2007 NPRA Q&A and Technology Forum: Answer Book

Hilton Austin
Austin, Texas
October 9 – 12, 2007

NPRA

FCC
Reliability and Safety

Question 2

Which type of valve technology or design is typically utilized in units with high catalyst withdrawal rates? Do you continuously withdraw catalyst? From a reliability and safety perspective, what type of hardware are you using for control? What is the best withdrawal line design?

Ralph Thompson (Chevron Products Company)

Valve selection for FCC catalyst withdrawal service is dictated by temperature and erosion considerations. FCC catalyst is very erosive, and when withdrawn from the Regenerator is typically 1200 F+. These considerations, coupled with high velocities when purge and carrier air are injected, lead to very aggressive conditions. We have developed a Best Practice for catalyst handling systems, and the information presented here generally follows those guidelines.
We have experience with 4 types of valves in catalyst withdrawal service:

- Conventional gate valve with and without hard facing
- Tapco “Mini Slide”
- Everlasting Rotating Disc valve
- High performance ball valve

Gate valves have generally been poor performers, giving 1-3 year life, even with upgraded trim and coatings. Both the Tapco “Mini-Slide” and the Everlasting Rotating Disc valve have provided good service, lasting multiple runs between replacements. We have limited experience with high performance ball valves in this service.

Continuous catalyst withdrawal from the Regenerator has been suggested as a way to even out the swings in level and catalyst activity which occur when batch withdrawal is used. We have no experience with using continuous catalyst withdrawal but have several locations interested in trying it. Locations with PRTs use a form of continuous catalyst withdrawal for third stage separator underflow.

For intermittent or semi-batch operation, the valve types described earlier are used for throttling. Block valves are most commonly low-chrome gate valves with hard-faced seats. Temperature monitoring of the withdrawal line is recommended to prevent over-temperature of downstream equipment. Some units have added fins to the withdrawal line to aid in cooling the catalyst. Carrier air also acts as a cooling aid.

Catalyst withdrawal lines are subject to leaks due to erosion at wear points. Coatings such as boronizing have been suggested for mitigating erosion but have not been widely applied. Erosion generally occurs at turns. We recommend using cushion tees in place of sweep ells to reduce erosion. Air purging of valves can create localized erosion and should only be used to clear the seat area when opening or closing the valve. We have experienced severe erosion and short life of primary regenerator catalyst withdrawal valves when the purge air has been used continuously.

Question 3

Carbonate stress corrosion cracking (CSCC) has been identified as a cause of failure in FCC main fractionator overhead systems. What changes in feed quality, unit operation, or configuration would lead to increased risk of CSCC? What parameters do you monitor to determine whether a system is susceptible to CSCC? While CSCC can be alleviated through post-weld heat treating, has the problem been significant enough to warrant either comprehensive PWHT in potentially affected areas or localized PWHT when problem areas are identified?

Ralph Thompson (Chevron Products Company)

Carbonate stress corrosion cracking (CSCC) is characterized by intergranular, somewhat branchy, scale-filled cracks. It is believed that ammonium carbonate (NH4CO3) is the main contributor to the cracking mechanism. The scale is typically black magnetite (Fe3O4) corrosion product and sometimes iron carbonate (FeCO3). This is unlike sulfide stress corrosion cracking, where the scale is iron sulfide.

Chevron finds that the work reported by Kmetz and Truax* in 1989 still holds true. Very briefly, carbonate SCC (CSCC) is a threat under the following conditions:

- Susceptible material: (i.e., non post-weld heat treated or poorly PWHT'd carbon steel)
- pH levels above 9.0 and carbonate concentrations above 100 ppm, or
- pH levels between 8.0 and 9.0 and carbonate concentrations above 400 ppm
- Electrochemical potentials between -500 and -600 mv (SCE)

Stainless steels are immune and have been used selectively as an upgrade where CSCC and other corrosion issues were an identified.

We primarily monitor the parameters of pH and carbonate levels to determine if we are in the SCC range, especially if we have non-PWHT'd equipment. As a practical matter it is easiest to monitor the pH. If we have a good sense of carbonate ranges with a particular plant feed and process conditions the pH may be the only parameter requiring periodic monitoring as long as it is outside the SCC range.

Higher nitrogen levels will lead to higher ammonia levels and could increase the pH into the SCC range. Similarly, anything that promotes CO2 will increase carbonate levels. The move from non-promoted, partial-burn operation to fully-promoted, full-burn operation was a significant contributor to the increased CSCC risk in many units. We recognize that some other companies pay particular attention to the S/N ratio, and while that can be useful we still put the most stock in the direct measurement of pH and carbonate as outlined above.

Regarding the use of PWHT as mitigation against CSCC, we are convinced it is very effective if the heat treatment itself is done thoroughly, and there are not unusual externally applied stresses. We found that we needed to beef up our PWHT practices for CSCC, primarily in going somewhat above the Code minimum temperature requirements, ensuring that we had good temperature measurement, and increasing the heating band widths. Our standard practice is to call for PWHT for all new systems, and even for existing systems that may be coming into the CSCC range we seriously consider it on a risk-basis. We try not to wait for leaks to force our hand and (without trying to "jinx" ourselves) in the past ten years we have not had significant CSCC issues.

*Reference: Kmetz and D.J. Truax, Carbonate Stress Corrosion Cracking of Carbon Steel in Refinery Main Fractionators Overhead System, NACE Paper #206 CORROSION 90.)

Sam Lordo (Nalco Energy Services)
The most identified change in operation that may have resulted inn carbonate stress corrosion cracking (CSCC) was the reduction of H2S through FCCU feed hydrotreating and an increase in ammonia from total feed nitrogen. Operational differences such as full or partial burn do not seem to increase CSCC potential.

From API 581 and NACE the identified environmental factors that increase the risk of CSCC are:

- >50 ppm H2S in the liquid water or pH>7.6
- Non-stressed relieved carbon steel
- PH >9.0 and carbonate (CO_3^{2-}) >100 ppm, or
- 8.0<pH<9.0 and CO_3^{2-} >400 ppm

Another parameter that may play a factor is the ratio of total feed sulfur to total nitrogen (S/N) on a ppm basis. It has been reported that cracking occurred in units with a S/N ratio of 0.7, while units that had no cracking had a S/N ratio of >6.0.

NACE has a task group, TG347, which is generating a document concerning this phenomenon. It is currently under review. The title of the report is "Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters".

Post weld heat treating (PWHT) appears to reduce the potential, however, there were several industry reported cases of PWHT equipment developing CSCC damage. This may be attributed to a low metal surface temperature during the PWHT process.

Another effective mitigating approach is the use of specialized filming amine products. Nalco has applied these products in units that have shown to be susceptible to CSCC.

Question 4

Does your refinery/company adopt a time-based rather than inspection-based replacement strategy for FCC reactor and regenerator hardware such as feed nozzles, air distributor, cyclones, cyclone support systems, and flue gas expansion joint bellows? If so, what is the planned service life for this equipment?

Ralph Thompson (Chevron Products Company)

The service life of each component is highly dependant on the application, and varies from unit to unit. As a result, we generally use inspection-based replacement frequency as opposed to time-based. We use results of the unit inspection coupled with run history to predict the need for replacement of key components at the next (or subsequent) turnaround. Unit monitoring is very important, since we want "no surprises". As an example, cyclone erosion predictions are used to forecast wear and identify "at-risk" systems.

We have adopted an upgrade strategy for high wear/low reliability components. We generally plan for a minimum of a 5 year turnaround interval when evaluating need for upgrades. We address the root cause of failure to extend service life where possible. We also identify high wear/low reliability components and selectively upgrade them. We have developed Best Practices to address critical components and systems.

Our expectations of the typical service life for well-designed/operated/maintained components are as follows:

- Feed nozzles: 5-10 years
- Air distributor: 15-20 years
- Reactor and Regenerator cyclones: 15-20 years
- Cyclone support systems: 15-20 years
- Flue gas expansion bellows: 15-20 years

Obviously operating conditions and run history have a major bearing on these service lives. In general, we find that frequent shutdowns have a significant adverse affect on service life and, in particular, component life predictability.

NPRA 2000 Q&A FCC Operations Question 1 addressed a similar issue and is a suggested reference.

Question 5

What is the shortest possible time between oil out and entry for maintenance on large inventory, high capacity FCC units? How is this achieved?

Regan Howell (Holly Corporation)

Holly has two FCCs, neither of which would be described as large inventory or high capacity. With that said, during discussions with the panel members who operate larger units, we found similar performance, regardless of the inventory and capacity of the units. Historically, Holly has obtained our first entry permits for FCC vessels between 36 and 48 hours from "oil out". During a recent unplanned outage, we still were able to open external manways for visual inspection at approximately 48 hours from the time feed was removed. Our first entry was 24 hours later (72 hours from oil out), but we were unable to enter the reactor for three more days – mostly due to coke buildup in the reactor vessel and the fact that we were unable to steam the unit because of the circumstances of the outage.

With our infrequent FCC shutdowns, Holly has found the best method for ensuring safe, quick entry is a set of "evergreen" procedures. The latest version of the procedure is stored electronically on our intranet. Several days prior to shutdown, operators conduct a Safety Task Review with their supervisor, the engineers, and operations management. The procedure is read through with a critical eye and updates may be made at that time. As the unit is shut down, procedures are checked off and annotated so that, post-shutdown, our current experience can be included in the procedure for the next turnaround.

Ralph Thompson (Chevron Products Company)

FCC shutdown timing is set by the requirements to isolate the equipment and remove both catalyst and oil to allow safe entry. We would consider 3 days oil out to entry "pacesetter". Most of our units are in the 4-5 day range. We find that the roadblocks to rapid entry are catalyst removal and cooling, and reaction mix blind installation. To speed catalyst withdrawal and cooling, we use multiple catalyst withdrawal points and external temporary catalyst coolers.
We are specifically addressing reaction mix blind installation by installing reaction mix valves. We have installed Zimmermann and Jansen isolation valves on two units and have plans to

install these on other units. Although these valves greatly speed the isolation process and reduce exposure to hazardous conditions, we do not consider the isolation they provide sufficient for entry, and use additional blinding for that purpose.

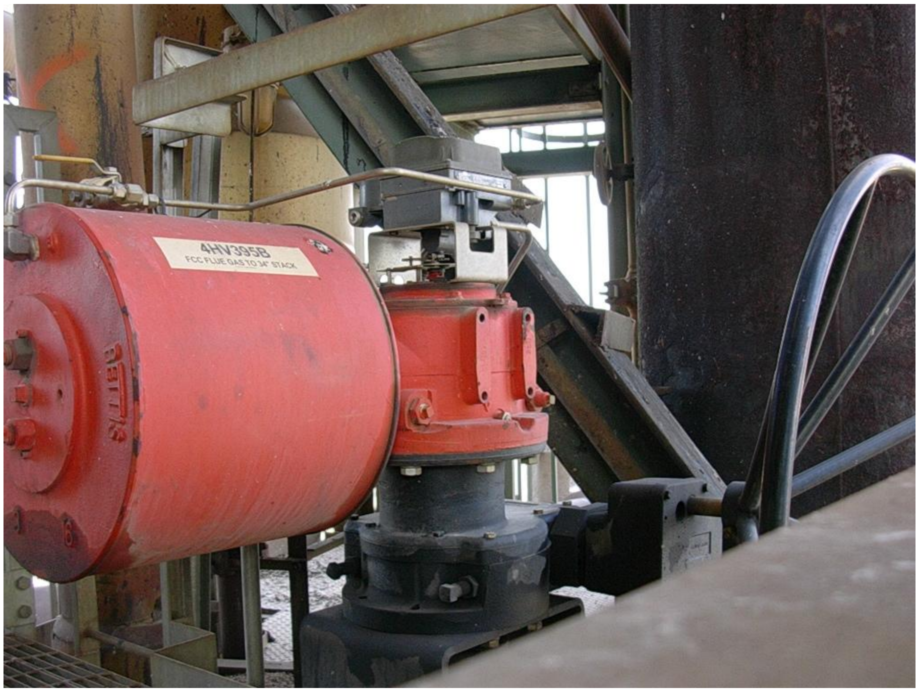
Question 6

Some CO and waste heat boilers operate with bypass stacks separated by seal pots or isolation valves. Maintenance of these seal systems can be expensive and these seal systems can be sources of poor reliability. What design upgrades and operating practices have enabled you to eliminate these bypass systems?

Regan Howell (Holly Corporation)

Holly continues to use bypass stacks with diversion valves at both refineries. These stacks are allowed by permit and used during startups, shutdowns, and in upset conditions.

Both Operations and Maintenance groups are assigned weekly preventative maintenance routines to ensure operability when these valves are needed. Weekly partial exercise of both the valve and the positioner is conducted. During scheduled turnarounds the valves are disassembled, inspected, and often, reworked. We foresee no major design changes to these systems, and certainly no elimination of these valves, in the near future



Ralph Thompson (Chevron Products Company)
We would agree that CO Boiler reliability has generally been poor and often does not meet the desired FCC run-length requirements. This necessitates decoupling the FCC from the CO boiler. We have taken two approaches to this problem.

The preferred approach, where possible, is to operate in complete CO combustion, eliminating the need for a fired CO boiler. This generally requires modifications to the regenerator to improve catalyst distribution. Air demand will also increase, possibly requiring supplemental air or oxygen. This approach has the benefits of improved catalyst regeneration, increased catalyst activity, and improved yields.

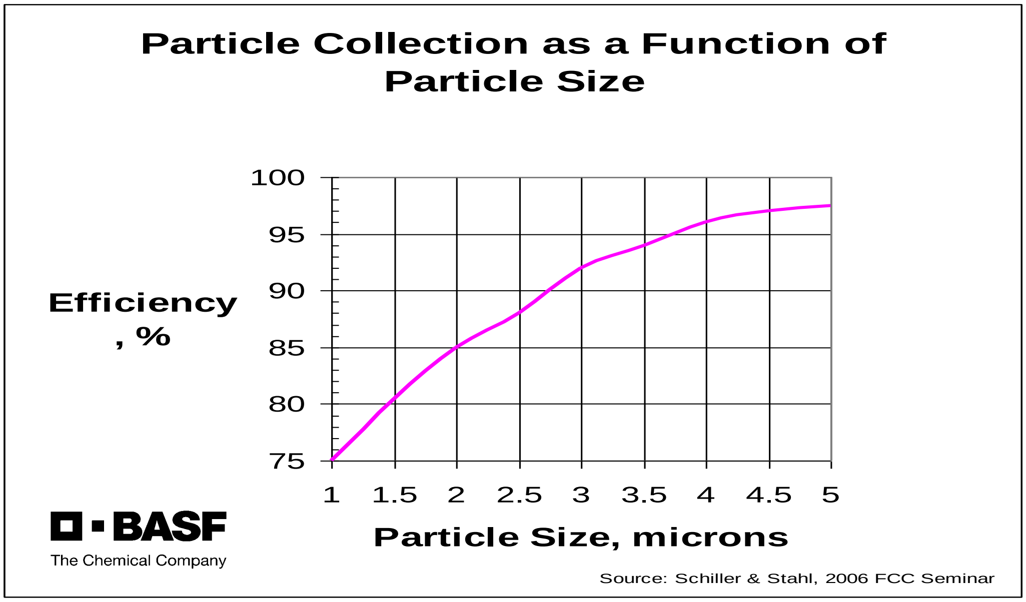
For those units feeding heavy feeds, operation in complete combustion may not be practical. We operate units of the SWEC R2R configuration which use two-stage regeneration. The first stage operates in partial combustion, and the flue gas from first stage is combusted in a CO incinerator before being combined with the second stage flue gas. An unfired waste heat boiler is used for the combined flue gas heat recovery. The CO incinerator does have a bypass and has not been a reliability or run length issue.

Environmental

Question 8

What level of $PM_{2.5}$ particulate removal do you expect (or have achieved) with flue gas fines separation and removal equipment such as third-stage separators, fourth-stage separators, electrostatic precipitators, or wet gas scrubbers?

Rex Heater (BASF Catalysts, LLC)
Below is a graph of ESP particle collection efficiency versus particle size presented by Martin Schiller of CSI Engineering in the 2006 FCC Seminar.



Source: Schiller & Stahl, 2006 FCC Seminar

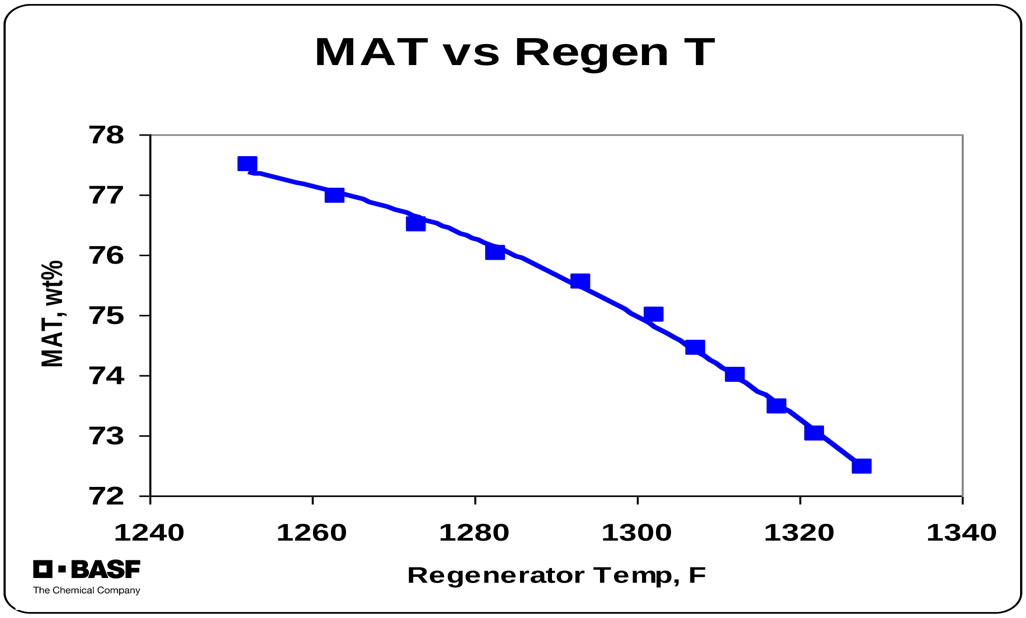
Catalyst

Question 9

Are there specific lab studies or commercial examples regarding the effect of regenerator temperature on catalyst deactivation and particle integrity, specifically attrition properties, apparent bulk density, and morphology?

Rex Heater (BASF Catalysts, LLC)

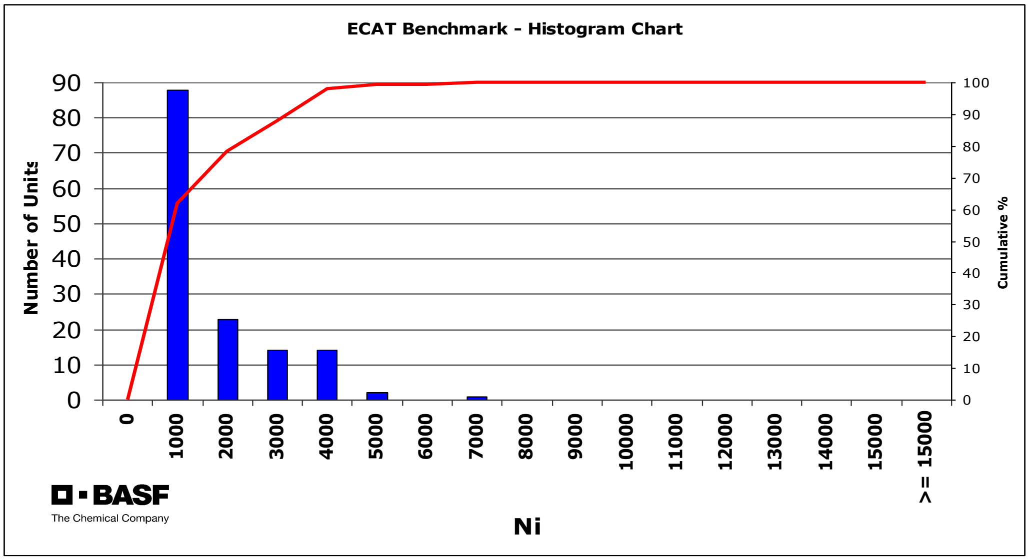
The subject of thermal deactivation of catalyst has been covered several times in past Q&A meetings. The plot below represents the correlations we use in our model to estimate thermal deactivation. Of course, there are other factors to consider in the deactivation equation, including the presence of steam and its relative volume, as well as ecat metals levels.

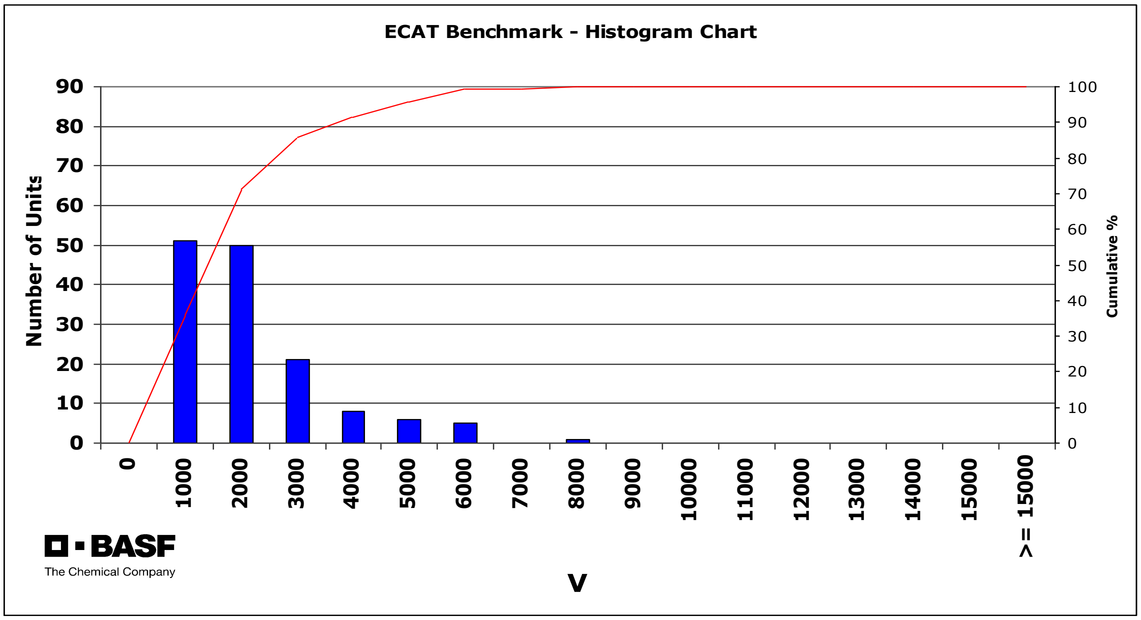


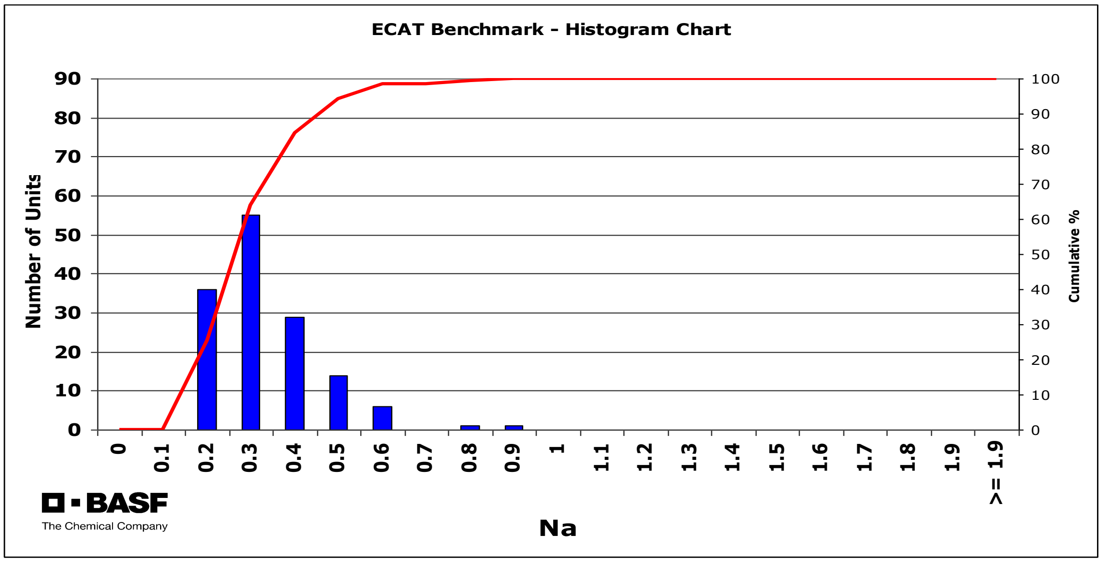
Question 10
What is your recent experience regarding the maximum level of equilibrium catalyst metals (Ni, V, Na, Fe, Ca) in FCC units processing residual feedstocks? Have there been any recent improvements in vanadium passivation technologies? At nickel levels approaching 10,000 ppm, have you experienced increased catalyst deactivation as evidenced by lower equilibrium zeolite surface area?

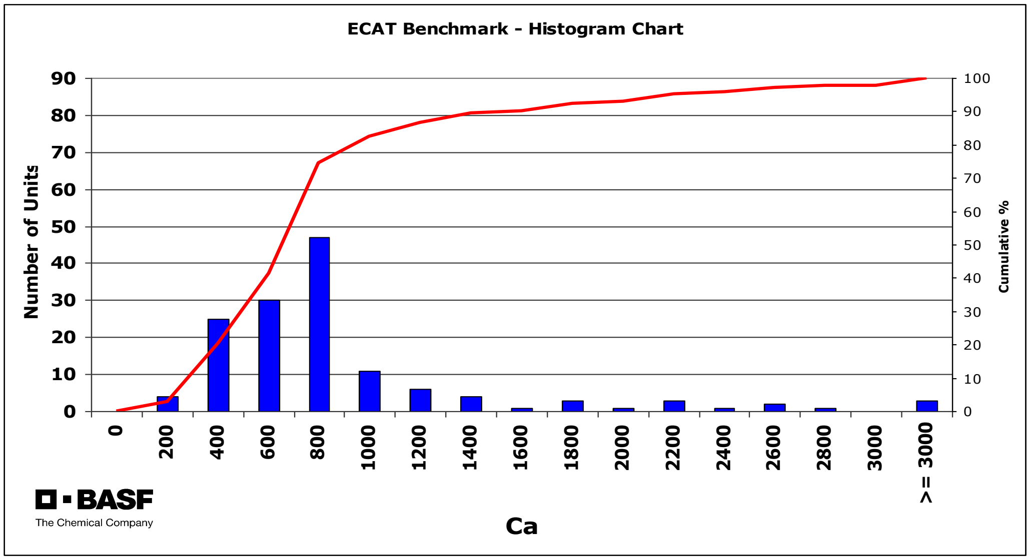
Ralph Thompson (Chevron Products Company)
We have only few units that operate with high levels of metals on equilibrium catalyst. The maximum nickel/vanadium levels are 5-6000 ppm each, but we have not seen the effects mentioned earlier. Other contaminants, such as iron, calcium, and mercury are becoming important as more opportunity crudes are processed. We have considerable experience processing high iron gas oils and reduced crudes in FCCs. Iron generally reduces bottoms cracking, giving a higher slurry yield and gravity. At least two units see an effect of iron on catalyst circulation. The effect occurs at moderate (<1.0% Fe) iron levels. This shows up as poor catalyst circulation and erratic pressure differential on slide valves.

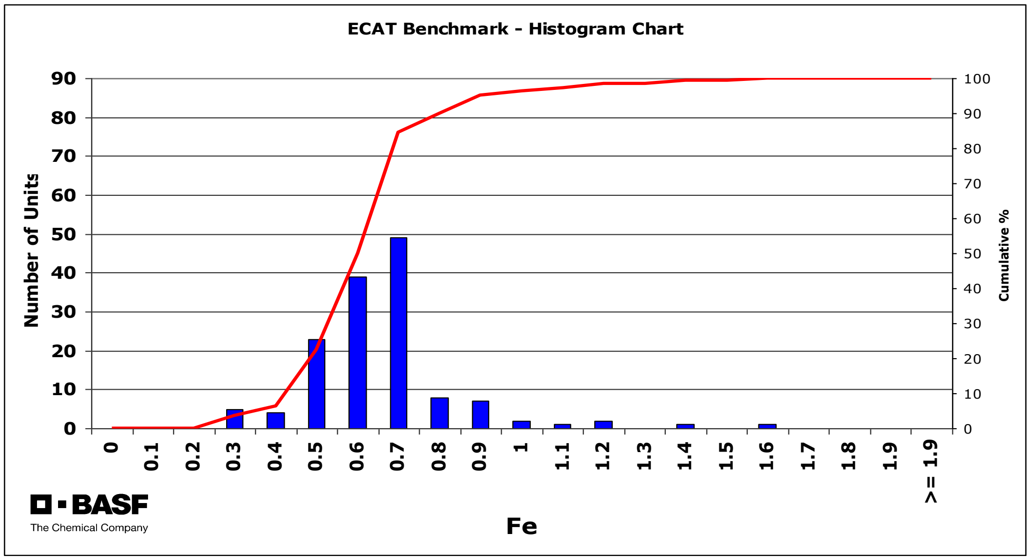
Rex Heater (BASF Catalysts, LLC)
Below are histograms from our benchmarking database showing the relative number of units at varying metals levels:


ECAT Benchmark - Histogram Chart
Number of Units
90
80
70
60
50
40
30
20
10
0
Cumulative %
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
>= 15000
BASF
The Chemical Company
Ni


ECAT Benchmark - Histogram Chart
Number of Units
90
80
70
60
50
40
30
20
10
0
Cumulative %
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
12000
13000
14000
15000
>= 15000
BASF
The Chemical Company
V


ECAT Benchmark - Histogram Chart
Number of Units
90
80
70
60
50
40
30
20
10
0
Cumulative %
100
90
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
>= 1.9
BASF
The Chemical Company
Na


ECAT Benchmark - Histogram Chart
Number of Units
90
80
70
60
50
40
30
20
10
0
Cumulative %
100
90
80
70
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800
3000
>= 3000
BASF
The Chemical Company
Ca



Process

Question 11

What process or catalyst options are available for shifting yield selectivity's from gasoline to distillate while minimizing the impact on light olefin yields? How are the product properties impacted? How does change-out rate impact the viability of the catalyst options?

Ralph Thompson (Chevron Products Company)

The suggested process options for maximizing distillate and light olefin yields are as follows. Gasoline can be undercut, with the heavier portion dropped to distillate. Cat:oil can be reduced to reduce conversion of distillate to gasoline, which will also increase the olefinicity of the C4s. Reducing cat:oil will increase HCO relative to LCO.

The suggested catalytic options for maximizing distillate and light olefin yields are as follows. Catalyst matrix surface area can be increased to maximize conversion to LCO while minimizing bottoms. This will reduce gasoline yield relative to LCO while maintaining or increasing olefin yield. A bottoms cracking additive can be used as a quicker way to achieve this effect. The downside to increased matrix surface area is increased coke make. ZSM-5 can be used to increase light olefins at the expense of gasoline. This option has the advantage of quick response but it needs to be used in conjunction with process changes to increase distillate yield. Catalyst zeolite content can be decreased to minimize cracking of distillate to gasoline. Zeolite rare earth can be optimized to enhance LCO quality. Decreasing rare earth decreases hydrogen transfer from LCO to gasoline and light olefins and improves LCO product quality. Rare earth changes, as well as other catalyst modifications, need catalyst testing to verify the optimum.

There is not much potential for making distillate when processing very paraffinic or heavily hydrotreated feed, since the conversion tends to be high, and gasoline and light olefins are favored over distillates.

Question 12

For FCC units with closed riser termination device (RTD)/cyclone systems, do you operate with the primary separator sealed or unsealed in the stripper bed? What differences in performance do you see between these modes? Which do you prefer?

Ralph Thompson (Chevron Products Company)

We have 7 units with closed cyclone riser termination devices which use diplegs, as follows:

	Sealed	Unsealed
Direct coupled cyclones		2
Rough Cut	2	
Ramshorn	1	1
Steerhorn	1	

The choice between sealed and unsealed operation is often dictated by the hardware design, since some units can only operate in one mode. For those that can operate either way, the choice is usually dictated by either dry gas make or catalyst losses. One unit starts up unsealed and switches to sealed mode when the unit operation stabilizes.

Question 13

With the move toward greater utilization of "opportunity crudes" such as Canadian synthetic crudes, what shifts do you expect in FCC product yield and quality and how will this impact the operation of the FCC unit?

Regan Howell (Holly Corporation)
Holly's choices for "opportunity crudes" are somewhat limited by our position as inland refiners, away from many crude pipelines. Holly is making substantial changes, both in operation and capital investment to maintain our product slate with crudes of varying quality.

We have already experienced increased levels of traditional FCC catalyst poisons. Our response to that situation has been increased catalyst makeup, evaluation of additives, and consideration of custom catalyst blends.

Holly is adding mild hydrocrackers at both refineries so we expect to see large changes in the heat balance of our FCC, when our gas oil is coming from our current crude sources. If our crude sources change to include previously "upgraded" stock, or bituminous blends, we expect to see coke yield and heat balance move back in the direction of current values.

Like the rest of the industry, Holly's ultimate goal is to maintain quality and to maximize yield from those feedstocks available at some discount from benchmark price. We are making the necessary capital investments, catalyst changes, and additive use to meet that goal.

Rex Heater (BASF Catalysts, LLC)
With the shift toward "opportunity" crudes, FCC feedstocks are becoming "heavier", with lower API, and are increasingly derived from Canadian synthetic crudes and bitumen blends. While sweet synthetic blends make up the majority of Canadian bitumen-derived crudes on the market, some sour synthetic, bitumen and condensate blends (Dilbits, SynBit, SynDilBit) are also available. Processing implications for the FCC refinery will be a function of the type of bitumen-derived crude imported and should be evaluated on a case-by-case basis. However, general trends can be drawn based on the compositional differences between conventional refinery feeds and these "opportunity" crudes.

Compared to conventional crude oil, synthetic crude oil (SCO) provides a larger volume of FCC feedstock with no residue and low total sulfur, nitrogen and metals, but with a larger aromatic content. On the other hand, Canadian bitumen contains a larger volume of highly aromatic 650ºF+ material, lower API gravity, lower hydrogen content and higher levels of sulfur, nitrogen, nickel, and vanadium. The central issue is the high throughputs required to process the additional feed that is now of poorer quality.

Refiners will see a significant shift in the FCC yield pattern when processing vacuum gas oils from most bitumen-derived crudes. The aromatic nature of SCOs limits FCC bottoms conversion with an increase in decant oil and light cycle oil yields. Other differences will be observed in the decrease of yield, especially naphtha and LPG, and quality of valuable products, with higher sulfur content in the naphtha and LCO cuts, and an increase in levels of coke precursors and reactor coking for heavier feedstocks. Also, the LCO produced will have low cetane number due to its high aromatic content. To a certain extent, yield improvements are possible with an increase in the catalyst-to-oil ratio, which can produce pressure balance issues, standpipe and slide valve sizing increases, and the need to improve/debottleneck the catalyst stripper. The large percentage of VGO-range material in these unconventional crudes may result in the FCC unit capacity becoming a bottleneck. A higher unit throughput can be accomplished at a higher reactor severity, but this would be limited by FCC hardware constraints. All the above – the contaminant levels, composition of bitumen-derived crudes and high feed volumes – make these opportunity crudes more challenging to upgrade into cleaner fuels and development of tailored FCC catalyst technology plays a key role in addressing these challenges.

Thanks to our friends at NCUT for assisting with this answer.

Question 14

What reactions lead to acetone formation and how can they be mitigated? We have measured acetone concentrations between 100 and 1200 ppm in the FCC butanes/butylenes stream.

Ralph Thompson (Chevron Products Company)

We have not detected acetone in FCC butane streams. Oxygenate testing conducted several years ago on butane streams associated with an MTBE unit did not indicate the presence of any acetone. The presence of significant acetone in the products from an FCC GRU would be surprising given the contact with water which occurs in the front end of the plant. One potential source is an extraneous stream such as a stream from a cumene unit which is fed to the back end of the GRU.

Question 15

What variables influence gasoline aromatics? In particular, please address feed properties, catalyst, and FCC operating conditions.

Ralph Thompson (Chevron Products Company)

The three key variables which influence gasoline aromatics are feed properties, catalyst properties, and unit operating conditions.

Lower feed hydrogen content translates to lower product hydrogen, i.e., more aromatic products. Naphthenic feeds make more aromatic products compared to paraffinic feeds.

Catalyst properties are also important. Low hydrogen transfer (low unit cell size/low rare earth) catalyst produces a more aromatic gasoline. ZSM-5 increases aromatics by concentration effect: olefins are cracked out, leaving behind aromatics.

Operating conditions are the third major factor. Increased riser temperature increases gasoline aromatics by dealkylation of larger aromatics and cracking of paraffins, leaving aromatics behind. Cutting deeper to produce more gasoline also increases aromatics, since the aromatics tend to be concentrated in the heavier fractions.

Question 16

A number of refiners are adding a chloride dispersant to address FCC main fractionator overhead system plugging issues. What is your experience with these products and have you had issues with downstream gasoline product quality?

Regan Howell (Holly Corporation)

Holly does not have experience with chloride dispersants at the FCC main fractionator. Conversations with our process treatment vendor lead me to believe such use is uncommon in our area. Since all chemical filmers have some dispersant qualities, the typical response at Holly was to question whether such use might simply be "repackaging" of existing technology and products by chemical treatment vendors.

Ralph Thompson (Chevron Products Company)

The processing of increased amounts of imported FCC feed, both gas oils and reduced crude, has resulted in increased chloride salts in the FCC Main Fractionator. Ammonium chloride salt dispersant is a chemical which is used to move (disperse) ammonium chloride salts to prevent plugging of FCC Main Fractionator. It is injected into the Main Fractionator reflux and ultimately removed through the heavy gasoline and LCO draws.

The use of a chloride salt dispersant may reduce corrosion by tying up ammonium chloride. Corrosion may still be an issue where the salts accumulate, however. Water will make salts very corrosive. The dispersant is not very effective at moving salts where low velocities are present so they may accumulate in low velocity zones further down the column. One unit experienced massive salt buildup and severe piping corrosion in a low velocity reflux line.

No product quality effects for either gasoline or light cycle oil products have been reported at facilities using the dispersant. However, most units treat the FCC products prior to sales, and that treatment will generally remove the salts. There has been evidence of chloride salts downstream of the unit which resulted in increased corrosion, but it is unclear whether the dispersant was involved.

Reference on Chloride Dispersants
William F. Minyard, Ammonium Chloride Salt Fouling Control in FCC Units, Stone and Webster Twelfth Annual Refining Seminar, October 10, 2000, San Francisco California.

Randy Rechtien (Baker Petrolite Corporation)

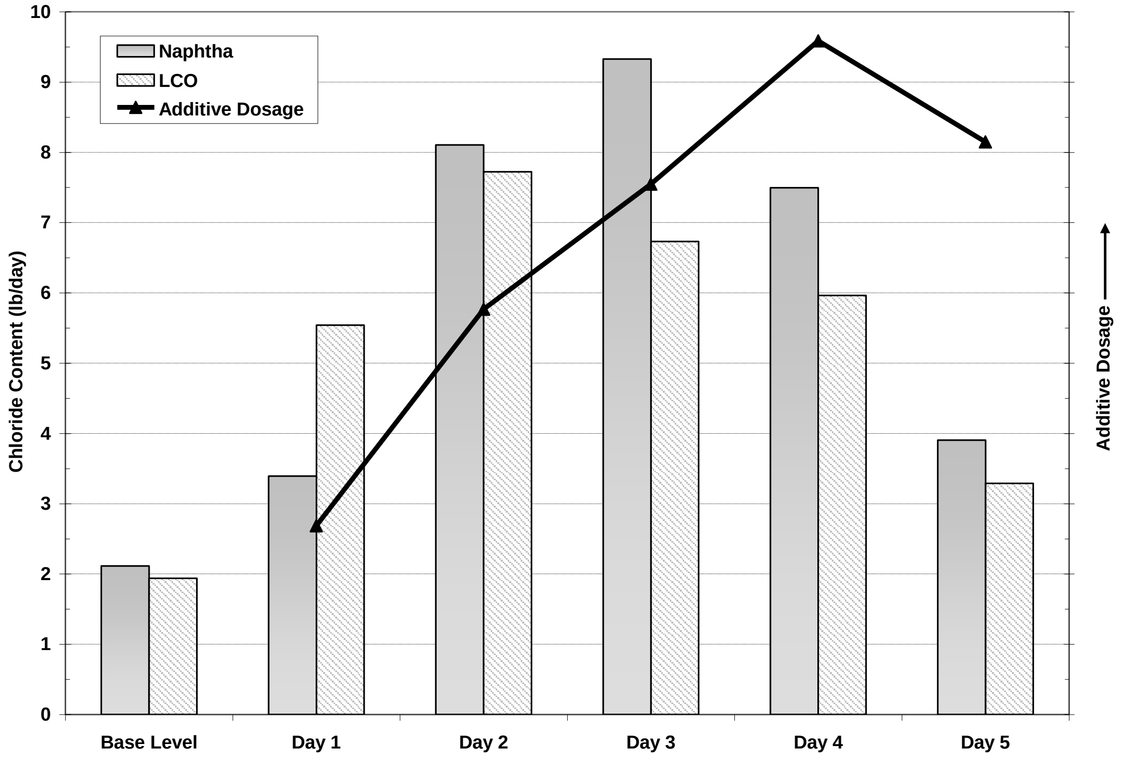
Baker Petrolite has successfully mitigated the fouling effects of ammonium chloride salt deposits in several FCC fractionators using dispersant additives. These additives applications are typically short-term in duration (3-5 days). Proprietary additives, specially formulated with enhanced surfactancy, are injected into tower reflux streams. Chloride levels in the tower side-cut streams are closely monitored before, during and after the additive is applied. In addition, to determine the effects on tower operation, key operational variables are monitored. These operational variables include tower pressure drop and distillation end-points of overhead naphtha and side-cut products.

By way of example, details about a recent application are provided below. A US refiner had historically experienced ammonium chloride deposition on the upper trays of the FCC fractionator which resulted in poor fractionation efficiency. Before using the dispersant additive, the refiner had used on-line water washing of the tower to remove the salt deposits. Though the water wash was beneficial, it adversely affected tower operation by generating high volumes of off-spec material which required re-processing. It was also necessary to reduce FCC charge rates by about 40% during tower washing.

To help mitigate the fouling effects, Baker Petrolite applied a salt dispersant in step-wise dosage increments to the tower reflux over several days. The improvement to tower operations was immediate and dramatic: large amounts of salts were removed via the heavy naphtha and LCO product streams and tower performance was greatly improved.

The graph below shows the increased chloride content in tower product streams during additive treatment. As shown, chloride levels in both the naphtha and LCO increased 3-5 times above their pre-treatment levels. These results confirmed that salts were successfully removed from the tower.

Salt Removal from FCC Tower with Additive Usage



In addition, the additive treatment improved tower fractionation efficiency such that the difference between the end-point of the FCC gasoline (overhead naphtha) and the 10% cut-point of the heavy naphtha decreased by some 20 degrees F.

Using this additive program, the refiner realized significant economic benefits when compared to the inherent shortcomings of on-line tower washing. Note that, during the period of additive treatment, there were no detrimental effects on the quality of downstream products.

Paul Fearnside (Nalco Energy Services)

Nalco has a number of clients who are successfully using the chloride salt dispersants on a continuous basis with no reported gasoline product quality issues. We have other clients who use the salt dispersants on an intermittent basis, one – two days, at much higher dosages to alleviate internal tower delta P concerns. During this type of treatment the products are slopped for later rerunning. This is due mainly to concerns from the high chloride salt content of the side streams while the deposited salts are dispersed and removed.

Question 17

What minimum nozzle velocities are required in air and steam distributors to prevent catalyst backflow and subsequent erosion? Please consider both upward and downward pointing nozzles.

Ralph Thompson (Chevron Products Company)

We generally focus on nozzle pressure drop rather than velocity as the key criteria for distributor nozzle design. We limit nozzle velocities to 250 ft/s and prefer velocities below 200 ft/s. We have recently designed air distributors at 80-100 ft/s. The key criteria for nozzle design is to have a pressure drop at turndown greater than 30% of the bed pressure drop for upward pointing nozzles and 10% of the bed pressure drop for downward pointing nozzles.

Rex Heater (BASF Catalysts, LLC)

The FCCU has many distributors, including combustion air, stripping steam, various fluffing distributors, and even the feed nozzle system.

Good distributor & nozzle design is about half the battle in good FCC operation. Many routine FCC problems are the result of poor distributor operation. This can include poor yields due to poor oil/catalyst contacting, poor stripping due to lack of catalyst/steam contacting, and excessive catalyst attrition due to distributor damage.

Unfortunately, distributor design is challenging in many FCC services, with too many design requirements and not enough degrees of freedom to satisfy all of them.

Distributor designs differ from designer to designer, but there are some common points:

1. The standard for FCC design is a system that incorporates dual diameter nozzles, meaning an orifice controlling the pressure drop to ensure even distribution and no catalyst back flow, and a nozzle diameter that sets an acceptable outlet velocity.
2. Sufficient distance from the orifice to the nozzle such that there is fully developed flow in the nozzle before it exits the nozzle
3. Sufficient coverage of the process area to ensure good vapor/catalyst contacting, but this is done 2 different ways. The more common manner is to have a lot of nozzles, as many as 1 per square foot of process area coverage, with appropriate sized nozzles & orifices to ensure even flow. The second manner is to have nozzles with high outlet velocity and rely on jet penetration for good process coverage.

Typical distributor & nozzle designs include the following parameters:

- orifices sized to give pressure drop equal to 30 % of the bed static height above the distributor
- nozzle outlet velocity of 90 to 150 fps
- minimum nozzle length of 5.2 times the difference between the nozzle diameter and orifice diameter, with some safety factor applied. Engineering firms use a factor of 1.5 – 3 times this length to set an acceptable safety factor.
- Drains to allow wet media to discharge freely

In terms of keeping catalyst from back flowing into nozzles, there are two separate answers, but they are related.

In the event of a single nozzle (like an emergency steam nozzle), the industry rule of thumb is to have 25 fps velocity in the orifice area of the nozzle. This results in low velocity, and should keep the orifice area of the nozzle clear, but catalyst will likely be back mixing into the nozzle diameter area downstream of the orifice. This means the nozzle must be designed for catalyst temperature.

If there is a distributor (ring, pipe grid, horse-shoe type designs), the minimum parameter used to prevent catalyst backflow is distributor delta P. Industry guidelines vary from a minimum of 10 % bed static height upwards to 30 % bed static height. A common industry belief is that 10 % minimum bed static height for distributors with downward pointing nozzles, and 30 % minimum bed static height for upward flowing nozzles.

The most likely way that we have direct experience with catalyst backflowing into distributors is by loss of pressure of the flowing media into the distributor. This can result in an instantaneous back flow into the distributor. If this happens, it may very well plug nozzles until the next scheduled maintenance turnaround on the unit allows entry to the vessel to clear the distributor.

Question 18
Some refiners have installed gas injection in FCC secondary cyclone diplegs to increase capacity and avoid defluidization problems. Please describe your experience operating with gas addition in the diplegs and any maintenance issues. What advice would you give to others considering this installation?

Ralph Thompson (Chevron Products Company)
Cyclone dipleg aeration is a technique used to improve cyclone dipleg fluidization. It involves adding a stream of purge gas, usually air or steam, to a location near the bottom of the cyclone dipleg ahead of the trickle valve. It assures that the cyclone dipleg does not defluidize and plug. This can be a problem for secondary cyclone diplegs that are lightly loaded.

We have two similar units with dipleg aeration of both the Reactor and Regenerator secondary cyclone diplegs. One Regenerator has 3 sets of 2 stage cyclones and the other has 2 sets. The 2nd stage diplegs each have an aeration purge in the sloping mitre bend section of the dipleg just ahead of the vertical trickle valve. The purge medium is plant air. The Reactors have a single set of close coupled cyclones and the 2nd stage dipleg has a steam purge, again in the sloping mitre bend section. The trickle valves are in the dilute phase and the stripper bed level operates approx 1.5 meters below the bottom of the trickle valves. The purge flows are small and regulated via restriction orifice as per normal instrument purges. Purge piping for the cold wall Regenerators enters the top of the vessel and is routed along the diplegs. Purge piping for the hot wall Reactors enters the vessel near the bottom.

These units have had good experience with secondary cyclone dipleg aeration. One unit was originally designed with dipleg purges on both primary and secondary cyclones of both the Reactor and Regenerator and operated this way successfully for many years. It was converted to close coupled cyclones but did not install purges on the reactor cyclones. After experiencing plugging after startup (for an unrelated reason) they decided to install a purge on reactor secondary cyclone dipleg. No dipleg plugging has occurred since aeration was installed. Dipleg aeration was installed in the other unit after it experienced dipleg plugging.

The purges need to be commissioned before catalyst loading to avoid plugging the aeration point. Erosion at the injection points has not been an issue. The routing of the purge piping needs to consider thermal expansion as well as impingement. Failure of the internal piping is a concern. However, this has not been an issue for either unit.

Question 20

Several refiners are considering continuous operation of the combustion air heater to maintain a minimum regenerator temperature when processing light, severely hydrotreated feedstocks. What control systems, design features, and other general precautions should be considered?

Regan Howell (Holly Corporation)

As I previously mentioned, Holly is constructing mild hydrocrackers at both our refineries. Of obvious concern, both from Operations and Engineering, is where our FCC units will “settle out” on heat balance.

Our company does not yet have experience operating the FCC with severely hydrotreated feedstock, but this appears to be a creative solution. The combustion air heaters are not always models of reliability, either during, or perhaps because of, their infrequent use. Reliability issues and safety shutdown system design would be required before Holly would consider use of these air heaters as a solution to our new operating conditions.

Question 21

When operating with one or more catalyst coolers on a regenerator, what control philosophy do you employ (e.g. constant heat duty, constant regenerator temperature, etc.)? What are the advantages and disadvantages for each approach? How does operating in full or partial burn impact the control decision?

Ralph Thompson (Chevron Products Company)

We have four units with catalyst coolers. They are used on either single stage regenerators or full burn stage of 2 stage regenerators. We have no experience with a catalyst cooler on a partial burn regenerator. The catalyst coolers are operated to minimize regenerator bed temperature to a limit, usually air or catalyst circulation. Catalyst cooler optimization is an advanced control application. We only use straight duty control if a cooler or steam system limit is reached. The benefits for minimizing regenerator temperature include: maximize catalyst circulation, minimize dry gas production, minimize swings during feed changes, and reduce catalyst deactivation.

Question 22

With the introduction of modern riser termination devices (RTD's) and the advent of severe FCC feed hydrotreating, what is your experience (typical values) with the ash content of the main fractionator bottoms (MFB) product (please provide typical values for: wt% ash, BS&W, particle size distribution, etc.)? Please describe the testing methodology utilized and the recommended testing frequency for this stream. What process, practices, and/or equipment changes can be, or have been, employed to reduce the ash content of the MFB product?

Ralph Thompson (Chevron Products Company)

Typical ash content data for various RTDs range from 0.005 to 0.2 wt% ash, with most in the 0.05 to 0.1 wt% range. Testing is done in accordance with ASTM D-482. We normally do not run a particle size distribution on the fines, but have used photomicrography as a qualitative monitoring technique.

For units which are required to meet stringent ash content specifications, slurry settlers, filters, and ESPs (Gulftronics) have been used. All have been problematic and the filters and ESPs require considerable maintenance. Filter plugging due to asphaltenes and waxes has been an issue at one location. The recycle stream generated by the backwash from these systems has caused feed system fouling and reactor coking.

Randy Rechtien (Baker Petrolite Corporation)

Baker Petrolite has been successful in reducing the ash content of FCC fractionator bottoms using our proprietary line of slurry settling aids. Settling aids function as surfactants to remove the hydrocarbon layer on the particle’s surface, enhancing the particle’s ability to drop from the liquid phase. These additive applications allow refiners to capitalize on the higher market value afforded to slurries (decant oils) with lower ash content.

Ash composition can vary greatly from one refinery to another. Though the primary ash components are inorganic (catalyst fines, metals, corrosion scale), heavier organic molecules can also be present which stabilize the ash in solution. Baker Petrolite offers an extensive line of settling aids to address these slurry variations.

Additive applications have been used on slurries with the following properties:

- Ash Content (wt%): up to 1.0%
- Gravity: as low as -10^{o}API
- Mean Particle Diameter (micron): 1 to 10

In general, the larger the mean particle diameter, then the more readily particles will fall out of solution. The table below shows particle diameters and ash content for three slurries of varying quality. As shown, higher particle sizes result in lower slurry ash content. Slurry additives, then, help to promote this settling effect.

REFINERY	MEAN DIAMETER (MICRONS)	UNTREATED ASH (%)
A	**9.4**	**0.027**
B	**5.9**	**0.056**
C	**1.5**	**0.97**

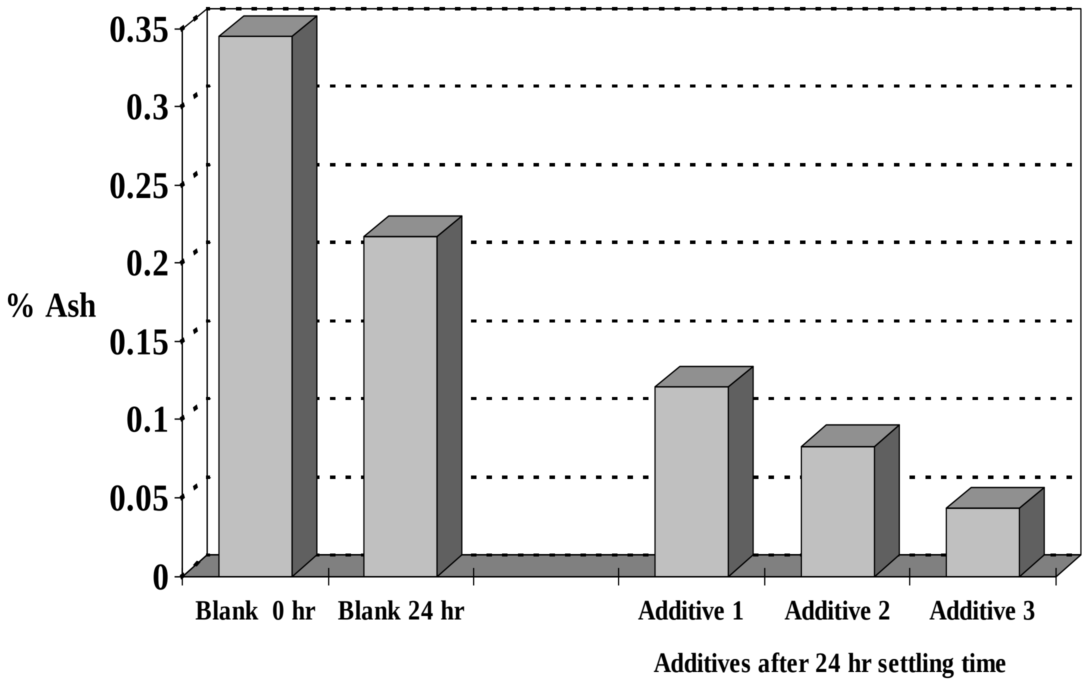
The market price for saleable decant oil is strongly a function of ash content. Therefore, refiners can realize significant economic benefit if the ash content of the slurry is below these specs---typically 0.05% ash or less. In addition, an additive application is often more economically viable than alternate operational/mechanical options (e.g., filtration) to reduce ash content.

The testing procedure for screening additives comprises the steps given below:

- Heat sample to the anticipated additive injection temperature in the field
- Dose the sample with additives to be tested
- Thoroughly mix the sample
- Cool the sample to anticipated storage tank (settling) temperature in the field
- Maintain the sample at the settling temperature for at least 24 hours
- Thief a small volume off the top of the sample
- Perform ashing of small volume to determine additive performance

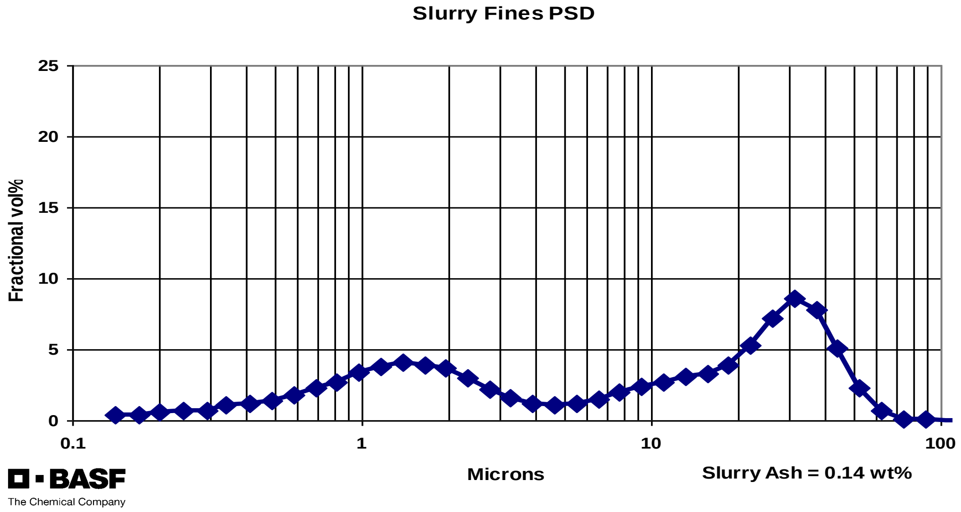
The graph below provides an example of additive testing results. As shown, the performance of settling aids should always be compared to that of settling alone. While all additives showed improvement over the untreated sample, one additive in particular produced a low enough ash content to meet the desired refinery spec of 0.05%. These test results were confirmed with a successful field trial. Currently, this refiner is using Baker Petrolite's settling aid to sell clarified slurry into the more lucrative "carbon black' market.

Reduction in Ash Content with Additive Usage



Rex Heater (BASF Catalysts, LLC)

Below is an example of a typical slurry ash particle size distribution. It demonstrates the typical bi-modal distribution of fines. The first (left) peak shows the smaller particles that are generally a result of attrition. The second (right) peak shows the larger particles that result from reactor-side cyclone inefficiency.



CRUDE/VACUUM DISTALLATION AND COKING

Process Safety

Question 23

High acid crude processing increases mechanical integrity risk. What steps do you take to ensure piping and vessel integrity when running these crude oils? Please discuss:

- *Safe limits of operation (SLO's) for crude acid number, sulfur, temperature and velocity;*
- *Metallurgy upgrades;*
- *Chemical additives;*
- *Inspection techniques, including smart pigging, eddy current testing, UT and inspection frequencies; and*
- *Inspecting furnace convection sections and other equipment that are difficult to access.*

Sam Lordo (Nalco Energy Services)

Defining the safe operating limits is critical during the initial assessment phase of a high acid crude evaluation. Assessments should include a thorough review of existing equipment, unit configuration, metallurgy, flow rate (velocity and shear stress), and stream composition.

Depending on the outcome of the assessment coupled with the operating plan will determine what mitigation strategies are needed.

Typical operating parameters regarding increase risk from high temperature naphthenic acid corrosion are:

- TAN>0.5 in whole crude and TAN>1.5 in side streams. However, damage attributed to naphthenic acid has been observed at TAN levels lower than these guidelines. In addition, some units have experienced no corrosion at TAN level greater than this guideline.
- Liquid flow velocity of >5 ft/s
- Metallurgies less than 316SS, such as, Carbon Steel, 410SS, 5 Chrome, 9 Chrome, etc. are susceptible. The commonly used resistant metallurgy is 317SS.
- Temperature >400°F (200°C)

Mitigation techniques used include crude blending, upgrading metallurgy, letting the metal corrode, using high temperature corrosion inhibitors such as Nalco's SCORPION products or a combination of all of these.

Nalco has successfully used inhibitors for the past 25 years in a number of units to protect various metallurgies with differing process conditions (towers, pumparound circuits, furnace transfer lines, etc.).

Question 25

Coker drum operations have several areas of risk. Please describe your current practices and plans for minimizing risk in the following areas:

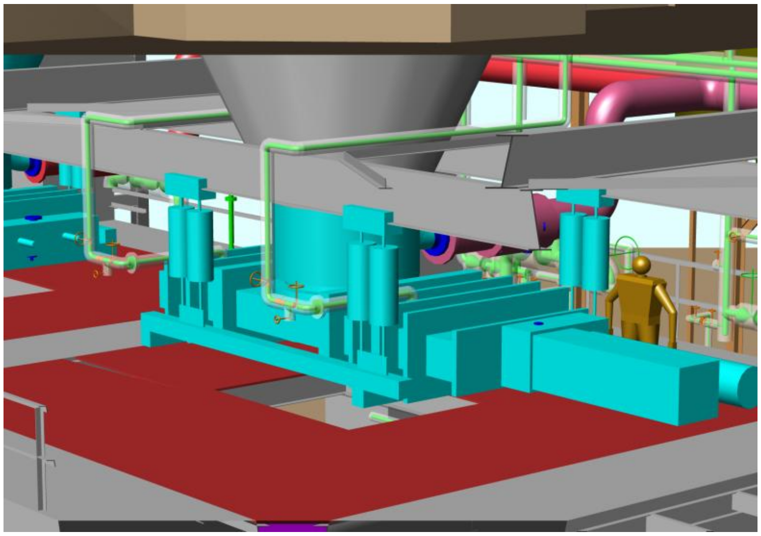
- *Bottom head;*
- *Top head;*
- *Drilling; and*
- *Switching.*

Is remote operation of unheading and drilling operations a feasible target?

Eberhard Lucke (CB&I):
Utilizing the latest and proven developments in equipment design and functionality, CB&I's design includes the following features:

Bottom Head

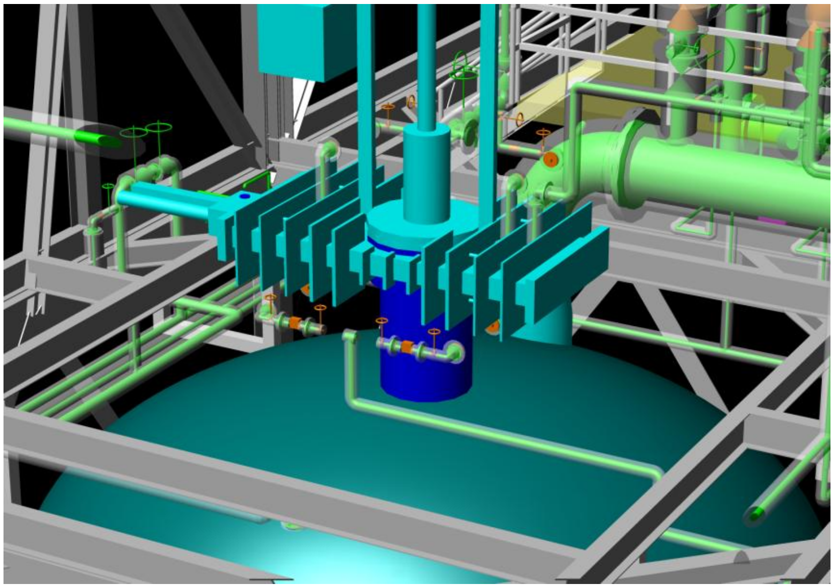
The bottom head is an automated gate valve attached to the coke drum cone flange with a fixed telescope to the coke chute or to a crusher inlet chute (see picture 1). The gate valve control panel is placed in a remote and safe location to eliminate any risk for the unit operator



Picture 1: CB&I Bottom Head – Conceptual Design

Top Head

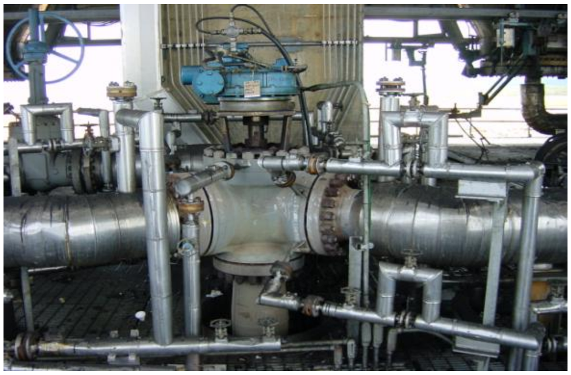
The top head is an automated gate valve attached to the top head flange. On top of the gate valve sits a containment dome including a vent line to route steam and vapor to a safe location. The cutting system has an automatic switching tool which can stay enclosed in the dome (see picture 2). This design also minimizes the risk for the unit operator and allows the operation of the system from a safe, remote location.



Picture 2: CB&I Top Head – Conceptual Design

Coke Cutting/ Drum Switch

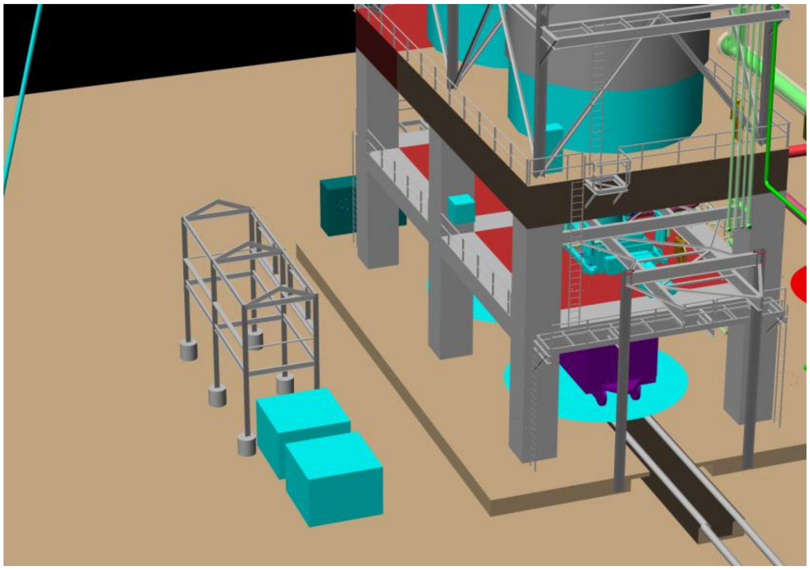
By using the automated coke cutting equipment and a motor driven 4-way ball switch valve (see picture 3), the manual steps for drum switch and coke drilling/cutting are minimized.



Picture 3: 4-way Ball Switch Valve

Remote operation

All main operating and monitoring functions for drum switch, opening/closing of top and bottom head, and coke drilling/cutting will be performed from a remote and safe shelter (see picture 4). The location of the control shelter is selected so that the operator can see the drum bottom head, the telescope and the coke receiving and handling system underneath the coke drums.



Picture 4: Coke Drum Operating Shelter

Richard Conticello (Foster Wheeler USA Corporation)

In the past 15 years, there has been an increased emphasis regarding operator safety of the coke structure specifically regarding coke drum unheading. Older manual unheading devices required maintenance operators to be on the unheading and cutting decks to first remove bolts, lift flanges, and remove the unheading devices. The semi-automatic devices are usually designed to be operated from a remote location such that the operator is at a minimum risk. However, the semi-automatic devices still require bolts and in some circumstances, flanges to be removed prior to operating the unheading device. The most recent development is the slide valve model unheading devices. Slide valve unheading devices allow the operators to operate the valves from a remote location with a minimum risk to their safety when either the top or bottom coke drum heads are opened. The slide valves do not require removal of bolts and flanges to be operated. One slide valve vendor has a safety pin that must be removed and placed in a specific area on the opposite side of the valve prior to allowing the valve to be operated. When operating the valves from a remote location, operators are at minimum risk to exposure to H2S and also should have a clearer path for emergency egress if necessary.

Drilling of the coke drum is usually performed in a dedicated operator cutting shelter. Emergency trip logic regarding the drill stem location in the coke drum is one safety aspect that is part of the cutting equipment vendor's standard supply package. In recent years, some of our clients have requested one common cutting shelter for multiple drums (6 coke drums) for cost reduction, operator safety, as well as egress. There is a device that is being marketed by one cutting equipment vendor that combines the drill stem enclosure with a slide valve top unheading device. Auto-shift tools have also been used to keep the drill stem in the coke drum for the entire cutting operation.

With the current industry practice of a valve interlocked system around each coke drum, if properly installed and maintained, the operators should be at a minimum risk when the coke drum switching operation is performed. The interlocked system is configured in such a manner that the operator cannot switch into an open drum or open a live coke drum.

Foster Wheeler is currently exploring with several clients the operation of the unheading devices, coke cutting, and valve switching from a remote location not on the cutting or switch decks with the main goal of getting the operator off the structure during the critical times thus providing additional operator safety.

Brian Doerksen (ConocoPhillips)

- Continuous improvement
- Safety reviews / standards
- Valve type unheaders
- Remote drilling and remote auto drilling
- Safety interlocks
- Emergency egress / water deluge

Opportunity Crudes

Question 26

What is your experience with crude containing high levels of mercury? What are the operational and safety issues?

Andrea Foster (Johnson Matthey Catalysts)

Levels of mercury in crude vary greatly depending on the location. Reported mercury levels in crude range from 30,000 ppb in California to a few ppb in Africa.

Mercury contained within the crude can plate out on metal surfaces it contacts. This can cause issues relating to personal exposure during maintenance and also issues relating to the disposal of mercury contaminated equipment at end of life.

In high mercury containing streams elemental mercury has been seen to collect at low points and drop out during draining or when the pipes are opened up.

Crudes which have had mercury removed from them can be sold for a premium. Downstream operators require low mercury feeds to protect their equipment and precious metal catalysts.

Failure of equipment due to the presence of mercury has been seen via two separate mechanisms, liquid metal embrittlement (LME) and amalgam corrosion. LME affects aluminum alloys, copper alloys and some steels. Amalgam corrosion affects aluminum alloys.

Sam Lordo (Nalco Energy Services)
From industry observation we find no one having any operational issues that are attributed to the mercury content in crude. There are numerous reports of product quality (primarily naphtha and fuel oil) and wastewater unit impacts. It can also be related to corrosion in overhead when it is present in the mercuric sulfide form.

Once in the wastewater unit it can cause concerns with respect to heavy metal discharge limits. Nalco has developed a patented additive that when used in conjunction with separation equipment can remove mercury from water to <1 ppb levels.

Precautions are required during turnarounds in units that have processed mercury-bearing crudes to limit personnel exposure. At a recent NACE meeting it was shown that radiographic techniques (X-Ray) can be used to find elemental mercury in piping.

Question 27
What are the low-temperature aqueous corrosion impacts of processing high TAN crudes? How do you mitigate those impacts?

Glenn Scattergood (Nalco Energy Services)
One impact we have observed is what appears to be an increase in chloride salt hydrolysis in the crude unit preheat, atmospheric and vacuum furnaces due to the presence of naphthenic acids, this increases the chloride loading in the crude and vacuum tower overhead systems. When crude TAN increases the refiner should pay close attention to proper overhead neutralizer injection dosage, water wash (if applicable) and monitoring to make the necessary adjustments.

Nalco has also observed increases in organic acids in the crude unit tower overhead systems.

One commonly identified acid is acetic acid. Acetic acid in crude tower overheads can increase when processing some of the various types if high acid crudes (such as, Doba, Kuito, etc.) due to additives containing acetic acid used in oil production.

Another source for both acetic and other light organic acids is from the decomposition of the large organic acids (naphthenic acids) in to smaller, volatile organic acids under atmospheric or vacuum heater conditions. These lighter acids go overhead in the crude and vacuum towers and can cause a decrease overhead water pH.

Decomposition of naphthenic acids, under atmospheric and vacuum heater conditions also may liberate CO2 into the overheads, which will also lower the overhead water pH.

On-line corrosion monitoring tools should be consulted to determine if the corrosion control program should be adjusted to against these acids.

Desalting

Question 28

How do you increase the capacity and performance of existing desalter systems without major capital investment?

Bill Cates (Hunt Refining)

By understanding the function and design of a single stage desalter system, a systematic approach of looking at each controllable variable will yield what steps can be undertaken without spending major amounts of capital dollars. First a look at each variable will independently to determine its affect on the desalter system.

1. Since desalters depend on gravity settling (per Stokes Law) at low rise velocity to remove water from the crude, crude charge rate through the desalter plays a major role in desalter performance. Crude charge rate determines the relative rise velocity within the desalter. As flow rate increases, the upward velocity increases. This increase in velocity will determine the size and weight of water droplets that will have sufficient mass to overcome the upward velocity and settle to the bottom of the desalter. Contact with the desalter manufacturer will help to determine the maximum crude charge rate of a particular crude or crude mix.

2. Crude API gravity is also a determining factor in the ability of water to settle through the crude. Desalters, by design, depend on density differential to cause the water to settle in the bottom of the vessel. As the density of crude approaches that of water, the ability to gravity settle water is diminished as the weight difference between the heavier water and the crude decreases.

3. Inlet temperature of the crude will affect the density differential of the crude and water. Running the temperature at the maximum without flashing hydrocarbon or water liquid to

vapor or exceeding the internal equipment safe maximum operating temperature of 325 ^{o}F will increase the ability to separate the crude and water. Be aware, however, that water solubility in the oil increases as the temperature goes up. This water will be free of salts but will leave the salt particle available to precipitate out if there is not enough water available to absorb the salt.

4. The majority of the salt contained in the crude is soluble in water. For this reason, a "fresh" water source is used to inject the water in the crude. This water is low in chlorides and thus is thought to be fresh due to its ability to absorb salt. The water and crude mixture is agitated to get the water and salt in contact with each other. When the water settles out in the desalter, the absorbed salt goes out with the water.

5. Mixing is required to get the fresh water in contact with the salt in the crude. This most generally accomplished right at the desalter through a specially design double ported mix valve. In going through the mix valve, the water is dispersed throughout the crude in various sized droplets which contact and absorb the salt. The water droplets will then either settle to the bottom due to being heavy enough, remain suspended or will rise with the oil into the electric grid.

6. In a low velocity desalter, the water/oil interface level in the desalter acts to provide two basic functions. This hard interface must be a minimum level above the inlet distributor in order to insure that the oil distributes evenly across the entire desalter. The second function is to provide a wash bed through which the oil must flow that will help to coalesce the water droplets.

7. The electric grid or grids function to combine the smaller water droplets into larger droplets that have the mass to overcome the upward velocity and settle to the bottom. Since a pure hydrocarbon is completely nonconductive, water carried up to and through the electrical grid acts to set up a path for the electricity to travel between grids, in essence creating an electrical short. The electrical conductance ability is increased as the amount of water enters the grid. The flow of electricity through the minute particles of water will act to cause the particles to adhere to each other, thus gaining in size and weight. As the particles gain enough mass, these large particles settle to the bottom of the desalter.

8. Water mixed with the oil tends to create a stable emulsion that will not separate without the aid of a primary emulsion breaker chemical. This chemical is designed to break water out of the oil. Basically, the water droplet is surrounded with oil the acts to isolate the water particle. The function of the emulsion breaker chemical is to destabilize the surrounding oil molecules so that the water can contact each other. When this happens,

the water particle grows in size until it has sufficient mass to overcome the upward velocity of the oil.

9. Using a split feed for either the wash water or the demulsifier chemical could improve the desalter performance.

    - In the wash water case, part of the wash water is injected into the oil just downstream of the charge pump. This water gets intimate contact with the oil in route to the desalter. Another side benefit is the water's ability to keep the raw crude side of exchangers cleaner. Care must be taken that this does not create a stable emulsion.
    - In the emulsion breaking chemical case, putting part of the chemical into the wash water acts to get the emulsion to the more stable emulsion layer quicker. This could result in a better break of the primary stable emulsion. The remaining emulsion breaker chemical is injected in the traditional spot to contact and break the secondary, weaker emulsion layers.

10. Additionally, other chemical treatment programs such as a reverse emulsion breaker designed to remove oil from water can help to clean up the desalter bleed stream.

11. Mud washing the desalter to remove solids from the very low velocity areas of the desalter helps to keep the maximum cross-sectional area available to be used. This effectively helps to keep the rise velocity to the minimum to allow smaller water particles to settle out of the crude.

Now that the controllable variables have been identified and explained, the following things can be done to potentially improve the normal operation of the desalter.

1. Decreasing throughput, while this is most often not a desirable option, will have the affect of improving desalter operation especially if the unit is being operated very close to or in excess of the maximum throughput rate. The decrease in rise velocity will allow smaller water particles to settle to the bottom of the desalter in accordance with Stokes Law.

2. Repiping the crude unit heat exchanger train can help to move additional heat in front of the desalter. Many desalter vendors and chemical vendors state that the desalter needs to be operated at >280 ^{o}F range for heavy crudes. This maximizes the thinning affect heat has on the crude oil to best set up the largest density differential possible without flashing any material to vapor. The optimum temperature is also dependent on the operating pressure inside the desalter.

3. Analyze the source of the wash water. Many refineries use a waste stream to provide the wash water. The pH of this water may have an affect on the performance of the desalter. If the water source is high in pH, using a weak acid, like citric acid, to adjust the pH to a slightly basic range of 8.0 – 8.5 can improve the desalting efficiency.

4. Modifying the injection system for the wash water can help to remove additional salts. Splitting the water injection point so that part of the water is introduced at the front end of the heat train while the rest is injected just prior to the mix valve can have the affect of getting better water contact with the salts thus improving the removal efficiency. Additionally, the water that is injected in the front end of the preheat train will be effectively preheated to the same temperature as the crude. The percentages of the splits will need to be determined on individual units.

5. Preheating the wash water that is injected in front of the mix valve, if not being done, will assist in maintaining the temperature entering the desalter at its maximum. The exchanger to do this job would not be very large so the cost should not be prohibitive. Various sources including the desalter blowdown stream or steam are usually readily available to provide this heat source. Attention needs to be paid to not preheat this small water stream past the bubble point so that steam is being injected instead of the liquid.

6. Accurate calibration during outages of the level transmitter is imperative to good desalter operations. This device needs to accurately display where the oil/water interface resides. During normal operation, use of the tricocks on the desalter will help to monitor if the transmitter is drifting.

7. If the taps on the transformer are on the lower power voltage taps, changing to the higher voltage taps may assist in the desalter’s ability to coalesce the small water droplets.

8. Exploring the vast range of emulsion breaking chemicals may determine a better breaker than is presently used. Additionally, use of a reverse emulsion breaker injected along with the wash water may help to further remove the water from the crude.

9. Install a mud wash system if one is not being currently used. This system will help to remove built up solids that affectively reduce the cross-sectional area available and will thus increase rise velocity.

10. If the desalter has multiple separate bottom drains, look at using each drain on an individually alternating basis to assist the mud wash system in removing solids. Typically, using one drain at the start of the mud wash and then switching to another after is effective in removing solids that tend to settle in areas remote from the drain. By alternating during the mud wash cycle, the solids have to travel a lesser distance to reach a drain point to be removed from the desalter.

These are some opportunities to improve desalter performance without spending large capital dollars to achieve. Past this point, major investments will be necessary to improve the overall desalting of the heavy crudes.

Sam Lordo (Nalco Energy Services)

Without incurring major capital investments some improvements can be achieved by improving level control, crude preconditioning in tankage, use of asphaltene dispersants, solids removal additives, and reverse demulsifiers. Other aspects can include crude blending to prevent incompatibility and development of a slop management program.

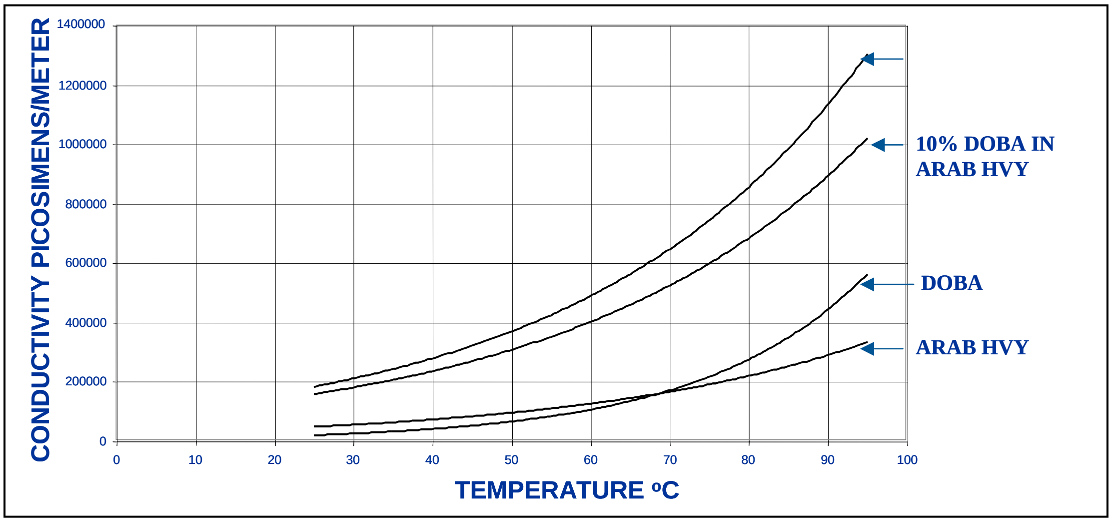
Developing a sound desalter mudwashing procedure and mix valve optimization studies can also improve desalter performance, especially after there has been a major change in the type of crudes being processed, such as going from medium gravity crudes to low gravity crudes.

Question 29

What operating strategies do you employ when desalting high conductivity crudes? What operational and/or equipment changes mitigate the problems caused by high conductivity?

Sam Lordo (Nalco Energy Services)

The real issue is that you may not be able to do much to lessen the impact of crude conductivity. Blending in some cases does not reduce crude conductivity; in fact it has been shown to actually have an unexpected increase. The graph below is a blending experiment that demonstrates this phenomenon.



So you are left with limiting the amount of the specific crude causing the problem and or upgrading the electrical section of the desalter.

Question 30
What options are available to minimize the impact of high BS&W crudes on desalter operation and wastewater treating?

Sam Lordo (Nalco Energy Services)
Several steps can be taken to lessen the impact of high BS&W crudes. These include:

- Crude preconditioning in tankage to promote desalter dehydration
- Tankage dewatering of the high BS&W crudes
- Monitoring upstream of the desalter, using online devices or sampling, so increases in BS&W coming to the desalter are not unexpected. Changes to operations, such as reducing desalter washwater, decreasing mix valve, can be made in anticipation of the change in crude quality
- Since one of the most common impacts is oily brine, or requiring a lower of the water level resulting in oily brine, installation of a brine break tank allows a second chance to clean the brine before passing it the wastewater unit.

Question 31

What are the challenges in desalting heavy or synthetic crudes such as those from western Canada or Venezuela? What are your experiences?

Sam Lordo (Nalco Energy Services)

The primary challenge is the change in crude viscosity (usually an increase) and in many cases a decrease in desalter temperature due to preheat heat exchanger alignment. Following Stokes' Law, both of these tend to decrease the effective size of the desalter.

Our experiences show that chemical pretreatment in tankage and use of asphaltene dispersants can be used to minimize the impacts of running these heavy crudes whilst maintaining charge rate.

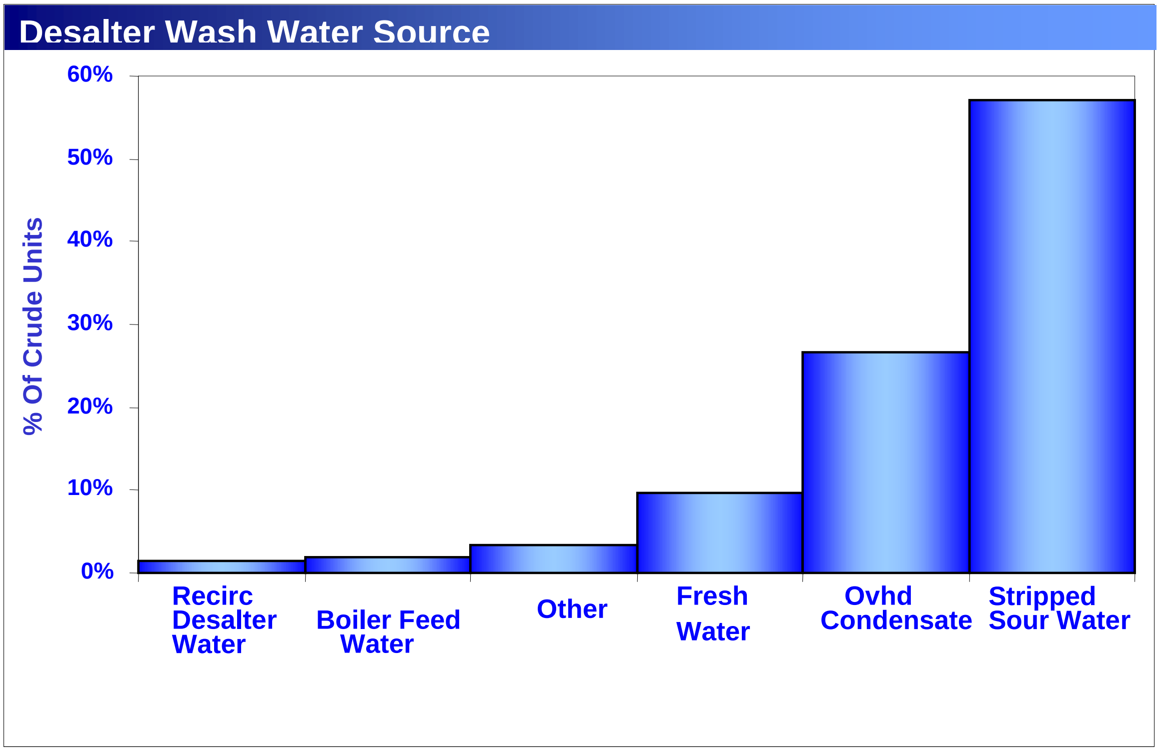
Quesition32

What are the best practices for minimizing desalter make-up and, consequently, desalter effluent volumes? Is it technically or economically feasible to utilize desalter effluent as make-up water for cooling water or boiler feed water service?

Regan Howell (Holly Corporation)

A separate question addresses, in detail, the variables affecting desalter performance. There is a minimum level of desalter makeup water and, consequently, a minimum amount of desalter effluent. If refiners can utilize other "waste" water streams as desalter makeup, there is a corresponding decrease in refinery effluent.

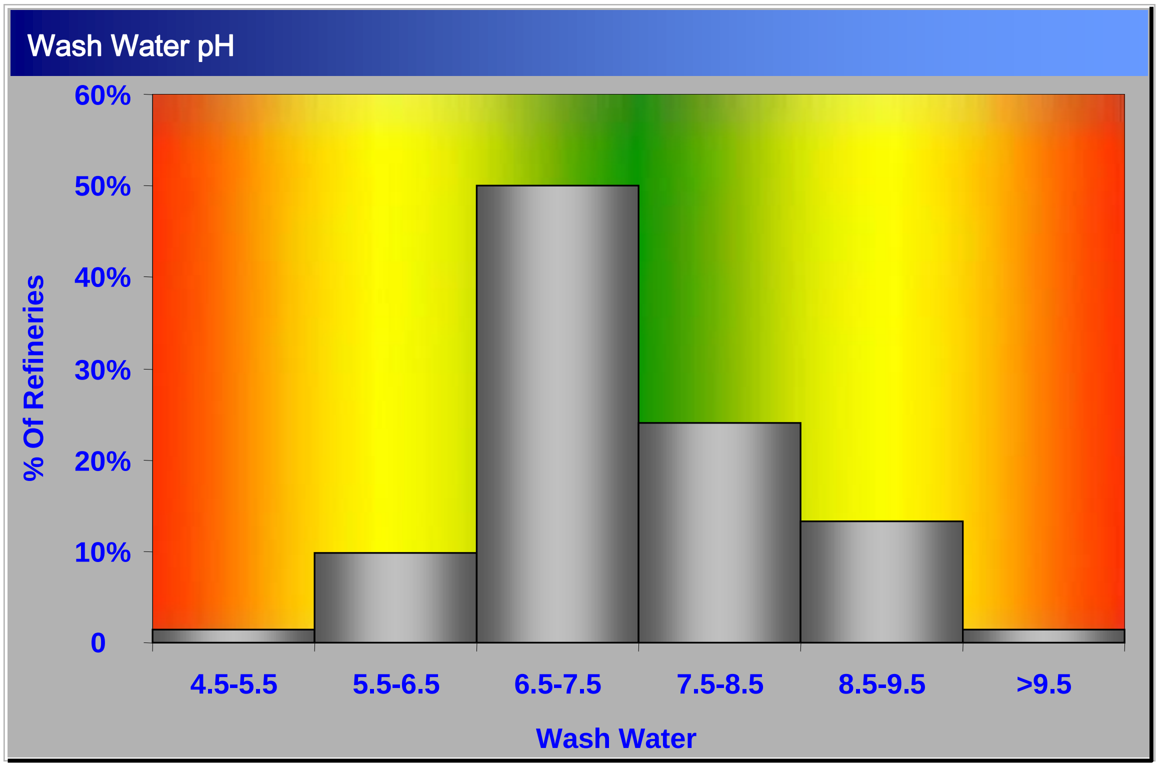
The attached histograms depict the results of a survey by GE Water & Process Technology of 188 crude units. Nearly two-thirds of those units use stripped sour water as desalter makeup. Condensate from the water boots of the crude overhead system accounts for makeup on one-quarter of the crude units. Fresh water is used in only about ten percent of those crude units. All other sources account for makeup at less than ten percent of those crude units surveyed. Holly utilizes stripped sour water as makeup in both of our refineries.



Courtesy of GE Water & Process Technologies

The widespread use of stripped sour/foul water as makeup water for crude desalters requires careful balancing of the steam operating cost at the sour water stripper and chemical cost at the crude unit overhead. If steam to the sour water stripper is decreased, ammonia levels in the stripped sour water will increase. If water with high ammonia content (> 50 ppm) is fed to the desalter, corrosion rates will increase in the overhead of the crude unit. Oftentimes, an increased rate of corrosion-control chemistry must then be fed to the crude overhead system to counteract the higher ammonia level.

Other waters are possible candidates for desalter makeup water. The following chart shows the pH range of desalter makeup water in the same 188 crude units previously mentioned. pH ranges where the background is green and yellow are acceptable (5.5-9.0); oranges and reds are not (>9.5 or <5.5).



Courtesy of GE Water & Process Technologies

Use of boiler feed water as makeup can be problematic due to the chemicals typically present in BFW, especially the polymers and neutralizing amines. Recirculated desalter water is suitable until the contaminant level reaches the point where the gradient for salt and contaminant removal from the crude diminishes and fresh water must be added. Recirculated water also does nothing for the overall water balance, since internal recycle streams do not affect the water "balance" at steady-state.

Neither Holly's experience, nor the best judgment of others in the industry indicate the technical ability or economic incentive to process other refinery effluent waters for use as desalter makeup water.

Sam Lordo (Nalco Energy Services)

The only practical way to minimize desalter make up water is to recycle a portion of the brine into the desalter washwater. However, this is not without risks. If the brine being recycled is emulsified oil or heavy with solids this can make stable emulsions in the desalter. Other strategies include the reuse of waters from outside the crude unit, such as, stripped sour water, selected tower overhead condensed water, and deareated wastewater effluent, as part of the desalter washwater make up.

Technically it is feasible to utilize desalter brine effluent as cooling tower or boiler feedwater through the use of osmotic membranes, ion exchange, clarification processes, filtration, etc.; however, it is probably not economically feasible except under the most drastic conditions.

Crude/Vacuum Distillation

Question 34

What impacts are oil field additives having on crude unit operations? What mitigation strategies do you use? Please describe your experiences.

Sam Lordo (Nalco Energy Services)

Raw crude oil is often processed further to remove light gases and excess water. The processes also use a variety of chemical additives. Table 1 shows a number of the commonly used additives in oil field production. Some of the additives will not have any impact on crude tower or unit corrosion. Others can potentially increase the likelihood of corrosion if they are not removed before the crude oil is shipped to the refinery.

Postproduction processes, such as crude dehydration, often reduce the residual amount of these chemical additives to levels that are not an issue in the refinery or to levels that are not easily detected. In some cases, though, the type of residual or amount is sufficient to cause issues.

In one example, a new crude was brought into a refinery as part of the feed slate (25-30%). The crude still contained some of the well stimulation fluids at a level that the overhead halogens increased from 10-20 ppm to >200 ppm. The unit has caustic injection to control chloride hydrolysis; however, in this case the caustic injection capacity was undersized for the intermittent halogen spikes. These spikes increased the corrosion rate (from corrosion probes) from 5-10 mpy to 50-60 mpy. The halogen identified was bromine and it was learned that some of the completion fluids had contaminated the crude shipment.

Acid injection can be used in the crude dehydration step. The most commonly used acid is acetic acid. This has been found to remain in the crude, probably as soluble acetic acid and dissolved in dispersed brine. It can also exist as a complex (i.e., calcium acetate), only to decompose in the crude furnace releasing the acetic acid function. Another type of emulsion breaking additive that could cause increased chlorides in a crude overhead, if not removed completely, are metal salt additives, such as, zinc chloride, aluminum chloride, etc.

Most corrosion inhibitors used in raw crude production and transportation are similar to those that are currently used in crude unit overhead corrosion control (i.e., Imidazoline). These compounds will decompose to harmless hydrocarbon fractions in the crude unit furnace. Some corrosion inhibitors added to the crude oils are suspected to carry through the raw crude and refinery process then decompose in the crude furnace. The corrosion inhibitors of most concern are those that are much more water soluble, such as quaternary amine chloride. Other corrosion inhibitors are diamines or polyamines, which could decompose to simple amines. Their decomposition temperatures and products are unknown.

Some paraffin control products used to clean wells are known to be chlorinated hydrocarbons. Historically, the use of these types of paraffin solvents was wide spread. However, industry placed restrictions in the form of specifications on the amount of chlorinated solvents, which reduced their usage. Recently, some crude oils have been suspected to contain these types of compound again. Their usage is seasonal and transitory and therefore hard to identify. Existing analytical testing is time consuming so shipments are often processed before the contaminant can be identified.

Enhanced recovery techniques using carbon dioxide (CO_2) can contribute to overhead corrosion. This is especially an issue for those crudes that are transported from the oil field to the refinery via pipeline. This mode of transportation does not allow enough time for CO_2 to disengage.

In most cases the only mitigation strategy that is quick to perform is to make rudimentary inspections such as, salt content, amine content, etc. More complex analysis can be done such as laboratory pilot testing to identify desalter, corrosion, and fouling impacts, but these are not easily or quickly done.

Table 1: Upstream Additives

Contaminant	Application	Could it Impact Crude Unit Corrosion?
Mineral acids (HCl, HBr, KCl, H3PO4, HF)	Well Stimulation, Emulsion Breaking, Scale Control	Yes
Organic Acids (Formic, Acetic, Citric, Glycolic)	Well Stimulation, Completion Fluids, Emulsion Breaking	Yes
Other acids (alcoholic HCl, EDTA, Fluoroboric acid)	Well Stimulation, Completion Fluids, Scale Control	Yes
Gelling Polymers	Well stimulation, Completion Fluids	No
Oxyalkylate resins	Emulsion Breaking	No
Solvents	Paraffin control	Some (chlorinated solvents)
Water treating polymers	Emulsion Breaking	Low probability (water- based)
Metal salts ($ZnCl_2$, $AlCl_3$, poly(aluminum) chloride)	Emulsion Breaking	Yes
Polydimethylsiloxane	Antifoams	No
Fluorosilicones (rarely used)	Antifoams	Yes
Methanol	Hydrate inhibitors	No
Phosphate esters, Phosphonates	Scale Control, Corrosion Control	Yes
Polyacrylic acid	Scale Control	Yes
Carbonic Acid	Enhance recovery	Yes
Neutralizing Amines (MEA, EDA, MMA)	Corrosion Control, H2S Scavenger	Yes
Quaternary Amine Chloride salts	Corrosion Control, Biocide	Potentially
Filming Amines (poly-substituted monoamines, Diamines, Polyamines, Imidazoline)	Corrosion Control	Potentially
Triazines	H_2S Scavenger	Yes
Chlorine, Bromine	Biocide	Yes
Ethylene Vinyl acetate Copolymers, Styrene/Ester Copolymer	Wax crystal modifiers	No
Polyalphaolefin polymers	Drag reducers	No

Dennis Haynes (Nalco Energy Services)
There are various possibilities that oil field additives can impact crude unit operations, but the most discussed and clearest impact recently are with respect to hydrogen sulfide scavengers. There are certain types of hydrogen sulfide scavengers that produce certain types of amines that have high salt forming potentials in atmospheric tower top internal sections. This has been reported in the industry as a problem; however, not all hydrogen sulfide scavenger chemistry

products have the same amine as a resultant. Therefore, it is important in hydrogen sulfide scavenging to apply the additive with a resultant amine with the lowest potential for salt creation. Nalco has a proprietary chemistry that is fit for this type of application, and has significant application experience with no reported problems from amine chloride salt formation with the Nalco product.

Crude Heater

Question 35

Please describe your experience with the latest generation of ultra-low NO_x burners. Please comment on operating performance (NO_x level achieved); flame height; operability; and sensitivity to fuel gas composition variability.

Regan Howell (Holly Corporation)

Holly is in the process of retrofitting several heaters with "next generation" or ultra-low NOx burners. Our experience in the design phase has included substantial effort to design ultra-low NOx burners without de-rating the heaters. In one particular furnace we found both the box too short and the burners too close together. Another heater simply did not have the underside clearance sufficient for ultra-low NOx burners. Fuel gas composition variability and fuel gas cleanliness are other issues we are incorporating into the overall design package.

Brian Doerksen (ConocoPhillips)

- For coker heaters, experience with ULNB
- Effect of cyclic duty
- Flame stability
- Length of flame

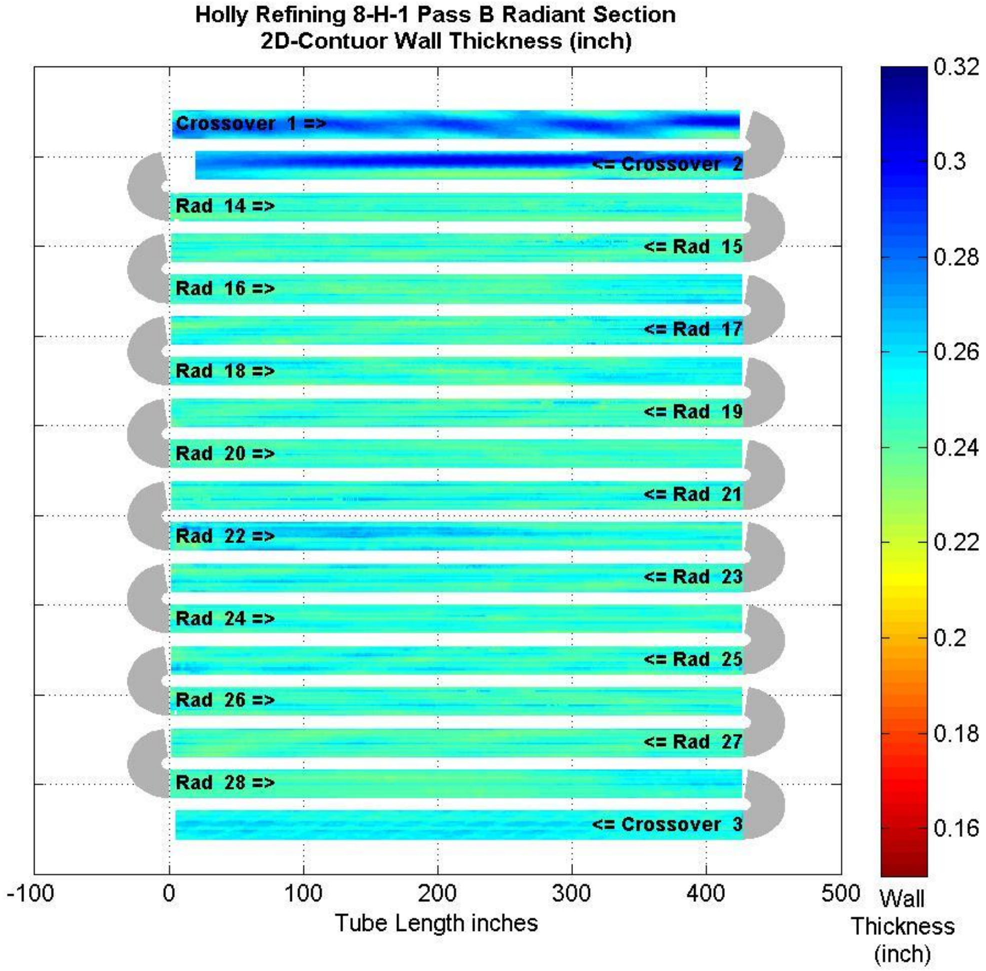
Question 36

During a unit turnaround, how are you assessing remaining life for convection and radiant coils in the short time available?

Regan Howell (Holly Corporation)

Holly's inspection groups are using many of the standard industry tools for non-destructive testing and determination of remaining life. Dragging a feeler gauge along the exterior of furnace tubes to identify creep or "ovality", Brinell hardness testing, and a fit-for-service evaluation per API 579 (using actual temperatures and time-in-service) are standards.

Recently, we have experienced impressive results with "smart pigging". The smart pig used in our Woods Cross crude heater gave impressive results in 5% and 9% Cr- ½ Mo steel tubes, both finned and bare.



While the graph shown here displays wall thickness, similar data can be gathered on variations of the inlet radius in a given tube; an indication of bulging or creep.

Holly has also used MPC Ω creep strain rate testing to determine remaining life in furnace tubes. This method requires too much time (months) to complete during a turnaround, but sections of representative tubes have been removed during a brief outage, then tested to justify action or inaction during the next turnaround.

Brian Doerksen (ConocoPhillips)

- Physical measurement for creep
- Use of Annex 'A' of API 530
- MPC 'Omega testing'

Question 37
What practices do you currently employ for exterior scale and process side coke removal in process heaters? What criteria are used to determine level of cleanliness?

Regan Howell (Holly Corporation)
Holly uses steam-air decoking and pigging, depending upon the particular heater, at one facility for process-side coke removal. The other refinery utilizes pigging only. Level of cleanliness is determined by the operators of the coke removal process. When steam-air decoking, the operators monitor O_2 levels and temperatures to give evidence of coke removal. When pigging, the pig-truck operators use a foam indicator pig to demonstrate consistent tube inside diameter. When the pig comes out mostly clean and minimally compressed, we consider the tubes clean.

Exterior scale is most often removed, while the furnace is down, with brushes and/or feeler gauges. On-line cleaning of the firebox-side of tubes by walnut shell blasting has been approved for use in our refineries but we've not yet had an opportunity to conduct and evaluate such a cleaning.

Like many in our industry, Holly has experimented with ceramic coatings on heater tubes. While we do not have "hard data", anecdotal and qualitative evidence suggests lower firebox-side scale on coated tubes than uncoated tubes.

Brian Doerksen (ConocoPhillips)

- OD Scale removal
    - On line
    - Entry
- Process side decoking
    - Pigging
    - On line spalling
    - Steam air decoking

Coker Heater

Question 38

What mitigation strategies have you used to reduce delayed coker furnace fouling? Were they successful?

Eberhard Lucke (CB&I):

For a Coker Revamp in a German Refinery, the following heater modifications have been implemented:

- Installation of additional steam injection points in the heater radiant section to change the velocity profile and delay the tube fouling
- Reduction of the number of tubes in the radiant section to reduce the residence time versus increasing tube heat fluxes
- Increase in spacing of the last 10 tubes close to the heater outlet to achieve a better heat flux distribution and lower peak heat fluxes
- Improvement of the burner performance and reduction of flame impingement by using a better burner tip design to move the flames away from the tubes toward the center wall

All these modifications allowed the refinery to switch the Coker unit operation from 100% atmospheric residue feed to 100% vacuum tower bottoms while maintaining the same heater performance and heater run length of 10 – 12 months.

Observations in old Coker units show that some of the older heaters show significant air leaks in the firebox walls which can cause maldistribution of heat in the firebox and disturbance of the desired flame profile. Improving the firebox wall insulation and closing air leaks in the walls can help significantly in improving burner controls and flame direction.

In a previous revamp in the same German refinery as mentioned above, the unit capacity was increased by adding a second pair of coke drums. Instead of replacing the main heater, a fired pre-heater was installed at the end of the feed pre-heat train. Such a fired pre-heater will help any operation to unload the main heater during unit expansions, which will allow operating the main heater at reasonable duties and fouling rates.

Patrick Bernhagen, Foster Wheeler USA Corporation
New Delayed Coker Heaters are supplied with the higher velocities for better inside coefficients and lower inside film temperatures. The fireboxes are generously laid out for coil to burner spacing and to provide a well stirred box. Individual pass firing and flow control allow tuning of each pass for the process conditions. Burners are selected to provide a specific flame pattern and the use of brick firing walls is standard practice. The combination of all of the above is coordinated to provide uniform heat flux to the tubes while minimizing any hot spots.

Existing Delayed Coker Heaters can benefit from replacing old style plug headers with contoured plug headers to reduce pressure drop through the coil. This reduced pressure drop can be utilized to increase velocity which helps reduce coking tendencies. Proper burner selection when faced with lower NOx emission requirements is a necessity; improper selection can cause flame impingement and hot spots.

Some refiners have used additives at the inlet of the coker heater to reduce coke buildup. There are mixed reviews on this process. Evaluations are ongoing.

Gregg McAteer (Nalco Energy Services)
Nalco has found a combination of coke suppressants and high temperature dispersants work well to retard the buildup of coke on furnace tubes. Proper feed analysis will help determine the likelihood of success. One of the side benefits to a coker furnace fouling control program is the decreased impact coker upsets have on the furnace. One customer finds this benefit to be the most valuable aspect of the program. Historically, an upset would bring the furnace down within weeks, whereas now they recover so well after upsets they normally make their planned run lengths.

Brian Doerksen (ConocoPhillips)

- There can be several contributing causes of fouling on the fire side and process side.
- Process side
  - Coke formation
  - Asphaltene precipitation
  - Deposition of inorganic salts
- Fire side
  - Combustion issues or scaling
- Coke formation
  - Thermal cracking process, time and temperature
  - Usually occurs in lower radiant outlet tubes
  - Furnace design

  - Keep flow turbulent
  - Distillate Recycle ^{TM}
- Asphaltene precipitation
  - Tends to occur in the radiant section
  - Problem with highly paraffinic resids or chemically or thermally processed feeds
  - Laboratory analysis to select distillate to improve solubility
- Inorganic salt deposition
  - Tends to occur in the upper radiant or lower convection section
  - Naturally occurring or result of chemicals used in production or transportation
  - Difficult or impossible to SAD or OLS, we often need to pig decoke
- Tube fouling due to fire side issues
  - Furnace design
  - Good basic firing practices
  - Consider ceramic tube and refractory coatings

Question 39

Is there a correlation between vacuum tower operating severity and delayed coker furnace fouling?

Eberhard Lucke (CB&I):

In general, there are four main aspects that determine the fouling rate and therefore the run length of a Coker heater:

1. The heater design
   Single fired heater versus double fired heater; average and peak tube heat fluxes; bulk fluid and oil film velocities; heater residence times total and at cracking temperature; burner arrangement
2. The Coker operating severity
   Unit recycle ratio; coil outlet temperature (COT); actual feed rate versus design feed rate; flame impingement on tubes; flow rate of velocity medium in heater tubes (steam or condensate)
3. The Coker feed quality
   Feed gravity; viscosity; Conradson Carbon content (CCR); asphaltene content; aromatics content; other feed components like resins, paraffins etc; metals content
4. Chemical Additives
   Additives used at production well site; additives used at refinery upstream units, example: caustic injection for corrosion control

In many cases, the vacuum tower bottom product (VTB) represents the main source, in some cases even the sole source for the Coker feed. In these cases, the severity of the vacuum tower operation will have a significant impact on the fouling rate and the run length of the Coker heater. Typical parameters of the Coker feed that will be discussed in more detail later are Conradson Carbon Content (CCR), asphaltene content and asphaltene to aromatics ratio, sodium content and viscosity. Due to the variety of crude oils processed in refineries, and due to the different heater designs and Coker operating severities, the impact of the Coker feed quality on the heater fouling rate can not be described in a simple correlation. But the following paragraph will give a qualitative description of the basic principles.

In very simple words, the fouling or coking rate in a heater tube is a function of temperature and time. Every adjustment to the heater design or operation that increases the temperature profile and/or increases the residence time at cracking temperatures will also increase the coking and fouling rate in the heater. Also, the more severe the vacuum tower operation (defined as high VTB cutpoint operation), the higher the VGO recovery and the heavier the VTB. The heavier the VTB is, the higher is the tendency of the Coker heater to foul faster and to show a decreased run length. Based on these principles, the following conclusions can be drawn:

1) The heavier VTB, as characterized by a lower API gravity, contains less heavy VGO components. As a result, at constant feed rate and constant unit parameters less of the feed material will vaporize in the Coker heater. This leads to lower velocities in the heater tubes and higher residence times at temperatures > 800°F. The ultimate consequence is higher conversion and increased fouling in the heater tubes.
2) The heavier VTB will have a higher concentration of asphaltenes, while at the same time less material like aromatics will be present to keep the asphaltenes in stable suspension. In the Coker heater, components like heavy aromatics start vaporizing and cracking, and the asphaltenes fall out of the suspension and combine to clusters, which form a layer of coke on the inside of the tubes. The higher the overall asphaltene content of the Coker feed, and the lower the asphaltene to aromatics ratio, the higher the fouling rates in the heater.
3) The increased viscosity of the VTB consequently causes a higher viscosity of the bulk fluid and of the oil film inside the heater tubes. This reduces the velocity in the tubes and increases the residence time of material at temperatures >800°F. As a result, fouling rates will go up.
4) The heavier VTB will have a higher concentration of metals and other impurities like sulfur, nickel, vanadium and – especially important for this case – sodium. At certain levels of concentration, sodium acts like a seed for coking and accelerates the fouling process in the Coker heater. As a rule-of-thumb, sodium concentrations > 25 ppmw are considered critical for accelerated heater fouling. Some operations can accept higher sodium concentrations; others limit their feed sodium levels to lower values. High

sodium concentrations can also be caused by caustic injection for corrosion control in upstream refinery units.

A qualitative assessment for the fouling rates of a Coker heater has to be performed for each specific operation. As mentioned above, there are multiple parameters that have an impact on the heater fouling rates, the feed quality being one of them. Increasing the VTB cutpoint in the vacuum unit feeding the Coker unit will most probably result in increased heater fouling and shorter heater run length.

Jack Buckley (Foster Wheeler USA Corporation)
The correlation to the severity of the Vacuum Tower operation vs. coker furnace fouling is only due to heavier feed being processed in the Coker Heater. Heavier feeds tend to lay down coke at a faster rate at constant coker heater throughput. The correlative criteria for coker furnace coking rate include asphaltene content, velocity and film temperature.

Brian Doerksen (ConocoPhillips)

- Heavier vacuum resid can have a significant effect on the rate of coking.
- Heavier resid vaporizes to a lesser degree.
  - Volumetric rate lower, velocities lower, less turbulent.
  - Increases film temperature and time to form coke in the tubes.
- Heavier resid also tends to have a higher ratio of asphaltenes to resins + oils

Question 40
Does your refinery (or refineries) have plugged headers (mule ears) on one end or both ends of the heater? Is this common in the industry? Are you planning to phase them out?

Patrick Bernhagen (Foster Wheeler USA Corporation)
Foster Wheeler Fired Heater Division recommends and supplies our Delayed Coker Heaters with Plug Headers on one end of the radiant section. Currently this is the only heater service where we recommend Plug Headers in normal circumstances. We still use plug headers not for heater operation but to allow recovery from external operational upsets that cause tubes to coke up to a point conventional decoking does not work.

These plug headers are welded to the tube while older practices had them rolled to the tube. All of our recent plug headers have contoured plugs allowing them to be mechanically pigged. The usual problems associated with plug headers are leakage during start up prior to the plug seating.

One aspect of their design is the plug is matched specifically to the hole in which the plug it was supplied. During maintenance of these plug headers it must be stressed that the plug must be handled properly so as not to score the seats or threads and that the plug be placed back into the same hole from which it was removed. This procedure may not completely eliminate the leakage but usually provides better results.

Brian Doerksen (ConocoPhillips)

- Yes, but on a very few remaining coker heaters.
- For the past 30 years, we've tended to use return bends in the fire box.

Question 41

How do you justify replacing major capital assets such as coker heaters and coke drums?

Michael J. McGrath, Foster Wheeler USA Corporation

The replacement of heaters or coke drums is typically based on economics. If a larger piece of equipment is required then the economics are based on the incremental capacity obtained by the unit with the replacement. This type of replacement is usually difficult to justify unless the item would soon be replaced for maintenance reasons. A replacement for maintenance reasons is also based on economics considering the ongoing repair costs and lost production time. In some cases, the item may be reaching its useable life and is being replaced to avoid safety issues in the future.

Coke Drums

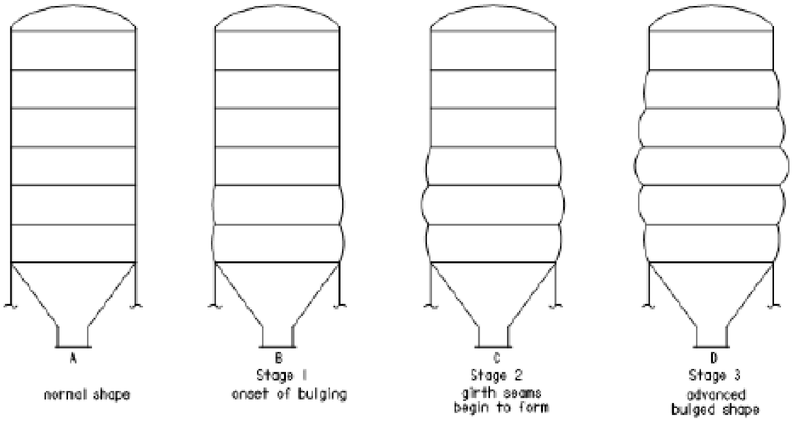
Question 42

What advances have been made on coke drum life expectancy, either through new drum designs or operating best practices?

Eberhard Lucke (CB&I):

There have been a number of improvements over the last years targeting increased coke drum life in both areas, coke drum design and operating best practices. While the improvements in drum design only apply to new Coker units and units where coke drums are replaced, the operating best practices help refiners with existing Coker units to maximize the life expectancy of the existing drums.

To evaluate the improvements in coke drum design and their effectiveness, one first has to understand the most common mechanism of coke drum failure. As has been shown in many reports and presentations in the past, the bulging and cracking is caused by the thermal stresses induced on the drum during the drum quench and the feed injection. Especially during the drum quench, the injection of cold water into the hot coke bed causes high thermal gradients in the drum material of up to 10°F per inch. As a result, over the increasing number of thermal cycles the drum experiences radial growth or bulging. At the same time, the circumferential weld seams in this portion of the coke drum tend to augment the bulging due to higher yield strength of the weld material compared to the base plate material. The result is a “constrained balloon shape” as shown in Picture 1.



A
normal shape

B
Stage 1
onset of bulging

C
Stage 2
girth seams
begin to form

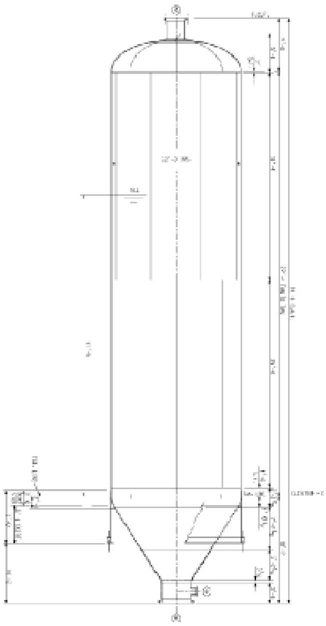
D
Stage 3
advanced
bulged shape

Picture 1: Successive stages in bulging deformation in coke drums (to an exaggerated scale)

In areas where the circumferential weld seams support the bulging, the base material tends to become thin and ultimately fails via through-wall cracking. The following paragraphs discuss the most common improvements in drum design and drum fabrication with reference to the failure cause as described above:

1. Elimination of circumferential weld seams (CB&I Vertical Plate Drum)

The same studies that showed the circumferential weld seams in the lower section of the coke drums as being the critical area for drum bulging and cracking, also show the longitudinal weld seams in the same area (outside of intersections with circumferential weld seams) were unaffected by the thermal cycling. Based on extensive research and analysis, CB&I concluded that the best solution to the problem was to eliminate the circumferential weld seams in the area of concern. Incorporating technology and know-how from other applications, CB&I developed a method for fabricating shell plates with the long side oriented vertically. Limited only by steel mill manufacturing capability, the longest vertical plate depending on specified thickness and alloy material can be up to 46' long. By introducing the Vertical Plate Coke Drum (patented), up to 5 circumferential weld seams can be eliminated, resulting in a cylindrical shell that can endure the severe thermal cycles (see Picture 2).



Picture 2: CB&I Vertical Plate Drum - Elimination of Circumferential Weld Seams

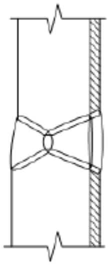
CB&I has successfully used the Vertical Plate technology for repairs, retrofits, replacements and new drums since 2000. Recent analysis of coke drums in service for over 2000 cycles (at 14 hour drum cycle times) have shown no significant deterioration or bulging in the critical areas of the drums.

2. Decreasing the weld metal yield strength

To minimize the difference in yield strength between the weld seams and the base plate material, the yield strength of the weld material should be decreased to be within +10% of the base plate material. This approach is very difficult to accomplish because the difference of the yield strength of the most common base plate materials compared to commercially available weld metals is typically higher than 10%. In addition, the yield strength of the base metals and the weld metals varies with temperature and may make the yield strength differential greater than 10% at operating temperatures. As a last remark, to control the weld metal yield strength to a tight specification in relation to the supplied base metal will require the use of weld processes that are not necessarily productive and cost effective.

3. “Blend grinding” the weld profile

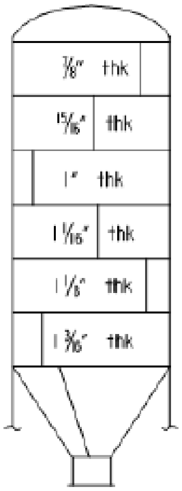
Blend grinding the weld profiles (see Picture 3) will reduce the geometric stress raiser effect near the weld seam and can extend the service life of the weld joint. This procedure can be cost effective if it is properly specified and managed. In any case, eventual repairs to the weld joint will be inevitable.



Picture 3: Weld Profile

4. Uniform shell thickness and thicker plates

As shown in Picture 4, older drum designs show a decrease in shell thickness for each course from the bottom to the top of the vessel. This design was based on the decreasing design pressure for each course, and allowed to minimize the total material cost of the vessel.



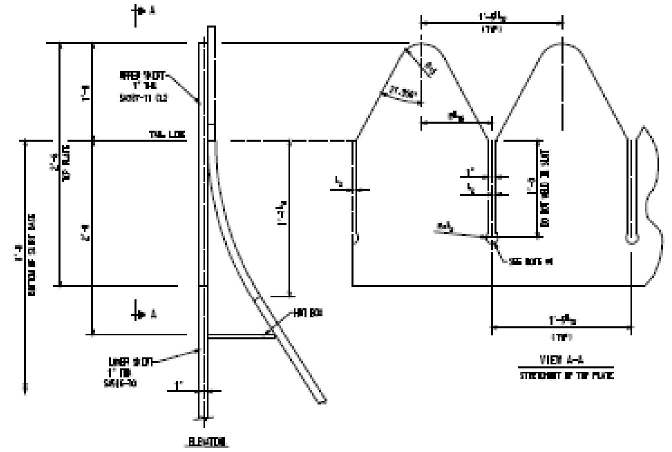
Picture 4: Typical shell thickness reduction

As a downside, this design does increase the stiffening effect of the weld metal used for the circumferential weld joints, and the thinner base plate will resist less thermal stresses during the life of the drum. The specification of very thick (> 2") and uniform shells reduces the stiffening effect of the weld seams and the peak stresses caused by the thermal cycles to some extend. But it will not completely eliminate the bulging and cracking mechanism in the drum shell, just slow it down. And it adds material and labor cost to the overall cost of the vessel.

5. Use of higher alloy materials
In theory, the use of higher alloy materials like 2 ¼ Chrome-1 Moly will make the vessel more resistant to the thermal cycling. This is based on the higher yield strength and the better creep and creep-fatigue resistance. In practice, drums of higher alloy materials in service haven't seen enough thermal cycles yet to determine if it is a major improvement. Also, using high alloy materials will also increase the cost of the vessel and make it more difficult to repair.

6. Non-destructive examinations (NDE)
Some of the new drum specifications require increased NDE testing and use a reduced acceptable flaw size. By doing this, more uniform weld joints should be produced. These procedures will increase the cost of the fabrication process without having any positive impact on the basic problem. Also, there are indications that show that the increased repair rate during the manufacturing process actually reduces the service life of the weld joint due to premature failures.

Another area of concern is the weld attachment of the skirt to the drum shell. This weld seams has been prone to cracking due to the same thermal cycles that cause the drum shell to fail over time. Several improvements have been made to the skirt-to-shell attachment. Picture 5 shows one of the improved designs, named T-Rex skirt (patented).



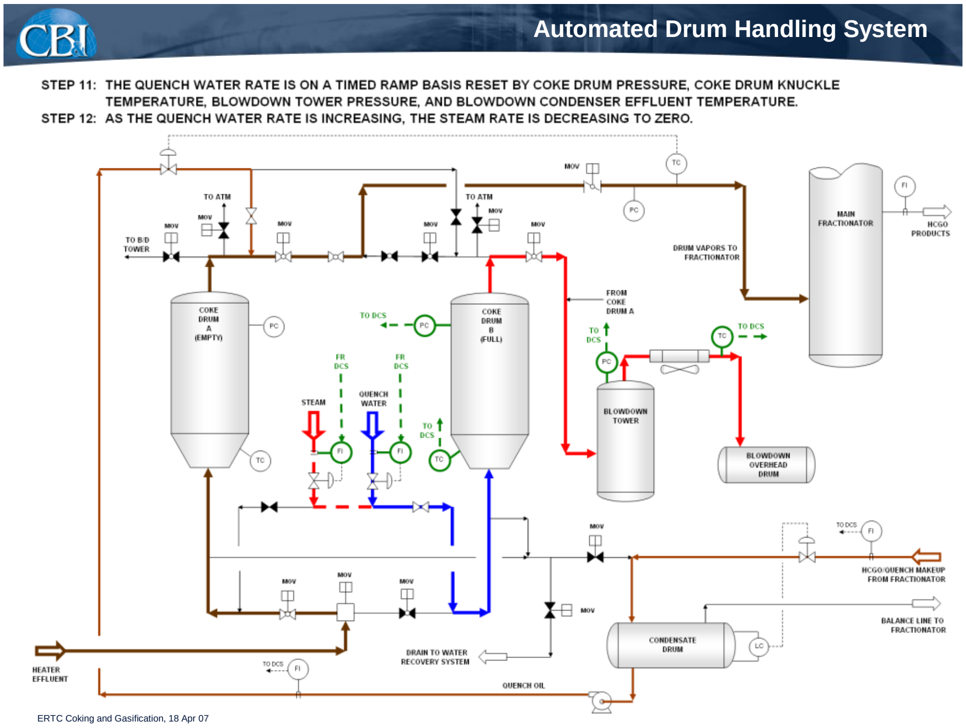
Picture 5: T-Rex Design

The T-Rex design, an improved skirt attachment based on the keyhole design, has been proven one of the most reliable skirts in service. Recent FEA studies have shown that this design significantly reduces the stresses on the attachment weld.

Another skirt design that is recently being developed is the so-called Wrapper skirt (patent pending). This design employs a fabricated, wrapper type skirt that adjusts to the geometry of the upper cone, the knuckle transition and the lower cylinder. It supports the drum primarily via bearing and frictional forces, not by load bearing weld attachments.

While the design measures discussed above apply more to new coke drums and drum repairs or replacements, the following paragraphs discuss operational best practices to reduce the thermal stresses induced on existing coke drums in service.

1. Drum Quench
Most operations today use a ramp function for the quench water; either automated (DCS) or manually adjusted. The quench step is typically started early during the last phase of the steam stripping step by injection a very small amount of water into the stripping steam. Then the ramp function is started at a low water flow rate, while the stripping steam valve is closed slowly (see Picture 1).



Automated Drum Handling System

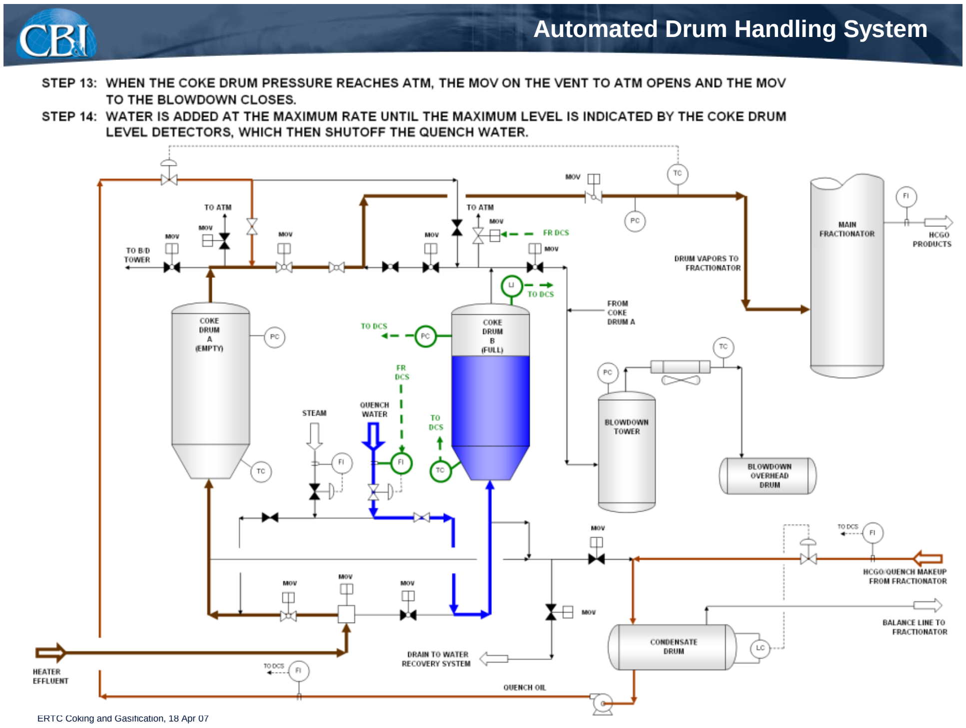
STEP 11: THE QUENCH WATER RATE IS ON A TIMED RAMP BASIS RESET BY COKE DRUM PRESSURE, COKE DRUM KNUCKLE TEMPERATURE, BLOWDOWN TOWER PRESSURE, AND BLOWDOWN CONDENSER EFFLUENT TEMPERATURE.

STEP 12: AS THE QUENCH WATER RATE IS INCREASING, THE STEAM RATE IS DECREASING TO ZERO.

ERTC Coking and Gasification, 18 Apr 07

Picture 1: Transition from Steam Stripping to Drum Quench

The quench water flow rate is increased at a pre-defined rate to minimize thermal stress. During that time, other parameters like drum pressure are observed and may impact the quench water flow control. Once the drum pressure is stable and steam generation in the hot coke drum is decreasing, the maximum quench water rate can be applied. Water is added until the water level is about 5' above coke level. Other parameters to monitor during the quench step are the drum temperature and the blowdown system pressure and temperatures (see picture 2).



Automated Drum Handling System

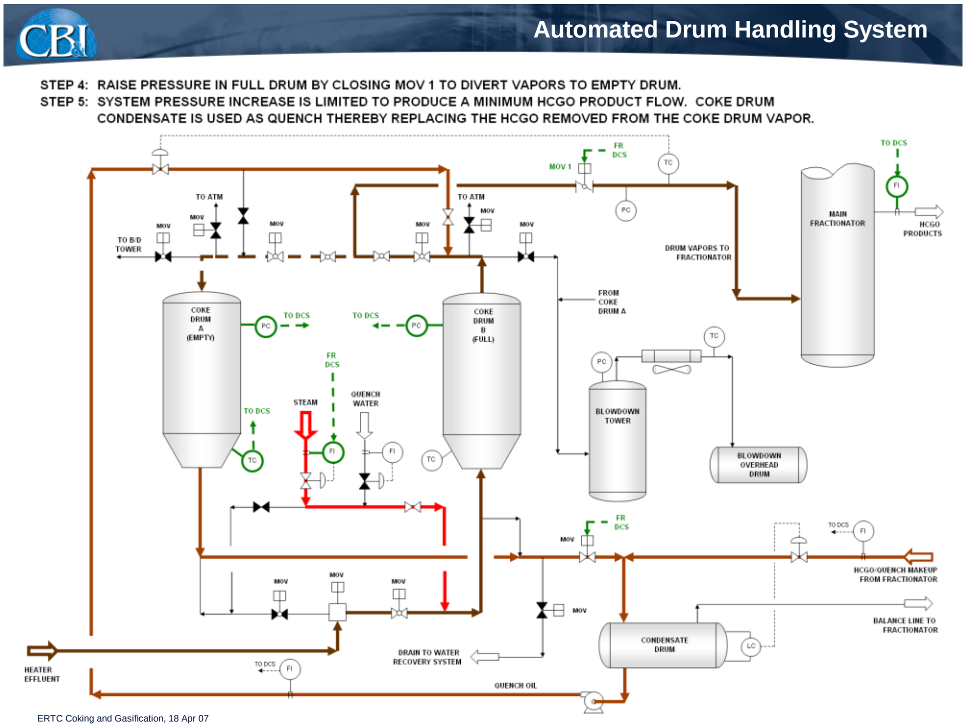
STEP 13: WHEN THE COKE DRUM PRESSURE REACHES ATM, THE MOV ON THE VENT TO ATM OPENS AND THE MOV TO THE BLOWDOWN CLOSES.

STEP 14: WATER IS ADDED AT THE MAXIMUM RATE UNTIL THE MAXIMUM LEVEL IS INDICATED BY THE COKE DRUM LEVEL DETECTORS, WHICH THEN SHUTOFF THE QUENCH WATER.

ERTC Coking and Gasification, 18 Apr 07

Picture 2: CB&I Quench Water Control Scheme

2. Warm-up and Drum Switch



Automated Drum Handling System

STEP 4: RAISE PRESSURE IN FULL DRUM BY CLOSING MOV 1 TO DIVERT VAPORS TO EMPTY DRUM.

STEP 5: SYSTEM PRESSURE INCREASE IS LIMITED TO PRODUCE A MINIMUM HCGO PRODUCT FLOW. COKE DRUM CONDENSATE IS USED AS QUENCH THEREBY REPLACING THE HCGO REMOVED FROM THE COKE DRUM VAPOR.

ERTC Coking and Gasification, 18 Apr 07

Picture 3: CB&I Drum Warm-up Control Scheme

As shown in picture 3, control schemes can be used to maximize the warm-up driving force to achieve optimum drum switch temperatures, In addition, the drum switch can be performed slowly or stepwise to allow the hot drum feed to warm up the cone section before switching to full feed flow.

3. Drum Cycle Automation

The use of an automated, PC controlled drum handling system as partially shown in pictures 1 to 3 can help to implement and sustain best practices for all critical drum handling steps like steam stripping, quenching and warm-up. These systems, like CB&I's automated drum handling system (patent pending), can be customized for each specific operation and can also be expanded in the future, e.g. for automated coke cutting.

Implementing best practices will reduce thermal stresses on coke drums and slow down the rate of bulging and cracking, therefore increasing drum life time significantly; has to be evaluated versus ultra short drum cycles and economic benefits of unit capacity versus coke drum reliability and repairs.

Brian Doerksen (ConocoPhillips)

- New Drum Design
    - Robust and Uniform wall thickness
    - Tight steel specification
    - Fatigue resistant weld design
    - Rigorous inspection and very tight inspection acceptance criteria
    - Skirt attachment design
    - Nozzle design
- Existing Drums
    - Drum life management best practice.
    - Inspection based on stage of life
    - Strain gage / thermocouples and evaluation of operating practices

Question 43
What on-line inspection techniques (after a drum cut) have you employed on coke drums? Have you used laser ID measurement or video inspection to detect incipient cracks?

Brian Doerksen (ConocoPhillips)

- Laser inspection with video record
- External inspections
- TOFd and manual UT
- Acoustic emissions

Question 44
Which coke drum weld seams are more prone to cracking (cone-to-shell attachment or 2nd or 3rd seam from bottom)? What techniques have you employed to repair these cracks?

Eberhard Lucke (CB&I):
This question has been partially answered with question 39. Please refer to the answer for question 39 for additional background and information. Several study reports have been published in the past analyzing the effects that lead to drum cracking and its root causes, for example Weil and Rapasky (1958), Penso et al., Livingston and Saunders, and the 1996 API survey. In short words, the thermal stresses induced onto the coke drum shell by the thermal gradients at the beginning of the drum quench cycle are found to be the most probable cause for drum bulging and as a consequence cracking. Drum bulging occurs slowly over the life of the drum with rates of as much as 0.3 inches per year. At the same time, the higher yield strength of the weld material in the circumferential weld seams tends to augment the bulging by causing a "constrained balloon shape".

As a result of the restraint caused by the weld seams, the base material over time becomes thin and ultimately fails via through-wall cracking. The bulging is most severe in the lower part of the cylindrical portion of the drum. This section experiences the highest thermal gradients during the quench cycle. Depending on the width of the plate used for each shell course, the section has up to four (4) or five (5) circumferential weld seams. Therefore, weld seams three (3) or four (4), counted from the cone attachment upwards, are the most likely ones to fail.

However, some drums may experience through-wall cracking in other weld seams closer to the cone or further up in the cylindrical section due to premature failures in the weld seam.

The skirt-to-shell weld attachment is another potential area of failure in coke drums. Since the attachment is near the bottom of the coke drum with high temperatures (in the area of 900°F) and high temperature gradients during drum quenching, it is just as prone to cracking and premature structural failure as the vessel wall.

CB&I's approach to crack repair is based first on the understanding that all possible safety precautions must be made before the defects are repaired. CB&I does not endorse or participate in repairs of this nature while the vessel is in service. Repairs of this magnitude must be made after the vessel has been removed from service, is cleaned and gas freed.

The exact repair technique depends on several factors, including extent of cracking, original vessel design and the expected life of repaired structure. Cracks deemed to be less severe, whether in the base material, weld metal or heat affected zone of a weld seam may be repaired by removing the defect and re-welding. The defect is removed by arc air gouging and the resulting cavity is inspected by MT or PT to verify that all trace of the defect has been eliminated. If the crack extends completely through the shell wall, the excavation will be made first from one side. Once the cavity has been filled by repair welding, the excavation will be made from the opposite side of the plate to assure that the entire defect has been removed. When gouging for defect removal takes place on the internal clad surface of the vessel, the cladding must first be stripped back away from the repair area so as not to allow the cladding material to be incorporated into the repair weld. Again, the repair cavity is inspected by MT or PT to assure entire defect removal.

The repair weld is made using the same welding procedure as required for the original construction. Specific welding techniques will be employed based on the position of the weld, type of material and mechanical test requirements for the vessel such as hardness or impact requirements. Stringer beads, weave beads, or even temper bead techniques may be employed to enhance mechanical properties as required. Preheat is maintained throughout the repair cycle at temperatures based on the type and grade of material being repaired.

Once the cavity has been welded, the clad surface is repaired by overlay welding using the appropriate welding procedure. Depending on materials, the completed weld may receive a post heat operation to allow it to be cooled to ambient temperature. Weld surfaces are generally ground smooth and flush to minimize geometric stress risers and NDE is again performed on the completed repair area. Finally, a complete band around the vessel circumference at the repair level is Post Weld Heat Treated with a final NDE after the PWHT operation.

When cracks are considerably more substantial, entire sections of vessel shell or skirt are often removed and replaced. When this repair methodology is used, the welding procedures and techniques described above are employed to prolong repair benefits. The keys to a successful repair operation are the same as for new construction. Proper selection of materials and consumables, proper welding procedures and techniques to achieve mechanical properties and proper post weld conditioning (grinding) and heat treatment to eliminate stress concentrations will give best results.

Brian Doerksen (ConocoPhillips)

- Other than skirt attachment welds, the circ seams about a third the way up the coke bed often seem prone to crack.
- Repairs
  - Blend grinding out shallow cracks
  - Proper repair with entry + PWHT
  - Temper bead technique with or without PWHT

Coker Operations

Question 45

Please describe your insulation system best practices for minimizing heat loss from a coke drum. Are there any correlations between coke drum overhead vapor temperature and coke make and/or liquid yield?

Eberhard Lucke (CB&I):

Per CB&I engineering standards for vessels and pipe with a diameter of 36” or bigger, or for a flat plate, in a temperature range of 800 to 1000°F, the minimum required thickness of the insulation material is 6”.

The impact of changes in insulation thickness on the coke drum heat loss and drum outlet vapor temperature is a complicated question since the impact of the “internal” insulation by the coke itself is unknown and will change from drum cycle to drum cycle.

“Best guess” approach:

Assuming ideal heat transfer, no wind, air temperature of 75°F, no interference between coke drums, no impact of coke as “internal” insulation material, an increase of insulation thickness by 2” may reduce the heat loss by maximum 30%. The estimated increase in vapor temperature at the drum outlet is 10 to 15°F. Using the conservative range of rule-of-thumbs for coking yields, this would result in 1.5 (max. 2.0) LV% more liquid yield (mainly HCGO), and in 1.0 (max. 1.5) WT% less coke yield. Actual numbers may vary widely due to non-ideal conditions.

Brian Doerksen (ConocoPhillips)

- Insulation design - ConocoPhillips have 2 standard methods
  - Insulation materials
  - Supports Jacketing
- Correlation between drum overhead temp and yields?
  - Yes. In general, we see a 1% by weight reduction in coke make with every 10F of increased overhead temperature based on a constant vacuum resid rate.

Question 46

What procedures do you use (or are considering) to reduce coke drum emissions during the decoking steps?

Brian Doerksen (ConocoPhillips)

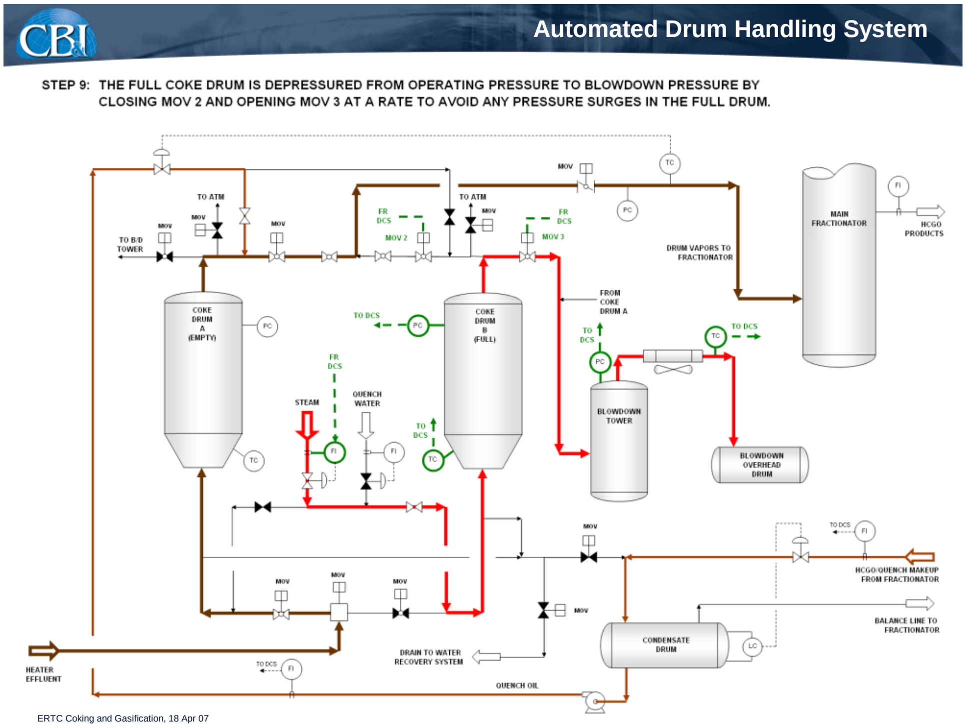
- For low pressure cokers, new designs route the closed blow down vapor during steam, quench, and backwarm steps to upstream of the wet gas compressor.
- For higher pressure cokers, route to flare gas recovery or a dedicated small compressor to boost to upstream of the wet gas compressor.

Question 47

When a full drum is switched to blowdown to begin cooling, we often see a rapid rise in foam level which is immediately reduced once water is introduced into the drum. What may be causing this and how might it be mitigated?

Eberhard Lucke (CB&I):

After a hot drum is taken out of service, the coke is steam stripped to the main fractionation tower to recover volatile hydrocarbon material. At this point, the drum stays close to normal operating pressure. Once this step is finished, the steam flow from the drum overhead is re-routed to the blowdown system. At this point, the coke drum is depressurized to blowdown pressure level, which allows recovering more volatile hydrocarbon material (see picture 1).



Automated Drum Handling System

STEP 9: THE FULL COKE DRUM IS DEPRESSURED FROM OPERATING PRESSURE TO BLOWDOWN PRESSURE BY CLOSING MOV 2 AND OPENING MOV 3 AT A RATE TO AVOID ANY PRESSURE SURGES IN THE FULL DRUM.

ERTC Coking and Gasification, 18 Apr 07

Picture 1: CB&I Steam Stripping Control Scheme

If this switch to blowdown is performed too fast, it will cause a pressure surge in the drum that will most certainly uplift the foam bed significantly. In some instances, foam and other material was sucked in the drum vapor line and caused severe fouling and plugging in the vapor line system. The reduced pressure also supports additional vaporization of material in the drum, which enhances the foaming and the entrainment of foam and coke fines.

Once water is introduced into the drum, the heat of the coke vaporizes a significant amount of the water. The produced steam will cause the pressure in the drum to increase again, and the foam front is knocked down.

The main strategy to avoid this problem should be to perform the switch to the blowdown system as smooth as possible. The actuation of the primary vapor line isolation valve and of the primary blowdown isolation valve should be coordinated in a way that minimizes the pressure surge in the vapor line and eliminates rapid decreases in coke drum pressure. If all involved valves are automated (motor driver installed), this process can be automated to increase consistency and eliminate potential errors. Automated systems like CB&I's Automated Drum Handling System (patent pending) include the switch to blowdown as a critical component of the drum cycle automation.

The control scheme can be optimized by using the stripping steam flow rate as injected into the coke drum to control the drum pressure during the switch to blowdown. This control scheme will increase the steam rate to maintain a minimum coke drum pressure during the process of the switch to the blowdown system, therefore minimizing the driving force that causes the foam bed to rise. The control scheme will also support the controlled depressurization of the coke drum to blowdown pressure level.

To achieve slow and controlled depressurization of the coke drum, the opening characteristics of the blowdown isolation valves and their drivers have to be checked. If only a few turns open already a high percentage of the valve, it will be difficult to control a slow flow of vapor and a slow decrease in drum pressure. In this case, we recommend modifying the existing valve/driver installation or installing new primary isolation valves with an opening characteristic that allows controlling the depressurization of the coke drums.

We would also recommend investigating the root cause itself, the foam bed. Depending on Coker feed quality and operating conditions, foaming can never be eliminated completely. But the control of foam on the coke bed at drum switch will help reducing the impact of pressure surges causing foam entrainment in general. The more foam is sitting on the coke bed, the more foam can be entrained into the vapor line. A good antifoam injection strategy will help minimizing foam on the coke bed. This includes selection of antifoam agent, selection of injection rate, selection of injection locations in the drum and review of the injection philosophy and timing. Some operations maintain antifoam injection to a drum even after it was taken out of service to control the foam bed during the above described drum depressurization stage.

Brian Doerksen (ConocoPhillips)

- If the blowdown system is much lower pressure than the fractionator, the sharp pressure drop may cause foaming.
- Mitigations can be operation techniques:
  - Open valve to blowdown slowly
  - Perhaps steam a bit longer to the tower
  - Investigate steam rate
  - Consider continuing antifoam until after switch to blowdown

Coker Blowdown System

Question 48
For refiners who have implemented or are implementing coke drum blowdown vapor recovery: How did the additional backpressure on the blowdown drum impact coke drum cooling and vapor recovery to the coker compressor and/or the flare recovery compressor? Were additional relief valves required to maintain the unit's relief capacity?

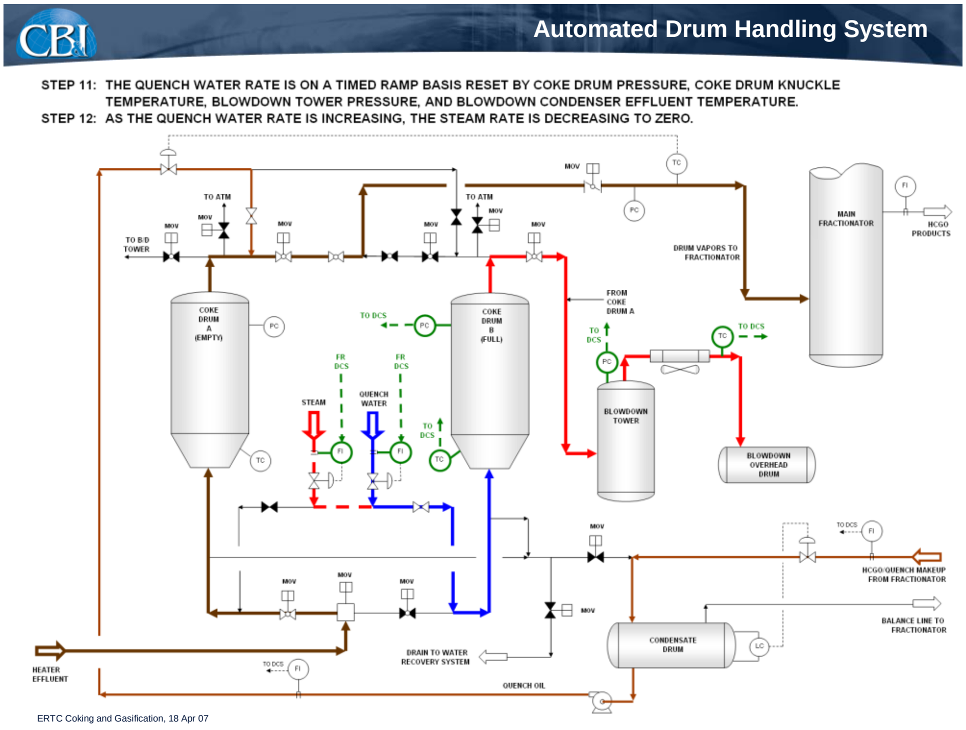
Eberhard Lucke (CB&I):
The recovery of Coker blowdown vapor can be achieved in different ways:

- Use of a Coker dedicated recovery compressor to receive the vapor leaving the blowdown separator drum and processing in the main fractionator overhead system/gas plant
- As an alternative, the vapor can be sent to a refinery wide flare gas recovery system, using a bigger compressor and preferably a central flare gas treatment system
- Especially low pressure operations have the option to let the blowdown pressure float on the WGC suction pressure, allowing the vapor to be recovered in the gas plant without the installation of a recovery compressor.

In any case, discharging the coke drum PSVs to the blowdown system induces high backpressure on these PSVs. The blowdown system is typically not designed to handle the full coke drum PSV relief load; therefore a high pressure drop can be expected caused by the blowdown equipment like scrubber tower and overhead condenser. High backpressure of 30% and more above the set pressure will require the installation of PSVs with balanced bellows. Following API procedure, the PSVs need to be de-rated by using the backpressure as parameter.

Depending on the de-rating of the SPV relief capacity, additional PSVs may be required to be installed to achieve the relief load for the coke drums. In many cases, an additional PSV also will be required on the blowdown separator to protect the drum against overpressure.

If the backpressure re-rating results in an unreasonable number of PSVs and/or valve sizes, or if the backpressure exceeds 50% of the set pressure, a different discharge location will be the better or the only option. Example: routing the discharge to the fractionator bottom.
The potential impact on the drum quenching should be kept at a minimum. If the blowdown system, especially the overhead condenser is sized correctly, the compressor will only handle the non-condensable material leaving the separator. In this case, the backpressure during quench should be low enough to not interfere with the quench water rate control scheme (see picture 1).



Automated Drum Handling System

STEP 11: THE QUENCH WATER RATE IS ON A TIMED RAMP BASIS RESET BY COKE DRUM PRESSURE, COKE DRUM KNUCKLE TEMPERATURE, BLOWDOWN TOWER PRESSURE, AND BLOWDOWN CONDENSER EFFLUENT TEMPERATURE.

STEP 12: AS THE QUENCH WATER RATE IS INCREASING, THE STEAM RATE IS DECREASING TO ZERO.

ERTC Coking and Gasification, 18 Apr 07

Picture 1: CB&I Control Scheme for Drum Quench

The separator drum pressure can increase if no compressor is used and the blowdown pressure is directly determined by the suction pressure of the wet gas compressor. This can become an issue if the unit operating pressure is high, for example in anode grade coke producing units. In all other cases, the quenching is impacted mostly by undersized blowdown condensers and an excessive steam flow going to the separator drum. In these cases, the additional steam rate can cause an increase in drum pressure up to a point where it activates the pressure override to cut the quench water rate. This will lengthen the quench step and can force longer drum cycle times.

GASOLINE PROCESSES

Process Safety

Question 50
What is the proper firefighting media to use when putting out a fire when both spent sulfuric acid and heavy hydrocarbon are present (e.g. in a spent acid tank or a diked area which has a layer of hydrocarbon floating on the spent acid)?

Ed Lowe (Pasadena Refining Systems)
When question was posed to several people, the predominant response recommended using a 3% Alcohol-resistant aqueous film forming foam (AR-AFFF). *Aqueous film forming foams (AFFF)* are water-based foams, frequently containing sodium alkyl sulfate, and/or perfluoro telomer as surfactants. They have the ability to spread over the surface of hydrocarbon-based liquids. *Alcohol-resistant aqueous film forming foams (AR-AFFF)* are foams with the properties of AFFF foams with additives to make the foam resistant to the action of alcohols.

In general discussions with Gasoline Panel members, it was disclosed that actual use of AFFF foam did not work well in real-life situations similar to the question's scenario. The fire kept lighting off because it was difficult to establish a foam blanket. Panelists recommended considering use of carbon dioxide.

There is a type of foam being used in Europe that should be considered for this particular application. The foam, which is a vapor suppressing foam, is intended for use on spills of acid materials.

Question 51

Reforming unit stabilizer column top trays and overhead condensers can experience fouling with ammonium chloride salts which are commonly removed by on-line water washing of the column overhead. What practices do you employ to reduce the risk of rapid corrosion and the potential failure associated with this fouling and subsequent water washing procedure?

Pedro Fernandez (Jacobs Consultancy)
Ammonium chloride salts deposition is a common problem in many naphtha hydrotreating and naphtha reforming units. Problem areas include reactor products condenser areas, compressor inlet areas and the overhead section of the product stabilizer.

Ammonium chloride salts form because of the presence of ammonia and chlorides in the reactor effluent stream. These compounds combine and precipitate as the streams are cooled and the effective concentration of the compounds increases in the gas phase.

The temperature at which these salts will start depositing will depend on the ammonia and HCl concentration, but in general it is possible to see salt deposits as temperatures drop below 400˚F.

Once formed, the ammonium chloride salts are hygroscopic, and readily absorb water. Once in contact with water, they form a very corrosive acidic solution, which if not managed properly will lead to extensive under-deposit corrosion in the areas where salts have deposited.

Good management of ammonium chloride deposits and corrosion starts with preventing the formation of compound. The two problem compounds are ammonia and chlorides.

Chloride is a necessary component of the reforming catalysis. It helps maintain surface dispersion of the key metal functions in the catalyst, and therefore can't be eliminated.

Ammonia is formed from the hydro-denitrification of organic compounds present in the feed. Proper pretreatment of the feed is the most important strategy to minimize the formation of the ammonia chloride salts. In general, reforming licensors and catalyst vendors recommend that the feed to the reforming unit should contain less than 0.5 ppmw nitrogen. We consider this to be the minimum standard of care. Many operators target values of less than 0.2 ppmw nitrogen in the reformer feed; we would encourage people to push their hydrotreating severity to achieve at least this level.

While it is relatively easy to meet very low levels of nitrogen with most conventional straight run naphthas, the story is different when processing thermally cracked materials, naphthas derived from heavy oil processing units, or from very high nitrogen content crudes.

One can calculate how much ammonium chloride will be formed in the reactor based on the amount of nitrogen in the feed. As a reference point, a naphtha reforming unit processing 20,000

BPD of naphtha with a nitrogen content of 0.5 ppmw will produce about 4,700 lb of salts (almost one hundred 50 lb sacks). This volume of salts will deposit and accumulate somewhere in the unit if unmanaged.

Several techniques have been used to mitigate or eliminate the formation and depositing of salts once the nitrogen has entered the unit:

The most effective technique—other than removing the nitrogen in the feed—is the Installation of chloride guard systems on the product separator liquid upstream of the stabilizer. By eliminating the chloride component, formation of the salts is eliminated.

Two types of systems have been used in this service: one is a scavenging solid adsorbent bed; several vendors including UOP, Sud-Chemie, and others offer materials that can be applied in this service. A second alternative is an alkaline (caustic) wash of this stream; Merichem has installed an alkaline wash-contactor system in a couple of units. Units with both types of systems report good results.

Some refiners try to adjust processing conditions to minimize the salt formation in the stabilizer. In our opinion, however, as long as the ammonia and the chloride are present, these changes only move the problem elsewhere—typically to the overhead condenser.

If the salts are formed and the refinery is forced to wash them out, the water washing technique used must include adequate precautions to avoid leaving wet salt deposits behind, since as noted earlier this could lead to severe under-deposit corrosion. The on-line washing technique that we are familiar with and has been used at several refiners involves using a large amount of water and slumping the tower during the process:

- Inject a large amount of water in the stabilizer reflux line and reduce the reboiler temperature so that the water comes out with the bottom product;
- Monitor the difference in the water conductivity between the inlet and outlet to determine when there are no more salts in the column;
- Reduce the water rate and increase the reboiler temperature so the water comes out on the overhead drum, wash the overhead condenser and receiver (again using the change in water conductivity as an indication of when the wash has been completed);
- Be very diligent in draining all water boots and low point drains.

Tina Drumheller, Frontier Refining

Primary locations for plugging in reformer stabilizer systems are the feed to the stabilizer tower and feed/bottoms exchangers.

Typically, separator level is the first indicator of plugging. When plugging occurs, water injection is used to mitigate pressure drop issues. Water is hard piped via 1” line to the tower feed, and a small amount of water is used to relieve plugging in the line. Caustic injection/water wash upstream of the feed coalescer and neutralizer injection in the overhead are used to mitigate corrosion. If a significant tower plugging problem is encountered, water wash is utilized. The tower is slumped and large volumes of water are used to flush the salts in the tower/overhead system.

Paul Fearnside (Nalco Energy Services)
Nalco recommends a procedure similar to what is being done successfully to mitigate salt fouling in the FCCU main fractionator (see question # 16). It is possible to severely reduce the frequency of the water washes by using a salt dispersant. The salt dispersant also has the added benefit of removing most of the " wet " corrosive salts that usually remain after the internal water washing procedure is completed.

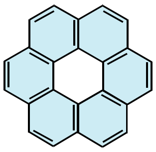
Malcolm Sharpe (Merichem Chemicals & Refinery Services LLC)
Merichem has been licensing CHLOREX^{SM} Technology since 1990 and currently has four (4) licensed units in operation. CHLOREX^{SM} units utilize Merichem's proprietary FIBER-FILM^{TM} Contactor to non-dispersively contact stabilizer feed with an alkaline water solution to effectively remove HCl. Since the FIBER-FILM^{TM} Contactor is non-dispersive there is no need to separate droplets out from the continuous hydrocarbon phase and as a result carryover and carryunder (and their associated drawbacks) are not an issue. Instead the aqueous phase (alkaline water in this case but also commonly caustic, amine and wash water) adheres to the fibers while hydrocarbon flows in between the wetted packed fibers. The result is the creation of immense interfacial surface area providing superior mass transfer without dispersion. For more information, an article reprint from Hydrocarbon Technology International and entitled "Eliminating Chloride Corrosion and Fouling of Reformer Stabilizer Columns" can be found on Merichem's website (www.merichem.com) under the Refining Technology/Product Literature tab.

Question 52
Have you found highly condensed aromatics (i.e. red oil) around the reforming unit, especially around heat exchangers and/or valve leaks? What safety precautions do you recommend for handling this material?

Jay Ross (Axens NA)
The PNA material formed is in the coronene ($C_{24}H_{12}$) or ovalene ($C_{32}H_{14}$) family of fused aromatics with a characteristic red/orange color. It generally is found in cold spots in the process

and can lead to plugging and pressure drop problems. The material is only really soluble in benzene and hence cleaning is by mechanical means with the waste treated as hazardous.

Others have commented on finding this material around the recycle compressor and the stripper reboiler when heated by reactor effluent (1996 Q&A). Operation under severe conditions of high temperature, high EP feed and low H/HC promotes formation of this toxic material.



Coronene: C24H12, T_b=525°C, T_{mp}=440°C

Alkylation

Question 53
In a hydrofluoric acid alkylation unit, what can you do to prevent plugging in the acid-soluble oil caustic neutralizer?

Ed Lowe (Pasadena Refining Systems)
Up until 2004 PRSI (then Crown Central) used a caustic (sodium hydroxide, NaOH) solution to neutralize acid soluble oil (ASO) and experienced the same problems as suggested by this question (i.e. – plugging in the ASO neutralizer). When the switch was made to using a potassium hydroxide (KOH) solution, the plugging problems were significantly reduced.

Currently, we use a KOH solution starting at strength 30% w/v. The KOH solution is recirculated in the neutralizer unit until it is depleted to 1% w/v strength. When the 1% w/v strength is reached [the strength is monitored by periodic in field testing by operators], the neutralizer recirculating solution is dumped to a holding tank, and the neutralizer is recharged with 30% w/v KOH solution.

Originally Crown Central had a spent KOH regeneration system process on site. By reacting the spent KOH solution with a lime (CaOH$_{2)}$) solution, KOH was produced along with the relatively insoluble calcium fluoride salt (CaF_2). The calcium fluoride was separated from the KOH solution and returned to the ASO neutralization process. The calcium fluoride salt was sold.

On site regeneration of the KOH now has been discontinued. Instead the spent KOH solution is regenerated off-site and returned to PRSI for use.

Tina Drumheller, Frontier Refining

Two of the common sources of plugging in acid-soluble oil (ASO) caustic neutralizers include scale resultant of corrosion and salt formation due to neutralization. Of the two, salt formation has been the more problematic.

Typically, one of two types of caustic is used in ASO neutralization: sodium hydroxide or potassium hydroxide. The basic chemistry for both is straight forward acid-base neutralization

$NaOH + HF \text{ -> } NaF + H_2O$

$KOH + HF \text{ -> } KF + H_2O$

Once salt formation exceeds solubility limits in solution, the salt crystals will tend to agglomerate as they settle out of solution.

The following are two means of preventing plugging

1. Maintain adequate circulation to prevent solids settling out.
2. For units with static mixers, ensure mixer design is adequate to ensure good mixing of caustic with ASO at the injection location.

If a plugging problem due to salt formation occurs, it can be mitigated by either water wash or steam out. If steam is used, stress cracking can occur with stainless steel in the presence of caustic and high temperature.

In Frontier's experience, solutions of both 10% NaOH and 5% NaOH have been used. With either solution system plugging at the mixer occurred frequently. Steam had to be used several times to relieve plugging, resulting in accelerated corrosion rates.

Conversion to 10% KOH resulted in prevention of plugging episodes with no other system modifications.

The increased operating expense associated with potassium hydroxide use was offset by installation of a caustic regeneration system.

Question 54
In a sulfuric acid alkylation unit, what can you do to minimize foaming and/or plugging in caustic wash or water wash systems?

Scott Alvis (Merichem Chemicals & Refinery Services LLC)
With conventional dispersive contacting devices such as static mixers, a conventional answer would be to monitor caustic strength. If strength is too high, precipitation can occur which leads to plugging. Reducing caustic strength requires a corresponding increase in circulation rate which leads to foaming. The best way to avoid both problems is to use a non-dispersive contacting device such as the FIBER-FILM^{TM} Contactor. Because caustic and water adhere to the fibers, there is greater surface area available for mass transfer without sacrificing the concentration gradient driving force. By avoiding dispersions, there is less tendency to form emulsions which also minimizes carryover and carryunder issues. In many cases, the FIBER-FILM^{TM} Contactor can be easily retrofitted onto existing separator vessels. For more information on the FIBER-FILM^{TM} Contactor, please visit www.merichem.com.

Question 56
In a sulfuric acid alkylation unit, there have been problems keeping the acid wash electrostatic precipitator (EP) operational. What steps do you recommend to improve the reliability of the EP?

Scott Alvis (Merichem Chemicals & Refinery Services LLC)
The sole purpose of the EP is to separate a dispersed phase from a continuous phase as a result of using dispersive contacting devices such as a mix valve. The surest way to avoid EP operational issues is to eliminate the EP altogether by using a non-dispersive FIBER-FILM^{TM} Contactor. Instead of dispersing the aqueous phase into the hydrocarbon phase as small droplets that are difficult to separate, the aqueous phase acid adheres to the fibers while hydrocarbon flows in between the wetted packed fibers. The result is the creation of immense interfacial surface area providing superior mass transfer without dispersion, thus avoiding the need for an EP to reduce acid carryover. For more information on the FIBER-FILM^{TM} Contactor, please visit www.merichem.com.

Question 59
For a hydrofluoric acid (HF) alkylation unit, what instrumentation do you recommend for controlling HF acid levels throughout the unit?

Ed Lowe (Pasadena Refining Systems)
Generally, the use of nuclear level indications/controllers are gaining wide acceptance in the industry. Several refiners have used nuclear levels in this service. External displacement level transmitters or interface level sensors are also acceptable. You should discuss this issue with your unit's technology licensor.

Tina Drumheller, Frontier Refining
Frontier has used differential pressure (dp) cells, magnetic float, and nuclear level measurement in HF alkylation units.

Both the dp cell and magnetic float level measurement became a reliability concern due to either instrument failure or plugging requiring instrument removal for cleaning.

Of concern in use of both types of instrumentation was the potential for exposure due to mechanical failure and maintenance requirements.

Nuclear level measurement has been successfully used in the following HF alkylation unit locations:

Acid settler

Depropanizer overhead boot

Acid stripper reboiler

Flare drum

Benefits of nuclear instrumentation include

1. Decreased risk of personnel exposure to HF
2. More robust level indication during start-up
3. Increased reliability

The main operational concern with nuclear level indication is susceptibility to x-ray. Procedures have been used to address the loss of nuclear level indication during periods when x-ray inspection is conducted. For example, automatic level control is set to manual during x-ray inspection that could interfere with nuclear level measurement.

Paul Hewitt (TRACERCO)

Due to the nature of the highly corrosive contents of a refinery alkylation unit careful consideration must be given to selection of an instrument to measure liquid level and interface between two immiscible phases.

The instrument selected must be reliable, as maintenance free as possible and ideally none contact with the fluids to minimize potential leak points on a process vessel.

Nuclear gauge technology is one measurement technique that meets all of the above criteria and is commonly used in alkylation process level control applications. The technology provides real time data, no moving or wetted parts leading to reduced maintenance and high reliability, is externally mounted and intrinsically safe / explosion proof.

Liquid Level Measurement

In the case of liquid level measurement a nuclear gauge is designed with a small radioactive source on one side of a vessel that is housed in a shielded container. The container is designed such that it emits a fan beam of electromagnetic radiation across the vertical length of measurement range required. On the opposite side of the vessel a sensitive detector is positioned within the fan beam. In the case of a level gauge, the detector will be positioned in a vertical orientation across the span of level range required. If a level alarm is used this will be positioned in a horizontal position at a specific vertical height. Figure 1 shows a typical arrangement for a level gauge

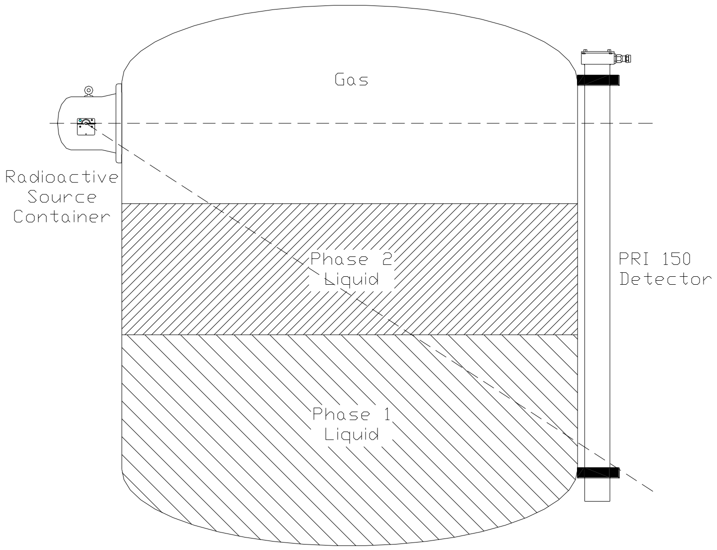


Figure 1 – Typical Level gauge Arrangement

When the vessel is empty the electromagnetic radiation penetrates the vessel wall, across the inside of the vessel and through the other wall providing a small radiation signal at the detector.

In the case of proportional level measurement, as the level of liquid in the vessel rises above the minimum, it reduces the amount of radiation reaching the detector over an increasing length of the vertical range. This causes a decrease in detector count rate. Using calibration data recorded within the instrument the detector response is directly proportional to liquid level within the vessel. The detector response is converted to a 4-20 mA and / or digital signal and relayed to a control system.

Alarms allow low level or high level liquid positions to be detected. In the case of a high level alarm the detector will measure a specific radiation signal when vapor is present between the vertical position of the radiation source and the detector position. As the liquid level reaches this vertical point the radiation is attenuated to background radiation levels. At this point, the detector can be used to send a warning signal to the control room (High Level Alarm) or actually trip a process activity. In the case of a low level this acts in the opposite manner. When liquid level covers the radiation signal between source and detector the radiation reaching the detector is at natural background levels. When the liquid level falls below this point there is a rapid increase in radiation reaching the detector. In much the same way as the high level system, the detector will send a warning signal to the control room (low Level Alarm) or actually trip the process activity.

In the case of nuclear gauge alarms it is very easy to test the systems on a regular basis. In the case of high level alarm testing the operator simply has to shut off the radiation using the shutter located on the shield. With zero radiation emitted from the shield, the alarm will act as if liquid level has reached the alarm set point and will trip. In the case of a low level alarm a small radiation test source can be manually positioned close to the detector. The increase in radiation signal acts in the same manner as if liquid level has fallen in the vessel and a low level condition has occurred. Due to the very sensitive detectors used, the test radioactive source is very small and will cause no safety concerns to process operators.

Finally, in order to minimize radiation source use, it is common within an instrument design to use one source of radiation and position a proportional level gauge across the measurement span together with critical alarm detectors at alarm and trip points. All of the detectors utilize the same radiation source.

Interface Level Measurement

Nucleonic interface gauges use a small radioactive source that is mounted internally through a 2" nozzle using a sealed 1" pipe that looks similar to a thermowell. The radioactive source is transferred from the shield external to the vessel to the end of the pipe inside the vessel. An external radiation detector is located on the outside of the vessel close by the internal pipe. The source is designed so that it can be pulled through the pipe and back into the shield. This allows the vessel to be entered with no safety concerns. Figure 2 shows a typical arrangement.

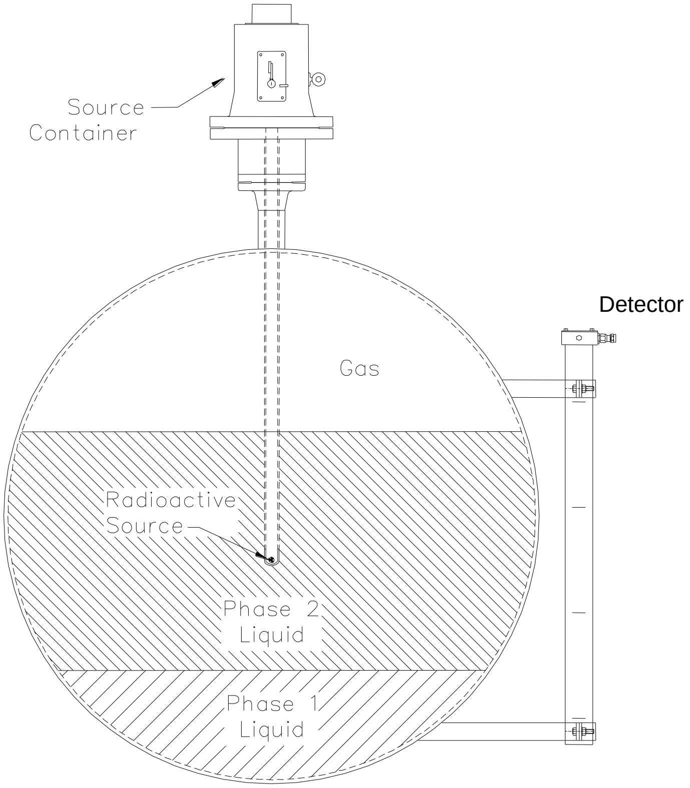


Figure 2 – Typical Interface gauge Arrangement

In the case of a proportional interface level measurement the radiation signal passes through the 1" pipe wall, liquid and vessel wall before reaching the detector. When the path between the source and detector is filled with the lower density liquid (alkylate) the signal intensity at the external detector is relatively high. When the higher density phase increases in height (HF solution) the radiation intensity at the detector is reduced. Through calibration of the system using the typical densities of both fluids involved, the interface position between the two immiscible phases within the vessel can be measured and controlled.

In a similar manner to liquid level measurement, detectors can also be positioned at specific vertical heights across the interface range to act as alarms. The detectors are tuned to alarm or trip at specific radiation signal strength. In the case of a high level alarm, radiation will be relatively high due to the less dense phase presence. If lower phase increases or an emulsion band moves upwards through the vessel the detector radiation signal will reduce and a signal will be sent to the control room warning of the condition. In the case of a low level alarm the reverse conditions would apply with an increase in radiation signal due to lower density liquid presence lower in the vessel.

Isomerization

Question 60

How do you detect leaks in an isomerization unit's steam charge heater? Have you been able to detect a leak before a significant portion of the catalyst bed was deactivated?

Pedro Fernandez (Jacobs Consultancy)

This question is related to the performance of any light naphtha isomerization units operating with a platinum on chlorinated alumina base catalyst. A common problem in these units is the deactivation of the catalyst because of the ingress of water or any other oxygenated compound that is transformed into water in the reaction section of the unit.

This is a familiar processing scheme: where the feed and make-up hydrogen gas are first dried and then mixed and preheated before being sent to the charge heater up-stream of the reactor. Because the reactor inlet temperatures are low, typically below 350˚F, many units have been designed with a steam-exchanged charge heater. The use of steam as a heating medium saves money and simplifies operations, but it opens the possibility of a cross exchanger leak that would permanently deactivate the catalyst.

An old rule of thumb was that 1 pound of water would kill about 100 pounds of catalyst. While different catalyst manufacturers may use different numbers, as a general rule this means:

10,000 Barrels of feed @ 225 lb/barrel @ 1 ppm of H_20 = 2.25 lb of water

or 225 lb of dead catalyst.

This number is important because it puts in perspective our general distrust in the use of analyzers as a safeguard to protect the isomerization unit catalysts. Small moisture changes lead to rapid deactivation rates.

In this respect, we believe that minimizing the risks and exposure to charge heater steam leaks should start with the proper design of the charge heater. We are very familiar with UOP design practices for these exchangers, which include:

1) Designing the steam side pressure lower than the process side pressure.
2) Ensuring that the charge heater tubes are welded to the tube sheet.

We are not aware of any refiner relying on a moisture analyzer as a leak detection mechanism. We believe this is a practical approach: unless the leak is caused by a major mechanical failure, leaks from these properly designed exchangers will result in a very small change in moisture content. Under this scenario, the simple reading from the moisture analyzer does not give the operator sufficient information to decide whether the leak is real. It may be just a bad instrument, a problem in the up-stream driers or a real leak.

One option to putting a moisture detector on the process side would be to put a hydrocarbon detector on the condensate coming out of the exchanger. A leak in the exchanger should register as a real spike in the hydrocarbon content reading.

Question 61

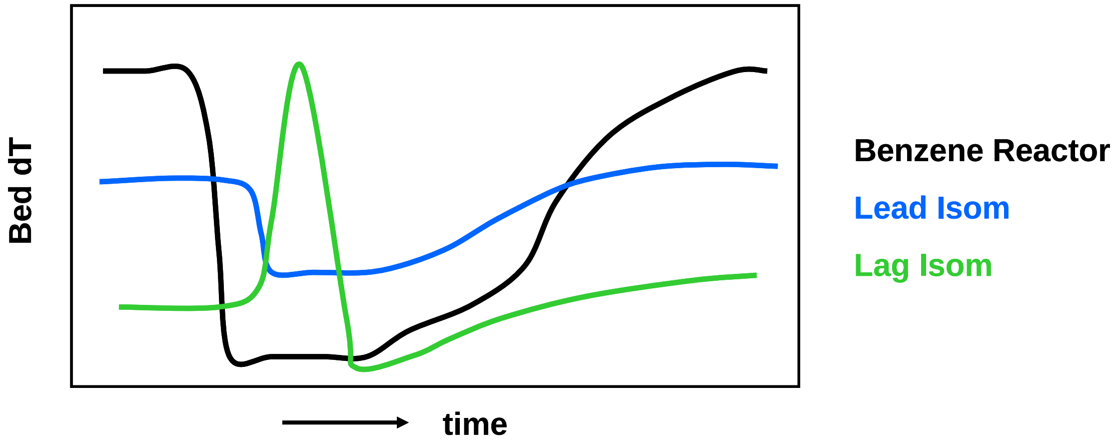
Have you found that you needed to install a methanator upstream of a chlorided catalyst isomerization unit to remove carbon monoxide (CO) from the feed? What is the source of the CO and how much of a difference has the addition of the methanator made to catalyst life? What is the expected payout for the cost of the methanator?

Jay Ross (Axens NA)

In general oxygenates, including CO and CO2 should be avoided in the hydrogen stream fed to an isomerization unit. CO and CO2 are often considered a poison due to possible water formation via methanation. As such, the CO+CO2 content in the hydrogen is limited to 10 ppm – a value well within steam reforming unit capabilities.

However, conditions in the isomerization unit will not promote significant methanation and a reversible inhibition by carbonyl formation is the main concern.

In one isomerization unit, an upset in hydrogen source led to high CO breakthrough and a deactivation wave passed through the lead benzene saturation reactor and then the isomerization reactors. The benzene reactor dT (delta temperature) dropped sharply as the Pt was temporarily poisoned by the CO. This led to transients in the heat exchange system and benzene passed to the isomerization reactors. As the hydrogen purity recovered, the unit activity recovered.



Although some methanation could occur leading to water formation and permanent catalyst damage, the normal operating temperature in an isomerization reactor is too low for this to occur to a significant extent.

Pedro Fernandez (Jacobs Consultancy)

This question is also related to the performance of light naphtha isomerization units operating with a platinum on chlorinated alumina base catalyst. In this case the culprits for the oxygen/water ingress are carbon monoxide and carbon dioxide that ingress into the unit as contaminants to the make-up hydrogen.

Low concentrations of CO are common in many of the available refinery hydrogen streams. Typical values are sufficiently low—in the 0 to 10 ppm range—that the catalyst deactivation caused by these streams will be barely noticeable. In this respect it is useful to look at some numbers:

10,000 BPD feed @ 300 SCF/B hydrogen make-up with 10 ppm CO =

0.08 lb of water equivalent,

or 8 lb of dead catalyst.

There are multiple potential sources of CO in the refinery hydrogen gas:

- Hydrogen from steam reforming plants contains CO and CO_2. In older hydrogen plants, CO_2 is removed by solvent extraction and the CO is removed in a methanation reactor. The hydrogen product from a methanation reactor typically has less than 10 ppm CO + CO_2, so this product should not be a problem for isomerization units.

- Modern hydrogen plants typically do not have a methanator because they use a PSA unit to achieve hydrogen purity. In general, modern PSA units are designed to meet single-digit ppm content of CO and CO_2. However, CO removal comes at the expense of hydrogen recovery and sieve volume, so higher contents of CO in PSA units that are being pushed in terms of capacity and or hydrogen recovery may be seen.

- An often overlooked source of CO is in the hydrogen from naphtha reforming units. CO in the hydrogen from naphtha reforming units may come from the regeneration step; the problem is more frequent in cyclic reforming units, because of the frequency of regenerations. A second source of CO in the net gas from naphtha reformers is water in the reactor circuit. Water will convert to CO to some extent in this environment. The problem is minor at normal recycle gas moisture levels but increases as the water content increases. CO content may also be high in Continuous Regeneration Reforming where the water generated in the reduction gas is not removed from the recycle gas system, particularly in low pressure units.

- Other sources of CO come from the FCC off-gas, and several other units' off-gases if they are used as a source for process hydrogen.

A few years ago, we examined a refiner's problem with catalyst poisoning in a UOP Penex process unit. One of the sources of the CO was clearly identified as coming from a very wet semi-regen reforming unit operation; however, it was difficult to quantify and isolate whether this was the only source of catalyst deactivation because the refiner had another reforming unit. To complicate matters, the perceived deactivation rate was higher than what one would expect based on the estimated oxygenates content in the make-up gas. The customer was very interested in installing a methanation reactor on this stream, but could not justify investing capital to fix a problem that was directly associated with bad operations.

We have spoken with other refiners who have experienced a similar problem. In one case, the refinery had significant amounts of CO in its hydrogen product—on the order of 100 to 1000 ppm CO in the hydrogen gas. This refinery recovers hydrogen from multiple sources though a cryogenic unit, including the FCC off-gas, hydrotreater off-gas and other streams through a cryogenic unit. The refinery installed a methanator and has reported years of stable operation.

In summary, methanators are definitely the ultimate solution for a CO/CO_2 contamination problem. They are relatively simple and offer a low capital cost solution—typically in the $750,000 to $1 million range to install. Before spending the capital, however, we recommend analysis of the following:

1. Is the source of the contamination fixable?
2. What is the real deactivation rate caused by this contaminant? Using the formula given above and the true hydrogen make-up requirements of your unit you will be able to calculate the pay-back.

Tina Moss (Johnson Matthey Catalysts)
Some refiners have installed a methanation bed upstream of the isomerization unit to reduce the CO content in the hydrogen source to <1 ppmv. In these cases, a small heater may also be required to increase the temperature to about 200°C. In absence of any poisons, the methanation catalyst can achieve a life in excess of five + years. The catalyst volume varies depending on the flowrate, desired CO conversion, and operating conditions. In cases where the hydrogen source is from a catalytic reforming unit, other purification beds may be needed since sulfur is a methanation catalyst poison. The contaminate levels are generally low so only a small guard layer above the methanation catalyst is needed.

Naphtha Hydrotreating

Question 62

How much coker naphtha can be added to the naphtha hydrotreater feed before you need to add a separate diolefin reactor?

Ed Lowe (Pasadena Refining Systems)
PRSI typically processes 9-10 vol% coker naphtha in our hydrotreater. We do not have a separate diolefin reactor. We are generally limited by silicon uptake on the NHT catalyst. The loss of activity caused by the silicon uptake leads to nitrogen breakthrough, forcing us to change the catalyst. Refiners can test for silicon in the ppm range using inductively coupled plasma optical emission spectroscopy (ICP) techniques. PRSI uses an external lab to perform this test.

Because olefin saturation reactions are exothermic, adding coker naphtha will lead to very high (100 deg. F) reactor exotherms. A rough rule of thumb is that the heat release from olefin saturation reactions is 8.6 BTU/SCF hydrogen consumed. Therefore, the coker naphtha limit can become the metallurgy limits on the reactor or feed/effluent exchangers. Perhaps conducting a test run with varying amounts of coker naphtha in the feed would help establish some operating guidelines. Catalyst vendors and technology licensors can also assist with this problem.

Finally, UOP specifies a maximum Bromine Index of 10. If you cannot meet this specification without violating NHT operating limits, you have too many olefins in the feed.

Pedro Fernandez (Jacobs Consultancy)

Unfortunately, the answer is: "It depends." The amount is not ruled by direct performance effects, but rather is mostly dependent on plugging and fouling. A general answer would be "Somewhere between 10 to 30%," although we have references of single bed reactor units operating with up to 40% coker naphtha.

A quick review of the general guidelines and concerns about coker naphtha: there are many single bed reactors processing coker naphtha, generally blended with other naphtha streams. What usually limits most refiners is not the di-olefin content of the naphtha but rather the following issues:

1) The first limit that most refiners hit is the ability to meet the product nitrogen and sulfur specifications. In general, most refiners will continue increasing the amount of coker naphtha in the blend, as long as they can meet these specifications.
2) The second limit is related to the olefins content and associated heat of reaction, which causes the unit to reach its reactor effluent temperature limit.
3) A third limit is the silicone and di-olefin content, which affect both the heat exchange system fouling and reactor plugging.

Di-olefins *per se* are not a major problem in the hydrotreating reactor. The heat of reaction associated with their saturation is larger per mol than the heat of reaction from the olefins saturation; however, the total di-olefin content is much lower than the olefin content. The major problem with di-olefins is that they will polymerize rapidly and cause plugging in both the reactor heat exchange circuit and on the top of the reactor bed.

The two main variables that affect the amount of polymerization and fouling in the reactor heat exchange circuit are temperature and concentration. Rapid di-olefin polymerization occurs in the 500˚ - 600˚F range. The wall tube surface temperatures of the combined heat exchanger and charge heater are generally at or above these temperatures and become a focus for polymerization reactions to occur.

Another important factor is the concentration of di-olefins in the stream. Maintaining a high recycle hydrogen rate, helps keep the di-olefin concentration low and helps reduce fouling. One word of caution may be appropriate for the few refiners with a liquid feed only preheat train: high temperature exchange surfaces should be avoided to prevent major fouling potential.

In summary: In an existing single bed naphtha hydrotreating unit, we would not be concerned about processing up to 10% coker naphtha without modifications to the unit. Units have been designed or are operating with up to 30% coker naphtha in the feed without a di-olefin saturation reactor. We have a reference of a refiner that processes 40% coker naphtha in its single bed hydrotreater but must deal with short catalyst cycles (the reasons for the short cycles vary between hitting the reactor outlet temperature limit, getting silicone saturation and associated catalyst deactivation, or simply reactor plugging, which is more typically associated with the di-olefins content). We have checked with some licensors and catalyst suppliers: each has different rules, but in general they all agree that below 20 to 30% coker naphtha in the feed, they would not include a di-olefin saturation reactor.

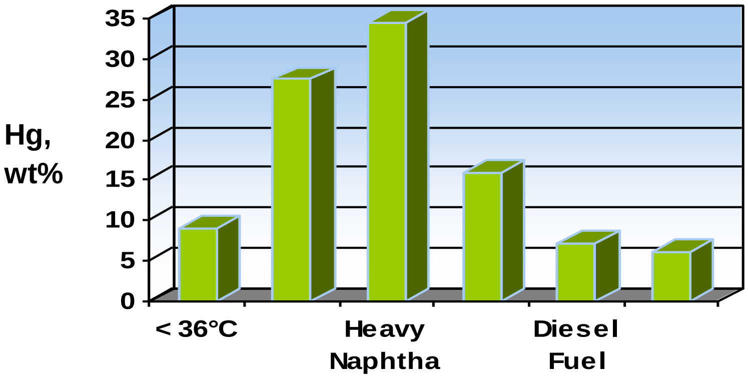
For a new unit processing more than 30% coker naphtha feed, we would recommend include a di-olefin saturation reactor. We believe that today's concerns about flexibility and on-stream availability justify the installation of this separate reactor, and all other coker naphtha design features such as a silicone trap type catalyst in the top of the main reactor and inter-reactor bed quench.

Steven J. Catchpole (Johnson Matthey Catalysts)
The main issue is the exotherm rather than the level of di-olefins. Di-olefins can be saturated with a good grading. Concerning the exotherm, one should aim to limit it to less than 60°C (110°F)

Question 63
What is the upper limit for mercury in catalytic reformer feed? What level of mercury in naphtha is removed in a naphtha hydrotreater? Does the use of cobalt/molybdenum (CoMo) or nickel/molybdenum (NiMo) catalyst make a difference in mercury removal? What is the typical hydrotreating catalyst capacity for mercury loading? If the mercury content in the naphtha is particularly high, is there an alternate method of mercury removal?

Jay Ross (Axens NA)
Mercury is commonly found in crude oil at a level of a few parts per billion (ppb) or several hundred ppb in select cases. Mercury is concentrated in the naphtha cut and found in both elemental and organically found forms. Condensates may contain 1000's ppb mercury and are the main source of concern for reformers, isomerization units and steam crackers.

Hydrotreaters will not capture Mercury, but organically bound Hg will be converted to elemental form which can be trapped downstream in a guard bed. Mercury trapping material such as CMG 273 by Axens will remove Hg to detectible limits of 1 ppb by irreversibly binding the Hg with sulfur.



Mercury distribution in Asian condensate

$Hg° + MS_x \rightarrow HgS + MS_{x-1}$

HgS is non volatile and not soluble in HC

Reformers (and other processes) often specify 1-5 ppb as the limit for Hg in the feed due to amalgam formation between Hg and many metals including Pt / Pd. The metal function of the catalyst will degrade, dehydrogenation in the first reformer reactor for example, and metal agglomeration will occur leading to a sharp drop in reactor dT (delta temperature). Catalyst regeneration is required to redisperse the Pt and restore activity.

The limit of Hg on the catalyst is a difficult question because Hg is relatively volatile and may not be found on spent catalyst, but rather passes through to products because the amalgams are only stable at low temperature. The precise disposition of the Hg is unclear due to volatility to products, low concentrations and detection limits.

Ed Lowe (Pasadena Refining Systems)
Mercury poisoning is most likely to affect diolefin saturation reactors at operating conditions of 200 °F to 300 °F. Mercury may show up in the sour water systems of NHTs although refiners would have to figure out how to test for it.

Mercury can be removed from natural gas and natural gas condensates using a metal sulfided catalyst on an alumina base. I am not aware of any applications of this technology in refining.

Andrea Foster (Johnson Matthey Catalysts)
Mercury is a particularly potent poison for precious metal catalysts operating at < 200 deg C. At > 200 deg C generally mercury amalgams are not stable and therefore any mercury in the feed should pass through the catalytic reformer into the product streams.

Similarly CoMo / NiMo catalysts are unlikely to assist in the removal of mercury. At typical hydrotreater operating temperatures any mercury present in the feed will pass through these beds. Due to the operating temperature of the hydrotreating beds the catalysts do not typically pick up mercury.

Removal of mercury from the feed naphtha stream using PURASPEC fixed bed absorbents is recommended upstream of the hydrotreating beds. They ensure that mercury is not present in downstream equipment and downstream catalyst is protected. These beds also prevent mercury from being emitted in vapor and liquid stream downstream. Surveys have shown that if mercury is present in a plant feed it will enter most of the associated gas and liquid streams.

Question 64

For an FCC heavy gasoline hydrotreater, how much arsenic (ppbw) do you see in the feed and how do you handle it?

Jay Ross (Axens NA)

This question was dealt with in general in the 1999 Q&A, p. 134. Although many of the issues are similar today, the specific application of FCC gasoline hydrotreating is more demanding with more precise selective hydrotreating to minimize olefin saturation and octane loss.

Much of the arsenic is found in the form of Arsine (AsH3) in FCC C3's, but arsenic can be found in organic-arsenic compounds in FCC HCN and LCO. Concentrations in these cuts range in the 10 to 100 ppb level.

Since Heavy FCC gasoline hydrotreaters operate at higher LHSV than diesel hydrotreater, the impact of arsenic is much higher and may result in short catalyst life. Guard materials are often recommended to increase catalyst life when arsenic is present. Axens has developed such material which is currently in operation in several Prime-G+ units.

Additional background information on arsenic can be found in well referenced articles by Reid et.al. ("Introduction to Arsine & Arsenic Compounds" and "Introduction to Arsine & Arsenic Compound Removal Methods", AIChE EPC Seminar on Arsine, March 1997)

Steven J. Catchpole (Johnson Matthey Catalysts)

We'd expect below 50 ppbw, but probably in many cases much less than this. Arsenic can be removed by metal guard grading material which would be desirable if arsenic levels are likely to exceed 50 ppbw. The capacity for the metal guard catalysts is pretty high and normally removes all the arsenic before the feed contacts the main hydrotreater beds.

Question 65

Have you been successful in reducing naphtha hydrotreater reactor pressure drop by the use of chemical injection to the reactor? What were the keys to success, and how much time did the chemical injection procedure add to cycle length?

Gavin Medine (Baker Petrolite Corporation)

Baker Petrolite offers an oil soluble, process-side proprietary blend of surface active agents designed to reduce the pressure drop of partially blocked catalyst beds. A U.S. patent has been granted covering the use of this agglomerant. This additive has proven effective in temporarily reducing the pressure drop across hydrodesulfurizer and hydrocracker reactor beds and thereby significantly increasing reactor run lengths. On average, additive treatment produces a 50% reduction in naphtha hydrotreater reactor bed pressure drop. When using this additive, refiners have increased reactor run lengths from one week up to several months.

One of the main benefits of the treatment is that it allows refiners to continue operating a reactor fouled with iron sulfide without reducing feed rates or shutting down the unit for catalyst skimming or replacement.

The keys to a successful treatment are based on the following application features:

- Proper additive injection methods and locations
- Correct injection equipment required for high pressure systems
- Dosage requirements to effectively act on deposited iron sulfide deposits
- Suggested monitoring to provide data needed to confirm performance

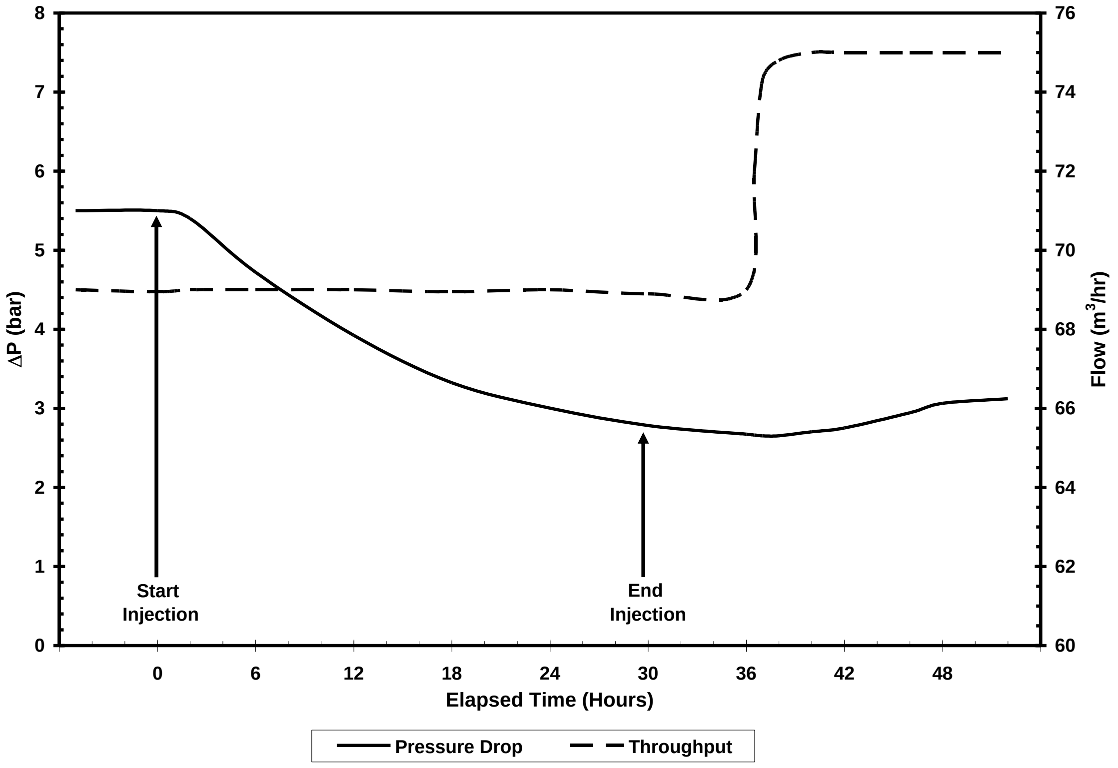
Some examples of Baker Petrolite's treatment of naphtha hydrotreaters with reactor bed pressure drop issues are provided below.

Example 1

A large, fully integrated European refinery was experiencing severe operational constraints due to a high pressure drop across the naphtha hydrotreater. Naphtha throughput was limited to less than 70 m^3/hour. A shutdown for a skimming operation was the only alternative to the refinery until they learned about Baker Petrolite's reactor bed agglomerant.

Additive was injected just upstream of the reactor bed for a period of about twenty-nine hours. The pressure drop began to decrease within a few hours of the initial injection. As shown in the graph below, after eighteen hours of treatment, the pressure drop had stabilized at 42 psi (three bars), representing a reduction of over 45%. By the end of the additive treatment period, the refiner was able to increase the unit throughput to 75 m^3/hour.

Additive Effect on Reactor Bed □ P and Unit Throughput



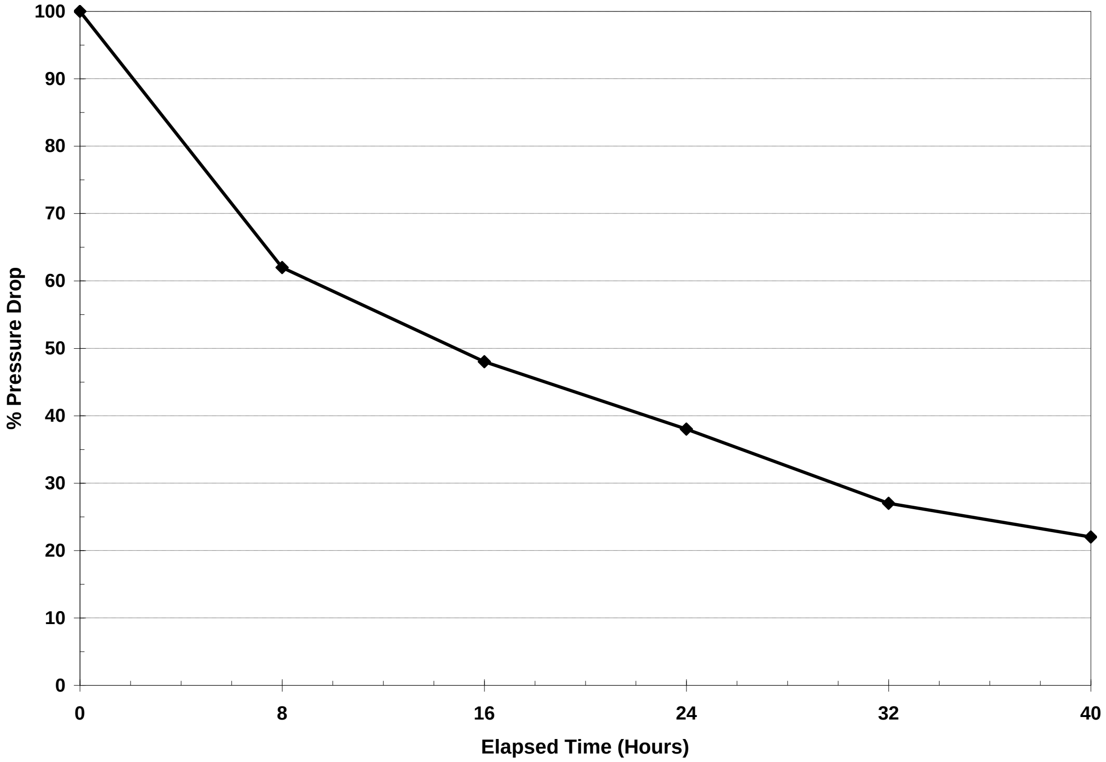
Example 2

A large Gulf Coast refinery experienced two process upsets within a two-week period. The first upset resulted in a two-fold increase in the delta P of the upper reactor bed, forcing the unit close to its operating limit. The second upset spiked the delta P beyond the operating limit. Unit charge rates were reduced by 20% to accommodate the pressure limitations. After reviewing the situation, Baker Petrolite recommended the use of reactor bed agglomerant to alleviate the pressure drop issues and control further fouling of the reactor.

After only eight hours of injecting the additive, the reactor delta P decreased to 62% of the upset value. The following day the refiner was able to return to normal feed rates on the unit while maintaining the reactor delta P at 50% of the upset value.

The graph below illustrates the impact of this application on the flow rate adjusted pressure drop across the upper bed. The pressure drop values are reported as a percentage of the original pressure drop at the upset condition.

Additive Effect on Reactor Bed ΔP



The refinery was able to extend the run length by several months with this application. Without the use of the agglomerant, the reactor bed fouling would have forced a complete shutdown of the unit.

Tina Drumheller, Frontier Refining

Cycle length in our heavy naphtha hydrotreater has historically been limited by pressure drop. Chemical injection at the top of the reactor was used twice in the last four cycles with negligible improvement and no manifested increase in cycle length.

Iron sulfide is probably not the largest component of fouling in the top of the reactor. For the most recent run, which began in April this year, new grating material was used at the top of the bed, and start of run pressure drop was 20 psi less than the previous 3 runs.

Brad Mason (Nalco Energy Services)
Reactor pressure drop increases can be caused by a build up of organic polymers, inorganic scales and particulates (such as FeS), or a combination of the two.

Organic deposits commonly result from oxidative reactions at both high and low temperatures. While some of these reactions involve molecular oxygen, many involve peroxides or organo-sulfur compounds coming from upstream processes; in this case, a simple oxygen scavenger or an oxygen stripper will not control fouling. Organic deposits can also occur as a result of non-oxidative polymerization reactions that are thermally or catalytically induced. Once formed, these materials can migrate to the reactor bed.

Inorganic deposits are typically composed of iron sulfide formed in-situ or carried as tramp iron from an upstream process.

Nalco has many examples of alleviating NHT reactor bed pressure drop caused by both organic and inorganic foulants through chemical addition. The keys to success in selecting the right additive for the situation are a high level of understanding of the unit processes and history, coupled with good discovery of the fouling problem and lab evaluation of foulant material and/or feed streams.

In most instances after applying the chemical additive, the reduction in reactor pressure drop starts to take place within the first hour. The usual treatment time is 24-48 hours. In one instance due to inorganic fouling, the reactor bed dP was reduced 20%. The refinery customer estimated this was worth >$5,000,000 in extended run length and higher throughput rates.

In another site a customer realized a reactor bed dP reduction from 32 psi to 11 psi within 24 hours. In this case the fouling source was identified as predominately organic polymers.

Question 66
We have experienced ammonium chloride fouling at several of our sites with the location of the deposits varying from unit to unit. Of particular concern are deposits around the recycle gas compressors. What washing fluid do you recommend for eliminating these deposits from the compressors? Can you mitigate these deposits by modifying the operating conditions? What is the best strategy to minimize ammonium chloride formation?

Ed Lowe (Pasadena Refining Systems)
There is some redundancy in this question with Question 51 posed earlier to the panel. Referring to these responses is also recommended.

In reformers, the key to reducing ammonium chloride (NH_4Cl) formation is proper Naphtha Hydrotreater (NHT) operation. UOP has an excellent paper on NH_4Cl corrosion in NHTs. The collective pool of experience at PRSI has not had much success modifying operating conditions to reduce formation of the salts. Obviously, however, eliminating the ammonia and/or the chloride will significantly reduce the formation of ammonium chloride. Keeping the nitrogen out of the reformer will help eliminate ammonia formation and subsequent deposition in the compressors and debutanizer (PRSI has experienced problems with NH_4Cl deposition in both of these areas). UOP specifies maximum reformer feed nitrogen content of 0.5 ppmw. In many cases it is nitrogen removal that limits catalyst life. Proper water/chloride balance is critical to minimizing the amount of chlorides in the recycle gas.

If you have a CCR, it is recommended for air going to the regenerator to be dry. UOP can provide more detailed information if that is necessary. In order to protect downstream equipment, installation of an alumina chloride scrubber will significantly reduce the amount of chlorides traveling with the hydrogen to other units such as hydrotreaters. (A contributor to answering this question worked in a refinery where the hydrogen line between two plants failed due to chloride stress cracking. The chlorides also damaged isolation valves at the battery limits of a hydrotreater). It is suggested that discussions with UOP and other technology licensors be held about the impacts of upstream units such as poor desalter operations and their contributions to chloride problems.

On-line remediation of ammonium chloride build up in and around compressors is quite common. Just recently at PRSI, we had a very successful on-line washing of our reformer recycle gas compressor with the help of our chemical injection vendor. While working for other refiners PRSI employees attest to similar success using naphtha, toluene, and/or kerosene as washing agents. When considering on-line remediation, if possible, collect samples of the material and do some bench testing to determine which chemicals work the best. Be sure to work closely with the reliability department and the compressor manufacturer to make sure you do not inject too much liquid at one time. Many compressors have case drains or other points to allow the injection and removal of deposits from the machines.

Randy Rechtien (Baker Petrolite Corporation)

Ammonium chloride formation in recycle compressors is a function of several operating variables:

- Nitrogen levels in the hydrotreater feed
- Chloride levels in the recycle gas
- Compressor type
- Compressor suction temperature
- Compressor suction pressure

Changes to operating conditions can minimize salt fouling. For example, the amount of ammonia produced in the reactor may be reduced by processing alternate feed stocks with lower nitrogen content. Ammonium chloride formation potential may also be reduced by increasing the temperature of the recycle gas to the compressor. However, in most cases, the refinery's ability to modify feed nitrogen levels or compressor operating conditions is usually limited. As such, the only variable that can actually be affected is the level of chloride in recycle gas.

Assuming that hydrogen produced at the reformer is used at the hydrotreater reactors, then the most common source of HCl in the hydrogen is the chlorinated solvent used to regenerate reformer catalyst. While operating methods (e.g., chloride guard beds) can prove useful in minimizing chloride levels, they never completely remove HCl from the hydrogen. The HCl content of recycle gas should be frequently monitored using gas detection tubes. Typical limits are 1-2 ppm HCl in the recycle gas. The absorbent materials in chloride guard beds should be replaced or regenerated as needed to maintain desired HCl levels in the treated hydrogen.

Baker Petrolite has been successful in alleviating compressor fouling using proprietary additives. These additives, which are formulated to provide increased surfactancy, help to disperse salts and solids which deposit on compressor internals. To evaluate the performance of these dispersants, compressor vibration and adiabatic efficiencies should be frequently monitored.

It is critical that the dispersant be injected along with a hydrocarbon carrier (naphtha or kerosene) to provide for proper additive mixing. Note that reciprocating compressors may not be viable candidates for these additive applications because of restrictions on the volume of liquid which they can safely tolerate.

Tina Drumheller, Frontier Refining

Salt deposits in reformer and hydrotreater recycle compressors have caused operating problems manifested in poor compressor performance and high vibration.

Continuous kerosene injection has been used to mitigate the effects of compressor fouling with marginal improvement. To prevent ammonium chloride salt build up in the hydrotreater recycle compressor, the recycle hydrogen was routed through the recycle gas amine contactor upstream of the compressor. Since that time, fouling has not limited compressor performance.

Use of high purity hydrogen in lieu of reformer hydrogen as feed to distillate and gas oil hydrotreaters has further prevented salt build up on associated recycle compressors.

To minimize ammonium chloride formation in the reforming units, nitrogen removal is targeted at a maximum 0.5 ppm in hydrotreated feed.

Compressors are cleaned during unit outages. Both chemical and hot condensate wash have been used. The current procedure calls for hot condensate flush until effluent pH is neutral.

Steven J. Catchpole (Johnson Matthey Catalysts)
Water remains the preferred choice for removal of ammonium chloride deposits though often applied in high pressure jets to speed-up removal. There is no real opportunity to modify process conditions to reduce the formation of these deposits. By far, the main option to remove chlorides from the feeds is to use chloride absorbents such as Johnson Matthey's PURASPEC products. It is important that these not only remove HCl, but also remove as much as possible the organic chlorides as both are precursors for the downstream ammonium chloride formation in combination with nitrogen sources.

Dennis Haynes (Nalco Energy Services)
Nalco has experience applying a salt dispersant chemistry into the inlet for gas compressors where ammonia chloride formation was causing a decrease in compressor efficiency and also causing vibrations. After application of the cleaning dispersant, the efficiency recovered and vibrations were eliminated to barely detectable limits.

Question 67
Have you seen increased catalyst deactivation in FCC gasoline hydrotreaters due to CO getting into the unit? What is the deactivation mechanism? What was the source of the CO and how did you mitigate its effects? How much deactivation did you experience?

Jay Ross (Axens NA)
The operating conditions of the selective HDS are such that the CO methanation level over the catalyst is lower than in conventional HDS. As a result, CO may build up in the recycle gas and inhibit the HDS catalyst. The catalyst will rapidly recover its activity once the CO is removed from the hydrogen make-up

Reforming

Question 70

A continuous reformer running at very high temperature and low H_2/HC ratio has sulfur injected as recommended by the licensor. However, there is still a large amount of coke build up between the scallops and the reactor wall. What is the likely cause of this coke formation and what steps do you recommend to resolve this problem?

Jay Ross (Axens NA)
Sulfur injection has proven very effective in suppressing metallic coke formation when the appropriate metallurgy is selected in the heater. With lower grade alloys such as P22 (2-1/4 Cr, 1 Mo), one must limit the heat flux and tube metal temperature even when proper sulfur passivation is used.

Operation at high WAIT and low H2/HC would magnify the problem of coke formation (higher tube temperature and lower hydrogen partial pressure). Coke formed in the tubes will migrate to the reactors and deposit behind the scallops or basket. The deposits have a H/C molar ratio ~0.1 and contain iron deposits, but contain no catalyst. They tend to grow under the conditions in the reactor and can put great pressure on the internals leading to damage over a period of months and ultimately affect catalyst circulation.

Axens specifies DMDS dosing (0.2 ppmw), proper heater metallurgy, heat flux limits & recommends monitoring furnace tube metal temperatures With P9 (9Cr 1Mo) or SS tubes, much higher heat flux and skin temperatures can be sustained before coking occurs (100 - 150° F higher than P22 tubes).

Ed Lowe (Pasadena Refining Systems)
The likely cause of the coke build up could be a case of metal-catalyzed coking. An analysis of a sample of the coke by UOP would greatly help in determining if it is indeed metal-catalyzed coking. UOP will use a high-powered microscope to analyze the coke.

In general, metal-catalyzed coke formation is caused by a variety of factors such as high temperatures (present) and low hydrogen partial pressures (present). In many instances, metal catalyzed coking appears in areas with a low superficial velocity. Partial plugging of the scallop screens with catalyst fines or other material can cause the low superficial velocity. Some early UOP reactor designs experienced issues with fines blocking the ventilation holes at the bottom of the outer baskets. Finally, if metal-catalyzed coking is occurring, consideration can be given to some metallurgies which appear to be more resistant to coke formation than others. The technology licensor should be consulted to provide input on the suitability of any recommended metallurgical substitutes.

Additional factors may be contributing to the coke build up. If the unit is running a feed that is a combination of naphthas (such as straight run and coker naphthas), check the end point of each stream individually (both the TBP and D-86) to check for a high EP tail that may be masked in the combined stream. Another factor to check for is to make sure that the air supplied to the regenerator is dry. High recycle gas moisture appears to contribute to coking.

Question 71
Do you use an oxygen stripper upstream of naphtha hydrotreater/continuous regeneration reforming units to remove absorbed oxygen found in purchased naphtha or naphtha that has been in storage? If so, what are the operating parameters of the oxygen stripper? Are there additive alternatives?

Tina Drumheller, Frontier Refining
Feed diolefin in the presence of oxygen can result in polymerization in feed/effluent heat exchangers and the reactor catalyst bed of naphtha hydrotreaters. This fouling can lead to run length and product quality limitations.

Feed diolefin is present in both virgin and cracked feedstocks with the latter typically containing the majority of the diolefin. Oxygen can be found in cold feed from storage and purchased naphtha.

Two main methods of addressing oxygen in the feed are

1. Strip oxygen from the feed upstream of the feed/effluent heat exchangers
2. Store naphtha in blanketed tanks to prevent oxygen from entering the feed

Two different designs for oxygen stripping include a reboiled stripper tower and a gas-liquid contact tower.

The basic design of the first can be described as follows:

The stripper is a basic stripper column with an overhead condenser, reflux and bottoms pumps, feed-bottom exchange, and the necessary instrumentation to properly and safely operate the unit.

Feed is heated via exchange with the bottoms product from the oxygen stripper, mixed with reflux from the oxygen stripper overhead receiver, and fed to the top tray of the oxygen stripper. A reboiler provides heat to the column. Oxygen stripped product is routed via the feed bottoms exchanger on column level control to the NHT Feed Surge Drum. The temperature of the oxygen stripped product is controlled by a TIC controlling the amount of bottoms material bypassing the tube side of the oxygen stripper feed-bottoms exchanger. The oxygen stripper bottoms temperature is set by the column pressure and the amount of boil-up, taking into account the bottoms composition.

The second design consists of a stripper tower with product lined up to the feed surge drum. The gas enters the column below the feed. The column operates in the range of 80-90 psig. Pumps deliver the cold feed from storage to the tower. The tower level control is cascaded to feed flow. The off gas exits the top of the tower and is let down to the fuel gas system via pressure control.

Both natural gas and reformer hydrogen have been used to strip oxygen from the feed. Use of natural gas caused a decrease in system hydrogen partial pressure due to evolution of absorbed methane. The use of hydrogen served dual benefit in systems with low hydrogen purity, resulting in increased system hydrogen partial pressure.

Brad Mason (Nalco Energy Services)

With respect to additive treatment, fouling of NHT feed/effluent exchangers due to ingress of oxygen in the feed to form either gums like deposits or inorganic foulant material is well documented.

One example where Nalco improved the efficiency of an oxygen stripper upstream of the NHT exchangers was with a refinery customer in Europe. Throughput to the NHT/CCR had to be routinely reduced as a result of inadequate stripping of oxygen. Average levels oxygen in the naphtha stream were up to 8 ppm, with a target of <1 ppm.

Through discovery of the root cause, an inorganic dispersant was implemented upstream of the oxygen stripper for the effective removal of iron sulfides and iron oxides from the oxygen stripper feed/effluent reboiler. By utilizing in-depth deposit analysis and specific monitoring tools, the fouling cause was treated and not the symptom.

The benefits to the refinery were steam savings worth some $300,000 annually and improvements to unit throughput.

Question 72

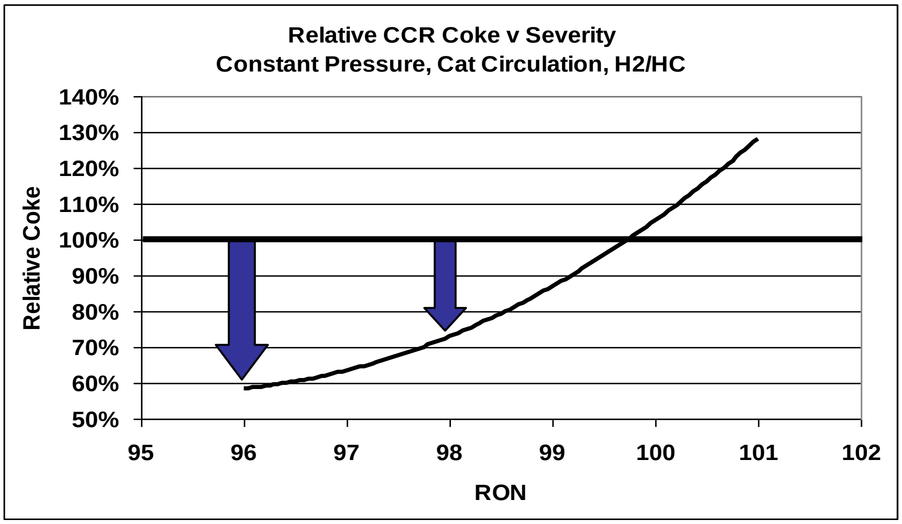
The mandatory addition of high ethanol concentrations to gasoline is reducing the reformate's required octane. What changes need to be made to a regenerator to allow it to run in a low coke mode?

Jay Ross (Axens NA)

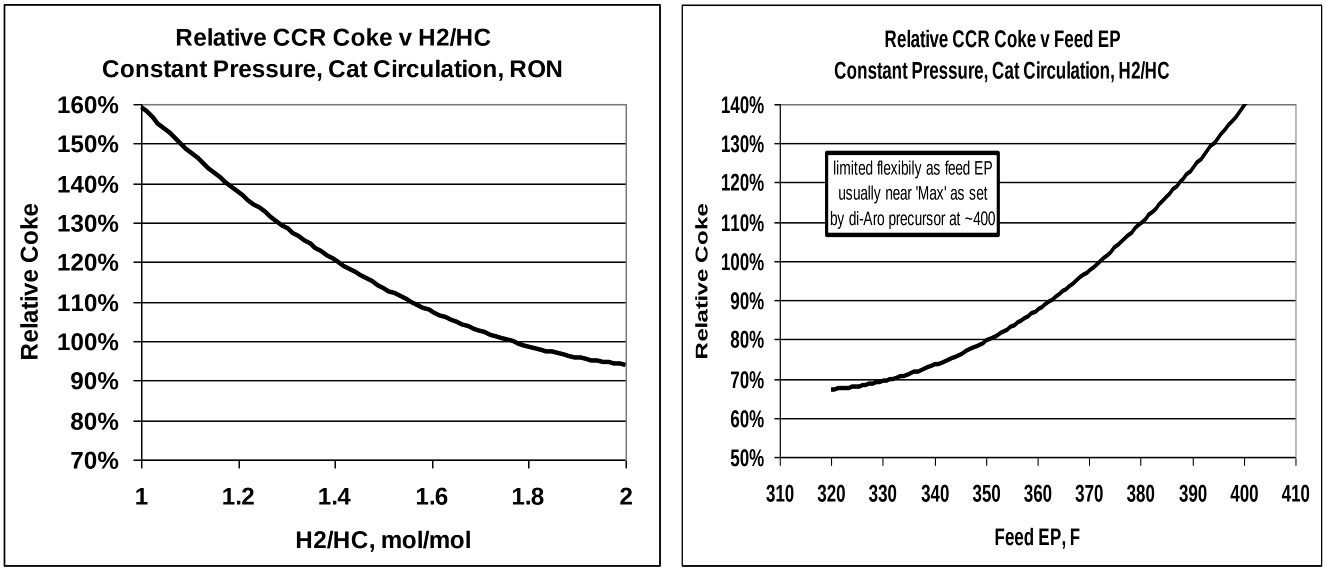
The inclusion of 5-10 vol% ethanol, displacing MTBE, may impact the pool octane by 1 - 2 RON, a value which is highly blend- and refinery-specific. The impact on the required reformer severity may be a reduction of 2 - 4 RON for a constant gasoline pool RON and a resultant reformate yield increase of 1 – 3 vol%. The reduced severity will result in a significant reduction in reformer coke production and potentially require operation and/or equipment changes.
Most CCR regenerators operate between 3 – 7 wt% coke on the catalyst. strategies to accommodate lower coke production will be highly unit specific:

- Slow catalyst circulation rate (build coke on the catalyst)
- Periodic shut down of the regeneration section
- Reduce oxygen content in the burn zone, if adequately controlled
- Increase feed EP or alter feed to make more coke
- Reduce the H2/HC ratio to make more coke
- Reduce unit pressure to improve yield selectivity (C5+ and H) and make more coke
- Permanent regen modifications as last resort

The most effective means of increasing or controlling coke make is by altering the H2/HC ratio or unit pressure within unit constraints. As the H2/HC is lowered, coke increases and there is a slight yield increase – see figure below.



Increasing the feed EP can also be effective, but most refiners operate near the recommended maximum value already – see figure below.



Effect of H2/HC and feed EP on relative coke production

Question 73
With the new stronger scallop designs, what is the next weakest link that will break when the catalyst bed pressures build to the point where something has to break? What causes high reactor bed pressure and what are you doing to address the problem?

Ed Lowe (Pasadena Refining Systems)
The scallops are still the weak link. After that, the technology licensor would have to provide that information. With a CCR, however, a good guess would be the center screen.

High bed pressures can be caused by coking (see #70), catalyst pinning, or other plugging such as fines from poor operation of the elutriation system (high catalyst flux, etc.). Check the pinning calculations to make sure that pinning isn't a problem. Minimizing fines formation can help.

Another key step in controlling bed pressure build is to keep moving catalyst at 10-15% of nameplate circulation rate as you are shutting down the reformer (CCR). The metal will cool faster than the catalyst. As the metal cools and the reactor diameter decreases, the bed pressures will increase. Heat ups and cool downs should be controlled to 50 deg. F/hr rate to reduce this issue.

Pedro Fernandez (Jacobs Consultancy)
We address this question from a general perspective and then provide information that comes directly from UOP.

There are two pressure mechanisms that can lead to failure of reforming unit internals, scallops and center pipe. The first, and possibly the most common one, has to do with plugged screens, bad circulation, and coke formation. Failure of internals in these cases is localized to the area where the coke formation is happening and is not related to the relative strength of the internals.

The second failure mechanism, which becomes more prevalent in larger size units, is associated with catalyst bed pressure buildup during the unit cool down. As the unit heats up, the reactor expands, increasing the available catalyst volume between the scallops and the center screen. The change in this volume is not a problem as long as the catalyst is circulating. When there is a unit shutdown, one of the first things to shut down is the catalyst circulation. The reactor cools down and contracts, reducing the available catalyst volume. Since the catalyst is not moving, it has no place to go, which leads to a substantial buildup of pressure from the catalyst against the internals. In general, the scallops or outer baskets are the first element to fail, but some of our colleagues have seen failures of the scallops, center pipe, or both.

UOP has maintained that scallops should be weaker than the center pipes. This makes sense: failure of the center pipe may lead to catalyst carryover out of the reactor to the heaters or compressor. In the past, scallop failures were less of a problem, in large part because the scallops in smaller reactors are relatively stronger mechanically, and because the expansion and contraction problems are less severe. However, this problem is more severe in the larger units.

UOP has made design and operating procedure modifications to help avert the potential problem of scallop and internal damages and failure. These changes include:

1. Increase the absolute strength of both the scallops and the center pipes. This change by itself is expected to give the scallops for larger reactors the same level of reliability as what has been traditionally experienced in smaller reactors.
   At the same time they have strengthened the center pipe by increasing both the profile wire thickness and the inner core of the center pipe.

2. Make provisions in the design to allow for the continuous circulation of catalyst during the cool down of the reactors to avoid the development of high catalyst bed pressures.

3. Make provisions in the design to avoid thermally shocking the reactors during emergency shutdowns and restarts and manage the heat up and cool down rate of the reactor.

In summary, the scallop remains the weakest point in the system—by design—but the design has been strengthened so that the potential for failure is minimized.

HYDROPROCESSING

Safety

Question 74

What are your best practices for mitigating the risk of hydrogen back flow to tankage during a hydrotreater feed pump trip?

Shaun Boardman (Jacobs Consultancy)
Best practices and best available control both continue to evolve over time. For this reason, best practices in new units differ from the logic and protection instrumentation applied in older units. We have not seen anyone specifically modify or update any of the older schemes where these have proved to be successful over time, such as the traditional double check, but most are applying more advanced protection schemes in addition to the check valves for new units.

Although this question refers specifically to hydrogen backflow to tankage, the same consideration can be given to all the backflow scenarios, namely feed oil, wash water and the lean amine supply. In most cases the Level of Protection Analysis (LOPA) generally requires that at least a single on/off chopper valve is required (SIL 2) in combination with closing of the flow control valve which are both activated by low flow.

Specifically on the feed case which includes a feed surge drum, the drum PSV could be sized for the backflow scenario and the feed system piping up-rated accordingly.

Scott Harper (Consumers' Co-operative Refineries Ltd)
We have a double check valve system and downstream of the check valves is a remotely activated shutoff valve in place on all the high pressure hydroprocessing units. In some units the minimum flow valve also acts as a check in the case of a pump failure. Between the feed tanks and high pressure feed pump are low pressure pumps, feed filters and a feed surge drum. Both the filters and surge drum have PSV protection to flare and the feed surge drum has a natural gas push/pull system to flare. We have not experienced any hydrogen back flow to tankage or for that matter to the feed surge drum during a feed pump trip.

Question 75

How do you protect against heater tube failures? Are operator observations adequate or must design and other monitoring features be incorporated? What are these features?

Scott Harper (Consumers' Co-operative Refineries Ltd)

On our fired heaters we employ skin thermocouples along with operator observations. All tube abnormalities and irregular skin TI readings, both high and low, are checked with the optical pyrometer. The catch to using the optical pyrometer for verification is to correctly set the emissivity for the tube. The optical pyrometer is set by adjusting the emissivity setting while taking a measurement close to a known skin TI reading until both the pyrometer and skin TI are in agreement. With the emissivity determined the irregular TI can be checked.

Operators are instructed to monitor the flame pattern of the burners when making rounds and board operators continually monitor stack analyzers for excess O_2 in the flue gas and draft conditions on the heaters. We have also periodically used infrared scans on line to check the entire heater confirming the thermocouples and checking the fire boxes for leakage and refractory damage. During a turnaround heater tubes are checked for metal loss via UT measurements. Once the UT measurement is confirmed and the tube thickness is found to be close to or below the corrosion tolerance it is replaced.

We feel that the critical factor is to verify all skin TI measurements. Both high and low readings can signal flow problems on specific passes of multiple pass heaters. Once the operators have confirmed that all the burners are firing equally, additional information can be reviewed to determine the accuracy of the reading. Variations in the outlet temperatures can be a sign of unbalanced flows which can cause high skin temperatures. Along with verifying the readings with the pyrometer we compare pass outlet temperatures, flows and valve openings to ensure that all the passes are balanced.

Yvonne Jeanneret (CITGO)

Refiners protect against heater tube failure using several techniques that are tailored to fit the degradation mechanisms that are active in their furnaces. For example, creep rupture and corrosion are frequently the cause of heater tube failures in refineries. Creep is a phenomenon that causes metals and other materials to deform and fracture when stress is applied long term to equipment operating at elevated temperatures. For heater tubes the primary source of stress is the internal process pressure, but structural loads on the tubes also play a role in creep failures. Regardless of the source of the stress, prolonged application of stress in equipment that operates at elevated temperatures can lead to creep damage and eventual failure. Whether or not creep damage occurs and the amount of damage that occurs depends upon the following factors:

- The alloy selected for the heater tubes
- The dimensions of the tube (used to calculate the stress in the tube wall)
- The stress level in the tube wall
- The tube metal temperature during past operations
- Tube wall loss rate due to corrosion or other damage mechanisms
- Other degradation mechanisms the tubes are experiencing such as loss of strength in steels due to spheroidization, graphitization, or decarburization.

During the 1990's the Omega approach to dealing with creep and other degradation of high temperature equipment was developed, and Omega software was written by the Materials Properties Council for the Oil Industry to make it possible to accurately assess the amount of creep damage that has occurred in furnace tubes and other equipment operating at high temperatures. Omega analysis also includes the effects of corrosion on the remaining life of heater tubes. Omega software is essentially a simulation program that makes it possible to determine how much creep damage has occurred in heater tubes and what the remaining life of those heater tubes is if the operating conditions remained the same. When long term corrosion rate information is inputted, Omega software calculates the effects of wall loss due to corrosion on the stress in the steel. As the wall corrodes away the stress in the heater tube wall increases making creep damage more likely. Omega software takes the creep damage and changing stress due to corrosion into account and predicts the remaining life of the heater tubes. In addition, the future operations can be included in the analysis to determine the impact of changing process conditions.

A good example of analysis of coker heater tubes is provided on the AIChE Chicago website: http://www.aiche-chicago.org/symposium06/wilks.pdf. Coker heaters tubes are particularly difficult to analyze because the process temperatures and pressures vary as coke forms in the heater tubes. This example uses daily temperature and pressure measurements, IR scans of the furnace, and a conventional furnace simulation along with Omega simulation software. It includes long term corrosion rate damage as well as damage caused by tube decoking. This analysis was used to determine when the tubes needed to be replaced, and the tubes were replaced before tube failures occurred.

Question 76

How are you applying API RP 579, Recommended Practice for Fitness-for-Service, to hydroprocessing unit fired heaters and steam/methane reformers? Are the inspection techniques and asset life modeling sufficient for improving turnaround management and extending turnaround cycles?

Scott Harper (Consumers' Co-operative Refineries Ltd)

CCRL does not specifically apply API 579 to our steam methane reformers to perform asset life modeling. We apply parts of API 579 along with inspection techniques to determine which tubes require a change-out. We gather information via operator observation and heater tube temperature measurement with an infrared optical pyrometer. Pyrometer readings are taken approximately 4 times a week and inputted into a spreadsheet for historical record keeping. The historical data is used to perform life predictions. The results of this analysis used to estimate the potential number of tubes that may require a change-out during the next scheduled shutdown. This enables maintenance to optimize the number of new tubes ordered into stock and schedule the appropriate amount of maintenance time to complete the estimated change-outs. During the turnaround all the tubes are UT scanned and measured for out of roundness to confirm the predictions. From the survey any tube that has 30% through wall cracking or 3% diametrical creep is changed-out.

Using this scheme we have never experienced a tube failure on the run on our terrace walled side fired reformer. The first re-harping of this reformer is scheduled for 2008 after 20 years of operation. Over the 20 years less than 10% of the tubes have been changed-out due to through wall cracking or out of roundness. The bigger problem that we have had to deal with is the outlet pigtail creep damage which has necessitated changing 25% of the pigtails.

Yvonne Jeanneret (CITGO)

Steam methane reformer furnaces and Hydroformer furnaces can be analyzed to determine fitness-for-service by using past equipment records along with Omega analyses to determine the remaining life of the tubes. API 579 describes Omega in Appendix F.7.3, and a draft procedure has been written for conducting the analysis. Therefore it is acceptable to use Omega to deal with all types of high temperature refinery equipment for fitness-for-service analyses. Frequently, refineries record furnace inlet pressures, outlet pressures, and tube metal temperatures for selected tubes (with thermocouples welded to the tubes and shielded). Also, periodic infrared scans are conducted to ensure the thermocouples are reading properly.

Pressures in individual tubes can be obtained from furnace simulations. Corrosion measurements are typically made during unit turnarounds. This information can be used with

Omega analyses to determine the remaining life of each tube in the furnace. Then if that life is sufficient to make it to twice the turnaround length, the furnace is fit-for-service till the next turnaround.

Steam reformer furnaces are more difficult to analyze but the same principles can be applied if acceptable data is available on the reactor tube temperature history. Since typically only a few tubes in a steam reformer reactor will have thermocouples a thorough assessment of the highest tube metal temperature is more difficult to obtain. Also, since hot spots can develop in a localized region of the tubes due to coke formation on the catalyst, the discovery of hot spots may not be rapid enough to provide data for accurate fitness-for-service assessments. Most refineries use operator observations of the tubes on a shift basis or daily to help to quickly identify hot spots on steam reformer tubes. While Omega analyses of steam reformer tubes may not be as accurate as the analyses of other furnaces that operate at relatively constant temperature and pressure, Omega analyses can be improved by testing samples cut from the tubes in the reformer furnace that have experienced hot spots. Omega testing of tubes that have been in service provides a more accurate assessment of remaining life.

Catalyst

Question 81

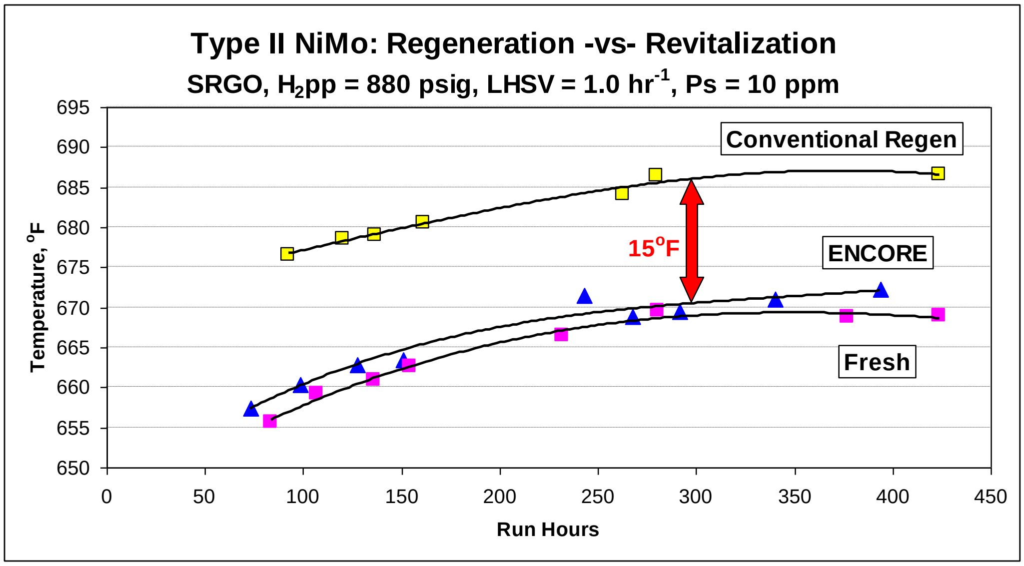
With the newer regeneration/rejuvenation processes for catalysts with Type II active sites, what has been your experience with reuse of these catalysts in ULSD or other services?

Paul Ceccato (Criterion Catalysts)
The application of standard coke removal regeneration techniques to spent conventional catalysts can sufficiently recover activity for reuse in similar or less severe hydrotreating applications. However, insufficient activity is recovered through these standard regenerations of catalysts containing Type II active sites to enable reuse in ULSD service for a cycle life similar or almost equal to fresh catalyst. For this reason, new methods to revitalize spent catalysts containing Type II active sites have been developed to allow reuse in ULSD service.

In a Type II catalyst, oxygen containing bridges between the active molybdenum and alumina base have not been formed, allowing complete sulfiding of the molybdenum to occur. Avoiding the formation of these oxygen containing bonds between the molybdenum and the support is performed through special manufacturing steps that are not reproduced during standard coke regeneration. In a revitalization process, the elimination of these oxygen bridges between the support and the molybdenum that occurs during the regeneration process is again accomplished in addition to carbon removal, resulting in complete sulfiding of the molybdenum during activation of the revitalized catalyst.

Criterion has extensive experience in reactivating spent CENTINEL and CENTINEL Gold catalysts having Type II active sites. Several years ago, Criterion developed a proprietary ENCORE Revitalization technology. This reactivation process includes a carefully controlled regeneration step to remove coke deposits, followed by several steps that recreate the original Type II surface chemistry of the CENTINEL and CENTINEL Gold catalyst. This technique has been successfully applied to both CoMo and NiMo catalysts, resulting in recovery of 90% to 100% of its fresh HDS and HDN activity in a range of services, including ULSD.

The following plot demonstrates the activity recovery by standard coke burning regeneration versus revitalization through ENCORE. Revitalization of a Type II NiMo catalyst results in near full activity recovery. The same catalyst is 15°F less active after conventional carbon burn regeneration, and if loaded into ULSD service, cycle life decrease by several months.



ENCORE Revitalization reverses deactivation caused by coking and agglomeration of the catalyst metals, but it does not remove contaminant metals from the catalyst. Hence it is important to evaluate the spent catalyst prior to ENCORE Revitalization. Mildly contaminated catalyst may still be revitalized with slightly lower activity recovery; however, heavily contaminated catalysts will likely be rejected in favor of fresh catalyst.

Question 82
What are the primary catalyst concerns when restarting the unit after a total power failure?

Paul Ceccato (Criterion Catalysts)
In most cases, a total power failure results in the loss of flow through the reactor due to shutdown of the recycle compressor, charge pump, and hydrogen make-up compressor. With hydrocarbon and hydrogen still in contact with hot catalyst, reactions continue to generate heat without transfer to the mass flow. As temperatures increase and hydrogen partial pressure decreases, soft coke can form and deposit on the catalyst. Over time, soft coke condenses to a hardened form which impacts catalyst performance and potentially flow distribution through the catalyst bed.

To minimize the impact of soft coke deposition, the catalyst should be cooled as quickly as possible by reestablishing gas flow, sweeping with hydrogen or nitrogen, or possibly continuing oil flow if absent of cracked stocks. Decreasing unit pressure within equipment limitations reduces reaction rates and assists with establishing flow through the catalyst. If power is not restored within a short period to enable a restart of the recycle gas compressor, the catalyst should be swept of oil and cooled to < 150^{o}F before blocking in under positive nitrogen pressure.

In hydro cracking applications, high energy releasing reactions promoted by high acidity catalysts necessitate the inclusion of facilities for immediate depressurization and initiation of catalyst cooling. Lacking immediate action may result in a runaway condition during which temperatures capable of damaging equipment and catalyst are reached as cracking reactions self perpetuate. Bed temperatures should be monitored closely upon securing the hydrocracking catalyst with particular attention to previously identified hot spot locations.

When restarting the unit after a power failure which has resulted in the need to cool down and depressure the reactor, we recommend a unit specific review of start up procedures. Some general guidelines are as follows:

The subsequent start-up should be gradual. The primary concerns are to make sure the catalyst remains fully sulfided and to strip the coke deposits from the recent deposition. After starting hydrogen circulation, the reactor should be heated to near the previous operating temperature or a maximum of 700^{o}F and held for a minimum of 8 hours while maintaining at least 1000 ppm H_2S in the recycle hydrogen. Temperatures should not exceed 475^{o}F if an H_2S concentration is not maintainable, but sour gas or sulfiding chemical can be added to allow further temperature additions.

After stripping the catalyst, temperatures should be reduced to less than 350^{o}F for reintroduction of straight run feed. A low temperature is advised due to the potential of localized coke formations which may retain heat and initiate reaction. The feedrate should be increased to a minimum of 70% of design and conditions held for at least 4 hours to pre-wet the catalyst.

With the recycle gas scrubber bypassed, temperatures can be increased to establish feed desulfurization while maintaining a minimum of 1000 ppm of H_2S in the recycle gas when exceeding 475^oF. Cracked stocks or normal mixed feed should be introduced while at lower temps but after identifying sufficient H_2S in the recycle gas and validating good flow distribution.

Steven J. Catchpole (Johnson Matthey Catalysts)
The main worry were the conditions during the shutdown, whether the catalyst at temperature has had feed without hydrogen present. If the hydrogen coverage was sufficient then no significant deactivation should be expected. Heating up with 40-50°C (70 - 90°F) an hour and bringing the unit slowly back on-line, should do the trick. If coking is expected, then a hot hydrogen strip or kerosene wash, might help, but this may not always be successful.

Process

Question 83

What are the "best in class" practices for ensuring adequate reserve quench in both ULSD hydrotreaters and hydrocrackers? How do you determine the reserve quench requirement?

Shaun Boardman (Jacobs Consultancy)
The approach of the licensors differs somewhat in their approach to this, and the extent of reserve depends much on the application.

Because actual heat release which promotes thermal instability is difficult to determine, a margin is normally applied over and above the normal operating quench requirement, and added to the recycle gas capacity as well as being applied to the sizing of the quench valves.

For Hydrotreaters, total quench is sized anywhere from 30% to 100% larger than the normal quench requirement. The range reflects the dependence on feed type, the type of catalyst used, and the application of any interstage heat exchange.

For hydrocrackers, the pre-treat section quench capacity is normally designed for anywhere from 50% to 150% of normal quench demand, while the hydrocracking section is designed with 200 - 300% of the normal requirement. The primary difference for the hydrocracker is based around the cracking function (acidity) of the hydrocracking catalyst.

An alternative approach to reserve sizing is to aim for 10% -15% of additional capacity on the calculated normal recycle gas compressor demand, but to design the quench requirement for tighter temperature control on each bed, limiting bed temperature rises to approx 2/3 of the expected maximum allowable for the catalyst function. The net effect is the same as the approach described earlier.

Steven J. Catchpole (Johnson Matthey Catalysts)
Quench itself would appear to be a logical step, but rather than specifically answering the question on rates etc, it is worthwhile considering a few points. It reduces the H2/oil in part of the reactor if the quench is gas phase or it can introduce a bypass in case of liquid quench. Thus what may seem an obvious solution may in itself cause more performance problems. Careful monitoring is essential to evaluate the success or not of use of quench once in action.

Question 84
With tightening fuel regulations and the increased severity of distillate hydrotreater operations, have you experienced any unanticipated problems such as corrosion, fouling or catalyst issues?

Gary Everett (Lyondell's Houston Refining LP)
We have two units that have been modified to produce ULSD. Both of these units are nominally moderate to low pressure (< 700 psig at reactor outlet) thus we had to use significant catalyst volume (LHSV < 0.45) and require very high purity make-up hydrogen to both units. These units both also operate with a very high percentage of cracked stocks (Lt. Cycle Oil and Coker Lt. Gas Oil) in the range of 50 to 70+%.

While we have not experienced any corrosion, fouling or catalyst issues per se as addressed in this question, we did have several unanticipated problems during our first year of ULSD production.

Our first (sort of) unanticipated problem was that while the revamp work for these units was based on an assumed design operating target of 8 ppm S to stay below the anticipated 10 ppm S pipeline limit, when we had to meet the more restrictive 8 ppm S max, we found ourselves operating significantly lower say 4 to 5 ppm to assure we did not go above the 8 ppm max. This was due to the fact that our refinery only produces one grade of diesel and if we went off specification we had insufficient tankage to rerun this material and would have to slop off spec product back to crude tower; therefore we did everything possible to stay below 8 ppm. We quickly realized as we increased Wt. Average Bed Temperatures (WABT) and watched our deactivation rates for HDS for the more severe treater (the one will all the LCO) exceed design expectations that this operating margin was far too great. This problem was initially exasperated by the problems we had with the on-line sulfur analyzers on each of the 2 ULSD HDS units. Relying on hourly lab analysis quickly taxes both Operations and Laboratory personnel and equipment. Frequent calibration and testing of on-line and lab (sulfur) analyzers is key to success. Of course it helps if both instruments are of the same type.

While each HDS unit had an on-line analyzer we did not have a similar set up for the precious few ULSD product tanks, thus if we went above 8 ppm S, we optioned to send to slop not knowing where the tank composite sulfur level was. We developed a sulfur totalizer calculation that helped Operations determine how much room or margin remained in a given ULSD product tank thus we were more confident to handle short term spec deviations. Ultimately, this led to us moving our target value to around 7 ppm (to meet the 8 ppm max).

The next unanticipated problem was the tremendous impact of LCO volume and more importantly, LCO end point. We knew from pilot testing with our ULSD technology provider that LCO was the worst component in our feed mix. Just to get LCO into our more severe HDS unit, we had to undercut the (simulated distillation) 95% point from 715 ºF to about 665 ºF. This material is effectively lost to FCC Clarified Oil which is a significant (price) discount to either LSD or ULSD. By design, we limited the quantity of LCO in feed to our ULSD HDS to < 29 %v. When doing process control network step testing, LCO was by far the most overwhelming control parameter. This meant that when we are high on product sulfur our 1st move is to kick out some LCO, and considering what discounted value this represents, this is not a desirable way to operate this unit.

The third unanticipated problem is the difficulty that wide variability (quantity and quality) of the Lt. Coker Gas Oil on these operations. We partially mitigated this impact for our most severe HDS unit with the rather unique conversion of an old idle reactor into a feed surge drum (FSD) specifically for the Lt. Coker Gas Oil feeds. The other unit partial manages these LKGO feed swings by fixing its flow of this material, sending the swings to the FSD. The (LKGO) FSD on the other unit provides a dampen flow swing to the reactor section. Even for the unit which had a coker gas oil FSD, these feed volume fluctuations likely added to overwhelming sensitivity of using LCO as the primary knob for controlling product sulfur. We are planning to add similar coker gas oil FSD for the other unit and go back upstream to see if some form of advanced process control can be used to help smooth these changes a bit more.

The four unanticipated problem was the sensitivity of make-up hydrogen purity on the operation of these two ULSD HDS units. As mentioned previously we set a design requirement for very high purity hydrogen to be fed to these two units. Due to some supply issues and additional unexpected hydrogen consumption for one of the units at its initial start-up, we only were able to achieve an 80/20 mix of SMR hydrogen (99.99+ %) and olefins hydrogen (95%) which lowered our make-up purity from 99.99% to 98.5%. While this does not seem like a significant difference, our discussions with the ULSD catalyst supplier (which is Criterion) indicated that this corresponds to a loss of 2-3 months cycle life (~ 10%) or reduction of about 1000 – 2000 BPD of LCO feed to the unit.

Our final (so we hope) unanticipated problem deals with end of run (EOR) conditions. Our LSD units typically reached EOR based on exceeding the product color specification of 2.5 ASTM at max temperatures around 735 ºF and WABT of about 715 ºF. However with ULSD, these EOR temperatures tend to be lower with WABT between 700 ºF and 705 ºF. We also found a significant relationship to LCO content in the feed and product color. One approach that we used to help hold off this EOR color phenomena was to alter our hydrogen quench strategy such that the last bed was operated relatively colder than the prior beds (which actually had to get hotter to keep the same overall WABT constant) and product sulfur at 7 ppm. This "negative temperature profile" is meant to maintain the reactor outlet closer to the optimum temperature for PNA saturation. As a result, color body formation reduced, allowing us to meet color spec. We started this change about 2 months prior to the expected EOR.

Finally, I would highly recommend that you monitor your ULSD feed components, [rate (especially if it is highly variable like LKGO), end point and percentage of cracked stocks], hydrogen purities both make-up and recycle and keep constant monitoring on product tankage to avoid unnecessarily slopping slightly off-spec product.

ISSUE	IMPACT	REMIDY
Product Sulfur Margin	Higher WABT & Increase Cat Activity Deactivation	On-line Sp analysis, tank totalizer & Adv Proc Control
LCO Quality	Higher WABT & Increase Cat Activity Deactivation	Control LCO quantity and EP via undercutting
LKGO Variability	Excessive Product Sulfur Margin	Dedicated LKGO Feed Surge Drum and APC
Make-up hydrogen Purity	High Sensitivity to minor changes – impact LCO processing & Increase Activity Decline	Maintain 3rd party high purity hydrogen source availability
EOR Color Issues	Lower EOR WABT and Max Bed Temperatures	Negative Bed Temp profile with last bed cooler than upper beds

Question 85
Please identify the possible causes of increased pressure drop in middle and lower catalyst beds. What solutions have you implemented to prevent pressure drop events?

Paul Ceccato (Criterion Catalysts)
Pressure drop development is not limited to the lead reactor bed, but may also occur across the middle and bottom catalyst beds. The following scenarios may result in pressure drop issues in a lower bed through a reduction in void space or restriction in the hydraulic channel:

- Inadequate cleaning of the catalyst support grid or repairs using smaller mesh materials in a lower catalyst bed;

- Loading catalyst containing a high concentration of fines or breakage of catalyst due to poor loading techniques;

- Loading insufficient or uneven support media which may result in catalyst migration through a support screen or grid;

- Creating an interface by the loading catalysts of smaller diameter or different shapes in a lower bed which may trap particulates passing through upper beds;

- Introducing corrosion generated particulates through gas and liquid quench lines or introducing water which can reduce catalyst crush strength or result in catalyst breakage upon vapor expansion;

- Poor flow distribution due to ineffective inlet distributor design or faulty installation, resulting in uneven particle and coke deposition,

- Reduced particulate migration at a dry point or location of increased vapor to liquid ratio from conversion or vaporization at elevated temperatures;

- Reversing flow due to inadequate or failed protection during an upset, breaking bottom catalyst or unevenly redispersing previously trapped particulates;

- The removal of Sodium and Iron in lower catalyst beds from migratory organo-metallic compounds which provide dehydrogenation activity and accelerate coking;

- Operation with minimal excess hydrogen at the reactor outlet or significantly reduced hydrogen partial pressure due to vaporization which accelerated coking;

- Clay fine precipitation from tar sand derived feedstocks as hydrotreating destabilizes the polar association between clay fines and aromatics.

Steven J. Catchpole (Johnson Matthey Catalysts)
In our experience, this is not a typical occurrence. This perhaps occurs in the case of liquid quench or if the lower bed(s) support screens or reactor outlet collector collapses.

Question 87
With the projected shift to making more diesel and less gasoline, have you modified the FCC feed treater to add conversion capability and make more diesel? What changes in catalyst type, reactor volume, pressure, or product separation are needed to do this?

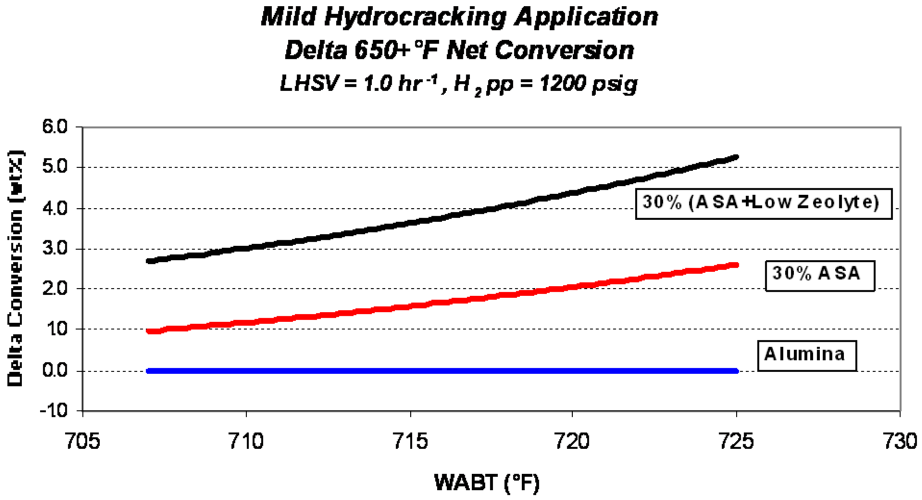
Paul Ceccato (Criterion Catalysts)
In its typical mode of operation, the FCC Pretreater reduces the sulfur content of the FCC feed while upgrading its quality through nitrogen removal and aromatic saturation. During hydrotreatment, partial conversion of heavy gas oil to diesel occurs to an extent dependent on catalyst type, unit pressure, and space velocity.

If desirable to increase diesel production at the expense of FCC feed, the catalyst loading strategy for the FCC Pretreater can be altered to include mild hydrocracking catalysts selective to diesel conversion. Positioning amorphous silica alumina (ASA) or low zeolite containing catalysts below hydrotreating catalyst will increase diesel production. With organic nitrogen affecting the mild acidity of both the ASA and low zeolite catalysts, the hydrotreating catalyst system must have high denitrification activity while maintaining a wide pore structure for stability when processing heavy feedstocks.

With a low cracking activity, sufficient ASA catalyst can be loaded below the hydrotreating catalyst to improve conversion without additional quench requirements. Conversion using ASA materials benefits from higher temperatures, so an ascending temperature profile is often preferred especially at SOR. Higher temperature exposure to the ASA catalyst will not impact its stability as expected for a hydrotreating catalyst.

When considering the use of low zeolite containing catalysts with higher cracking activity, a review of the heat balance and quench capability is necessary. Increasing the acidity of the catalyst through the inclusion of zeolite reduces conversion temperatures and increases yield at higher temperatures. In most cases, a dedicated bed with inlet quench is required for operational control. An added benefit of the dedicated bed is the ability to increase or decrease diesel conversion based on economics.

The following plot compares the observed 650+°F conversions in a Mild Hydrocracking Application when replacing 30% of the alumina hydrotreating catalyst with ASA or a combination of ASA plus low zeolite. As the cracking activity of the catalyst system increases, additional 650+°F conversion is realized. As temperatures increase, the delta conversions for the ASA and ASA+low zeolite systems further increase due to their higher activation energies. An increase in the zeolite content would result in additional conversion with a greater response at elevated temperature.



Question 88

Operating a FCC feed treater in aromatic saturation mode generally increases FCC liquid yields. Have you found that this increased severity leads to more refractory sulfur species in the LCO? If so, what options do you have to compensate?

Shaun Boardman (Jacobs Consultancy)

The one-line answer is that the boiling range of the LCO limits the species that could be present in the cut, and it's not a more refractory species that results, but a higher concentration of the refractory species which result.

Here is above view expressed with numbers:-

The sulfur content of FCC feed is resultant when operating a Cat Feed Hydrotreater in 'Aromatics Saturation Mode', and is generally around 200-700 ppm for medium sour feedstocks.

On the other hand, CFH hydrotreatment for meeting of 30 ppm in the overall gasoline pool is less severe and would produce more like a 1000 – 1200 ppm S in FCC feed.

Typically the S content of LCO is approximately equal to the concentration of S in the FCC feed, so the lower severity case above would show ~1000 ppm S in LCO, while the sweeter Cat Cracker would produce sulfur levels in LCO around the 300 ppm-400 ppm range.

In a speciation of the S distribution, the 1000 ppm S would typically contain around 200-250 ppm of refractory substituted DBT's while the 400 ppm material would contain something like 300+ ppm of these complex DBT's.

Generally the LCO yield from the deeper treated FCC feed case is reduced, so although higher in concentration, the net effect on total MDBT's to the diesel treater is approximately the same.

What is more likely to be a differentiator is whether the FCC riser temperatures have increased at the same time. Higher riser temperatures translate directly to a more aromatic LCO, and consequently increased levels of MBDT's converted from the HCO and VGO fractions. This would undoubtedly produce a more refractory LCO; however, there would be less of it…

In general I have not seen anyone adjust their ULSD operation to accommodate a change in the LCO quality as a result of switching Cat Feed Hydrotreater modes.

However, if you were looking for to adjust your ULSD operation for an apparent impact, options would include:

- Lower FCC reactor temp to hold constant conversion and LCO yield
- Utilize excess CFH conversion capacity by recycling LCO to achieve some LCO destruction.
- Lower LCO/DCO cutpoint temperature
- Raise SRD/AGO cutpoint to replace diesel lost due to lower LCO production (weighted average DHT feed composition may not change)
- Change FCC catalyst, some catalysts can alter sulfur distribution between reactor and regenerator as well as small distribution changes between gasoline, LCO, and DCO.

Question 89

When co-processing diesel and VGO for ULSD and FCC feed treating respectively, does this require a specialty catalyst and/or a modification of operating parameters? What is the impact on the FCC unit?

Gary Everett (Lyondell's Houston Refining L.P.)

We have two nominal 55 K BPSD VGO hydrotreaters that essentially treat all the VGO that goes to our nominal 100 K BPSD FCC unit. These Cat Feed Hydrotreaters (CFH) units are somewhat mismatched in that the older unit has a hydrogen partial pressure of about 650 psig and a LHSV of 2.0 which the newer unit has a hydrogen partial pressure of about 1100 psig and a LHSV of 1.0. For obvious reasons, we don't attempt to co-process any diesel in the older (low pressure) unit but have consistently processed 5 to 8 K BPSD of diesel boiling range material in the higher pressure unit. The bulk of this lighter material comes from undercutting the heavy coker gas oil (HKGO) to mitigate the tight processing capability of the old Distillate HDS units. When we were evaluating component streams for the production of ULSD, we were surprised to see that the once (severely) hydrotreated diesel drawn of the (high pressure) CFH unit appeared to be one of the most difficult to treat based on our ULSD technology/catalyst supplier (Criterion) just behind LCO. We all theorized that this was so because the remaining sulfur species obviously were the most refractive (difficult to remove).

Note that since we had earlier decided to rely on post FCC gasoline hydrotreatment to meet our Tier 2 gasoline compliance needs, we did not attempt to take the CFH product sulfur down to a level that our have likely produced a near ULSD spec product. Considering our very poor quality gas oil feed to the CFH and some verified maldistribution issues, the best we have been able to do is 3500-4000 ppm S in combined (from both CFH units) FCC feed (1500 ppm form the higher pressure unit) versus more like 300-500 ppm S in those FCC units that attempt to make 30 ppm S Tier 2 gasoline without post FCC gasoline treatment. These operations yielded a co-processed CFH diesel of nominally 600-1000 ppm S versus < 15 ppm required for ULSD. Our intended approach was to re-process this material in one of our modified ULSD hydrotreaters to make ULSD specifications. Since the source of this co-processed diesel is mostly from coker operations the nitrogen content of this CFH diesel is quite high around 1000 ppm since our overall HDN for this unit is < 50% level.

Once we actually began making ULSD, we were pleasantly surprised to see that this once severely hydrotreated diesel did not act like the highly refractory (sulfur) stream we anticipated but more like something between straight run diesel and Lt. Coker Gas Oil (LKGO). This surprising characteristic first showed up during the ULSD unit advanced process control set testing which attempts to identify the significant effect of variations of each of the component feeds. For this testing, the CFH diesel behaved much like something between straight run diesel streams and LKGO's. It is worth mentioning that the only stream overwhelmingly impacting ULSD HDS performance was LCO (which I discussed earlier my Question 84 response).

This mystery of sorts still baffles us in that we can not directly link any specific property differences from the earlier sample (evaluated by our technology provider) and the more recent CFH and ULSD operations. The properties for all three types of diesel components are shown below:

Stream	**CFH Diesel**	**SR Diesel**	**LKGO**
Property			
API Gravity	28.0	30.0	31.5
95% Sim Dist	707	684	675
Sulfur, %w	0.134	0.950	1.66
Nitrogen, ppmw	820	140	1100

For the last 4 months of the current ULSD catalyst cycle, we have tried to better manage the downgrades of LCO to either FCC clarified oil or cutter stock by co-processing 2000 to 3000 BPSD of LCO in the (higher pressure) CFH unit. This resultant CFH diesel stream still needed secondary processing but again its behavior was more consistent with something between SR diesel and LKGO. This is overall favorable as long as there is some capacity within the CFH unit. Typically Lyondell's Houston Refinery is long on VGO so our preference is to find a way to feed more LCO directly to the ULSD units by improving the LCO characteristics through better FCC feed treatment or improving the distillation effectiveness within the FCC Main Fractionation. Since this later option has to wait for our next FCC T/A several years down the road, we are in the process of upgrading our reactor internals to enable our CFH to operate in a more effective Aromatic Saturation mode. This will result in increased conversion, which will decrease the amount of LCO to process.

Steven J. Catchpole (Johnson Matthey Catalysts)
We expect little impact on the FCC unit, but block mode operation can deactivate the hydroprocessing unit faster if the catalyst is still hot whilst operation in cooler mode; so occurring during changeovers. In general frequent changes of operating temperatures increase the catalyst deactivation rate.

Question 92
Are you aware of any "runaway" reactions in ULSD hydrotreaters (a runaway is defined as a self-perpetuating reaction characterized by a large temperature increase)? Please discuss the factors that can cause such a runaway.

Shaun Boardman (Jacobs Consultancy)
There is some significant discussion within the industry around the risk of thermal run-away in ULSD hydrotreating, especially in light of the significant proportions of cracked feedstocks.

I tend to think of thermal run-away as a self-perpetuating, ***continually increasing*** process which will produce permanent catalyst or equipment damage unless drastic remedial action is taken.

A temperature excursion which levels out or drops off before any damage is done, does not qualify as a temperature-runaway. The processes in a temperature excursion are distinct from those of a run-away.

Runaways are restricted to acidic hydrocracking catalyst functions where the feed is also the fuel. The acidic catalyst promotes scission of the C-C bond, with a heat release of between 60 Btu/SCF - 70 Btu/SCF hydrogen consumed. The reaction is a first order kinetic reaction and the rate is promoted by temperature. As a result, if allowed too much temperature, the reaction can rapidly become self-promoting, and begin to run-away, reaching temperatures of 1800 °F – 2000 °F.

ULSD hydrotreating catalysts are generally alumina based (non-acidic) catalysts with little or no cracking function. Even where some cracking catalyst is applied to boost conversion yields, such as in the bottom bed of a reactor, the nitrogen / NH3 levels are sufficiently high to limit the acidic function of the cracking catalyst.

ULSD heat generating reactions are limited to sulfur / nitrogen removal, and olefin and aromatic saturation. Although the olefin and aromatic saturation reactions generate a significant level of exotherm, they are self limiting reactions.

High concentrations of highly olefinic light distillates could lead to 100+ °F temperature rise across a reactor, but are quickly depleted through the catalyst bed. The lack of an acidic function on the catalyst prevents this temperature from generating any hydrocracking conversion exotherm. Once the saturation reaction is depleted, the reactor temperature then stabilizes.

In the case of aromatics saturation, the ultimate limit is once again the quantity of aromatics in the feed, however, this saturation reaction quickly becomes equilibrium limited at elevated temperatures, limiting the full extent of reaction. Although these saturation temperature rises may be sufficiently high to be detrimental to the long-term catalyst activity if allowed to peak, they are generally not sufficiently high to be associated with equipment damage - These reactions qualify as having a potential to cause temperature excursions in the range of 800°F.

Since feed composition changes are generally slow, the risk of a saturation temperature excursion due to a feed changes is small. What is more common place is the basic level of concern at operating with large steady-state exotherms over a multiple quenched bed reactor in ULSD / cracked feed service. With multiple quench application, sudden loss of quench could lead to a saturation temperature excursion as described above.

There is one other situation which could be considered a thermal run-away since it causes significant damage to catalyst activity, and occurs too quickly to control - That is the temperature excursion which can occur during catalyst sulfiding.

The bulk of the sulfiding process is generally designed to take place at 450 °F - 500°F and complete at about 650°F.

High sulfiding agent addition rates coupled with a low heat sink capacity (low mass rates) could allow the sulfiding exotherm to pulse through in a wave of activity as the reaction is activated, generating a brief temperature excursion as high as 850°F.

The rapid reaction leads to the depletion of H_2S, and the high temperature provides sufficient enthalpy for the endothermic reduction of the promoter metals under the hydrogen environment.

Although reduced metals can be re-sulfided, reduction of the metals leads to agglomeration, destroying the metals dispersion over the catalyst.

In addition, sufficiently high temperatures will sinter the alumina substrate and cause a significant loss in catalyst surface area.

Both processes will permanently destroy the fresh catalyst activity.

Question 93

The recommended hydrogen circulation rate for ULSD service is typically higher than in pre-ULSD days (i.e. > 5:1 hydrogen available/hydrogen consumed). How are units operating at ratios less than 3:1 performing compared to predictions?

Paul Ceccato (Criterion Catalysts)

Treating the more difficult aromatic sulfur species in ULSD service requires at least partial saturation of the molecules to remove the sulfur atoms. The ability of a ULSD unit to treat highly aromatic feedstocks while operating for an extended cycle life is dictated by the hydrogenation environment created by catalyst type and hydrogen partial pressure.

The hydrogen ratio is only a surrogate (and simple) way to measure the quality of hydrogenation environment, so all contributing variables must be considered. The gas circulation rate along with gas purity, feed vaporization, yield shift, unit pressure, and hydrogen consumption define the hydrogen partial pressure. Higher gas circulation directionally increases the hydrogen partial pressure which enables operation at higher temperatures before reaching aromatic equilibrium constraints. In addition, enhanced denitrification prevents catalyst instability from organic nitrogen which interferes with deep desulfurization. Gas circulation including make-up must replenish consumed hydrogen and be available in sufficient excess to minimize both coking and the impacts of the increasing H_2S concentration on desulfurization down the reactor.

The impact of a reduced hydrogen circulation to consumption ratio is dependent on feedstock type and unit conditions. Processing cracked stocks or high end point SR materials at a reduced gas ratio will result in accelerated catalyst aging at lower than normal temperatures from aromatic condensation (coking). Reducing the gas ratio in units which already operate at low hydrogen partial pressures will create additional difficulty in handling feedstock severity swings and potentially result in step changes in activity due to increased coking.

Although most ULSD units were designed with 4:1 gas ratios, higher feedrates, undersized furnaces, and pressure drop issues have resulted in reduced treat gas rates for part of some cycles. We predicted and have observed deactivation rates increase by 1.5-2 times the normal rates (typically 2-2.5°F/month) when the gas ratio has been reduced from >4:1 to ~3:1, particularly in units processing LCO.

ULSD

Question 96

What best practices do you employ for the use of diesel fuel additives such as lubricity, conductivity, pour point stability, and cetane improvement?

Chuck Muth (Nalco Energy Services)

All four of the additives mentioned are "performance" based and can vary in performance with the fuel. In addition, the new ULSD's in the market respond differently to all 4 additives. Lubricity and Conductivity are further complicated by the addition at terminals outside the refinery guidance, yet both lubricity and conductivity are (or will be) ASTM specs.

A careful program of sampling and documenting is essential to make sure you are meeting specs. Distillate pour point depressant and cetane improver are added at the refinery and are subject to the refinery lab testing for approval to ship. The complication comes with the "opportunistic" crudes many people are bringing into refineries or the general trend in changing crude sources.

The crude source, processing schemes and final product blending ratios of various streams can all affect ULSD performance and response to additives.

Yvonne Jeanneret (CITGO)
Lubricity and conductivity are typically added at the terminal.

Stability additives should be injected into the least stable component as soon as possible after all processing units and dryers and once the stream is below 200F.

Cetane Improver, 2-Ethylhexyl nitrate, injection system design can be obtained from the chemical manufacturer.

All injection systems materials must be compatible with the additive. Certain synthetic materials should not be used. Also some additives are excellent solvents and can degrade gaskets and seals.

In humid areas evaluate if your additive tanks require nitrogen blanketing due to condensation. Some chemical tanks may require deluge systems. Appropriate secondary containment such as dikes or walls is required.

The ideal injection system would control the additive injection flow rate based on the diesel flow rate. The desired ratio would be input. This can be done by

a. using a metering pump with a pulse dampener and a prover gauge (for pump calibration) or
b. using a centrifugal pump with spillback, a coriolis-type mass flow meter and a control valve.

Question 97
How are you dealing with previously processed diesel streams that don't meet ULSD specifications (e.g. diesel from FCC feed treaters, ARDS, H-Oil or LCFiner units and biodiesel)?

Steven J. Catchpole (Johnson Matthey Catalysts)
Care is required when blending them into the feed of a hydrotreater. The sulfur in them is essentially all refractory. This actually means that the process condition are relatively severe for what would "appear" to be a standard hydroprocessing application.

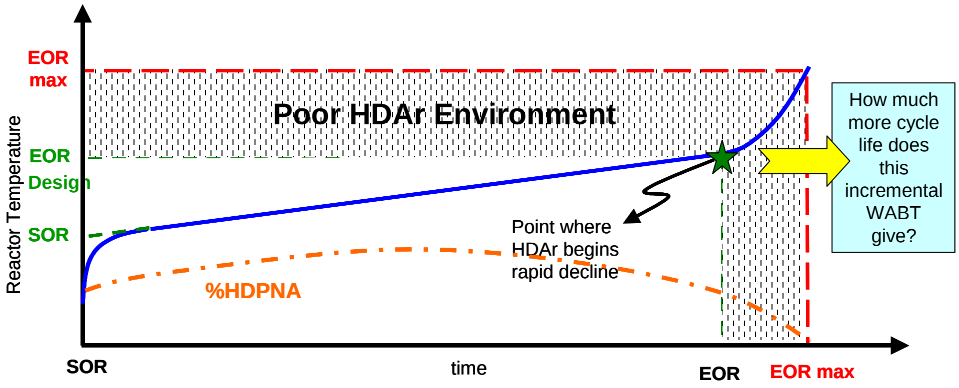
Question 98

What factors affect ULSD hydrotreater end of run (EOR)? Have there been any issues (other than color specification) due to high temperature at EOR? How do LCO percentage, operating pressure, feed gravity, and feed endpoint affect the EOR color?

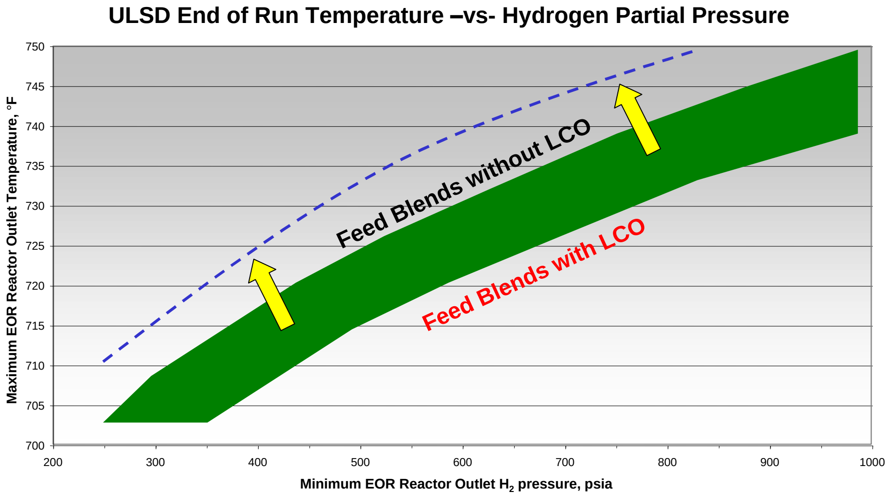
Paul Ceccato (Criterion Catalysts)

The production of ULSD involves both the direct and indirect removal of sulfur. For simple compounds, the sulfur atom is directly cleaved, but more complex sulfur species require aromatic saturation to gain access to the sulfur atoms prior to removal. Direct sulfur removal is kinetically limited, so reaction rates increase with increasing temperature. Since aromatic saturation becomes equilibrium limited and reaction rates decline at elevated temperatures, indirect sulfur removal dictates EOR conditions.

The following figure shows the expected catalyst temperature profile as the cycle progresses. After the initial catalyst break-in and an extended period of stable catalyst deactivation, aromatic equilibrium constraints create a poor saturation environment to continue ULSD production. Theoretically, EOR is defined by the onset of equilibrium constraints; however additional cycle may be achievable by increasing temperature to remove additional sulfur via the direct pathway. Unfortunately, accelerated coking at the elevated temperatures in the poor saturation environment permits only a short potential extension to the cycle.



The temperature defining the onset of aromatic constraints is a strong function of hydrogen partial pressure. The following plot shows a band of maximum temperatures versus hydrogen partial pressure with boundaries set by the feed aromatic content. As the partial pressure increases, the maximum allowable temperature increases for a longer cycle life. Extending the cycle life by increasing temperature while in a poor saturation environment is possible for feeds containing less refractive sulfur. For this reason, the cycle life for a SR feedstock may be extended, while the cycle life for an LCO containing feedstock will likely end for either desulfurization limitations or a decrease in diesel cetane.



Color issues may or may not become a factor at EOR. Color is created by aromatics in the product diesel and has dependency on the concentration and types of feed aromatics. When operating at temperatures beyond the equilibrium constraints, dehydrogenation and aromatic condensation potentially result in color problems. Color stability issues may also arise upon the reduction in denitrification toward EOR.

LCO is a stream of concentrated aromatics which increases the aromatic content of the blend and directionally increases the potential for color problems at elevated temperatures. Units operating at increased hydrogen partial pressure are more resistant to color issues due to higher allowable temperatures before reaching aromatic equilibrium limitations. Directionally, lower gravity and higher end point feeds include a higher concentration of aromatic species which may influence color issues at elevated temperatures.

Steven J. Catchpole (Johnson Matthey Catalysts)

These all need to be considered for their impact on the formation of poly-aromatics. LCO consumes more hydrogen reducing the hydrogen partial pressure, thereby increasing the formation of poly-aromatics. Higher feed gravity and feed endpoint indicates a more aromatic feed, so again a higher tendency to form PA. Higher pressure reduces PA formation.

Question 99

Initially, common carrier pipelines established very strict ULSD sulfur maximums to ensure that the product met end-use specifications. More than a year later, these same pipeline operators are considering relaxing their specifications. What options would you consider to take advantage of these changes?

Yvonne Jeanneret (CITGO)

It is true; Colonial Pipeline was considering raising the inbound sulfur limit for ULSD. Initially, they canvassed their shippers to get feedback on this. Their plan has since been put on hold, as they evaluate the feasibility of moving ULSD north of Baltimore on their system.

If or when Colonial or other pipelines relax the sulfur specification, ways in which you may take advantage of this are:

1. Reduced severity at the ULSD Hydrotreater, extending run length.
2. Increase endpoints of current feedstocks to maintain the same run length
3. Purchase additional feedstocks, such as Light Cycle Oil, for the ULSD hydrotreater
4. Blend higher sulfur streams to the hydrotreater product such as Hydrocracker Bleed in the 25-40 ppm sulfur range.

Question 100

How do you manage or avoid contamination due to the swing between jet fuel (up to 3000 ppm sulfur) and seasonal production of ULSK (ultra-low sulfur kerosene, <15 ppm sulfur)?

Gary Everett (Lyondell's Houston Refining L.P.)

While the question may have been intended to discuss transportation issues around moving jet fuel (kerosene) and ULSK to terminals through common carrier pipelines, my answer will deal with how to avoid contamination within the refinery battery limits as we do not transport ULSK out of the refinery but always blend into ULSD any barrels of this type of material produced in one of our distillate hydrotreaters. When Lyondell's Houston Refinery completed its post FCC gasoline treater for compliance with EPA's Tier II regulation, one of our moderately low pressure (< 400 psig hydrogen partial pressure) distillate hydrotreaters which had been used for

sulfur removal from heavy FCC naphtha was freed up for other potential uses. One such use was to have the ability for two nominal identical units to be use in the production of ULSK and jet fuel, simultaneously. By running considerably less feed rate in the ULSK designated unit, achieving ULSK sulfur specifications (< 10 ppm) was easily met. Thus when margins favored ULSD versus Jet (kerosene), we were able to boost the quantity of ULSD product by 10-12 M BPSD.
However, we still had to be concerned with contamination when we switched between these (jet and ULSK) operations. The first concern was to blind off all those “nodes” or connections to lines and manifolds where potential contamination could result. It was assumed that simple block valves were not sufficient to assure zero contamination. Having dedicated lines for each of these identical units also provided us added insurance that we would not contaminate a finished batch of < 8 ppm sulfur ULSD with jet fuel (kerosene) with its nominal sulfur in the range of 1000 to 2000 ppm.

There are no on-line sulfur analyzers on either of these distillate hydrotreaters so we had to rely on the ULSD product tank (sulfur) totalizer and frequent lab analysis to assure we stayed within specification. We are in the process of adding an on-line analyzer for the ULSK unit, similar to the main line ULSD units to allow for better control to a target sulfur limit much closer to the 8 ppm pipeline limit.

To date we have been very successful in managing the production of and use of ULSK into our main-line ULSD product tanks without putting any batches off-spec.

Question 101

New North American hydrocracker units have been designed to make ULSD rather than gasoline (typical of older designs). What design, catalyst, and process changes have been implemented to make this product shift and ensure that the more stringent ULSD specifications are met?

Shaun Boardman (Jacobs Consultancy)

Where an existing hydrocracker has been employed in ULSD, it has generally been used to remove all or part of the most difficult feedstocks (typically LCO) from the diesel pool, rather than to produce ULSD per se. A cracked distillate feed can be accommodated on a typical gasoline selective hydrocracker without major modification or catalyst change simply by co-processing the lower quality distillate with the normal unit charge. This is generally true to some extent as significant quantities of LCO will at some point impact the hydrogen capacity of the unit, and the fractionator capacities on naphtha.

For a new hydrocracker design, shifts in the refinery G:D can be accommodated too, where traditional FCC feedstock can be fed to a hydrocracker to produce higher yields of kerosene & diesel which meet finished ULSD specifications in place of cat gasoline.

For a stand-alone hydrocracker, a distillate shift is best accommodated by a single stage operation with recycle. Reduced acidic catalysts are employed and deep pretreat is needed to guarantee ULSD sulfur across the operating cycle.

Two stage designs provide greater flexibility between production of gasoline / diesel and Jet.

For refiners also having an FCC, combinations between once through hydrocracking and FCC conversion provide yet more options.

The new wave of hydrocrackers that are coming off the board have also been associated with wider refinery objectives such as increased capacities for heavier crudes, and in the interests of Capital Savings, these designs have become highly integrated with polishing reactors, dedicated LCO cracking reactors, parallel trains of VGO/HCGO hydrotreating, and employ numerous integration tricks with hydrogen systems, separators and recycled distillate draws for meeting ULSD specs.

NPRA

National Petrochemical & Refiners Association

1899 L Street, NW
Suite 1000
Washington, DC
20036.3896

202.457.0480
www.npra.org