limited to <50ppb in the feed to the reformer to ensure good performance. Typical symptoms of too much sulfur in the feed are hotspots/bands found ~1/4 of the way down the tube (the area with the highest propensity for carbon formation). The sulfur binds to the Ni to form Ni-S which is not active for reforming. Carbon is formed on the inside of the tube and functions as insulation thus restricting the endothermic reaction from removing the heat being supplied to the tube.

Topsoe's line of alkali-promoted steam reforming catalysts will significantly reduce the risk of carbon laydown in the top half of the tube where the propensity for carbon formation is highest.

Sulfur can be removed by eliminating sulfur in the feed, and the sulfur on the catalyst will gradually be stripped off the Ni crystal. The carbon that may have been formed due to the poisoning is more difficult to remove. Sulfur as well as carbon can be removed to some extent by steaming at high temperatures. In more severe cases, a steam-air decoke (regeneration) is preferred to remove the carbon completely.

<u>Sintering:</u>
Sintering refers to the coalescence of metal crystals due to high temperature. At elevated temperatures, the effective total metal surface area available for reaction is reduced as small crystals gradually merge to form larger crystals. See attached chart as reference for sintering rates. Sintering is irreversible and can occur anywhere high temperatures are present. Sintering is always present under typical SMR operating conditions, but as can be seen from the graph, the major part of the sintering takes place in the first few weeks of operation and mainly in the bottom of the tube where the temperatures are higher.

Sintering of Nickel Surface
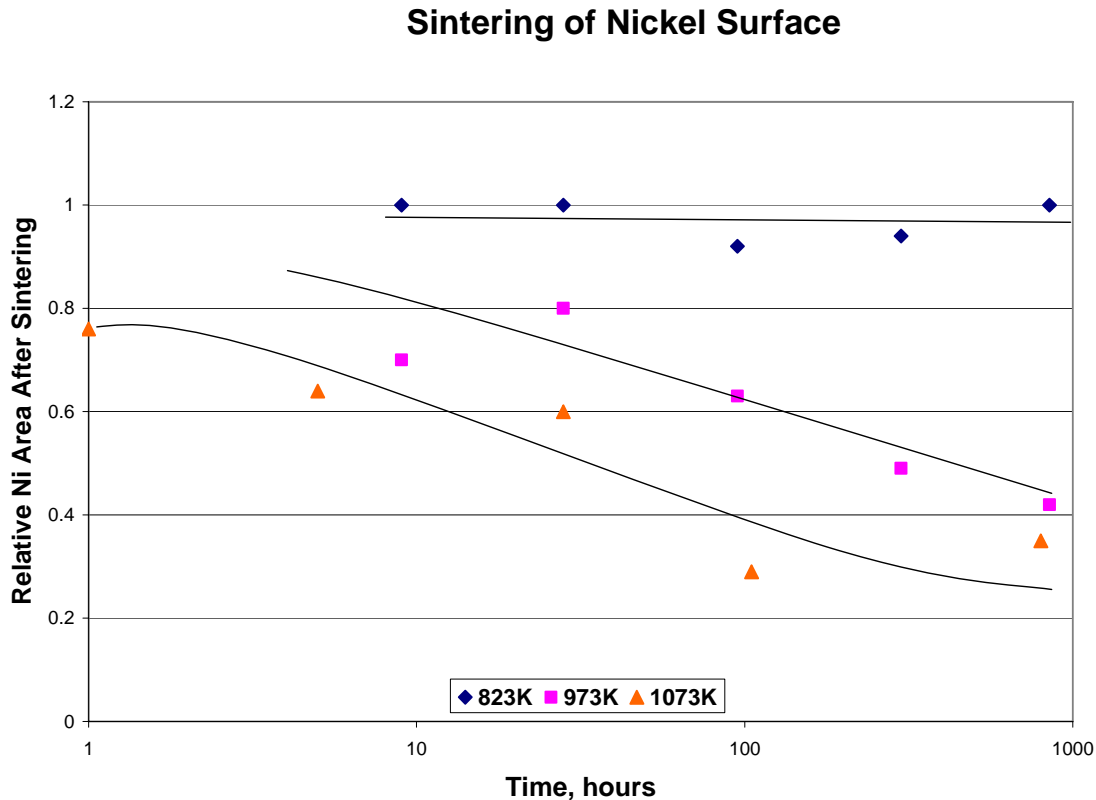
Question 58
What techniques do you use for steam-methane reformer catalyst loading? Are there others?
*What are their relative benefits?*

Tina Moss (Johnson Matthey Catalysts)
Correct loading is vital to both efficient steam reformer operation and steam reformer tube life. The two main objectives in steam reformer loading are to prevent the formation of large void spaces within the tube and to ensure even flow distribution through each tube. There are two general methods for loading steam-methane reforming catalyst: 1) sock loading; and 2) trickle loading.

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Johnson Matthey Catalysts has experiences with both loading techniques. However, our experience is that almost all users in the U.S. and Canada use the trickle loading method. In other parts of the world, trickle loading is also being utilized more frequently. The one we have the most experience with is the UNIDENSE™ technique. UNIDENSE™ technique was originally developed and licensed by Norsk Hydro, which recently sold the technology, and is now available through UNIDENSE™ Technology GmbH. The technique uses carefully designed springs on a cable, which are used to give a controlled and uniform free-fall of catalyst, minimizing damage, as it is poured into the tubes. There are other trickle loading methods that have been made available recently to help minimize the manpower required.

Experience from a large number of trickle loadings has confirmed that the technique is significantly quicker than traditional sock loading methods. It also produces less pressure drop variation and less need for tube vibration or re-loading of catalyst tubes.

The improved flow distribution resulting from the more homogeneous pressure drop across the reformer ensures optimized operating efficiency in the Primary Reformer by achieving uniform process gas exit temperature and methane slip. The improved operating efficiency also minimizes potential for tube failure by lowering and achieving a more uniform tube wall temperature, as illustrated in the figure below.

Tube Wall Temperature
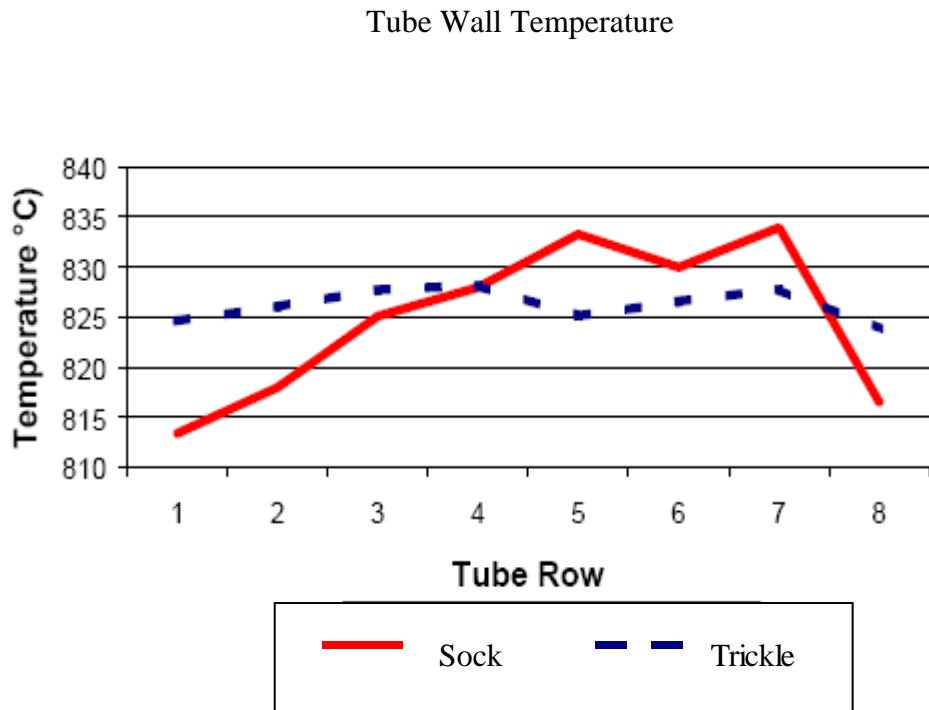
James Fleshman (Foster Wheeler USA Corporation)
Current technology uses a device inserted into the catalyst tube to slow the particles as they are poured into the tube. At least two variants of this are available – a brush and a spiral. Each system has its own equipment and techniques.

The older sock loading method requires a separate step to fill the socks, and the actual loading requires a longer shutdown and produces a less uniform fill than brush loading. However it does not require a license fee and may be economic depending on local conditions. At one time the catalyst tubes were filled with water and the catalyst poured in – this is not used due to the time required to dry the catalyst after loading.

Ted Hallen (Haldor Topsoe)
A typical steam reformer contains 100-500 tubes. For an acceptable catalyst loading, pressure drop across a tube should be ± 5% of the average.

There are four SMR loading methods that are commonly used in the industry today:
- SpiraLoad™
- Unidense™
- CatCade™
- Sock

The first three provide very similar results while the sock method is somewhat antiquated and provides lower quality results. The sock method may be a good choice for reloading a few tubes, but for a total furnace load, the other methods are preferred.

Many factors affect the quality of a loading. One critical factor is the quality of personnel performing the loading. None of the methods are completely automated, so the human factor is important.

A summary of the basic concept and advantages/disadvantages is shown in the tables below:

Loading Method	Licensor	Basic Concept
SpiraLoad^{tm}	Haldor Topsoe, Inc.	Plastic tube sections w/inner spiral lip slows catalyst as it falls.
Unidense^{tm}	Mourik Norsk Hydro Yara Int'l	Cable with springs to slow catalyst as it falls.
CatCade^{tm}	Cat Tech	Cable with plastic flaps to slow catalyst as it falls
Sock	N/A	Socks filled with catalyst are lowered with a rope.

Loading Method	Advantages	Disadvantages
SpiraLoad^{tm}	Uniform dP's (±5%) Very low reload requirements (<1 per 1,000 tubes) Good loading speed "Human error" virtually eliminated	Slightly higher cost vs. Unidense / CatCade due to more costly equipment
Unidense^{tm}	Uniform dP's (±5%) Good loading speed.	Slightly more risk of "human error" vs. SpiraLoad^{tm}
CatCade^{tm}	Uniform dP's (±5%) Good loading speed	Slightly more risk of "human error" vs. SpiraLoad^{tm}
Sock	No licensing fees	Less uniform dP's (±10%) Higher reload % required. Extra pre-socking step needed before loading. Slower than the other 3 methods.

Question 59
What is the expected life of adsorbents in pressure-swing adsorption (PSA) units? What contaminants affect or shorten life? What methods do you use to measure residual life?

Paul Zimmerman (UOP)
When the PSA is operated in accordance with the design parameters of the unit given in the operating manual for the PSA Unit, adsorbent expected life is the life of the unit. The majority of adsorbent replacements are due to revamps for a change in operating conditions, such as a feed change, or to improve performance for higher throughput or recovery.

The PSA has multiple layers of adsorbents. The type and quantity of adsorbent layers is designed to remove specific impurities given in the design feed specification. The contaminants that shorten the life will depend on the types of adsorbents used in each of these layers. For example, if the feed contains impurities such as C6 and heavier and the adsorbent system is not designed for it, then these may adsorb strongly onto an adsorbent layer and not desorb during the regeneration step. This effectively reduces the capacity of that layer.

When the unit is operated outside of the design parameters, some impurities such as CO_2 can also migrate to incorrect layers causing a loss of adsorbent life. Because of this, operating a PSA with a feed higher in impurities than design, or with higher than design impurities in the product can result in a reduction in adsorbent life. Other common causes of heavy impurities loading include long cycle times, improperly using the Manual Step Mode, valve leakage, liquid entrainment, and improper feed temperature.

The first indication of heavy impurities loading is a decrease in product purity followed by an inability to control pressure change functions. If impurity loading is severe enough, then replacement of the adsorbent may be required.

Another source of adsorbent failure can be through "dusting" of the PSA adsorbent. This occurs when the unit has been operating with the pressure swings outside of the design parameters, such as when the unit is operated with known valve failures, or operators override the step advance safeguards internal to the PSA program.

The health of the adsorbent can be checked by running a Performance Test. This procedure is provided with the Operating Manual supplied by UOP. A performance test is conducted by operating the PSA at a steady state with the product as close to design specification as possible.

For example if the PSA is designed for a product specification of 10 ppm CO, the product should have between 5-10 ppm CO. In addition the feed pressure and tail gas pressure should be maintained as close to design as possible, as these impact unit performance. Once this is achieved for 12 to 24 hours, samples of the feed, product and tail gas are taken and fully analyzed. For these analyses a material balance is done to determine the overall hydrogen recovery from the unit. If the hydrogen recovery is less than design, measures can be taken to help "clean-up" the adsorbent to restore it back to the original capacity. This "clean-up" involves running the unit for a period of time with high purity product.

James Fleshman (Foster Wheeler USA Corporation)
PSA adsorbents are unlikely to "wear out" in normal service, but they can be permanently damaged if heavy components reach the wrong part of the bed.

PSA systems use a series of adsorbent layers – what is essentially weak adsorbent at the inlet to remove heavy or more easily adsorbed components, followed by stronger adsorbents to remove the lighter or more weakly adsorbed gases. Liquids or high levels of heavy components can cause problems.

In SMR gas service the most common culprit for bed damage is liquid water carryover. For mixed or hydrocarbon-rich feed streams, changes in composition can be a problem since high levels of heavy hydrocarbons (C4+) in the feed can pass through the first layers and be irreversibly adsorbed if they reach the wrong adsorbent layer.

Liquids need to be removed from the inlet gas, and heat tracing of the inlet piping or a small heat exchanger to put a few degrees of superheat into the gas might be considered if liquid carryover is a problem. Uniform feed gas composition is important in hydrocarbon systems.

Ted Hallen (Haldor Topsoe)
Under normal circumstance, the expected life of adsorbents in a PSA unit is the life of the unit (15+ years). The adsorbents are fairly forgiving for most components in the vapor phase at ambient temperature. Certain acids, such as HCl vapor may react with the adsorbent and cause damage. The liquids carried over as liquid droplets or mist choke the pores of the adsorbent, making it ineffective. Carry over of liquids such as compressor oil, amines, condensed hydrocarbons is known to have caused damage to the adsorbent. The extent of the damage will depend upon the amount of liquid carried over into the adsorbent beds, and it will be reflected in reduced throughput capacity or difficulty of meeting the purity specification.

The adsorbent can also be damaged by lifting or crushing of the adsorbent. This may be caused by mal-operation, or equipment failure. The crushed adsorbent may cause excessive pressure drop, gas mal-distribution in the beds, and carryover of adsorbent dust into the product as well as in the purge gas.

It is difficult to predict remaining cycle life of PSA adsorbents. Vessel inspection schedule and the age of the adsorbent are typically used in conjunction to decide when it is time for a replacement. Damage to a part of the adsorbent may reduce the unit throughput. Replacement of the damaged adsorbent may be necessary to get back the full capacity.

Safety & Reliability

Question 60
How do you monitor furnace tube metal temperatures? Compare the relative reliability and accuracy of tube skin thermocouples with that of thermography.

Paul Zimmerman (UOP)
There are four categories of furnaces – very hot (steam hydrocarbon reforming heaters), hot (catalytic naphtha reforming heaters), medium temperature (crude unit heaters, hydroprocessing recycle gas heaters or combined feed heaters) and cool (reboilers). UOP recommends the following for each category:

- Very Hot – tube skin thermocouples tend to not last long in this service and oxidation of the alloy tubes is not severe. UOP recommends using an infrared camera to monitor the tube metal temperature. Selection of the proper infrared camera and training of the technician(s) assigned to use the camera are critical to achieving a reliable tube metal temperature reading.

- Hot – roughly one-fourth of the tube skin thermocouples will develop a significant offset in the hot direction after 6 to 36 months of operation in this service. Operators will respond by either skewing the heat profile in the furnace or limiting the unit's throughput. Therefore, UOP does not recommend using tube skin thermocouples in this service. For furnaces that do not foul on the ID of the coil, stay within a defined operating boundary (flux, bridgewall temperature, etc) and use calculation methods to trend the tube metal temperature. For other furnaces, either have Cetek ceramic coat the 9Cr-1Mo tubes (Cetek has the quality control necessary to maintain an even thickness) or upgrade the coil metallurgy to an alloy that will not appreciably oxidize. Then use an infrared camera to monitor the tube metal temperature.

  If company policy or local regulations demand that tube skin thermcouples be used, UOP recommends purchasing the Gayesco Xtracto-Pad style thermocouples for two reasons. First, the sheaths can be replaced easily during downtime without welding. Second, Gayesco provides excellent service during the installation process. The service aspect is critcal as there are several pitfalls to successfully installing tube skin thermocouples of any style. Make sure that Gayesco is heavily involved in every step of the installation process including designing how the sheath will be routed and clipped, training of the welders doing the installation and providing consulting services during the installation. UOP recommends installing two tube skin thermocouples at each location with only one connected to the junction box such that when a skin couples starts to read high it is possible to switch over to the backup thermocouple. Replace all thermocouple sheaths every turnaround.

- Medium – In this service, tube skin thermocouples provide a more reliable and accurate tube metal temperature than an infrared camera. Use Gayesco tube skin thermocouples in sets of two as described above. Also as described above, have Gayesco heavily involved in the design and installation process. Conduct a quarterly infrared scan of the coil to check for hot spots that may develop away from the skin couples. During each turnaround, grind the oxide scale off the tubes in an area approximately one foot above or below the tube skin thermocouples. Tune the infrared camera to read the same as nearest thermocouple prior to conducting the quarterly survey.

- Cool – tube skin thermocouples are not required. Conduct a quarterly infrared scan of the coil. Ensure that the maximum allowable tube metal temperature is set correctly. Many fired heater vendors set the temperature at the minimum required by API 560 (25°F above the calculated maximum tube metal temperature). Most heaters in this service have Sch 40 AW coils operating at stress levels far below the elastic allowable. Therefore most coils in this service have an allowable tube metal temperature that is much greater than 25°F above the calculated maximum tube metal temperature.

Note: infrared cameras cannot be used to monitor the tube metal temperature of any coil in oil fired service as the camera is only capable of seeing the outer surface of the oil ash that collects on the OD of the coil surface.

Tom Kiliany (ExxonMobil R & S)
Hydrogen reformer tube metal temperatures are usually measured using three techniques. The first method is direct visual observation of the all of the tubes via the furnace peep holes. With this method, an operator can quickly determine, via color, if a given tube or portion of a tube is higher in temperature compared to the other tubes in the row. Also, the approximate absolute tube temperature can be determined by the color or lack or color to about ± 50ºF.

A second method of determining tube metal temperatures consists of attaching a properly shielded thermocouple directly onto a tube. Given the difficult high temperature environment, the thermocouples have a tendency to fail. While operational, these contact thermocouples provide accurate readings at the limited locations where they are attached.

A third method of measuring tube metal temperatures is infrared pyrometry. A pyrometer measures the infrared radiation and converts it to tube metal temperature. The emissivity of the reformer tubes must be accounted for when using an infrared pyrometer. Values of emissivity range from 0.85 to 1.0. In general, the temperature readings from an infrared pyrometer are 20-30ºF high. By reading a higher than actual tube metal temperature, the tubes are protected since a furnace temperature reduction will be undertaken before damage occurs.

Alfred Faller (Foster Wheeler USA Corporation)
Tube skin thermocouples have generally given poor service life in reformers. They can be made to last but attachment details are important. Optical pyrometers are the norm for monitoring TMTs in steam reforming furnaces. In coker furnaces, TMT thermocouples give reasonable life.

Question 61
What do you use to blanket your hydrotreating feed drums? What are the pros and cons of each blanketing medium?

Paul Zimmerman (UOP)
A variety of gas streams have been used for feed surge drum blanketing. Fuel gas is the most common and there usually is no disadvantage to using this material. For some hydrotreating units blanketing with fuel gas, the amount of LPG sponged out of the blanket gas has caused problems.

The next most common are makeup gas and nitrogen. These are used when the fuel gas minimum pressure is low. It is desired to maintain a certain pressure in the drum to be able to provide enough differential pressure for the backwash filter, about 40 psi. If the fuel gas minimum pressure is below this, then alternate sources are considered. Nitrogen and makeup gas are more expensive than fuel gas and so are not favored economically. Also, the chloride content in makeup hydrogen blanketing gas has been an issue in some units. One unit plugged up the charge pump suction strainer with chloride salts and had to shut down a couple of times as a result of chlorides picked up from the blanket gas.

James Turner (Fluor)
A survey of 20 hydroprocessing units, designed by different companies, showed the following streams for feed drum blanketing:

Blanketing Gas	# of Units
Fuel Gas	14
Natural Gas	3
Hydrogen	2
Process Gas	1

While not a scientific survey, these results clearly show that the dominant gas used for feed drum blanketing is fuel gas. Advantages are that it is normally readily available, and relatively low cost.

The vast majority of these designs use a "push/pull" drum pressure control scheme, where on high pressure, the gas is vented to the flare or to an LP gas recovery system, and on low pressure, the supply gas enters the drum. A few designs "float" on a process gas supply header, and the pressure in the drum is not directly controlled.

Advantages to using fuel gas or natural gas are availability and low cost. A potential disadvantage is dissolved gas in the feed, which can sometimes impact the recycle gas purity.

An advantage of using hydrogen is that dissolved gas will not dilute the hydrogen concentration in the reactor loop. Disadvantages are higher cost, and the hydrogen may only be available at high pressure, increasing the likelihood and severity of valve failure relief cases.

The survey did not find any cases where nitrogen was used, although we know some units use nitrogen. A disadvantage of using nitrogen is high cost. In addition, dissolved nitrogen in the feed can theoretically have a small impact on the recycle hydrogen purity, if the nitrogen reaches equilibrium with the feed, and there is no purge. A process simulation shows that the recycle purity may be reduced 1-2%. However, in most situations, the blanket gas will not be in equilibrium with the feed (normally there is not enough turbulence or mixing of the feed and the blanket gas), so it is unlikely that this effect would be seen in an operating unit.

Question 62

How do you ensure that emergency depressuring valves and interlocks are functioning properly during long periods of non use? Are there on-line methods to determine whether this equipment will operate when needed?

Paul Zimmerman (UOP)

UOP specifies that emergency depressuring valves and interlocks be operated by a high reliability safety system or interlock system that includes a logic solver. UOP specifies that the logic solver shall be a fault tolerant, redundant programmable logic controller, with self diagnostic coverage. Diagnostics shall include the I/O interfaces. The diagnostic functions are expected to detect certain latent (hidden) failures, and associated alarms inform operators that maintenance may be required to confirm functionality of the system.

UOP also specifies a testing frequency for safety instrumented systems, and specifies that the refiner shall determine a testing frequency for interlock systems. The maximum test interval for safety instrumented systems is specified to be every year for field sensors, logic solvers, and solenoid valves, and every four years for shutdown valves.

It may not be practical to fully test an entire interlock system on-line because a single cause may have many effects. For example, actuating the high rate depressuring hand switch in a hydrocracker may simultaneously open the high rate depressuring valve, stop the recycle gas compressor, stop the charge pumps, shut down the makeup gas to the reactor section, shut down fuel to the combined heater, stop the wash water pumps, and stop the lean amine pumps to the recycle gas scrubber. It does not seem feasible to test all those elements together on-line.
It may be possible to test certain individual elements on-line. Procedures for testing would need to be developed to ensure it doesn't activate an unnecessary shutdown and that the shutdown and logic systems are returned to normal operation.

UOP is aware that some refiners have bypass valves around shutdown valves or solenoids and the bypass valve is normally locked closed. UOP does not include bypass valves for testing purposes in standard UOP designs. This is to prevent solenoids and valves remaining in a bypassed position and failing to react to an emergency situation.

Tom Kiliany (ExxonMobil R & S)

During unit turnarounds and other shutdown periods, emergency depressuring valves and interlocks are tested. With some systems, testing can be accomplished on-line through use of parallel valves.

Catalyst

Question 63
What are the critical criteria for ULSD catalyst selection? Can catalyst selection be done by modeling alone or is pilot plant testing required? How do you predict catalyst stability / deactivation?

Larry Kraus (Albemarle Catalysts Co.)
Managing H_2 consumption and contaminant control are the most critical concerns in ULSD catalyst selection. In Table I, it is seen that as catalyst activity for ULSD increases, the associated H_2 consumption increases.

Table I
ULSD Catalyst Options: Activity and H_2 Consumption

| CATALYST:	HDS RVA (Product S < 10 wppm)	HDN RVA (Product S < 10 wppm)	RELATIVE H_2 CONSUMPTION (Product S < 10 wppm)
High Activity CoMo (STARS™ CoMo)	100 - 150	100 - 130	100 - 105
High Activity NiMo (STARS™ NiMo)	190	150	135
Bulk Active Metal (NEBULA™)	> 250	> 200	> 175

In order to fully utilize high activity catalysts in ULSD service, the H_2 consumption in a hydroprocessing unit must be in balance with the unit H_2 supply capabilities. The makeup H_2 supply must exceed the H_2 consumption in the unit and chemical H_2 circulation must be sufficient to ensure adequate hydrogen partial pressure (ppH_2) at the reactor outlet. ULSD catalyst selection must be made to balance catalyst activity/H_2 consumption and meet product property requirements without product quality (e.g. cetane) giveaway.

When H_2 consumption and H_2 supply are not compatible (out of balance) catalyst stability is reduced. Commercial data illustrating this are shown in Figure 1. Here the Normalized WABT as a function of TOS is shown for two catalyst cycles. In the first cycle a catalyst system consisting of STARS™ NiMo/Nebula™ was used. In the subsequent catalyst cycle a STARS™ CoMo/Nebula™ catalyst system was used to reduce H_2 consumption and better balance H_2 consumption/ and H_2 supply. In both systems the ratio of STARS™ Catalyst/Nebula™ was the same. Here it is seen that the rate of deactivation of the STARS™ NiMo/Nebula™ catalyst system is ~ 3.5 times higher than that of the STARS™ CoMo/Nebula™ catalyst system. This can be attributed to the 20 - 25% higher H_2 consumption with the STARS™ NiMo/Nebula™ and the accompanying reduction in ppH_2. This is expected given the higher aromatic saturation

activity of STARS™ NiMo as compared with STARS™ CoMo and the identical STARS™/Nebula™ ratios used in both catalyst systems.

In Figure 1 it is also seen that the initial activity of the STARS™ NiMo/Nebula™ catalyst system is significantly higher (lower SOR WABT required) than the STARS™ CoMo/Nebula™. However, this higher activity could not be fully utilized because of the rapid rate of deactivation with the STARS™ NiMo/Nebula™ system. These data are also an illustration of the potential danger in basing catalyst system comparisons and catalyst selections on initial or SOR activity/performance without accounting for the impact of H_2 consumption on catalyst stability. Clearly the STARS™ NiMo/Nebula™ system had higher SOR activity (lower temperature requirement). However, a longer catalyst cycle could be achieved with the STARS™ CoMo/Nebula™ system because of its greater stability under the operating conditions used.

Figure 1
Commercial Example
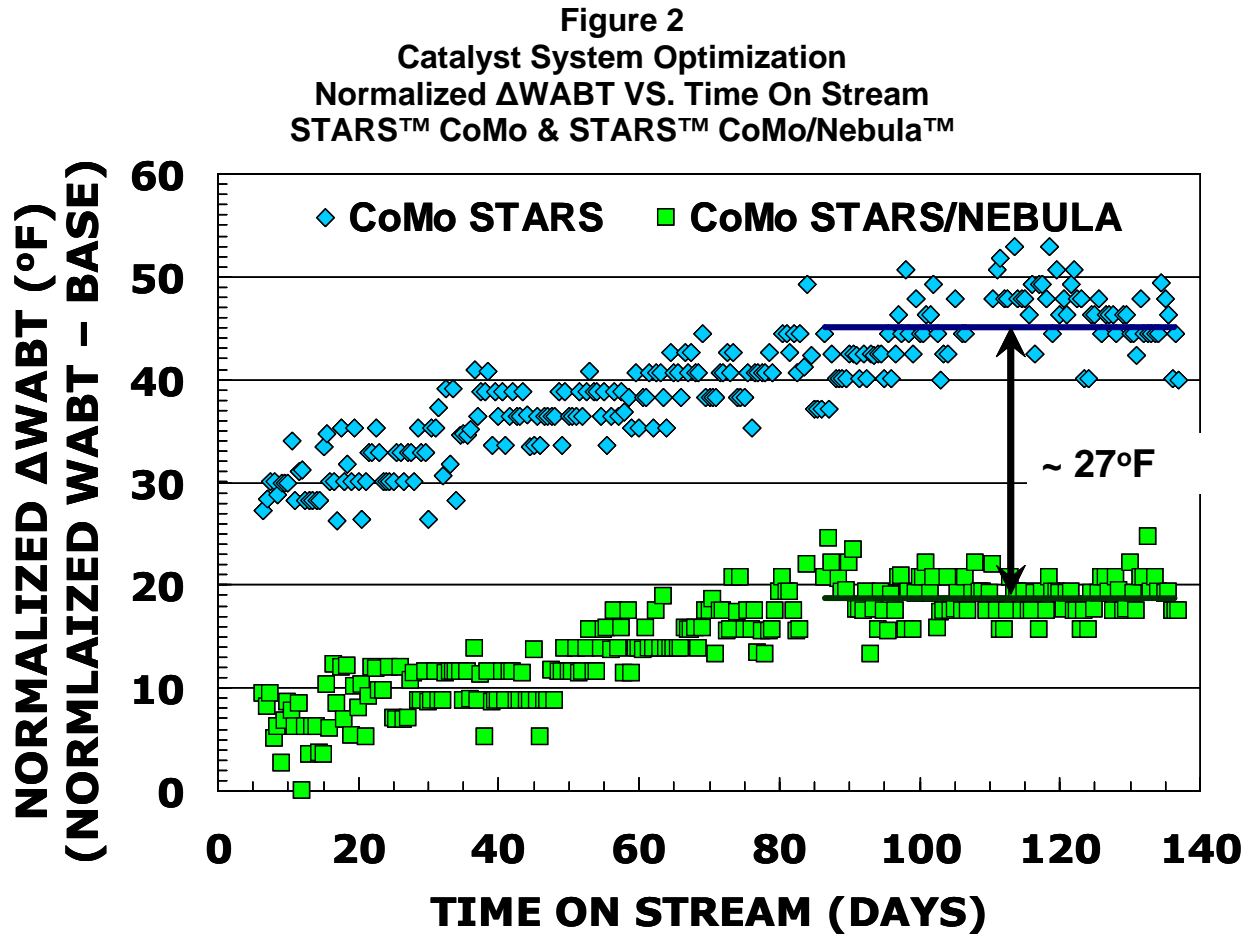Impact of Catalyst System on Catalyst Stability
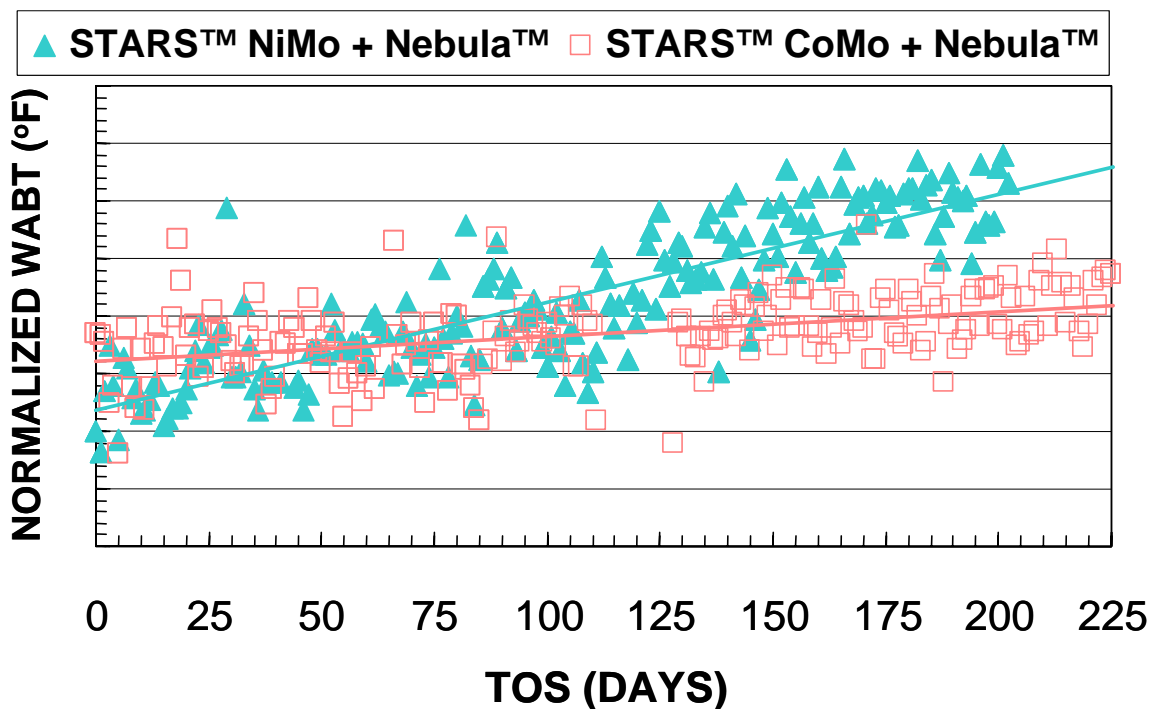
This commercial example clearly shows the critical impact of catalyst system design and selection on H_2 consumption/H_2 supply balance and catalyst cycle length. Also, this example illustrates that simply applying higher catalyst activity does not ensure an increase in catalyst cycle length.

Application of high activity catalysts in ULSD operations is an opportunity to increase cycle length, improve product properties, and increase unit throughput. The high H_2 consumption associated with these catalysts makes it critical to ensure that H_2 consumption is balanced with

H_2 supply to avoid catalyst stability problems. One approach to utilizing high-activity, high-H_2-consumption catalysts, like Nebula™, is to use them in combination with other catalysts. A STARS™/Nebula™ combination can significantly boost catalyst system activity while keeping H_2 consumption at a manageable level

Figure 2 shows the comparison of ULSD performance of CoMo STARS™ and Nebula™/CoMo STARS™ catalysts systems processing a straight run feed. The combined system contains ~ 25% Nebula™.

Figure 2
Catalyst System Optimization
Normalized ΔWABT VS. Time On Stream
STARS™ CoMo & STARS™ CoMo/Nebula™

From this plot it is seen that addition of Nebula™ to the catalyst system provided a significant activity boost while maintaining catalysts stability. The H_2 consumption with the combined system was 9 - 10% higher after achieving stable operation.

Pilot plant testing is recommended to verify H_2 consumption. Catalyst stability/deactivation is predicted from model correlations of process conditions (e.g. ppH_2) and deactivation rate.

Contaminant control is addressed in Question 64.

Ted Hallen (Haldor Topsoe)

For ultra deep desulfurization of diesel, it is the reactivity of the most refractive compounds (dibenzothiophenes with substituents in the 4 and 6 positions, the most common of these is 4,6-dimethyl dibenzothiophene) which determines the overall desulfurization rate. There are two different reaction pathways, which are both important for the removal of these refractive S-compounds: the direct sulfur extraction pathway, which is inhibited by H2S and nitrogen compounds, and the pre-hydrogenation pathway, which is mainly inhibited by specific basic nitrogen compounds.

Due to the different activities for removal of the basic nitrogen compounds, a catalyst primarily using the hydrogenation route (typically a NiMo catalyst) for removal of the refractive sulfur molecules will behave in a different way than a catalyst primarily using the direct desulfurization route (typically a CoMo catalyst).

The hydrogenation route does not become really important until almost all of the nitrogen compounds have been removed. At this point the hydrogenation route with the NiMo catalyst will have a higher reaction rate than the direct route with a CoMo catalyst for HDS of the more refractive compounds. Therefore, the three main factors, which are determining for the choice of catalyst (NiMo or CoMo) for ultra deep HDS, are:

- pressure (high pressure favors NiMo),
- amount of inhibiting nitrogen compounds (high content of nitrogen compounds favors CoMo) and
- LHSV (low LHSV favors NiMo).

Thus, it is found for deep desulfurization that CoMo catalysts generally perform better than NiMo catalysts at low to moderate pressures with feeds containing cracked stocks.

The pre-hydrogenation route is favored at high pressure, and therefore NiMo catalysts are often the preferred choice at high pressure.

At low pressure, there are three reasons why pre-hydrogenation reaction pathway is not favored.

- Firstly, the hydrogenation activity is low.
- Secondly, the deactivation rate for the hydrogenation active sites is high, and
- Thirdly, the hydrogenation reaction is limited by aromatics saturation equilibrium at higher reactor temperatures.

Some CoMo catalysts are designed to be heavily dependent on the hydrogenation route to provide a high HDS activity. Such CoMo catalysts suffer from the same drawbacks as NiMo catalysts with respect to the production of close-to-zero sulfur diesel at low pressures. When operating with such CoMo catalysts, aromatics saturation equilibrium may result in a poor activity response when the temperature is increased. Such a phenomenon has been reported in the literature as the "wall" effect. The technology used in Topsoe's CoMo BRIM^{TM} catalyst does not exhibit this "wall" effect problem.

Catalyst selection is often based on modeling alone, but in order to do this, the model has to be tuned to a lot of different pilot plant data and commercial unit data for different feedstocks. If the feedstock is not that well known, a sulfur and nitrogen speciation is important to guide the selection of the optimum catalyst and operating conditions.

Regarding deactivation, prediction of catalyst stability/deactivation is best based on the combination of carefully selected commercial data and very good pilot plant test data. The commercial data give the general deactivation tendencies, but if the distribution in the commercial unit is not perfect, the deactivation will also be higher than it should have been due to both the bad distribution and the higher than necessary SOR temperature. The pilot plant data can be used to investigate the effect of end point, other feedstock variations, H2/oil ratio, hydrogen partial pressure, SOR temperature and LHSV. However, in pilot plant testing, one has to be very careful to avoid what is often called artificially high deactivation, which is often presented in papers (deactivation of more than 5-7°F/month at not so severe conditions). In order to obtain useful deactivation data from a pilot plant test, it is important to make sure that a deactivation similar to that of an industrial unit is obtained for a given feed and operating conditions. Subsequently, the operating conditions or the feed may be changed.

Question 64
What are the most common contaminants in ULSD feedstocks? What are the relative impacts of arsenic, silicon, sodium, and other metals? Are the effects of these contaminants the same for cobalt/molybdenum (Co/Mo) and nickel/molybdenum (Ni/Mo) catalysts?

Larry Kraus (Albemarle Catalysts Co.)
As, Si, and Na are the catalyst poisons most commonly encountered in diesel hydroprocessing. Fe is a common diesel feed contaminant, typically resulting in pressure drop build-up, rather than catalyst poisoning. The impact of catalyst poisons on catalyst activity is controlled using guard bed (poison trap) materials. Pressure drop build-up from Fe deposition is controlled with size/shape grading and specialty Fe traps.

The relative toxicities (catalyst poison strength) of As, Si, and Na are shown in Table I. As is overwhelmingly the most toxic of the common diesel feed contaminants.

Table I
Relative Toxicity of As, Na, and Si

| Poison	Relative Toxicity
As	10
Na	0.3 – 1.0
Si	< 0.1

The origins of the common feed contaminants and their major catalyst impacts are shown in Table II. Arsenic is increasingly a concern in diesel hydrotreating as Canadian (and other) synthetic crudes become more common. Diesels derived from synthetic crudes can have As levels as high as 0.5 wppm (500 wppb). 1000 wppm of As on a catalyst will reduce its activity by ~ 50%.

Table II
Catalyst Poison Origin and Impact

Poison	Sources & Impact
As	- Crude (Synthetic Crude, Russian, Chinese, West African) - Drilling Mud Diesel - Present in All Fractions - Naphtha > Distillate > VGO - Major Impact: Catalyst Activity
Na	- Caustic - Seawater - Crude - Present in All Fractions - Major Impact: Catalyst Regenerability
Si	- Coker Feeds (Anti-Foam Chemicals) - Predominantly in Naphtha Fraction - Major Impact: Catalyst Regenerability

Producing ULSD from feeds having high As levels will require guard bed materials to protect high activity catalysts and maximize catalyst cycle lengths. Many high As feeds also have high Si levels. The As and Si capacities of several guard bed and high activity catalysts are shown in Figure 1. The specific guard materials selected and the relative quantities of the materials used will be based on the relative amounts of As and Si contaminants in the feed. Si deposition can reduce the As capacity of guard materials designed for high As uptake. When processing feeds with high Si levels, a guard material with a high capacity for Si (e.g. KF-647) must be used upstream of the As trap (KG-6).

Figure 1
Catalyst Relative Poison Capacity
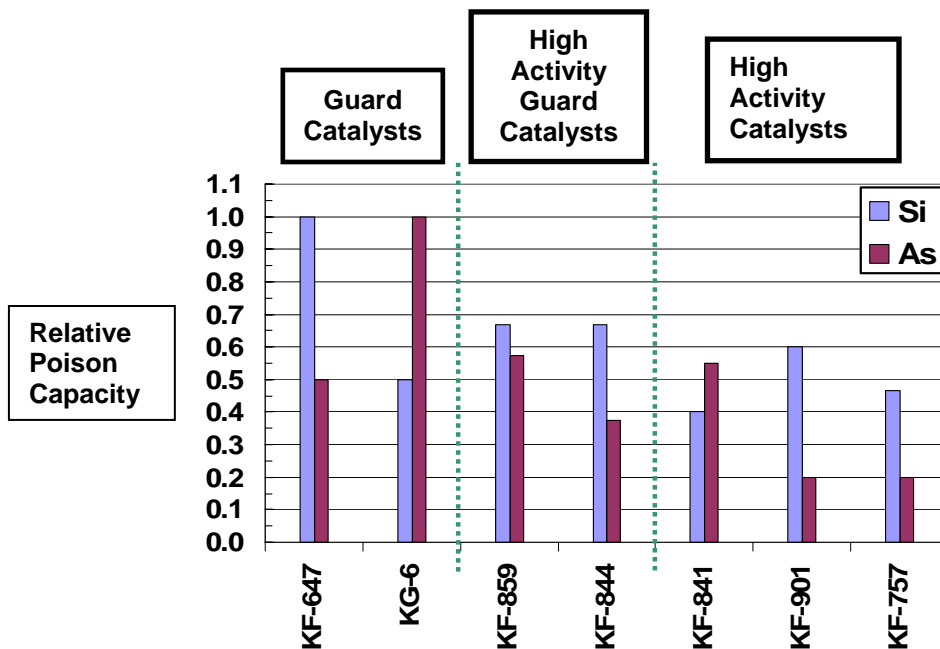
In commercial operations, it has been observed that NiMo catalysts are more sensitive to As poisoning than CoMo catalysts. This is consistent with the high affinity of As for Ni that is the basis of As trap guard materials.

Dr. Pierre Dufresne (Eurecat, S.A.) and Dr. Nilanjan Brahma (Eurecat U.S.)
ULSD stocks are much cleaner than VGO feeds and catalyst contamination is much less a concern for ULSD units than for FCC or Hydrocracker Pretreaters. The major contaminants which can be found are Silicon (if coker gas oil present), sodium, arsenic, iron. The effects of catalyst poisons are typically cumulative in regards to catalytic activity loss.

Ted Hallen (Haldor Topsoe)
In today's refineries, it is possible to encounter all sorts of contaminants and possible poisons that will potentially impact the hydroprocessing of hydrocarbon streams. In random order, some of the most common are:

Sodium	Iron	Solids
Silica	Lead	Phosphorus
Nickel	Arsenic	Vanadium

Here we should also differentiate between particulates entrained in the feed (inorganic), as opposed to those present in organic form.

Obviously, the former can be removed or reduced by feed filtering techniques. Any remaining solids can be handled by using an optimized graded bed system, for which Haldor Topsoe employs a large number of high void fraction, shape-optimized, and special function shaped catalysts.

In the production of ULSD, the nature and composition of the feedstock is normally such that the most commonly encountered contaminants would be silica, arsenic, and possibly sodium.

The relative impacts of Si, As, and Na on hydrotreating catalyst activity is shown in the attached Figures 1-3. For silica Figure 1), please note that the effect on HDN is much greater than it is for HDS.

With regard to the effect of the contaminants considered here on catalytic activity, this would be similar for NiMo and CoMo types. However, there could be other factors that dictate the specific use of CoMo or NiMo, which again could impact the performance of a particular catalyst in a specific service.
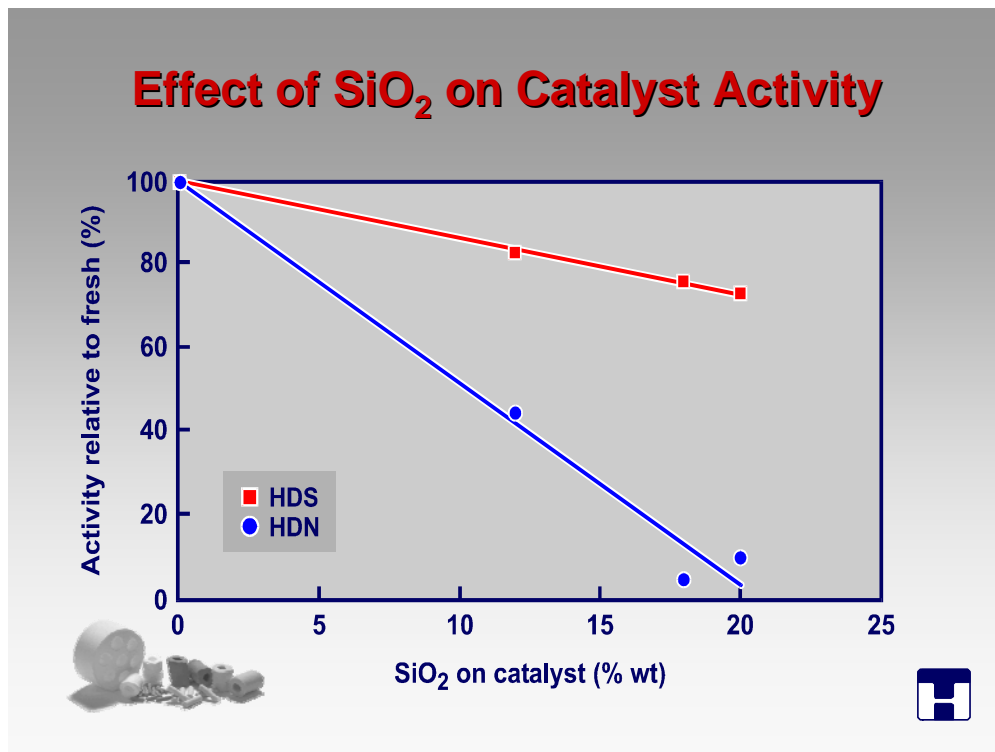
FIGURE 1

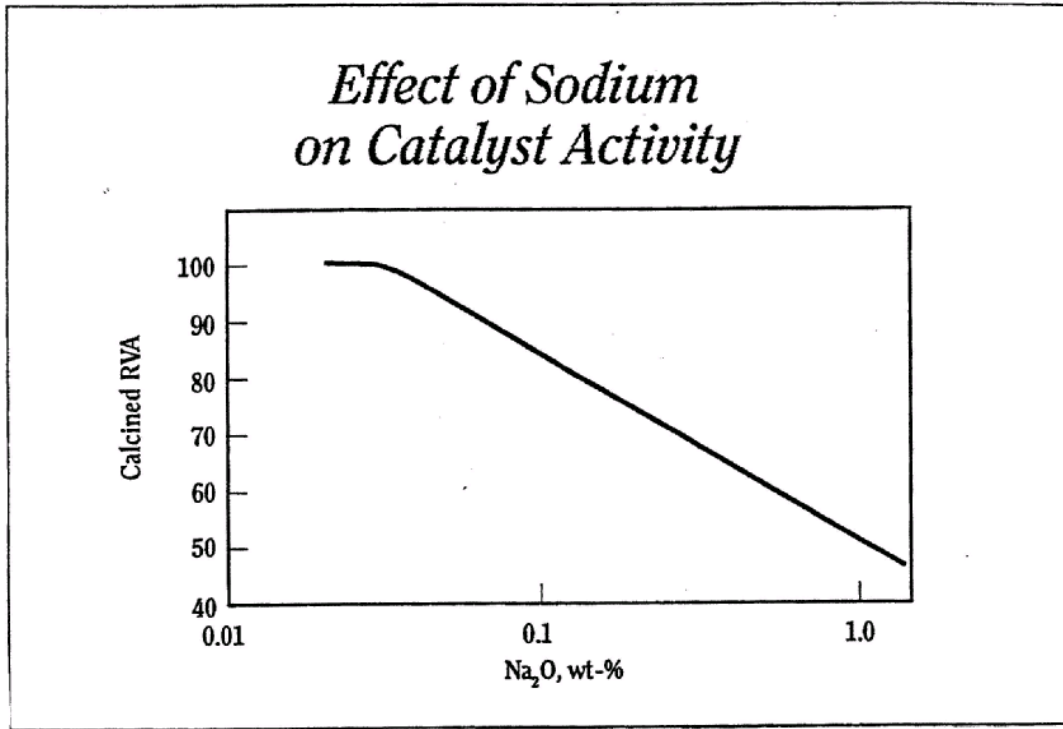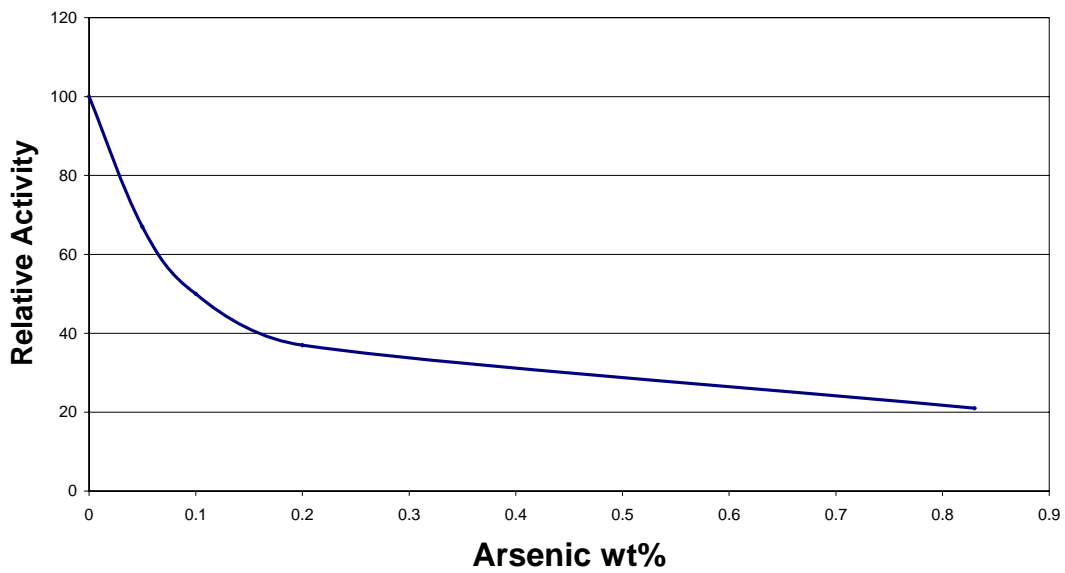**FIGURE 2**

Effect of Sodium on Catalyst Activity

FIGURE 3

Relative Spent Catalyst Activity with Arsenic Contamination

Question 65
Describe your experience with commercial regeneration of the newer Type II catalysts. What activity recovery did you achieve?

Dr. Pierre Dufresne (Eurecat, S.A.) and Dr. Nilanjan Brahma (Eurecat U.S.)
Standard regeneration techniques are not very effective for the newer Type II catalysts. In order to recover 90-95% of the original activity level, ALBEMARLE Type II catalysts require a treatment with their REACT process following a special regeneration technique. In the REACT process, the catalyst is transferred to a state comparable to when it was fresh. This will only be done on catalysts that have suitable physical and chemical properties with respect to surface area, poison levels, and size.

Larry Kraus (Albemarle Catalysts Co.)
Albemarle Catalysts has developed the REACT process for activity recovery of their STARS portfolio of catalysts with Type II active sites. REACT is a secondary treatment of regenerated catalyst in order to re-disperse the active metals and reintroduce the Type II active site configuration which is lost when carbon and sulfur are removed during regeneration. Activity recovery is typically over 90% of fresh catalyst but can be adversely affected by contaminant content and the severity of regeneration.

REACT has received wide acceptance and steadily growing use since its introduction.   These catalysts are often reloaded in the same unit as the fresh catalyst and have shown similar performance. Some of these catalysts have even been treated by the REACT process a second time, also with good results.

Paul Zimmerman (UOP)
UOP has had recent direct experience with REACT. Albemarle KF-848 pretreating catalyst was regenerated following a cycle in a hydrocracking unit processing a high endpoint VGO and other difficult feed components. Pilot plant comparison was done for the regenerated catalyst with and without REACT. The regenerated only catalyst had only 60 to 70% of fresh HDN activity, which is consistent with regenerated Type II catalysts without secondary treatment. With the REACT process, the activity was improved to 92 to 97% of fresh HDN activity. For this unit, this was a difference of 15 to 20°F activity loss from fresh without REACT versus only 1 to 3°F activity loss following the REACT process. The REACT treated KF-848 catalyst has been reloaded into the same unit and is performing within expectations.

Ted Hallen (Haldor Topsoe)
Before answering the question we would like to elaborate a little bit on the distinction between what is described as "Type I" and "Type II" catalysts. As mentioned at the 2005 NPRA Annual Meeting in San Francisco, Topsoe announced as early as in 1984 at a conference in Portugal that it is possible to enhance the activity on a hydrotreating catalysts by modifying the active Co-Mo-S structure. To distinguish between the "old" and the "new" structure, Topsoe's researchers named them "Type I" and "Type II". This discovery of Type II was a big step in the development of more active hydrotreating catalysts, and not only Topsoe but virtually all catalyst vendors have since then developed new catalyst preparation technologies to produce catalysts that contain Type II active sites.

Type II sites have thus been known for more than 20 years and there has been a continuous progress in catalyst development since these sites were first discovered. However, although the catalysts from several vendors all contain Type II sites, they are not produced with the same preparation technology, and it therefore stands to reason that the various catalysts will behave differently upon regeneration:

Topsoe´s TK-574 (CoMo) and TK-573 (NiMo) Type II catalysts, which were commercialized in the late nineties, are still today installed in and sold to a large number of ULSD hydrotreaters. These catalysts will typically exhibit 4-6°F lower activity compared to fresh catalysts after a conventional regeneration. Depending on the flexibility of a specific ULSD hydrotreater this can be sufficient activity for a reload. Other vendors have reported that ULSD catalysts lose a significant amount of the original activity after a conventional regeneration and will thus require a special post-treatment to achieve an acceptable activity recovery.

Topsoe's newest ULSD catalysts, TK-576 BRIM™ and TK-575 BRIM™, which incorporate our new BRIM™ activity sites as well as Type II activity sites, have been regenerated with good results. However, to maximize the activity of the spent TK-576 BRIM™ and TK-575 BRIM™, Topsoe recommends reprocessing the catalyst using "ReFRESH™," Topsoe's proprietary reactivation method, which practically restores the catalyst to its original activity.

Using Topsoe's reactivation method enables the refiner to use our newest ULSD catalysts more than once for maximum economical benefit to the refiner.

Question 66
ULSD catalyst suppliers reported expansion plans in 2005. What is the status of these announced plans and how will they affect catalyst supply and lead times for ordering catalyst?

Tom Kiliany (ExxonMobil R & S)
Several companies have announced catalyst plant expansion plans, including Criterion and Albemarle.

Larry Kraus (Albemarle Catalysts Co.)
Albemarle is currently in construction of its newest world scale HPC manufacturing facility in Bayport, Texas which is scheduled to be on-stream in the first quarter of 2007. This facility will enable Albemarle to continue to meet the growing demand for its leading technology HPC products, and further support the refining industry's objectives of producing clean fuels and processing heavier feedstocks. Albemarle expects that demand for top performing HPC products will continue to increase on a global basis for the foreseeable future, and therein we recommend to our clients that they continue to focus on 6+ month lead-time for HPC catalyst to ensure that they are able to obtain the optimal HPC system for their applications.

Ted Hallen (Haldor Topsoe)
Topsoe is in the process of expanding and modifying our manufacturing facility in Denmark. The expansion, which will be fully implemented before the end of 2006, will result in a 60% increase in capacity and additionally allow us to make some products that hitherto we have only

produced in our Houston facility. In addition, Topsoe has plans for revamping our plant in Houston. In the short term, we expect these measures to ease the supply problems that we have had in the past year and reduce our backlog from the peak of 10-12 months in late 2005 and early 2006 to a more manageable lead time of about 4 months.

ULSD

Question 67
How has ULSD catalyst performed relative to predicted performance? What monitoring tools are you utilizing to optimize unit performance and determine end-of-run for ULSD catalyst?

Ted Hallen (Haldor Topsoe)
Topsoe ULSD catalysts are currently installed and operating in more than 80 ULSD units worldwide. About 45 of these units were licensed by Topsoe's Hydroprocessing Technology Division. Practically all of the units have started up, and they are all operating satisfactorily and met predicted catalyst performance criteria. Only one unit has had problems related to feed contamination and not related to the catalyst performance.

As part of our Tech Service package, Topsoe uses our proprietary models to analyze unit data sent on a regular basis by our customers. This analysis results in a series of plots on unit performance, and, in particular, a normalized relative activity and normalized WABT plot that is used to determine the remaining run length on the catalyst charge.

Question 68
Describe you experience producing ULSD in a single bed or an undersized reactor.

Paul Zimmerman (UOP)
The task is challenging, especially if the unit is also at low pressure. However, ULSD has been produced in single bed hydrotreaters. For example, one single bed unit operating at ~650 psig and >3.5 LHSV has been meeting ULSD targets for several years. Feed, however, is straight run diesel with no cracked stocks. To make sulfur specs, the feed is cut with straight run kerosene to sufficiently reduce desulfurization severity. The kerosene requirement was reduced substantially by retrofitting with an UOP UltraMix liquid distributor above the bed and by using a stacked bed catalyst loading of CoMo catalyst over NiMo catalyst.

Ted Hallen (Haldor Topsoe)
It is possible to produce ULSD in a single bed reactor, depending upon the difficulty of the feedstock and the cycle length that is desired.

Three factors to consider are:

1. More reactive feedstocks consume more hydrogen very quickly which results in high heat release and temperature rise.
2. The maximum reactor operating temperature is reached sooner in a single bed reactor resulting in shorter operating cycles.

3. Flow distribution can degrade through a long catalyst bed which reduces catalyst utilization through the reactor. This can be somewhat mitigated by installing a high efficiency distribution tray at the top of the reactor

Although it is possible for ULSD to be produced in single bed reactors, single bed reactors are not found in newly designed ULSD units due to the three limiting conditions listed above.

Refiners may elect to use existing single bed reactors. In such cases they will be more successful if they select easier feeds that require less hydrogen for the three reasons identified. In such cases, a high activity catalyst such as Topsoe's TK-576 BRIM^{TM}
catalyst will be advantageous, as it will give the lowest SOR temperature.

One of our customers has used Topsoe's TK-576 BRIM^{TM} catalysts in single bed units with success. In these units, the refiner is using SR feeds to minimize the temperature rise and extend run length as much as possible.

Question 69
Are you using a hydrocracker to produce ULSD? If so, how is it integrated into your operation?

Paul Zimmerman (UOP)
The hydrocracker is well-suited for producing ULSD because it produces highly saturated products with very low sulfur. The majority of hydrocrackers outside of North America are producing ULSD from the diesel product. Most of these units are standard hydrocracking flow schemes processing VGO feeds. Some have more difficult feed components such as cycle oils, coker gas oils, or de-asphalted oil. Within North America, most hydrocrackers primarily produce naphtha but ULSD production is growing.

In addition to the traditional hydrocracking flow schemes, there are also novel flow schemes that allow integration of hydrotreating with the hydrocracker. UOP has designed parallel reactor systems that allow one reactor to hydrotreat diesel to produce ULSD and the other reactor for hydrocracking to convert streams like LCO to gasoline. Also, UOP's HyCycle and APCU flow schemes allow co-processing diesel for ULSD production in a finishing/post treating reactor. These flow schemes take advantage of engineering innovations of an enhanced separator (EHS) to separate hydrocracked products and heavy unconverted oil from hydrocracking section so that lighter products and additional diesel can be hydrotreated in the post treating reactor. The flow scheme makes use of recycle gas and heat from the main cracking reactor section.

Question 70
How do you handle cracked stocks in ULSD units? Please discuss the percentage of cracked stocks in your ULSD unit feedstock. Describe your practices for "phasing in" cracked stocks in an ULSD unit.

Paul Zimmerman (UOP)
It is a UOP practice to avoid subjecting fresh catalyst to a severe service in the initial operation after catalyst sulfiding. This is because during the catalyst induction period, the catalyst sites are susceptible to accelerate coking reactions. Managing the period of straight run feed processing

and avoiding highly deactivating feeds such as cracked stocks or heavy feeds reduces coke precursors on the catalyst.

UOP recommends operating on straight run feedstock for the first three days minimum and preferably the first seven days. Once the period of straight run feed processing is complete, the best practice is to gradually transition to a blend of cracked stock and straight run feed. UOP recommends about two weeks of blend stock processing with increasing cracked stock portion in 25% increments in the blend spread over the interim period. After the initial three weeks, the operating severity can then be increased to design conversion with design feedstock.

Dr. Pierre Dufresne (Eurecat, S.A.) and Dr. Nilanjan Brahma (Eurecat U.S.)
The general advice is not to introduce any cracked feedstock for the first 3 days after startup in order to prevent premature coking of the active sites. A suitable alternative available from Eurecat is a catalyst pretreatment especially tailored for this application. Called TOTSUCAT CFP, this presulfiding and activation treatment allows cracked feeds to be directly introduced to the unit during start up at 120-250F without the need for additional straight run feed. With Totsucat CFP, the unit will produce on spec product using cracked feeds at startup without adversely affecting cycle length.

Ted Hallen (Haldor Topsoe)
The reactivity of each individual stream in the feedstock blend should be carefully determined in order to select the optimal catalyst system and operating conditions for a given ULSD hydrotreater.   I would refer you to our answers on question 63 regarding catalyst selection. The amount of metals/contaminants in the cracked fractions (for example Si in the coker fractions) will also contribute to accelerate the catalyst deactivation and therefore these contaminants should be carefully considered in the choice of the catalyst system.

Virtually all of Topsoe's ULSD catalyst applications in North America include FCC cycle oil and/or light coker gas oil as feedstock components. Worldwide, 40 out of 80 ULSD units using Topsoe's catalysts process cracked feeds. The percentage of cracked stock varies widely from about 15% up to 100% of the total charge. A representative summary of ULSD feed compositions from recent Topsoe licensed ULSD technology projects in the U.S. are tabulated below.

Unit	A	B	C	D	E	F
%SR Distillate	84	55	64	74	42	60
%LCO	-	45	17	26	29	40
%LCGO	16	-	19	-	29	-
Sulfur Content, wt%	1.0	0.4	1.7	0.7	1.2	0.7

Topsoe specifies that the catalyst is sulfided with straight run distillate in either once-through or recycle mode. Following the activation procedure, ULSD conditions are immediately established with the straight run feed. Topsoe recommends that the introduction of cracked stock to the unit be delayed by 48 hours following line out of the SR feed. After this initial delay, the cracked feeds are slowly introduced in step wise fashion and reactor temperatures increased as required to maintain the ULSD product sulfur target. In the first days of operation, freshly

sulfided catalysts exhibit higher than normal aromatics saturation activity together with corresponding increased hydrogen consumption and heat release. Especially with cracked feeds, it is possible to see hydrogen consumption exceed makeup supply during this initial highly active phase of operation and the addition of cracked stock should always be managed to avoid loss of hydrogen pressure in the unit.

Our experience shows that ULSD applications can be lined out with complete introduction of cracked stocks in three to four days following presulfiding. This philosophy has resulted in successful startups of all of our ULSD projects with catalyst activity and resulting stability in line with the predicted performance.

Question 71
How have the qualities/properties of FCC light cycle oil (LCO) changed following implementation of high severity FCC feed hydrotreating? Is it easier or harder to process the LCO into ULSD?

Paul Zimmerman (UOP)
The LCO sulfur content will vary with feed sulfur, and while the LCO sulfur wt% will decrease with more severe feed hydrotreating, the percent of feed sulfur that appears in the LCO product will be higher relative to the feed. This is because hydrotreating removes the lighter sulfur species first, so the remaining sulfur species are more likely to appear in the heavier FCC products. For straight run VGO, the LCO wt% sulfur content is almost a 1:1 ratio with feed wt% sulfur (1 wt% S VGO and 1 wt% S LCO). With severe hydrotreating, the LCO wt% sulfur can approach a 2:1 ratio with feed wt% sulfur (0.08 wt% S VGO and 0.15 wt% S LCO).

A cleaner feed with higher hydrogen content will allow the FCC unit to operate with a higher conversion, so the LCO yield generally will decrease. The aromaticity of the LCO is controlled more by the FCC operating conditions and catalyst properties than by feed quality, so with a constant boiling range product and constant catalyst type, this will not change very much. LCO is generally difficult to process to ULSD. This is due in part to the higher concentrations of difficult to convert sulfur compounds and in part to the presence of poly-aromatics which have been identified as inhibitors in ULSD operations. However, as a general rule, the LCO produced from a hydrotreated FCC feed is easier to achieve ULSD sulfur requirements than from an unhydrotreated feed. There may be cases depending on the FCC operating conditions (very high FCC conversion, high riser temperature, certain FCC catalysts used) where it would be more difficult to achieve cetane requirements.

Tom Kiliany (ExxonMobil R & S)
Most, if not all, of the U. S. West Coast refineries have some form of FCC feed hydrotreating due to gasoline specifications mandated by the California Air Quality Management District (CaAQMD). Many of the FCC feed hydrotreating units have been on stream for 15 or more years, thus providing a very good data base of experience. The properties of LCO after startup of a FCC feed hydrotreating unit are improved depending upon hydrotreating severity, for example, a 80-90% reduction is sulfur content, a 40-50% reduction in nitrogen concentration. The aromatic content of the LCO increases because the FCC is operated at a higher conversion to naphtha. Subsequent processing of the LCO into ULSD is easier from total sulfur content, but to

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accurately predict the hydrogen consumption, the increase in aromatic content needs to be considered.

Larry Kraus (Albemarle Catalysts Co.)

It is well known that producing ULSD with cracked feedstocks like LCO and coker distillate is much more difficult than with straight run diesel feeds. The main factors causing this increased processing difficulty are higher contents of nitrogen, aromatics, and sterically-hindered sulfur.

The effects of high severity FCC pretreatment on FCC operation are well understood. Reduced nitrogen and increased hydrogen contents of the FCC feed allow the unit to operate at higher conversion. Also, the sulfur contents of FCC products are lower and the aromatics contents of cycle oils are higher.

Does the benefit of lower sulfur in LCO from a severely hydrotreated feed overcome the negative effects of higher aromatics content? This is a difficult question to answer because there is rarely a case where a FCC unit operates with a feed composed of untreated and severely hydrotreated material. By inference between LCO's originating from different FCC units, we conclude that the negative effect of higher LCO aromaticity more than offsets the benefit of lower LCO sulfur content. In practice these effects are difficult to compare because the volume of LCO produced from highly hydrotreated FCC feed is less than that from unhydrotreated feeds.

The above assumes 100% hydrotreated FCC feed, which is seldom the case.
When hydrotreated feeds are blended with unhydrotreated feeds the net effect is typically negative for LCO treatability to ULSD. The partially hydrotreated FCC feed can be operated at significantly higher conversion than unhydrotreated feed, increasing LCO aromaticity, while sulfur content remains relatively high due to the high sulfur content of the unhydrotreated feed. This is the worst of both worlds and, in our experience, results in some of the most difficult LCO's to hydrotreat.

Question 72
Have you used hydrocracking catalyst in the last bed of an ULSD unit to improve performance such as desulfurization or aromatic saturation? Describe your experience.

Paul Zimmerman (UOP)

Depending upon the nature of the feed stock, hydrocracking catalyst in the last bed of a hydrotreating unit can give an advantage in aromatic saturation and reduction of multi-ring aromatics to allow ULSD production. The chemistry that enables this is by ring opening from the cracking function. Acidity of cracking catalyst also enhances desulphurization for refractory hindered sulfurs present in streams like LCO.

However, there are several considerations that need to be taken for this approach. First, the hydrocracking catalyst must be selected to balance activity with the hydrotreater operating temperature, pressure, LHSV, and deactivation rate. If the activity is incorrect for the operation, then it will either not be active enough for the desired cracking and ring opening reactions or it will be too active causing excessive cracking or even a temperature runaway. Unit design also needs to be evaluated for controllability of hydrocracking reactions, such as quench rate, bed

size, temperature rise, and emergency systems. Startup and emergency procedures may need to be modified.

One unit uses HC-24 hydrocracking catalyst in the bottom of a hydrotreating unit processing a blend of LCO and LGO at about 1000 psi hydrogen partial pressure. The objective is to improve cetane through API upgrade by running low conversion in the cracking bed. Although it would have been desirable, pilot plant confirmation was not done before loading the hydrocracking catalyst. The first load had a small amount at the bottom of the reactor. Subsequent cycles have used greater amounts of hydrocracking catalyst based on experience with its performance.

Tom Kiliany (ExxonMobil R & S)
We have examined the possibility of using hydrocracking catalyst in the last bed of ULSD units and decided that it was not suitable for our configuration.

Question 73
How do you handle off-spec product when producing ULSD? Are off-spec products immediately routed to different tankage or are other options considered? When making these decisions, are you relying on lab data or an on-line analyzer?

Paul Zimmerman (UOP)
ULSD specifications allow almost no margin to correct off-spec product so product quality must be monitored closely. In some operations, off-spec product is recycled. Alternatives include off road diesel blending, slop oil and hydrocracker or FCC feed.

One refiner has installed analyzers in the tank farm in addition to the analyzer on the ULSD unit product rundown. They have identified issues with product contamination in transfer piping and storage which they want to be able to flag prior to the tank final QA before shipment.

Question 74
Does the actual (post start-of-run) hydrogen consumption in your ULSD unit(s) match the design conditions? Have you had to rebalance your hydrogen system?

Tom Kiliany (ExxonMobil R & S)
Good agreement between actual hydrogen consumption versus the projected hydrogen consumption based upon the design conditions for Ultra Low Sulfur Diesel (ULSD) units has been observed. This is not surprising given the large experience base with 500 ppmw sulfur product diesel units. The additional hydrogen necessary for heteroatom (sulfur/nitrogen) removal from 500 to 15 ppmw sulfur is incremental and readily calculated. The larger factor in predicting hydrogen consumption of ULSD units is the aromatic saturation needed to convert the remaining more refractory sulfur containing molecules, for example benzothiophene and dibenzothiophene. Combinations of modeling and pilot unit test runs were used to design ULSD units.

As for rebalancing the refinery hydrogen system as a result of ULSD implementation, the results range from small adjustments to more complex changes. Some refiners have had to purchase/make significant quantities of additional hydrogen.

Process

Question 76
When processing unusual feedstocks such as aromatic extracts from lube oil processing, de-asphalted oils (DAOs), low-metal resids, etc. in hydroprocessing units, what issues have come up (e.g. poly-nuclear aromatics condensation, excessive hydrogen consumption, severe deactivation, etc.)? What reliable correlations or analyses are available to characterize unusual feedstocks, predict their hydrogen consumption, yield pattern, and product quality, etc.?

Paul Zimmerman (UOP)
There are many types of feeds that are difficult to process in a hydroprocessing unit. In addition to the feedstocks mentioned in the question, we could also consider heavy cycle oils, coker and visbreaker gas oils, and difficult crude sources such as Maya or Synthetic crudes. The capacity to process unusual stocks such as these is obviously plant specific and depends on the exact nature of the stock and the percent inclusion in the feed. The bulk properties of the feed blend are not sufficient to evaluate the ability to process. The source and properties of each of the feed components needs to be considered. Often, individual compound classes may need to be analyzed to properly characterize very difficult feedstocks.

Lube extracts are not common feed components in hydroprocessing units. The concentrated presence of multi-ring aromatics can result in significantly increased coke deactivation rates, especially in recycle hydrocracking units. Light extracts can be processed at very modest concentration levels in some once-though hydrocrackers and hydrotreaters, but with an adverse impact on cycle length. For example, a hydrocracking unit increases deactivation rate about 4 times greater when processing up to 10% lube extract compared to 100% straight run VGO processing. The ability to process a light extract can be assessed by an evaluation of the SimDist 98% point, the 4-ring & 5-ring aromatic content, carbon residue, and nitrogen content.
DAO has been included in hydroprocessing feed blends. The quality of the DAO must be closely managed so as to adhere to metals, carbon residue and asphaltene specifications. Successful processing requires proper catalyst selection including an appropriate loading of demetalization catalysts for quantitative metals removal upstream of the main treating beds. In hydrocrackers, catalysts must be capable of converting the heavy end of the DAO. Unit configuration and design also needs to be considered. In recycle hydrocracking applications, a mechanism of HPNA rejection is necessary to avoid accelerated coke deactivation of the cracking beds.

Some units have processed VGO from a resid hydrotreater. Compared to a straight run VGO, the bulk properties of VGO from a resid hydrotreater may seem benign with modest levels of nitrogen, low sulfur, and low multi-ring aromatics. However, conversion of nitrogen compounds into the VGO boiling range results in more complex compounds than seen in straight run VGO. As a result, this nitrogen is very refractory requiring significantly higher hydrotreating temperatures. HPNA formation in the hydrocracking catalysts is also much higher. Substantially higher deactivation rates have been observed on hydrotreating catalysts when processing VGO from a resid hydrotreater.

Question 77

What do you do to take a hydroprocessing unit to a "safe condition" for interruptions that you expect to be brief, e.g. a power outage that may last a few hours? What do you do for a smooth recovery to full operational status? What do you do differently when the interruption may last 3-4 days or more?

Paul Zimmerman (UOP)

UOP believes each operation interruption should be examined on a case-by-case basis depending on the duration and cause of the shutdown and other refinery logistics. It is prudent to determine the specific safe condition for each interruption scenario, planned or unplanned, instead of applying a global safe condition to all the interruptions. In developing the specific safe conditions, the main objective is minimizing catalytic reactions, which is usually achieved by lowering catalyst temperature to a non-reactive point and removing feed. Once reactor temperature is lowered to a safe level, the next consideration depends on the duration and type of the interruption. Holding operating pressure and/or maintaining gas circulation at low temperature are preferable and acceptable as long as the interruption is brief and can be maintained safely. Power outage is an emergency requiring a response specified in emergency procedure.

The fractionation section should also be included in the planning for the safe condition. If possible, the fractionation can be placed in a closed loop warm circulation for a short period to allow a smooth recovery once the reactor section is on-stream again. If the circulating liquid is heavy with high pour point issues, then replacing the high pour point liquid in the circulating stream may be necessary. Finally, if a closed loop fractionation section circulation is not feasible, then it will need to cool down, stop flow, and hold levels until restart.

A shutdown during catalyst activation is a special case since that is when the catalyst is most vulnerable to damage. To prevent reduction of the metals, it is critical reduce the temperatures to below 400°F, preferably less than 350°F. If safe and feasible, H_2S should be maintained in the recycle gas. To proceed with activation, an additional amount of sulfiding agent may need to be obtained to account for losses during shutdown and restart.

Tom Kiliany (ExxonMobil R & S)

If a hydroprocessing unit has a power interruption of a known short duration, then, in general, the catalyst temperature should be lowered to stop the chemical reactions especially coking. Depending upon the configuration of the unit, one of the following conditions exist;

Make-up gas compressor(s)	Recycle gas compressor(s)
1) Electric driven	Electric driven
2) Electric driven	Steam driven
3) Steam driven	Electric driven
4) Steam driven	Steam driven

For the first condition, the unit would have to be depressured to flare to prevent catalyst and potentially reactor vessel damage due to high temperature.

For the second condition, the steam driven recycle gas compressor would have to be increased to maximum flow to cool the catalyst temperature.
For the third condition, the steam driven make-up gas compressor would have to be increased to maximum flow to cool the catalyst temperature.
For the fourth condition, the catalyst temperature could be slowly reduced to stop the desulfurization reactions and await restoration of electric power.

To restore to full operational status, restart any electric driven compressor(s), restart the liquid feed (at low temperature) and relight the feed furnace. Increase the catalyst temperature until specification product is obtained.

If the power interruption is of three to four day duration, then initially the steps taken above would still be completed. Next the temperature of the catalyst would need to be lowered to less than 400°F to prevent reduction of the sulfided active sites on the catalyst.

Ted Hallen (Haldor Topsoe)
The measures to be taken in case of upsets in a hydrotreating unit requiring (or resulting in) a shutdown very much depend on the reason for the upset (power failure, pump trip, compressor trip, etc.). The automatic emergency shutdown system (EPS) should be carefully programmed according to trip diagrams, cause and effect diagrams, etc. to safely and as quickly as possible bring the unit in a stand-by position where risk of injury to personnel and damage to equipment and catalyst is minimized.

A normal shutdown is a controlled cooling of the reactor and removal of oil from the catalyst. It is recommended to cool the catalyst to 480°F before sweeping oil from the catalyst. In case of short-term shutdown, it is recommended to cool the reactor to 400ºF, while maintaining the normal operating pressure as to facilitate a smooth restart of the unit. However, for long-term shutdowns (more than 2 days), it is recommended to depressure, add nitrogen, and further cool the reactor.

In order to protect the catalyst from damage, especially during emergency shutdowns, it must be kept in mind that the catalyst may be damaged by:

1) Hot hydrogen without hydrogen sulfide or oil
This will tend to strip sulfur from the active/sulfided catalyst and at prolonged exposure to these conditions, there is a risk of reducing the metal sulfides to free metals with consequent permanent loss of catalyst activity.

The risk of reduction of the catalyst is much greater when it is in the oxide state during a time when it has been presulfided and you are in shutdown or emergency shutdown operation.

A short example from a start-up of what can happen. We are aware of one refiner that loaded a small amount of ex-situ presulfided catalyst in the bottom of a reactor, but the majority of the catalyst load was not sulfided. During the sulfiding step on the start-up of the unit, the refiner noticed H_2S breakthrough shortly after the start of heat-up and therefore continued raising temperature. However, the breakthrough was only the result of H_2S evolution from the small

portion of ex-situ presulfided catalyst and H_2S was not uniformly present throughout the reactor. The result of prematurely raising the temperature was a reduction in the metals on the catalyst back to their metal state and on lineout with fresh feed the catalyst performance was about 60% below expectations.

2) Hot oil without hydrogen
Operating with hot oil on the catalyst without any hydrogen will result in coke formation on the catalyst, leading to loss of catalyst activity and increased pressure drop.

3) Contact with water
Exposing the catalyst to liquid water or high water vapor concentrations at elevated temperatures can result in loss of catalyst strength. Therefore, any slugs of water in the reactor inlet streams must be avoided.

4) Back-flow
Back-flow through the reactor must be avoided due to the risk of lifting of the catalyst bed and support.

Question 78
What options are available for low pressure hydrotreaters (total pressure < 500 psig) for production of ULSD and low aromatics products? What is the quantity and quality of the LCO that can be processed in these low pressure units?

Paul Zimmerman (UOP)
The feedstock that can be processed in low pressure (<500 psig total pressure) hydrotreating units to produce ULSD or low aromatics products is mostly limited to straight run diesel. Light cycle oil contains much higher concentrations of polycyclic aromatics and refractory sulfur compounds than straight run material. This makes it difficult to process a typical LCO in a low pressure unit to produce ULSD or a low aromatic product. The primary issue plaguing low pressure hydrotreating units is thermodynamic equilibrium limitations. Aromatic saturation is exothermic and reversible, and is therefore subject to equilibrium limitations. The potential also exists for thermodynamic equilibrium limitations to dictate the lowest achievable product sulfur and nitrogen concentrations when operating at low pressure.

The reversible stop of the hydrogenation route for desulfurization of sterically hindered sulfur species, such as substituted dibenzothiophenes, is the saturation of at least one of the aromatic rings of the sulfur containing heterocyclic aromatic compound. Data has shown that the temperature response can become sluggish in low pressure units suggesting an equilibrium effect may dictate the low achievable sulfur concentration. As pressure increases, the temperature response is much better allowing production of ULSD. These data highlight the impact that pressure has on the position of the equilibrium and the potential problems that may be encountered when attempting to produce ULSD in low pressure hydrotreaters.

Hydrodenitrogenation (HDN) can play a significant role in ULSD production due to inhibition of HDS by organo-nitrogen. The nitrogen compounds of primary concern are nitrogen containing heterocyclic aromatic compounds. Hydrogenation of the nitrogen containing aromatic ring is

required before nitrogen extraction is possible. As such the rate of nitrogen removal can be impacted by the hydrogenation equilibrium, decreasing under conditions where hydrogenation is not favorable. If the nitrogen concentration ceases to decrease with increasing temperature due to the thermodynamic equilibrium, the HDS activity will be adversely affected.

The options available for low pressure hydrotreaters are very limited when ULSD and low aromatics products need to be produced. The extent of aromatic saturation, desulfurization, and denitrogenation will be limited at low pressure, particularly at end-of-run when the reactor temperature is elevated. The minimum achievable sulfur level is influenced by numerous factors including concentration of sterically hindered dibenzothiophenes, nitrogen content, hydrogen partial pressure, space velocity, and catalyst type. There may be reason to believe that the aromatic content of the feedstock ought to be added to the list of factors influencing the minimum achievable sulfur level at a given pressure. In light of these factors and the equilibrium considerations discussed, the feedstock that can be processed at low pressure to produce the desired products is mostly limited to straight run diesel. Low amounts of LCO may be processed in some units depending on these factors.

Ted Hallen (Haldor Topsoe)
It is well known that the catalyst has to remove the sterically hinderered sulfur compounds to produce ULSD, and that this can be accomplished via the direct desulfurization route or via the prehydrogenation route. Desulfurization via the prehydrogenation route is fast, and if it is thermodynamically possible this is the preferred route. However, in oil there exist specific basic nitrogen compounds which absorb to the hydrogenation sites on the catalyst, and until these nitrogen compounds have been removed the desulfurization will occur via the slower direct route. At low operating pressure and/or if the concentration of feed nitrogen is high it is not possible to convert the inhibiting nitrogen compounds to ammonia, and then it only possible to make ULSD using the direct route. Basically, the preferred catalyst in a low pressure ULSD hydrotreaters therefore has a high activity for desulfurization via the direct route and it is especially important that the activity of the direct desulfurization sites are high if the feed also contains cracked material as this will increase the concentration of inhibitors.

Topsoe's licensed technology has been used for the design or revamp of 45 hydrotreaters producing diesel with less than 10 wtppm S, and 4 of these ULSD hydrotreaters operate at a pressure below 500 psig. In addition, we have many loads of catalysts installed in non-Topsoe licensed ULSD hydrotreaters, which also are operated below 500 psig. In these hydrotreaters, CoMo catalyst (either TK-574 or TK-576 BRIM™) is used. Both types are developed by our researchers with a dedicated effort to maximizing the activity for the direct desulfurization and as such they are indeed suitable for ULSD production at low pressure even if the feed contains LCO. The amount of LCO that can be blended in the feed will depend on the LHSV and hydrogen availability, but typically it is in the range from 10-25%.

In these units, saturation of aromatics is equilibrium-limited, and, with hydrotreating at 500 psig or lower, mono-aromatics are not saturated.

Question 79
What experiences have you had with high pressure drop in a reactor's lower bed? What were the likely causes? Do you have any effective techniques for preventing it?

Jean-Luc Nocca (Axens North America)
Axens has seen pressure drop build in the lower bed of CFH units, especially when processing high end point feeds. We have identified the cause to be heavy molecules lay down in the later sections of the Hydrotreater where there is insufficient Hydrogen to continue the break down of these molecules as well as smaller pore structure catalysts which have diffusion limitations.
As the temperature is increased, such molecules tend to break down into large poly-condensed molecules resulting in poor compatibility with the partially hydrotreated feed. They lay down on the catalyst forming coke, resulting in delta P issues.

A catalyst arrangement with a staged pore size design has been very effective in a number of units to alleviate this problem and significantly increase cycle length.

Paul Zimmerman (UOP)
Pressure drop normally builds up on the lead bed. When a lower bed has high pressure drop, the first item to check is if the readings are correct and making sure the instruments are functioning properly. However, pressure drop problems in a lower bed of a multi-bed reactor are more common than might be expected.

The most prevalent cause for high pressure drop in lower beds seems to be the accumulation of fines; in most cases iron sulfide fines. Iron sulfide particles are small enough to be swept through the catalyst beds by the momentum of the process fluid. These particulates may drop out in a lower bed in a zone of low liquid to vapor or at a dry point. A change in flow direction, such as around an outlet collector has been identified in several instances as the cause for iron sulfide fines accumulation. Small particles can also filter out when passageways become constricted, such as from a smaller catalyst size or dense loading. In some cases this is due to significant coking associated with high bottom bed operating temperatures, typically at end of run. Once fines start to deposit, they serve as a filter for further accumulation. In a few cases, hydroprocessing catalyst fines or FCC catalyst fines have been the cause of lower bed pressure drop.

Excessive coking in a catalyst bed has also been linked to high pressure drop. Massive coking is often the result of a temperature runaway; which in some instances has been known to fuse catalyst. Consequently, in cases of severe temperature runaway, UOP recommends dumping and screening the catalyst. Extensively damaged catalyst will need to be replaced.
Loss of catalyst containment often leads to quench distributor tray plugging and elevated pressure drop. This kind of pressure drop increase is usually more abrupt.

The best prevention to avoid pressure drop problems in any catalyst bed includes feed filtering, proper internal cleaning and installation, and proper catalyst selection and loading.

Technical Memorandum: NPRA Hydroprocessing Q&A Panel

18-September-06

From:	Luke Byerly - Criterion Catalyst and Technologies
To:	Hydroprocessing NPRA Q&A Panel

Subject: High Pressure Drop in Lower Bed of Reactors

	Pressure Drop Increases At Reactor Bottom		
	Cause	**Effect**	**Prevention Technique**
1	Hydrogen Starvation	Increased Pressure Drop due to Accelerated Coke Formation (Coke Balls)	Implement Necessary Alarms to ensure hydrogen purities and hydrogen to oil ratios are always above a specified minimum (online H_2 analyzer). If these minimum specifications are not met, decrease charge, remove cracked stock, increase hydrogen purity, or increase hydrogen flow.
2	Faulty/Damaged/Improperly Installed Outlet Collector	Catalyst migrates to downstream Heat Exchangers causing increased pressure drop in the bottom bed of the reactor. Outlet collector becomes plugged with catalyst/coke/debris and pressure drop increases in the reactor bottom.	Ensure refinery engineers and inspectors physically inspect the outlet collector. Ensure proper process and mechanical design is applied for new outlet collectors. Ensure current installations are still mechanically sound.
3	Dirty Screens at the Reactor Outlet	Reactor Outlet Screens that have not been properly cleaned can cause high SOR pressure drop at the reactor bottom. Depending on the severity of the pressure drop, early shutdowns can occur.	Ensure refinery process engineer physically inspects the screens. It is the process engineer's job to ensure there are no problems with the outlet screens.
4	Faulty Catalyst Loading (poor loading, material left in reactor, etc…)	SOR Pressure drop is usually higher than design. Either maximum rates cannot be achieved, or pressure drop eventually becomes to high. Either scenario causes an early shutdown.	Ensure Catalyst Loading Company has a good reputation. Refinery Process Engineer should oversee the loading. Take regular outages to ensure the beds are level and no debris is left in the reactor.
5	Significant Residual Oil Entrainment	If the Asphaltene content is high during a severe operation (70-80% Aromatic Saturation), the asphaltenes can precipitate out of solution and eventually agglomerate. This can cause a pressure drop increase at the reactor bottom. It tends to occur at the reactor bottom because aromatic content is the lowest in that location.	Refinery should routinely monitor VGO color (at least weekly). If the VGO color is greater than or equal to 7, resid is entrained in the VGO.
6	Faulty/Damaged support grid in interbed of reactors	If support grid/screens are installed improperly or are damaged during a turnaround, catalyst can migrate/collapse into the quench zone/distributor region. The gas quench can cause catalyst attrition and fines generation. As a result, increased pressure drop in the reactor bottom can occur	Ensure refinery engineers and inspectors physically inspect the reactor internals . Ensure proper process and mechanical design is applied for new installations. Ensure current installations are still mechanically sound.
7	Operational Upset Causing a Pressure Reversal (Catalyst is "fluffed")	Unplanned shutdowns or equipment failures can cause the reactor pressure to switch (Pressure is higher at the Reactor outlet). As a result, flow is reversed abruptly. The catalyst is "fluffed" causing severe mal-distribution and possible reactor internal damage. As a result, pressure drop increases can occur at the reactor bottom. A decrease in catalyst activity can occur as well.	It is difficult to design for upset conditions or abrupt shutdowns. However, check valves are recommended in necessary locations (unit dependent).
8	Debris/Foulants in Quench Hydrogen	Iron Sulfide scale and other contaminants can enter with the quench hydrogen. This can result in an pressure drop increase at the lower section of the reactor.	Routinely sample the quench hydrogen (if possible). Install Duplex Strainers so the quench hydrogen is continuously filtered, and it can be cleaned online.
9	Dry Point Operation/Low Liquid Flow	Dry Point Operation can cause low liquid flow that can deposit micro-particulates and begin void fraction reduction. Low Liquid mas flux can cause poor flow distribution and can result in hot spot. Hot spots can lead to increase in Pressure drop.	Ensure the Liquid Mass Flux is greater than 2000 pph/ft^2. Be aware of % vaporization at reactor outlet.
10	Micro-Particle Migration	Specific types of crudes (especially synthetic) contain micro particles that are not removed by feed filters, grading, or main bed catalyst. As a result, these particles build up at the reactor bottom, and pressure drop increases occur.	Know which crude sources can cause these types of problems. Be cautious when purchasing these crude types. Chemical Injections may help keep these particles in solution.

Ted Hallen (Haldor Topsoe)

In Topsoe experience, most iron sulfide contamination problems can be effectively handled with a well designed graded bed using Topsoe's high void graded bed product line. In severe cases, we would recommend Topsoe's TK-25 or "TopTrap" a macro-porous product designed to capture fine particulates. Carbon deposit resulting in lower dP is usually the result of an operations upset or poor loading that leads to maldistribution.

More unusual causes of high pressure drop in a reactor's lower beds can be found in two types of units:

1. Fixed bed resid hydrotreating units
2. Hydrotreaters processing tar sands derived crudes.

In resid units, a problem that can occur is asphaltene precipitation. In this case, aromatics in the feed keep the asphaltenes in solution. As the run progresses, the percent aromatic saturation increases with the increasing temperature in the hydrotreater because of normal catalyst deactivation. Eventually, the aromatics concentration is decreased to the point where it is not high enough to keep the asphaltenes in solution, and they begin to precipitate. The aromatics are of course more saturated in the lower beds, and eventually the precipitated asphaltenes fill the void spaces in a lower catalyst bed, thus resulting in a noticeable increase in the pressure drop.

In tar sands processing units, we find that fine sand/clay particles precipitate in a similar fashion to that of asphaltene precipitation in resid units. Probably the unit most prone to lower bed delta P increase is the VGO hydrotreating unit. There are three possible mechanisms that have been postulated:

1. The fine sand/clay is suspended by the aromatics and as aromatics get saturated via the hydroprocessing environment the sand drops out in a lower bed.
2. The fine sand/clay is suspended due to molecular charges between the oil and the clay. Again, the hydroprocessing environment affects this molecular charge, such that the precipitation occurs in the lower bed of the unit.
3. The third mechanism is more related to the physical environment changing in the hydrotreater. Early in the run, a larger portion of the feed remains in the liquid phase. Therefore, there are higher liquid rates within the catalyst beds. These higher liquid rates have a high enough velocity to physically move the fine sand/clay entirely through the reactor. As the run progress, temperatures are raised increasing the percent vaporization of the feed. Therefore, the liquid rates are decreased and the sand/clay stops being washed through the bed but deposits much like a sand bar in a river bed.

Whatever the mechanism, it is best handled by shifting from dense loading to sock loading in the region/bed where the increase in pressure drop occurs. Also, one can shift to a larger sized catalyst particle in that particular bed. These actions will increase either the size of voids and/or the void space, allowing more room for the deposited material that is being precipitated.

Question 80
Are you using real-time optimization (RTO) of hydrotreater/hydrocracker operations based on on-line analyses of feed and product qualities? Do you adjust operating conditions based on catalyst activity/deactivation modeling?

Tom Kiliany (ExxonMobil R & S)
For some applications, such as ULSD, reliable on-line instruments exist and are being used to provide closed loop information to adjust furnace outlet temperatures at several of our refineries.

A catalyst activity/deactivation model is applied to nearly all units. In actual practice, operating conditions are adjusted based upon lab analysis of the unit products, rather than anticipating the change from a model prediction. This approach allows the catalyst activity model to be adjusted and improved or it identifies a need to double check lab results.

FCC

Environmental

Question 82
To what extent does electrostatic precipitator (ESP) performance decline over the operating cycle in terms of opacity trends and daily fines collection? Can a performance curve be generated assuming constant conditions (similar upstream processing, no change in regenerator cyclones performance, and well maintained insulator purge)?

(CSI Engineering)
Performance degradation of any FCCU electrostatic precipitator may be due to various factors. However, not all perceived degradation can be attributed to the ESP alone. Over a multi-year run, loss of regenerator cyclone performance may occur due to wear resulting in increased particulate loading to the ESP. Increased fines generation within the FCC process may increase particulate loading and decrease particle size, both of which affect electrical performance and stack emissions. If loading and conditions to the ESP are constant, performance degradation may or may not occur and the effects may vary widely according to the site and situation.

The most predictable change in ESP performance may take place during the first few weeks after flue gas is introduced to a clean precipitator. Clean collecting plates, clean discharge electrodes, and clean insulators together produce optimum, but non-sustainable, levels of performance. It is not possible, nor desirable, to maintain completely clean collecting plates: Some dust cake must be allowed to accumulate so small particulate can agglomerate for the ultimate removal. As catalyst dust accumulates on surfaces in the precipitator, sparking may increase, current may decrease, and the uniformity of the electrical field may be adversely affected. A fall-off in performance over the first few weeks is often evidenced by a slight increase in stack opacity and a reduction in transformer-rectifier power levels. After the initial period, performance may continue to decline and the cause of any decline, whether in the precipitator itself or upstream in the FCC process, may be difficult to identify.

One possible cause of long-term performance degradation is the depletion of charge-carrying ions in the collected dust layer. Under the influence of the electrical field, sodium ions may migrate within the dust on the collected plates. The ions move toward the outer dust surface where they are rapped off, leaving behind a sodium-depleted layer close to the collecting plate. This depleted layer develops high electrical resistivity that interferes with the electrical operation of the precipitator. The usual solution to sodium depletion is complete cleaning of the precipitator during periodic turnarounds.

ESP performance and efficiency are largely affected by the condition of the grids. The grids are susceptible to corrosion due to the presence of sulfates in the flue gas. Maintaining temperatures throughout the ESP that are above the dew point for a given sulfate concentration is critical. It is also important that the design of the ESP promotes even flow throughout the cells, avoiding any dead spots. Adequate insulation is also imperative to prevent any localized condensation.

Fouling of insulator surfaces may play a role in electrical degradation. Even with continuous insulator purge, some dust, carbon, and sulfuric acid may deposit on insulator surfaces, providing an alternate path for electrical current. The result may be increased sparking and decreased operating voltages. For this reason, it is essential to thoroughly clean the insulator surfaces whenever the precipitator is shut down for maintenance. During the run, it is important to monitor the volume, pressure, temperature, and reliability of the purge air supply.

Evacuation difficulties may result in overfilling of hoppers. Depending on the precipitator's gas flow distribution, overfilled hoppers may cause chronic electrical problems and increased opacity; the source of which can be difficult to identify and correct. A good-quality hopper design includes electric heating pad, well-installed thermal insulation, and gamma ray level detectors.

In precipitators with less than optimum gas flow distribution and poorly designed flow control devices, buildup on vanes, perforated plates, and horizontal surfaces may distort gas distribution, causing performance degradation. These problems can be corrected in the short term by cleaning of the precipitator. Long-term solutions may require redesign of the flow control devices.

Other causes of degradation may include inadequate maintenance, inappropriate transformer-rectifier control settings, variation in rapping, and inattention to operation requirements such as hopper evacuation, insulator purge, etc. Variation in ammonia injection rates for flue gas conditioning, where required, may be at fault. The precipitator is highly subject to fluctuations in process conditions and must therefore be continuously monitored to ensure that the ESP is tuned to the process and the process is amenable to good performance of the ESP. Regarding a performance curve, the operation of the ESP is so much affected by the above-mentioned factors that the premise of constant conditions is probably not realistic.

Question 83
Our side-entry regenerator dense bed has three temperature indicators (TI) whose readings are over 100°F apart (colder near the spent catalyst inlet). The unit has a modern air grid and a dense phase "ski jump" spent catalyst distributor. We use the average bed temperature in heat balance calculations. Typical temperatures are 1230-1315°F in the bed, 1290-1335°F in the dilute phase, 1350-1400°F at the cyclone outlets and 1405°F in the flue gas. Flue gas NOx is very low with less than 0.5 vol% O2 in the stack. What are the incentives for better bed temperature measurement and for reducing afterburn (and bed maldistribution)? What are the incentives for improving the spent catalyst distributor design? Will oxygen enrichment improve or worsen temperature differentials? How can we minimize the risk of increasing NOx emissions if we make any modifications?

Dalip Soni (ABB Lummus Global)
Improved spent catalyst distribution and discharge can reduce both afterburn and NOx emissions. ABB Lummus Global has revamped a unit of similar design with a relatively low cost spent catalyst distributor design that reduced afterburn by 15 degrees and NOx emissions by 50% at the same time reducing promoter addition by 50%.

Question 85
Selective catalytic reduction (SCR) units have recently been added to reduce NOx from the FCC stack. What issues may limit the SCR unit from matching the 5-year cycle length for the FCCU?

Joe Prince (Foster Wheeler USA Corporation)
One of the most significant issues to be addressed in the design of the SCR system is preventing the catalyst and revamped downstream heat recovery equipment from potential deposits of ammonium bisulfate and ammonium sulfate (ABS) particulates. The bisulfate particulate is the most troublesome because it is sticky and not effectively removed by soot blowing. These salts are formed by conversion of the sulfur trioxide in FCCU off gases. Its formation is directly related to sulfur trioxide and ammonia concentrations as follows:

Ammonium Sulfate and Ammonium Bisulfate form from the reaction of NH3, H2O and SO3.

Ammonium Bisulfate is a "Sticky" solid that is formed by the following reaction:

$$NH_3 \text{ (g)} + SO_3 \text{ (g)} + H_2O \text{ (g)} \rightleftarrows NH_4HSO_4 \text{ (l,s)}$$

Ammonium Sulfate is powdery solid that is formed by the following reaction:

$$2NH_3 \text{ (g)} + SO_3 \text{ (g)} + H_2O \text{ (g)} \rightleftarrows (NH_4)_2SO_4 \text{ (l,s)}$$
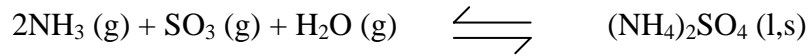
Because it is sticky, Ammonium Bisulfate tends to form deposits on the catalyst and heat transfer surfaces.

Preventing these deposits is accomplished by designing the SCR system to operate at sufficiently high temperatures to prevent formation of these salts, generally above 650^oF. Reducing excess air in the CO Boiler is also an effective way to reduce sulfur trioxide concentrations. In the heat recovery section, elevating boiler feedwater temperatures is an effective preventative method. Reducing the SCR's ammonia slippage is also very effective in this area. It is therefore critical to know the operating temperatures that will prevent these deposits and consider them in the SCR and heat recovery system revamp design. Unfortunately there is a wide variation in the research on this subject. Considering the variation in data, using the most conservative predictions is the best choice for the critical FCCU service.

Equipment

Question 91
The addition of wet flue gas scrubbers and possibly selective catalytic reduction (SCR) units increase the backpressure on CO boilers or waste heat boilers. What are the issues that must be considered if forced draft or induced draft fans are added to keep the existing boiler from being modified? Have you chosen to install fans in this service?

Patrick Bernhagen (Foster Wheeler USA Corporation)
Foster Wheeler has studied and revamped adiabatic combustor CO Boilers for higher backpressures needed due to WGS additions. The units require a review of the casing for the higher operating pressure, the burner usually requires replacement for the higher pressure and the FD fans must be replaced. In many cases 15 to 20" W.C. (or more) is added to the operating pressure for WGS.

CO Boilers require fans for the burners.

Question 96
What performance benefits have you realized from installing structured packing in an FCC catalyst stripper? What operating difficulties have you encountered? How many turnaround cycles has the packing been in service and what was the condition of the structured packing when inspected during a turnaround?

Dalip Soni (ABB Lummus Global)
ABB Lummus Global has developed next generation stripper internals that eliminate some of the drawbacks of structured packing. These new internals are based on the use of baffles that are arranged and oriented in such a way that all of the stripper cross sectional area is available for catalyst flow. These baffles are formed into Modular Grids that can easily be stacked one over the other. These new internals have been commercialized on a UOP stacked unit with a side stripper. Regenerator temperature dropped by 10°F even after reduction of stripping steam by 30 to 40 %.

Process

Question 102
What are the potential causes of excessive foaming and carryover in LPG liquid-liquid amine contactors?

(Aminetech and UOP)
There are several reasons for foaming/carryover in LPG contactors: High amine concentration may cause carryover due to higher viscosity resulting in difficult disengagement of the amine and hydrocarbon phases. The concentration at which carryover becomes excessive varies with each unit. Generally, however, concentrations over 40% can cause this problem. Another cause of carryover, also related to high amine viscosity, is a low lean amine temperature. This may be difficult to avoid, particularly if the lean amine also serves gas contactors which require low amine temperature to maintain adequate H2S recovery. Contamination with heat-stable salts can cause corrosion in the system resulting in fine particles of iron sulfide which aggregate at the

amine/hydrocarbon interface and hinder disengagement. Providing efficient solids removal via filtration is essential. If the amine is also being used to treat FCC or coker gases, the trace amounts of oxygen in these gases will accelerate the degradation of the amine. Likewise, the exposure of any amine to excessive heat in the regenerator will cause degradation products to form. One other thing to be aware of is that many of the newer high-molecular weight amines have a significant solubility in LPG. In a warm contactor, the amine will dissolve in the LPG and then, as cooling takes place in downstream equipment or tankage, amine will separate and drop out. This has frequently led refiners to think that amine is "carrying out" of the contactor when in actuality amine was in good condition and the contactor was operating just fine.

Another very common reason for amine carryover from LPG liquid-liquid contactors is variations in LPG rate at the same time that the contactor is being pushed near its ultimate capacity. In these cases, if the LPG feed rate is not kept very steady, the little surges in rate that can take place during operation can cause short periods of high hydrocarbon velocity that will lift amine out the top of the extractor. This problem is very common in treaters where some of the LPG comes from a delayed coker. The change in LPG rate that takes place over the drum cycle can have more effect on the extractor than people realize. To minimize the effect of changing LPG rates, the upstream level control needs to be a level to flow cascade tuned to keep the flow rate, not the drum level, smooth.

With most pushed amine systems, foaming can only be prevented by an aggressive program to maintain the quality of the amine.

Question 107
Describe your experience processing extraneous naphtha streams in the FCCU. What types of streams can be upgraded? What factors are considered to determine the best injection point: pre-feed nozzle; mixed with feed; upper nozzle; stripper; or gas plant?

Dalip Soni (ABB Lummus Global)
Naphtha streams that are olefinic in nature (for example coker naphtha) can be processed in the FCC unit by injecting these upstream of the main feed injectors. High catalyst temperature and catalyst to oil ratio, can crack these streams to light olefins/LPG. If the naphtha streams are mixed with the main feed or injected down stream of the main feed injectors, cracking will be very minimal or none at all.

Question 109
What are the possible causes of coke formation in the first 10 feet of the riser above the feed injection point? How is coke formation impacted by feed distillation and riser mix zone design?

Dalip Soni (ABB Lummus Global)
Bad feed injectors can cause this coking. Heavier feed coupled with bad feed injectors can worsen the coking effect. ABB Lumuus Global has solved such a problem in some units by replacing the original injectors with their *Micro-Jet* design.

Question 111

When designing or revamping a FCC, under what operating conditions would you consider adding a catalyst cooler? In a retrofit case, what needs to be checked when adding a catalyst cooler?

Dalip Soni (ABB Lummus Global)

Catalyst cooler is considered to keep regenerator temperature within acceptable limits when processing residual feedstocks. It is desirable to put a catalyst cooler if regenerator temperature goes above 1350 F. Some residua can be processed in existing units without the need for catalyst cooler. Also running the unit in partial combustion should be explored before employing catalyst cooler.

Question 112

For units that operate in partial burn, what are typical compliance practices to meet the MACT II 500 ppm CO standard when the CO boiler is shut down? What are the typical operating handles used in transitioning from partial burn to full burn if this option is used for compliance? What are some ways to optimize the unit in this mode of operation?

(Engelhard and UOP)

It is highly unlikely that 500 ppm CO could be met without going to full combustion operation. Fortunately, it is fairly easy to put a regenerator into full combustion. In the transition to full burn, CO promoter should be added at a relatively high rate. However, this could cause a problem if there is a NOx limit. There are a number of low-platinum and zero-platinum promoters available with good commercial success rates. It is also important to make sure that the stripper is optimized with respect to steam rate. Once the unit is in total combustion, the feed temperature will typically be significantly reduced to pull as much heat out of the regenerator as possible and to keep the catalyst-to-oil ratio from being too low. It will be essential to make sure that the heat that was previously removed from the slurry pumparound loop to preheat the feed can be dumped somewhere else without upsetting the main column. The bigger question is can the unit mechanically operate at the new conditions? The regenerator, the flue gas system, and the regenerator standpipe must be mechanically designed for this higher temperature. The refinery steam balance may also be limiting. For many units it will be necessary to reduce the feed rate to allow for the extra air that is required to operate in total combustion. Higher excess oxygen concentrations will also help reduce CO emission, but again, NOx emissions may be a concern. I think that it is obvious that the possibility of operating a unit not designed for total combustion in a total combustion mode is something that can only be determined by a careful study of the mechanical design and operating constraints of that unit. For many such FCC units the higher regenerator operating temperature and very different operating conditions needed make it impractical to operate in total combustion without some mechanical modification to the unit.

Question 113
For resid FCC units converted to operation with lighter feeds, what options are available to prevent regenerator temperature from dropping below acceptable levels? What are the operating and economic considerations for each option?

Dalip Soni (ABB Lummus Global)
Run the unit in complete combustion if it is running in partial combustion
Recycle main fractionator bottoms
Increase unit severity

Rick Johnson (NCRA)
The term resid feed is not rigorously defined or uniformly used throughout the industry but generally the term resid refers to feeds with moderate to high (>2%) concarbon and high levels of other contaminants such as nickel and vanadium. In recent years as refiners have gone to lighter, sweeter crudes or started feeding more heavily hydrotreated feeds to the FCC unit as part of a low sulfur fuels strategy, some have faced the problem of too low of a regenerator temperature. When the regenerator temperature drops too low, the coke burning kinetics do not allow the unit to completely burn all of the coke off of the catalyst. Regenerator carbon monoxide levels may increase leading to FCC stack environmental issues. Additionally, the unit may become catalyst circulation limited. Therefore, a refiner should adjust operating variables which can raise the regenerator temperature. Resid units that were originally designed to operate in partial combustion may choose, if possible, to operate in full combustion. Resid units which are equipped with catalyst coolers may minimize or turn off this service.

Beyond this, the process variables that may be manipulated to raise the regenerator temperature include the following:

(1)   Main column bottoms recycle.
(2)   Increase catalyst activity through formulation or higher addition rate.
(3)   Change to a less coke-selective catalyst.
(4)   Increase riser feed temperature.
(5)   Increase reactor top temperature.
(6)   Decrease or eliminate stripping steam.
(7)   Using torch oil (in extreme cases).
(8)   Increased use of combustion promoter can help reduce CO emissions from a cold regenerator.

I make the assumption that the unit when it was designed for resid operation had a catalyst cooler as part of the design. Also, I am assuming that by "lighter feed" is meant a full range VGO or high API type resid that will make less coke. The first problem to be addressed is the drop in regenerator temperature that will result from the lower coke make. With a UOP designed catalyst cooler it is possible to continuously control the heat removal and hold the regenerator temperature as an independent variable at the desired point. This type of cooler can usually be shut down completely without damage to the cooler. By doing this the catalyst circulation can be kept in the design range for the standpipes and slide valves. Such units can usually transition back and forth between resid and VGO feed with a minimum of regenerator operational

problems. For a non-adjustable cooler (such as a coil in regenerator design) the heat removal is constant and as the coke make goes down the regenerator temperature will decline and the catalyst circulation needed to heat the reactor will increase. The point where the catalyst circulation is at the maximum possible in the standpipe you will be at the lightest feed possible to operate the unit with. When transitioning to a lighter feed it is normal that the gasoline production will increase and the LCO and bottoms make will decrease. The capacity of the fractionation equipment and product cooling systems to handle the changed load must be evaluated. Surprisingly the most significant problem can be minimum flow rate that the net bottoms product cooling system can be operated at without fouling or plugging problems. Another problem to consider is the operation of the flue gas system to operate at the new conditions. Often the lower conductivity of a lower SOx content flue gas will cause problems keeping the efficiency up with an existing ESP system designed to treat high SOx gas. If there are no significant bottlenecks in the product handling systems the major economic benefit of running a resid FCC on a lighter feed is the increased feed rate that is possible. The exact economics though is a very complex question involving the costs of the different feeds, unit capacity, product yields and values, lower catalyst make up rates required by the FCC, different product qualities, and loss of co-product steam from the catalyst cooler. Only a detailed study for a particular question can give any meaningful results.

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