2008 NPRA Q&A and Technology Forum: Answer Book

Omni Orlando Resort
at ChampionsGate
Champions Gate, Florida
October 5 – 8, 2008

NPRA

Q&A and Technology Forum:
Questions & Answers

HYDROPROCESSING

Safety

Question 1
What are your experiences taking reactor effluent samples? What safety issues do you consider when taking samples? What do you consider to be best practices?

Edwin Yuh (UOP)
UOP has traditionally included sampling capability in our licensed units when there are multiple reactor systems. For example, a sample point is typically installed at the pretreat reactor outlet before the cracking reactor in hydrocracking units to measure nitrogen slip. Many UOP licensees collect reactor effluent samples routinely. Quite a few recently licensed units are designed as integrated hydroprocessing units processing different feeds with different catalyst systems. UOP has added sampling capability at each stage in the unit so that we can monitor catalyst performance individually to optimize unit operation.

Occasionally we have had problems with sampling systems. Over the years, we have made modifications. Several considerations are important in the design of a reactor effluent sampling system,

1) The sample is normally at high pressure and high temperature containing H_2 and H_2S.
2) The sample is taken at the bottom of a horizontal process pipe.
3) A two-phase sample needs adequate cooling in a cooling water pot.
4) The sample system has an intermediate holding reservoir designed at operating pressure. The holding reservoir has pressure let-down capability to flash the light gaseous components to flare.
5) Proper metallurgy and piping class are used for the entire sampling system.
6) Reliable valves are important that tolerate frequent use.
7) The sample station has adequate temperature and pressure indications.
8) The system should have proper relief considerations.
9) The system should also have various purging capabilities to deal with viscous fluids.
10) Sufficient purging of the reactor effluent sample needs to occur in order to collect a representative sample.
11) The purged liquid is sent to appropriate destinations.
12) The sample system has appropriate back flow prevention.
13) The system should use a closed sample system to avoid environmental release.
14) The sampling system requires a detailed set of operating procedures.
15) The operators require proper training and safety gear when taking the sample.

Question 2

Do you re-evaluate your unit operating procedures at regular intervals? How often? What principles/standards are these procedures reviewed against?

David Rapavi (HOVENSA)

HOVENSA reviews and re-issues unit operating procedures in accordance with OSHA Standard 1910.119 paragraph (f)(3), which states "Operating procedures shall be reviewed as often as necessary to assure that they reflect current operating practice, including changes that result from changes in process chemicals, technology and equipment, and changes to facilities. The employer shall certify annually that these operating procedures are current and accurate."

Unit operating procedures are updated throughout the year to reflect any changes from Management of Changes, PHAs, Incident Investigations, and recommendations from operating personnel and subject matter experts. All changes are communicated to the affected employees both at the time of implementation of the change and during procedure recertification.

Unit operating procedures are reviewed and recertified by Operations on an annual basis, and over the years we have used different types of recertification methods to assure our procedures are current and accurate. Some of the methods include reviews of the procedure by subject matter experts as part of their job responsibilities, reviews by training supervisors as part of new operator training, and our current method of reviews by the Operations shift team done during a job pre-task.

Before we execute a unit operating procedure, a job pre-task is done by the Operations shift team, which includes the operators and shift supervisor. During the job pre-task, all the steps of the procedure are reviewed and discussed, what-if scenarios are assessed, and concerns regarding the unit operating procedure are addressed. The supervisor completes a job pre-task form which includes list of attendees, topics discussed, potential reliability or safety problems and mitigation plan. Any procedural changes are redlined, and the redlined version is used to complete the work. After the work is completed, the redlined procedure is submitted by the supervisor to the PSM department which updates the procedure and applies a new revision number and date. All effected operators are then retested on the procedure.

For unit operating procedures that are not executed during the year, the procedures are recertified using the same job pre-task method by evenly distributing them over the operating shifts.

We have found the job pre-task method very effective in not only assuring that unit operating procedures reflect current operating practice, but it also facilitates training and understanding of our relatively inexperienced workforce with approximately 50% of the operating population having less than five years of experience.

Regarding hydrotreating units, the unit process engineer will have the catalyst vendor review catalyst activation and hot hydrogen strip procedures and incorporate all necessary changes by submitting a redlined copy to the PSM department before the job pre-task.

Chad Perrott/Mike Pedersen (UOP)

As a licensor, UOP evaluates operating procedure as part of our Schedule A work process. In other words, the frequency for review is much higher than a typical refiner's procedural review. UOP considers any significant changes to design configurations and any new catalyst considerations. This is followed by an update to the general procedures in the operating manual we provide to our licensees.

During the procedure review in the engineering stage, UOP focuses on the overall issues leaving the individual numbering/line references to the refiner. This provides a learning opportunity for the refiner's responsible parties (engineers, operators, management) by using the UOP general procedure and developing a procedure specific for the refiner. This insures that the systems of the new unit are understood and site specific considerations are included. The detailed unit specific procedures are reviewed onsite by the UOP startup staff for consistency between UOP's general procedures and the intent of the refiner's developed procedures. UOP startup staff also participate in any procedure revisions learned during startup.

In the event of loading a new catalyst into an existing unit, the same general procedural review is followed by UOP and the refiner is made aware of any changes they must make to insure successful catalyst activation to retain maximum activity.

For operating units, HAZOP reviews also provide a good prompt for updating procedures. HAZOP findings will guide some of the procedure modifications. Feedback from refiner's is that input from the process licensor is valuable.

Question 3

Have you experienced an uncontrolled exotherm in a hydrotreater when processing coker naphtha, light or heavy coker gas oil, or streams derived from synthetic crudes? Describe this event. What was damaged as a result of this exotherm? What are the remedies to avoid a re-occurrence?

Mike Pedersen/Chad Perrott (UOP)

While there have been a number of temperature runaways in hydrotreaters, feed slate, including the presence of Coker products, has typically not been a primary contributing factor. Problems have been the result of failure to follow procedures, either during startup or in not adequately reducing temperature or hydrogen pressure during emergency shutdown.

Since hydrotreating units processing cracked feedstocks have higher risks of uncontrolled exotherm when the unit is upset, UOP recommends initiating manual depressuring when recycle gas flow is lost and depressure the unit until reactor temperatures are 50°F below normal operation. When the recycle gas compressor is re-established, continue to cool the reactor to unit restart conditions.

Gordon Low, Manager Refining Licensing, Haldor Topsoe-California

Topsoe has not experienced a temperature excursion in any of our licensed coker naphtha hydrotreaters. Indeed, the reactor temperature rise of a naphtha hydrotreater designed to process a mix of straight-run and coker naphtha can be considerable. For a unit processing 100% coker naphtha, the temperature rise can be as high as 300ºF. Some methods that designers use to limit this temperature rise are: feed composition control, multiple feed injection points, gas-to-oil ratio, liquid quench, and product recycle. In addition to managing the temperature rise during normal operation, the unit must also be designed to minimize the likelihood and severity of any temperature excursions caused during upset conditions. High temperature alarms, safety interlocks to trip feed and heater, emergency depressurization, plus designing the equipment and piping to withstand a temperature excursion are some of the methods used to avoid plant damage during an upset. Finally, having clear, well-written procedures and well-trained operators are also necessary to maintain safe operation.

Question 4

What level of change in feed quality or product specification would trigger a management of change (MOC)?

David Rapavi (HOVENSA)

We use MOCs to communicate any changes to unit upper and lower limits, procedural changes, physical equipment changes, and responses to any newly introduced process hazards.

We purchase and blend crudes and other purchased feedstocks to keep the overall unit feed properties (sulfur, nitrogen, TAN, oxygenates, product yields, etc.) within certain boundaries. So, we do not do MOCs for hydrotreater feed quality changes for feedstocks that are of similar distillation range and process derivation (process derivation being straight run product, FCC products, Coker products, etc.) because of our relatively consistent crude or unit feed properties. As an example, we would not do a MOC to process straight run No. 2 Oil in a hydrotreater that historically processes straight run No. 2 Oil regardless of what crude unit or crude it originated from.

Product specification changes typically do not require a MOC because no new hazards are introduced and the unit is still bound by the same upper and lower operating limits. The major consequence of a hydrotreater product specification change is the impact on catalyst deactivation, which we consider an economic decision.

We do MOCs for hydrotreater feed quality changes that are of different distillation range or process derivation before initially processing that feed in the unit. As an example, we would do a MOC to process straight run naphtha in a hydrotreater that historically only processed straight run No. 2 Oil because of the change in distillation range. Another example, we would do a MOC to process Coker Light Gas Oil in a hydrotreater that historically processed straight run No. 2 Oil and FCC Light Cycle Oil because of the change in the process from which the feed was derived.

We also do MOCs to increase a percentage of a particular feedstock when a prior MOC or historical unit condition limited the percentage of feedstock in the feed blend.

Question 5

What measures do you recommend to ensure that personnel are not exposed to hazardous materials such as nickel carbonyl, Ni(CO)4, or arsenic-contaminated dust during and after reactor shutdown?

Vinny Nair/Mohamed Abuedia/Mike Pedersen (UOP)

Nickel carbonyl is a highly toxic and volatile substance. $Ni(CO)_4$ is most likely to form during startup and shutdown of a hydroprocessing unit. Brief exposure to relatively low concentrations may cause severe illness or death even though initial symptoms may be very mild. The OSHA permissible exposure limit is an eight hour Time-Weighted-Average of 0.001 parts per million by volume ppmv (i.e. 1 ppbv). It is always better to assume that spent hydroprocessing catalyst contains nickel carbonyl.

The best way to prevent exposure to nickel carbonyl is to avoid its formation. Carbonyls will not form if the circulating gas during cooldown is essentially free of carbon monoxide. In most cases, a specification of <10 ppm carbon oxides in the makeup hydrogen is the key. When nickel carbonyl is suspected, heat up the catalyst bed with recycle gas to above 400°F and clean up recycle gas before cooling. All unregenerated catalyst should be cooled below 150°F and unloaded under nitrogen.

Some spent hydroprocessing catalysts can contain up to 0.5 to 1 wt-% of arsenic especially in the first two beds of hydroprocessing units. The arsenic on the catalyst can be present in catalyst dust formed during unloading. Permissible exposure limit for inorganic arsenic at concentrations is less than 10 micrograms per cubic meter of air (10 ug/m^3), averaged over any 8-hour period.

High arsenic content spent catalyst requires isolation. That includes segregation of workers for decontamination (temporary showers) prior to exiting from the reactor area and contacting other workers. Arsenic contaminated catalyst requires encapsulation in silica prior to landfill.

Question 6

What are the conditions that require activating a high rate depressurization on a hydrocracker? With regard to temperatures, which is the governing value, rate of change or absolute level? If voting logic is used, how is it implemented?

Edwin Yuh (UOP)

An emergency which occurs in hydrocracking units must be recognized and acted upon immediately. UOP licensed hydrocracking units are designed with a depressuring system having two depressuring rates. A restriction orifice in the line downstream of the depressuring valve governs the rate of depressuring. Depending on the emergency situation, the operation procedure and instrument setup call for different unit depressuring.

The high rate depressuring is activated in case of a serious emergency such as a fire or a temperature excursion. High rate depressuring can be initiated manually by the board operator as well as automatically. High rate depressuring is activated automatically when any cracking catalyst bed temperature or cracking reactor outlet temperature reaches the vessel design temperature, or when any cracking reactor skin temperature reaches a temperature 10°F or 5°C below the design temperature.

Because of the localized nature of hot spots, voting is not done. If any one temperature rises to the trip point, then automatic depressuring is initiated. To minimize nuisance trips, thermocouples associated with the automatic depressurization system are configured for downscale burnout. A relatively new feature UOP has added is a one second time delay that is specified upon detection of high temperature prior to initiation of the high rate depressure trip. The purpose of the time delay is to prevent nuisance trips due to short-term electrical noise in the temperature signal line.

The shutdown depressuring system has worked well in the UOP licensed units. In addition to the shutdown system, a well defined and understood emergency procedure by all the operating staff is a must to safe guard the unit.

Process

Question 7

What best practices do you recommend for ensuring reliable level measurements in the cold high pressure separator? Please comment on shielded taps, magnetic float indicators, radar detectors, and others.

Don Eizenga/Charles Van Zile (UOP)

For small level ranges, the use of displacement type level instruments has been successfully used in both hydrocarbon level and hydrocarbon-water interface level measurements. For larger ranges, differential pressure measurement with or without capillary seals has been used for hydrocarbon level service. Radar detectors have been used for water interface measurement. UOP is not in favor of magnetic level instrument due to concerns about fouling the float. None of the alternate measurement devices/methods have proven sufficiently reliable such that an online spare instrument would not be recommended for this critical and difficult service. Hence, best practices would include the following:

- Two instruments for each service with independent taps and isolation valves rather than a single instrument with gauge backup (magnetic or otherwise)
- Hydrocarbon-water interface level devices selectable with a switch for online maintenance
- Hydrocarbon level devices with high signal selector to minimize chance for liquid carryover to the compressor or amine scrubber
- 2oo3 high level shutdown instrumentation should be located on the Separator as any liquid carryover will cause compressor problems either directly or through foaming in the Recycle Gas Scrubber with minimal advanced warning
- Instruments with flowing process (non-DP cells) should have free draining connections without low points and minimum piping/valving
- The separator should be lined with stainless steel to avoid excessive corrosion leading to instrument plugging.

Question 8

Is ultra-low sulfur kerosene (ULSK), i.e. with less than 15 ppm sulfur, suitable for the jet fuel/kerosene pool? If not, what are the issues? Are there new operational issues that arise when operating a jet/kerosene unit in ULSK mode? Have you encountered any problems when switching from conventional jet/kerosene to ULSK operation and back?

David Rapavi (HOVENSA)

We have a hydrotreating unit that produces jet fuel/kerosene 95% of the time and ULSK approximately 5% of the time. The ULSK produced is blended with ULSD to meet a cold filter plugging point (CFPP) requirement of -20^{o}F for a winterized ULSD blend and is not blended into the jet fuel/kerosene pool. The unit processes less than 5% cracked stocks and operates at nominally moderate to low pressure (<625-psig reactor outlet pressure) with a LHSV of 3.

The American and European aviation fuel standards, ASTM D-1655 and DEF STAN 91-91, have a maximum sulfur specification of 0.3-wt%. Like diesel, kerosene hydrotreated to ultra low sulfur levels will have lower lubricity. In comparing our ULSK and jet fuel / kerosene, the ULSK had approximately 20% lower lubricity (or 20% higher wear scar diameter result). However, these results were measured by the HFRR test method used for ULSD and not BOCLE (Ball-On-Cylinder-Lubricity Evaluator) test method, ASTM D-5001, which is the standard lubricity method for aviation fuels. All of the other fuel properties remained relatively unchanged.

The European aviation fuel standard, DEF STAN 91-91, has a minimum lubricity requirement of a maximum wear scar diameter of 0.85-mm, but it only applies to fuels containing more than 95% hydrotreated material where at least 20% is severely hydrotreated (reactors with hydrogen partial pressure > 1015-psi). The American aviation fuel standard, ASTM D-1655, does not have a minimum lubricity requirement because low lubricity fuels are commingled with high lubricity fuels in most distributions systems and the resultant fuels no longer have low lubricity. However, where there are concerns about lubricity, lubricity improver additives can be added to the fuel up to specified concentrations.

Producing ULSK requires higher reactor temperatures; for our unit, an increase in WABT of approximately 40^{o}F is required and the reactor outlets are typically less than 650^{o}F. We have a dedicated ULSK product tank, and since the unit does not have an on-line bottoms product sulfur analyzer, we increase our bottoms product sampling frequency from twice per day to six times per day. We have not experienced any color or stability problems.

The unit does not have feed/effluent exchangers with seal welded tubes, so there is a concern it may not be able to produce ULSK when needed. Therefore, at the beginning of each ULSK blending season, we do not commit to selling the first cargo of winterized ULSD until the ULSK is made. As feed/effluent exchanger bundles are required to be replaced, we are considering replacing them with seal-welded tube bundles.

Using this approach, we have had no issues meeting specifications when switching from conventional jet fuel/kerosene to ULSK operation and back.

Steve Mayo (Albemarle)

Many refiners produce ULSK as a blending stock for the distillate fuel pool. Since the boiling range of kerosene excludes the most difficult to hydrotreat sulfur species, it is possible to produce a ULSK blend stock with near zero sulfur at fairly mild hydrotreating conditions. This ULSK blend stock can be used to offset higher sulfur from ULSD operations typically requiring much more severe operating conditions. It is well known that even a few ppm of higher sulfur in the ULSD hydrotreater can extend cycle length and reduce severity. The ULSK blend stock allows the ULSD unit to operate without over-treating since it acts as a buffer for sulfur excursions from normal operation. Undoubtedly some of this ULSK has found its way into the jet/kerosene pool as well. At one time there were fears that ultra low sulfur jet might cause problems with aircraft engines but to date there is no indication of this and no limitations to minimum sulfur content in jet fuel.

Traditionally, jet/kerosene hydrotreating has been a mild operation for virgin feedstocks and a more severe operation for cracked feedstocks. Smoke point and/or color have been the main drivers for a more severe operation. The sulfur species present in the kerosene boiling range are removed via the direct desulfurization route so moderate pressure and LHSV are sufficient. Color and smoke point, requiring removal of poly aromatics (and in some case monoaromatics) will almost by necessity also reduce sulfur to ULSK levels. ULSK units are, in general, relatively easy to operate -- certainly in comparison to their ULSD counterparts.

Operating in block ULSK and jet/kero mode is practiced and is generally not problematic. Depending on the unit operating conditions there may be little benefit to catalyst cycle life for block mode operation as compared to operating in ULSK mode for the entire cycle. If the feedstock quality deteriorates for the lower severity blocks, it can take quite some time for the catalyst to desorb aromatics and nitrogen and aromatics. It's important when switching to ULSK to allow sufficient time for these species to desorb before operating severity is increased.

Question 9

Synthetic Canadian crudes are of increasing importance in the U.S. Have there been significant issues when processing Canadian crude-derived feedstocks? Specifically, are there any known catalyst fouling mechanisms, deactivation, and/or product quality issues?

Gary Brierley (UOP)

There can be numerous different problems when trying to process Canadian synthetic crudes, depending upon the exact type of crude purchased. The term "synthetic" is generally taken to mean a blend of upgraded or partially upgraded naphtha, distillate, and gas oil range materials, with no resid (1050°F+ or 565°C+ material). There are also several bitumen blends available where whole bitumen has been blended with condensate, sweet synthetic crude, and heavy conventional crudes.

The majority of synthetic crudes and bitumen blends derived from mined bitumen will have some BS&W (fine clay particles) that will cause pressure drop problems in fixed-bed reactors. Bitumen produced using steam-assisted gravity drainage (SAGD) technology generally do not have a BS&W issue. Fully-upgraded synthetic crudes will have sulfur and nitrogen levels comparable to light, sweet conventional crude, but the remaining sulfur and nitrogen is very difficult to remove since the upgrader that produced the stream has already removed all the easy-to-treat contaminants.

Bitumen is a very aromatic feedstock, so the distillate produced has very poor ignition quality. Kerosene smoke points as low as 13 mm, and full-range diesel cetane numbers as low as 33 are normal for specific synthetic crudes. The VGO cut of synthetic crudes generally make very poor FCC feedstocks. Because of the high aromatic content, conversion in the FCC can drop by as much as 20%, while the yields of LCO and decant oil can triple. Proper FCC feed pretreating is the key.

A summary of the various synthetic crudes and bitumen blends available, and the implications for running these crudes, can be found in the NPRA paper AM-06-16 from the 2006 Annual Meeting.

Henrik Rasmussen (Haldor Topsoe, Inc.)

Processing of synthetic Canadian crudes will typically require more coking capacity as well as more hydrotreating capacity and additional hydrogen availability. Therefore, before starting to process synthetic crudes, it is necessary to do a detailed evaluation of the infrastructure of the refinery to determine the effect of these more severe feedstocks. Topsoe is currently revamping a significant number of hydrotreating units to accommodate large quantities of synthetic Canadian crudes. In most cases, co-processing of small amounts of synthetic crude is possible without a refinery revamp. However, the reactivity of the naphtha, diesel, and VGO fractions originating from synthetic crudes is typically lower than the reactivity of feedstocks originating from most conventional crudes, resulting in a higher required WABT to obtain the same product specifications for otherwise unchanged operating conditions. Some of the synthetic feeds have already been partially hydrotreated; so, even though the overall sulfur level may below, it is important to remember that the remaining sulfur species (DBT's) are difficult to hydrotreat.

With more of the crude passing through the delayed coker, the downstream hydrotreaters will also see larger amounts of silicon contamination as well as higher olefin content, resulting in higher catalyst deactivation, higher hydrogen consumption, and higher temperature rises across the catalyst bed. We are also seeing higher quantities of arsenic, which is a significant poison, deposited on catalyst exposed to synthetic Canadian crudes. Therefore, it is imperative that the catalyst load used in the hydrotreaters is designed with a robust graded bed system to handle olefins and associated coking potential. It is also required to use proper guard bed catalyst to pick up silicon and arsenic to protect the downstream main bed catalyst. Topsoe's graded bed catalyst system and our BRIM^{TM} catalyst are currently used in an increasing number of hydrotreating units processing large amounts of synthetic feedstocks without any issues.

Catalyst

Question 10
Catalyst Supply/Availability Update – Panel and Audience Comments

Question 11
Large quantities of spent ultra-low sulfur diesel (ULSD) catalyst will soon be coming available. What are the options for reuse? How successful has regeneration, rejuvenation, or reactivation of Type II sites been?

Scott Fritsch (UOP)/Steve Mayo (Albemarle)

The vast majority of spent catalysts from ULSD operations are Type II. Type II active sites have a weak connection to the substrate which, unfortunately, is strengthened when the spent catalyst is regenerated and the active metals converted from sulfides to oxides. Regenerated Type II catalysts may be as low as 60% of the activity of fresh catalyst of the same type. This level of activity may be adequate for lower severity hydrotreaters but reuse in ULSD units will likely result in very short cycles or an inability to produce ULSD at all.

Rejuvenation/Reactivation processes have been developed to take the regenerated Type II catalysts (now Type I) and reintroduce the Type II characteristics. This typically restores spent catalyst activity to >90% of the underlying fresh catalyst. Pilot plant testing has been done at Albemarle and at UOP comparing fresh KF-848, regenerated KF-848 and regenerated with REACT procedure, as well as additional testing of KF-857 and other STARS catalyst at Albemarle. The regeneration with REACT was found to result in catalyst very comparable to fresh performance with just slightly less activity.

Reactivated STARS catalysts have had broad application in ULSD units. More than 10,000 tons of STARS catalyst have been processed by Albemarle's REACT process. Typically, a portion of the spent catalyst is rejected due to poisons and breakage. The remaining portion is reactivated and loaded with fresh catalyst to fill the reactor volume. Performance of these units has been very good. In general, there has been little difference in the temperature required to produce ULSD. Multiple reactivation cycles have also been successful, with up to three cycles being proven.

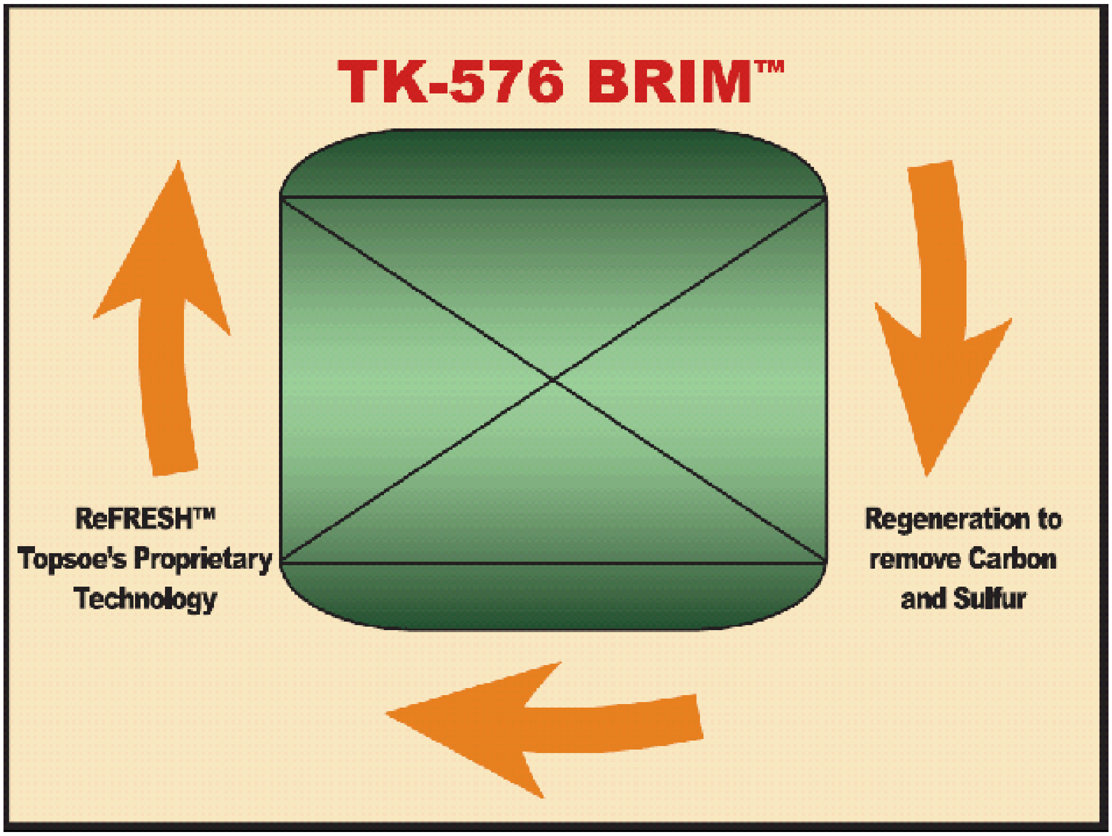
In conclusion, regeneration and REACTivation are viable means for reuse of spent catalyst. Albemarle’s REACT technology can help customers who require mainly catalysts with high activity, operate units with high margins (i.e. hydrocracker pretreatment, ULSD units), or want to upgrade spent STARS catalyst that otherwise would have been disposed of.

Lars Skyum and Henrik Rasmussen (Haldor Topsoe A/S)

There are several options for reusing spent ULSD catalysts. It is our experience that many refineries either use regenerated or reactivated catalysts in less demanding service, for instance in the production of heating oil. A number of Topsoe's clients are using Topsoe’s ReFRESH™ technology to reactivate the catalyst for reuse in ULSD service, either as a partial or a full load.

The catalyst preparation techniques for Type II catalysts are different for each vendor, so the treatment of the spent catalysts and the resulting activities are also different. With Topsoe's BRIM™ Technology it is possible to regain typically 80-85% of the original fresh catalyst activity with just a conventional and proven regeneration procedure, which is sufficient for many applications. The unit performance with a regenerated catalyst is of course not as good as with a fresh load, but if the refinery can accept a slightly shorter cycle it is a cost effective solution. It should also be noted that the SOR pressure drop will be a little higher with reused catalyst due to the extra handling of the catalyst.

If more activity is required for ULSD service, our ReFRESH™ Technology can be applied to the regenerated catalyst after which our BRIM™ catalyst will regain up to 95% of fresh catalyst activity. This technology offers substantial savings compared to fresh catalyst. Our ReFRESH™ TK-576BRIM™ is current used successfully in a number of ULSD units.



Question 12
What specific variables guide your selection of catalyst type for ULSK production?

Steve Mayo (Albemarle)
The main variables to be considered for ULSK catalyst selection are process objectives. An operation where sulfur is the primary objective will almost always find CoMo catalysts provide the best cycle length. Operations where color is the main constraint may use CoMo or NiMo or a combination in order to balance cycle length and operating temperature. Operations where smoke point improvement is the main objective will typically use NiMo catalysts or, in extreme cases, a separate noble metal aromatic saturation stage. Secondary considerations for catalyst selection are feedstock type and unit pressure. Virgin feedstocks and lower pressure units will typically favor CoMo catalysts while cracked feedstocks and higher pressure units may favor some or even all NiMo catalyst. High activity, Type II catalysts are generally preferred for ULSK. Reactivated Type II catalysts are also a good choice.

Kim Knudsen and María Jesús Lorences Pérez (Haldor Topsoe A/S)
The catalyst choice for ULSK production will be determined by the feedstock properties (mainly specific gravity, distillation curve and nitrogen content), which in turn will influence the level and type of sulfur compounds to be removed as well as the type and concentration of inhibitors affecting HDS activity. Generally speaking, a NiMo catalyst will be the preferred choice for a light kerosene with a low nitrogen content, while a CoMo catalyst would be better for a heavy kerosene feedstock. Additional product requirements such as significant improvements in smoke point will of course play an important role in the catalyst choice.

ULSD

Question 13

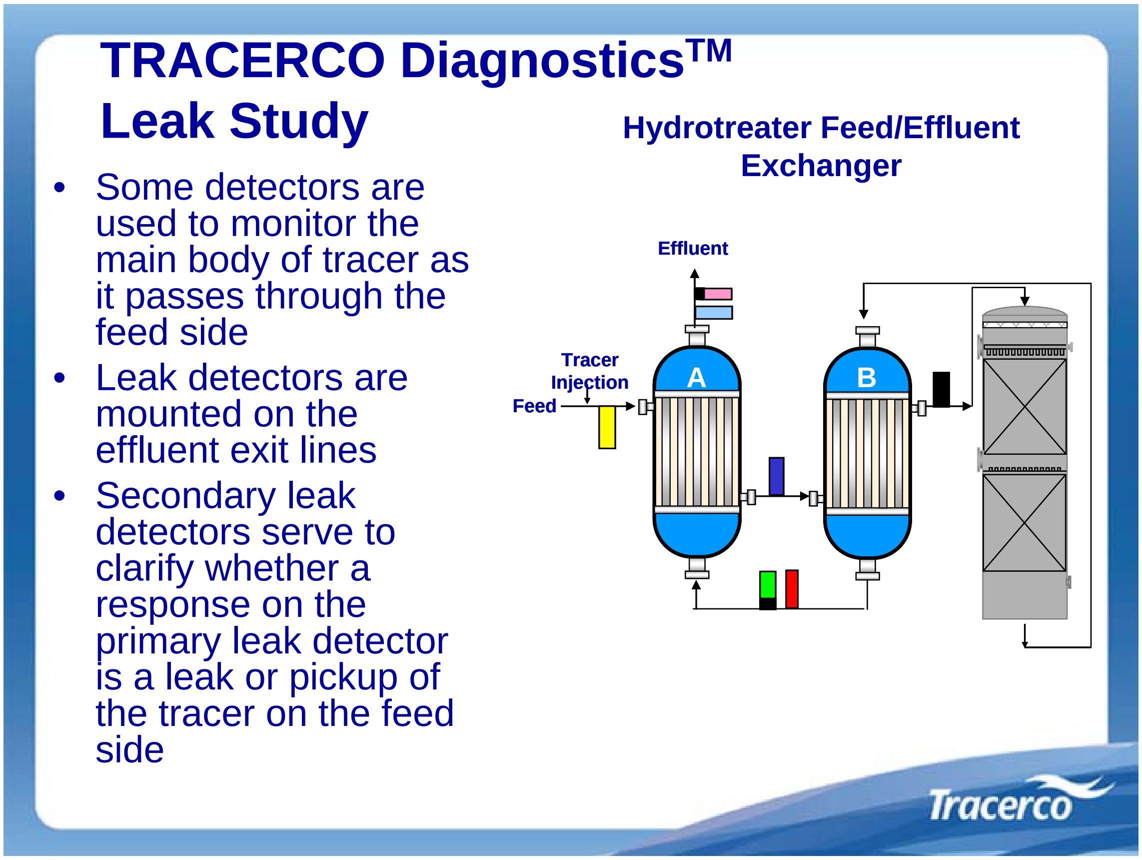
What technologies are available for finding leaks in feed/effluent exchangers and what are the detection levels? Is seal welding of tubes required to prevent significant leaks?

David Rapavi (HOVENSA)

There are several on-line techniques or technologies for finding leaks in the feed/effluent exchangers and the choice of method depends on the size of leak expected.

Sulfur speciation of the feed and product streams is done to determine if any easily converted sulfur species are present in the product. Feed leaks as low as 0.05-vol% in the product can be detected. However, unless you are able to sample the effluent of each exchanger or set of exchangers, it will not be possible to identify exactly which exchanger is leaking until the unit is shutdown and the exchangers are pressure tested.

For leaks greater than 0.5-vol% of the feed flow, radioisotope tracers can be used with external detectors (see Figure 1).



TRACERCO Diagnostics™

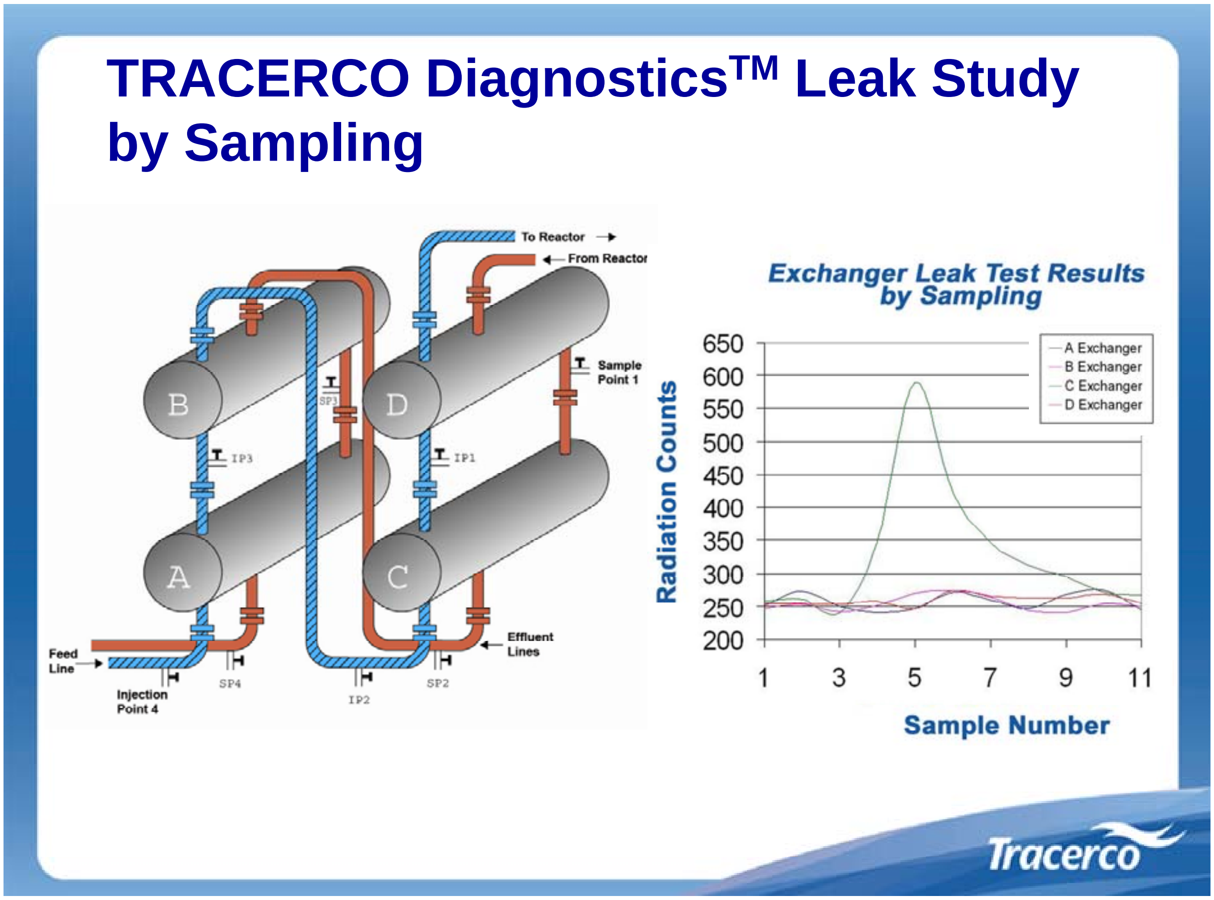
Leak Study

- Some detectors are used to monitor the main body of tracer as it passes through the feed side
- Leak detectors are mounted on the effluent exit lines
- Secondary leak detectors serve to clarify whether a response on the primary leak detector is a leak or pickup of the tracer on the feed side

Hydrotreater Feed/Effluent Exchanger

By placing detectors on the effluent side of each exchanger or set of exchangers, it is possible to identify which individual exchanger or set of exchangers has a leak to help with maintenance planning. On our ULSD unit, we installed the nozzles and valves on the feed side of each reactor effluent exchanger to improve our chances of detecting an exchanger leak.

If the leak is smaller than 0.5-vol% but greater than 100-vol-ppm, radioisotope tracers can still be used, but samples of the effluent stream must be collected and analyzed on site for the presence of the tracer (see Figure 2).



TRACERCO Diagnostics™ Leak Study by Sampling

Gas tracers, such as helium, can also be used for finding small leaks on-line, but the leak size may be difficult to quantify under 0.1-vol% due to problems of obtaining a good representative sample. So gas tracers are sometimes used just to confirm or deny the existence of a leak instead of quantifying it.

With ULSD units, very small leaks are threats to product quality and catalyst run length. TRACERCO has developed a group of chemical tracers that have better detection limits than radioisotope tracers to find these very small leaks. These non-radioactive, chemical tracers are selected to closely match process fluids. They are very stable, flashing in the high temperatures of a hydrotreater, and then condensing with the effluent, without degrading or reacting. The chemicals can be detected in the samples at concentrations as low as 1-ppb. Theoretically, a leak rate as low as 1-vol-ppm can be detected. To date, the smallest leak found by TRACERCO with this technology was a 44-vol-ppm leak. One disadvantage of the chemical tracer compared to the radioisotope tracer is that the samples containing chemical tracer have to go to a lab for analysis. Another disadvantage is unless you are able to sample the effluent of each exchanger or set of exchangers, it will not be possible to identify exactly which exchanger is leaking.

The TRACERCO on-line leak detection technology is described in *TRACERCO News Volume 2 Edition 3* "Chemical Tracers Find Elusive Leak in Hydrotreater Feed/Effluent Exchangers."

To date, HOVENSA has only used sulfur speciation and radioisotope tracers with external detectors for finding leaks in feed/effluent exchangers.

We do not feel that seal welded tubes are required to prevent significant leaks, but feel that they are required for any new ultra low sulfur production. We have installed them on our ULSD and LSG units and as feed/effluent exchanger bundles are required to be replaced our kerosene hydrotreater (which produces ULSK approximately 5% of the time), we are considering replacing them with seal welded tube bundles.

Steve Mayo (Albemarle) / Edwin Yuh (UOP)

In the past, many different methods have been used to detect leaks in feed/effluent exchangers -- with varying degrees of success. Radioactive tracers can be used if the residence time in the reactor is large enough to notice the delay in picking up a signal. With the advent of sulfur speciation analytical techniques there is little reason to use any other method. The technique is relatively simple in that a leak is present whenever light sulfur compounds are found in the product. These sulfur species are easily removed in the hydrotreater so their presence implies they must be entering the product via a feed/effluent leak. Sulfur speciation provides a very clear qualitative and quantitative indication of exchanger leaks and does so without the necessity to sample the reactor effluent or other non-routine sample points. Sampling between banks of exchangers can help pinpoint the specific bundle which is leaking -- potentially saving a lot of time for repair. From the exchanger design perspective, in UOP's opinion, strength welding the tube to tubesheet joint is very valuable in minimizing leakage and is superior to seal welding.

Rasmus Egeberg and Torkil Ottesen Hansen (Haldor Topsoe)

A heat exchanger leak may be to blame if the reactor temperature in an ULSD unit is much higher than expected and the product sulfur does not respond well to reactor temperature increases. Our clients have employed two methods to determine heat exchanger leakage on line. One method is to inject a radioactive isotope upstream the exchanger and measure the response time downstream. Another method involves a sulfur speciation analysis e.g. by a gas chromatograph equipped with an atomic emission detector (GC-AED) where the feed and product are analyzed for sulfur species. If easily converted sulfur species are identified in the product, then it is a good indication of exchanger leakage. Topsoe did a lab study by blending small amounts of a 1.2 wt% S feed with a 10 wppm S ULSD product, which showed it was possible using this method to detect leaks below 0.05 wt% of feed. At this level, such a leak would add 6 wppm of feed sulfur to the product. .

We always specify strength welding of the exchangers in ULSD service to minimize the risk of leaks.

Question 14

For ULSD units, what product specifications besides sulfur content (e.g. API uplift, cetane number, cetane index, endpoint shift, aromatics, or others) govern unit operation? For these product properties, what magnitude of improvement have you experienced?

Lars Skyum and María Jesús Lorences Pérez (Haldor Topsoe)

The most common product specifications driving the operation of ULSD units (besides sulfur content) are cetane number/index and API uplift. The magnitude of improvement depends on the feedstock properties and operating conditions. Topsøe has designed ULSD units with the objective of obtaining a cetane number improvement as high as 10 and 8º in API gravity. Depending on the feedstock being processed, these values are normally achievable in a single-stage high-pressure unit. A more flexible solution would be a two-stage HDS/HDA unit where the saturation of mono-aromatics can be further increased and controlled during operation. Product aromatic contents as low as 1 wt% can easily be achieved by utilizing this option.

Question 15

What are the causes of off-spec color problems at end of run (EOR)? How does EOR operation affect other product properties, yields, and hydrogen consumption? What unique or novel approaches have you used to overcome these problems?

Steve Mayo (Albemarle)

Color problems at EOR are almost always due to reduced aromatic saturation in the reactor. Depending on the pressure of the unit, and especially the hydrogen partial pressure at the bottom of the unit, it is quite possible for EOR conditions to operate well past the thermodynamic optimum for aromatic saturation. Under these conditions, not only are aromatics not effectively removed but condensation reactions may create poly-nuclear aromatics (PNA's) larger than those in the feed. Not all PNA's are color bodies but most color bodies are PNA's. Since the concentration of color bodies required to affect color is quite low, conditions which promote PNA formation must be avoided. Tracking delta T and hydrogen consumption are both effective tools for determining when conditions are being created which are favorable for PNA formation. Low or even negative delta Ts in the bottom bed and declining hydrogen consumption are both strong indicators that the aromatic equilibrium point has crossed from kinetic control to thermodynamic control.

There are few simple solutions to overcoming color problems. Catalyst selection can sometimes be used to extend cycle length by reducing SOR temperature and expanding the operating window before reaching EOR temperatures. Improving hydrogen partial pressure can have a large impact on color by raising the temperature at which the aromatic saturation begins to decline. Increasing hydrogen purity, increasing gas circulation rates, decreasing feed initial boiling point, etc. will help raise hydrogen partial pressure. Good liquid distribution is important, especially when processing a feed like kerosene where the unit operates with high, but not complete vaporization. Block mode operation should be avoided as this may cause adsorption of PNA's in the catalyst bed during the low severity blocks. If the unit has multiple beds and inter-bed quench capabilities, running a descending temperature profile at EOR may extend cycle.

A fail safe solution is to add a trim reactor with inter-reactor quench. The trim reactor is operated at low temperature to avoid conditions in which PNA's are formed. This allows the main reactor to operate at conditions where PNA's are formed because they can be removed by the trim reactor. A post clay treater or other PNA removal process can allow the hydrotreater to operate past EOR temperatures which cause color to be formed.

Suheil Abdo/Tim Cowan (UOP)

Color bodies in the distillate range tend to be aromatic in nature. Regarding off-spec color problems at EOR, as catalyst temperature is increased to offset loss in activity, a point can be reached where aromatic saturation is equilibrium limited. Equilibrium constraint may favor the presence of some residual multinuclear aromatics and consequently coloration of the product at high temperatures and low pressure. Some of the aromatic color bodies which were saturated at SOR may not be saturated at the higher EOR temperatures.

A detailed analysis would have to be carried out to determine if the color in the unit is a result of deficient catalyst hydrogenation function (kinetic constraint) or due to equilibrium limitations under the conditions prevailing in the reactor. We would propose catalysts with a strong hydrogenation capability for the former case or doing what's possible to lower the operating temperatures and/or increase hydrogen partial pressure for the latter.

At EOR temperature, distillate cetane is also slightly affected by the lower aromatic saturation function. It is not uncommon to see a 2 or 3 number loss in cetane number over the course of a conventional hydrocracking cycle. More strongly affected is kerosene smoke point. A stringent specification on kerosene smoke point often dictates the operating pressure of the unit. Higher pressure units can operate to higher EOR temperatures before reaching an equilibrium limited regime.

Yields of heavier products tend to decline as the catalyst deactivates. Higher operating temperatures result in the production of more light ends at the expense of distillate. Although cracking to light ends requires more hydrogen, this is more than offset by the reduced aromatic saturation function of the catalyst. In general, there is a slight decline in chemical hydrogen consumption over the course of a run.

The above problems can be managed by recognizing the impact of operating temperature and pressure on product quality and yields. Catalyst design plays a major role in managing this, since a more stable catalyst will be able to operate for a given cycle length at a lower EOR temperature for example. For new units, an appropriate pressure can be specified to mitigate these problems. For existing units, there are several catalysts that can be utilized to ensure the proper trade-off between activity and yield selectivity are optimized.

Simon Ivar Andersen (Haldor Topsoe)

Off-spec color problems at EOR conditions are related to the presence of very small amounts of aromatic structures with several conjugated rings (4-6 rings). A strong apple-green color may be obtained with as little as 10-50 ppm of 5 ring aromatics, which will also give a fluorescent appearance. These aromatics are formed by condensation of smaller aromatics, naphtho-aromatics or naphthenes at the high temperature toward EOR. At Haldor Topsoe, in order to predict the color of products, we have developed correlations between feed properties and color at EOR conditions. This tool is used to assess if color might be a problem. However, for a specific feedstock and operating condition, very small amounts of aromatics responsible for the color can only be detected using advanced techniques such as fluorescence spectroscopy. We have undertaken an in-depth study of the formation of these color bodies using Synchronous Fluorescence Spectroscopy, looking at both feedstock types and process conditions as well as line-out phenomena. The conclusion was that the concentrations were so low that it was merely a cosmetic problem, and that the aromatic content had no impact on other fuel properties or performance. The study also showed that blending was not always a possible route for dilution of the color, as a diesel of low color but fairly high in mono- and diaromatics content may actually increase the color of the blend, because the small aromatics can act as a vehicle to carry electrons between the large fluorescent color body molecules. This would amplify the color intensity. Again the lack of any large effect of dilution does not imply that there is a large content of color bodies, but only that the color appearance in liquids containing aromatic substances is a very complex phenomenon, taking place at extremely low concentrations. Nitrogen compounds are present in such low concentrations in ULSD that these are not the source of the color. Based on our experience and knowledge of the kinetics of color removal, we have been granted a patent for removal of color bodies. Using this technology, we have licensed several units and solved the color issues.

At low pressure and at reasonably high SOR temperature, aromatic saturation of polyaromatics will decrease towards EOR, and the hydrogen consumption will therefore decrease or stay constant due to the opposite effect of increased hydrocracking (see below). This will give a higher density of the diesel and a lower delta T in the reactor. At high pressure and low SOR temperature and medium EOR temperature, the saturation of polyaromatics to monoaromatics may increase, and if the nitrogen content is low enough in the reactor, also the monoaromatics may be saturated to naphthenes, thereby increasing the hydrogen consumption. This will lead to a lower density of the diesel and a higher delta T in the reactor. At low pressure and from SOR to EOR, the trend seen will depend on the feed and operating conditions.

From SOR to EOR, the cracking activity will increase, thereby increasing the yield of gas. The naphtha will often increase, and the diesel yield will decrease due to the lower aromatic saturation. However, the extent of this will be determined by the feedstock and operating conditions.

Question 16

Comment on the use of additives, dewaxing catalyst and associated operating conditions, or feed management to address ULSD cold flow properties.

David Rapavi (HOVENSA)

Additives called anti-gel additives, pour point depressants, cold flow improvers, diesel operability additives, CFPP additives, LTFT additives, cloud point depressants, and others are used to improve the low temperature properties of diesel fuel. Most function by crystal modification reducing the size and shape of the wax crystals. A few reduce the temperature at which crystallization takes place.

We add a pour point depressant to ULSD at a dosage of approximately 20-vol-ppm per every 5^{o}F reduction in pour point. Because ULSD tends to have a higher wax content and narrower wax distribution than LSD, some additive suppliers have developed additives specifically for ULSD, which require lower dosage rates when treating ULSD than with additives designed for LSD.

We have a hydrotreating unit that produces jet fuel/kerosene 95% of the time and ULSK approximately 5% of the time. The ULSK produced is blended with ULSD in a 20%/80% ratio and additized with 400-vol-ppm of CFPP additive to meet a -20^{o}F cold filter plugging point (CFPP) requirement of a winterized ULSD blend.

We do not process highly paraffinic crudes or use dewaxing catalyst because the ULSD cold flow properties can be achieved economically with additives and blending.

Vasant Thakkar/Vern Mallett (UOP)

ULSD processing by nature produces product that is highly saturated and thus could have poor cold flow depending upon feed source and severity of processing. While some pour point depressants are effective, additives for cloud point reduction and cold filter plugging improvement provide only small benefits.

Cold flow properties of ULSD operation can be managed to greater extent by using UOP HC-80 hydrodewaxing catalyst stacked with hydrotreating/hydrocracking catalyst. UOP has experience with HC-80 application in several hydrocracking and hydrotreating units. The catalyst provides superior diesel product cold flow properties by selectively acting on straight chain paraffins in the feed. Depending on the catalyst operating temperatures, feed properties and other operating conditions, diesel cold flow properties can reach minus 30-35°F for “winter” grade ULSD.

UOP also has new hydrocracking catalyst like HC-215 and HC-120 that inherently have better isomerization activity so that the product iso-to-normal ratio is significantly higher thus achieving better cold flow quality.

Besides catalytic solutions, the cold flow property can be managed by feed endpoint management but reducing endpoint effectively lowers diesel yield. Other options can be feed blending i.e. if product is more cyclic it will have better cold flow if cetane is not limiting. The addition of a stream like LCO helps improve cold flow to some extent. This is normal practice to blend No. 1 diesel into No.2 diesel to adjust cold flow for the winter season, both components need to be ultra low sulfur level.

Peter Bendtsen (Haldor Topsoe, Inc.)

Meeting cold flow properties is increasingly seen to be a limiting parameter for refiners. With the demand for high product quality diesel and the economic incentive of cutting deeper into the heavy part of the gas oil, cold flow properties can become a serious concern.

The ULSD cold flow properties typically measured are Cold Filter Plugging Point (CFPP), Cloud Point (CP), or Pour Point (PP).

Generally, these properties are adversely affected by the concentration of 'waxy' molecules, these being the normal and slightly branched paraffins, in the gas oil. The high melting point of the paraffins in the upper ULSD boiling range is mainly responsible for the cold flow properties and can cause the ULSD to become off-spec due to wax crystallization.

Common routes for improving cold flow properties in ULSD products are feed management, kerosene blending, use of additives and catalytic dewaxing.

a) Feed management is an effective but usually economically unattractive way to address these issues. The concentration of the long chain paraffins may be reduced by reducing the end point of the ULSD product. This directly improves cold flow properties but also reduces the potential diesel pool.

b) Blending in lower boiling streams, i.e. kerosene as a diluent, also directly improves cold flow properties. However, blending in kerosene might adversely affect other ULSD product properties such as Cetane Number, Flash Point, and Vapor Pressure.

c) The cold flow properties may be improved by addition of specialty chemicals (such as cloud point depressants). This method is effective in some cases; however, it occasionally requires addition of these chemicals in relatively high concentrations. This is especially the case in units coprocessing bio-fuels. Additionally - many chemicals are only very effective towards one of the cold flow properties, but less effective towards another cold flow property - thus requiring addition of several chemicals.

The first three routes have historically accounted for most of the corrective action to improve cold flow properties. However, with the increased demand, a fourth option is becoming more attractive.

d) Cold flow properties of diesel fuels can be effectively improved by catalytic hydrodewaxing. Using this technology, the improvements are achieved by selective isomerization and hydrocracking of the normal and slightly branched paraffins.

The hydrodewaxing catalyst is highly zeolitic in nature. It either selectively isomerizes or cracks mainly the normal-paraffins, which, as mentioned above, have poor cold flow properties. The dewaxing catalyst, only to minor extent, affects the other compounds in the diesel (naphthenes, aromatics etc).

Controlling ULSD cold flow properties by hydrodewaxing thus gives the potential for a larger diesel pool. However, an inherent phenomenon, related to the nature of these cracking type catalysts, is the formation of some lighter products from the heavier feed components - mainly formation of naphtha and some C1-C4 gas.

Historically, dewaxing catalyst was loaded into stand-alone units. However, lately there has been a shift more towards a combination of hydrodewaxing and hydrotreating in the same reactor, as a result of the increased need for dewaxing in existing units.

Traditional ZSM-5 based dewaxing catalysts give an unstable product containing a lot of olefins. The reactions are endothermic and thus harder to control. This catalyst type does not provide any activity for HDS, HDN or HDA, resulting in poorer product quality of the dewaxed product.

Besides the dewaxing function, Topsoe’s modern sulfur-tolerant dewaxing catalyst, TK-928, offers good HDS/HDN/HDA activity. The reactions across this catalyst are exothermic, and TK-928 can thus easily be installed in a conventional hydrotreater.

Loading Topsoe’s dewaxing catalyst in combination with hydrotreating catalyst is typically done having the dewaxing catalyst 'sandwiched' in between the hydrotreating catalyst near the outlet of the reactor.

Using this approach, the dewaxing function is switched on/off by temperature control in the last bed by the use of quench gas and reactor inlet temperature control. To activate the dewaxing catalyst capabilities during wintertime operation, reactor temperatures are increased. During summertime operation, the amount of quench gas injected before the last bed is adjusted to operate the dewaxing catalyst at lower temperatures to limit the function of the dewaxing catalyst and the associated higher hydrogen consumptions and yield losses.

Question 17

What are the issues associated with co-processing naphtha and distillate in the same unit with the objective of simultaneously producing ULSD and reformer feed? Comment on fractionation strategies, EOR constraints, contaminant issues (e.g. silica, arsenic, nitrogen), or other considerations.

David Rapavi (HOVENSA)

We have one LSD unit that was modified to produce ULSD and we co-process straight run heavy naphtha with distillates in it due to strong ULSD economics over gasoline. The Stripper tower operation is adjusted to maximize ULSD production up to a minimum flash specification of 130°F. The overhead naphtha product we produce is not suitable for reformer feed directly because it contains H_2S and the sulfur and nitrogen levels exceed our maximum reformer feed specification of 0.5-wt-ppm. To produce reformer feed grade naphtha, the operating severity of the ULSD unit would have to be increased, resulting in ULSD product over-treating and shorter catalyst run lengths. Furthermore, due to concerns of sulfur recombination in the naphtha product, the allowable end-of-run reactor temperature would be lower than the ULSD only operation. Also, the H_2S in the naphtha product would have to be removed before sending it to the reformer.

Adding naphtha in the feed of the ULSD unit may result in a higher deactivation rate due reduced hydrogen partial pressure from additional feed vaporization. If coker naphtha is processed, the unit must be designed to handle higher hydrogen consumption and contaminants such as silicon and diolefins which can cause catalyst poisoning and equipment fouling.

A co-processing unit can be revamped or built to produce reformer feed and ULSD simultaneously and the refiner can determine what best fits their situation of building and operating two separate units or going with one co-processing unit.

Laura Kadlec/John Kulach (UOP)
Some considerations for co-processing naphtha and distillate in the same unit are the feed rates and feed quality, which go into the selection of operating pressure, space velocity, and catalyst. Distillate hydrotreating for ULSD typically requires higher hydrogen partial pressure, lower LHSV and more active catalysts compared to naphtha hydrotreating, because of the need to convert stable sulfur compounds such as benzothiophenes and dibenzothiophenes. If the distillate feed includes Coker gas oils or other difficult to process streams such as extracts and condensates, the design would call for a more severe operation with higher reactor temperatures. Inorganic contaminants such as silica and arsenic can be removed from the feed upstream of the active desulfurization catalysts by using filters, particulate traps, and demetallization catalysts in the top of the reactor.

Naphtha hydrotreating for reformer quality feed requires sufficient catalyst and hydrogen partial pressure for sulfur and nitrogen removal. This is usually a low severity operation compared to distillate hydrotreating. The main concern for naphtha hydrotreating is recombination sulfur. Recombination is a phenomenon where olefins combine with hydrogen sulfide to form mercaptans. The rate of this reaction increases with temperature, so mercaptan formation is more of a problem as catalyst deactivates, requiring higher operating temperatures. Mercaptan sulfur in the naphtha product can rise to 2 ppm or greater at end-of-run, which is well over the maximum allowable for reformer feed. If Coker naphtha is included in the feed, the NHT will normally be designed for a more severe operation and may include a lower temperature trim reactor for mercaptan conversion. Coker naphtha can also contain high concentrations of Si which require a large volume of demetallization catalyst. Fortunately, these demet catalysts also have reasonable activity for nitrogen and sulfur removal.

While a typical distillate hydrotreater fractionation section would consist of a stripper column to remove light ends and meet flash point specification, a hydrotreater co-processing distillate with naphtha for reformer feed would require a more complex fractionation section. The fractionation configuration would depend on the relative rates of distillate and naphtha as well as the reformer feed specifications for C_6- material. If the naphtha rate is relatively small, a debutanizer and naphtha splitter on the stripper overhead liquid may be sufficient. If the naphtha rate is higher, an atmospheric fractionation column similar to what would be used on a distillate hydrocracking unit may be required.

Whether a co-processing unit is more economical than individual DHT and NHT units will depend on the relative feed rates, feed quality and product specifications. Co-processing would tend to be favored if the DHT pressure requirement is relatively low, and if the naphtha quantity is small relative to distillate.

To summarize the issues with co-processing for ULSD and reformer feed:

- The reactor must operate at conditions (hydrogen partial pressure, LHSV, temperatures) required for ULSD production, which is more severe than required for naphtha hydrotreating.
- There must be sufficient demetallization catalyst based on the level of inorganic contaminants in the combined feed. If processing Coker naphtha, the volume of catalyst required to prevent Si poisoning may be a significant portion of the total reactor volume.
- End of run temperatures will be higher than in a typical naphtha hydrotreater, increasing the potential for sulfur recombination and potentially requiring post-treating of the naphtha to meet reformer feed specifications.
- More complex fractionation is required to recover naphtha and meet reformer feed specifications.

Kim Knudsen and María Jesús Lorences Pérez (Haldor Topsoe)
Co-processing of naphtha in a diesel hydrotreater will result in a lower hydrogen partial pressure due to the vaporization of the naphtha stream. The lower hydrogen partial pressure will require a higher operating temperature to achieve the same product sulfur requirements. The catalyst deactivation rate will also increase. It will be very difficult to produce reformer feed at the "normal" operating temperature in a ULSD hydrotreater. The sulfur content in the naphtha fraction will usually be higher than required, due to recombination reactions. The contaminants (and inhibitors) present in the feed will also have an influence on HDS and HDN activity, but it is difficult to set generic considerations, since different contaminants and inhibitors will influence the catalyst activity in different ways. Having said this, a number of Topsoe's clients are successfully co-processing Naphtha in ULSD units. In these cases we will design the catalyst loading with a proper graded bed system as well as catalyst to pick up Si and Ar.

Question 18
What are you doing to maximize diesel production? Comment on strategies such as feed diet, conversion, and fractionation techniques.

Steve Mayo (Albemarle) / John Kulach (UOP)
While changing feed diet and fractionation techniques can add incrementally to diesel production, the only method to achieve significantly higher diesel output is by conversion of VGO or other feeds such as Coker gas oil or deasphalted oil. The main conversion processes where diesel output can be increased are the FCCU, FCC-PT and Hydrocracking.

Changes in catalyst and operating temperatures in the FCCU can move selectivity from gasoline to LCO. These techniques are fairly well understood, but unfortunately produce a diesel that is highly aromatic and completely unsuitable ULSD without high severity post-treating. New FCC catalysts are being developed which improve the situation but all the options still require post-treatment. These highly hydrogen deficient feedstocks will need significant hydrogen input in order to product a cetane value which is even moderately acceptable.
Operating the FCC-PT unit in mild hydrocracking mode can produce up to 30% distillate. The conversion which takes place is primarily thermal, producing a distillate stream that is still relatively high in aromatic content. Sulfur will also be higher than ULSD so post-treatment is required to produce an acceptable sulfur and cetane level. Depending on unit pressure, operating the FCC pretreater in MHC mode can reduce cycle length by up to 50%. If the unit is capable, it may be possible to revamp the unit to a partial conversion hydrocracker. These units are capable of 50-60% conversion to distillate.

Question No. 25 also deals with increasing diesel production from a new unit perspective. UOP will address various hydrocracking configurations.

Question 19
What reactor temperature strategies are you using for multi-bed ULSD reactors?

David Rapavi (HOVENSA)
We have one LSD unit that was modified to produce ULSD. It processes no cracked stocks and operates at nominally moderate to low pressure (<625-psig reactor outlet pressure) with a significant catalyst volume (LHSV <0.6).

The unit has three catalyst beds with inter-bed hydrogen quench. The quench flows are adjusted manually by valve output to operate at equal bed outlet temperatures throughout the run. Operating at equal bed outlet temperatures results in the lowest WABT, provides the most uniform catalyst deactivation rate, and should allow for longest the catalyst cycle length.

Lars Skov Jensen (Haldor Topsoe)
Generally, multi-bed ULSD reactors are designed with equal outlet temperatures from all beds. Operating with equal bed outlet temperatures results in longer catalyst life, because it results in the lowest peak temperature for a given weighted average bed temperature (WABT).

Especially for revamp units where it is not possible to further increase the recycle gas flow, it may be necessary to operate with an ascending temperature profile to ensure sufficient hydrogen availability at the inlet of the reactor.

Question 20
What operational changes are required to produce full-boiling range ULSD directly from the FCC pre-treat unit? Please describe your operating experiences (for audience).

Steve Mayo (Albemarle)
In our experience, producing full-boiling range ULSD directly from the FCC pretreater is not possible without taking extreme measures in the operation of the unit. ULSD can be produced at more moderate conditions in the FCC-PT unit when the refiner is willing to significantly undercut the diesel from the unit. This requires a high pressure unit (>1200 psi hydrogen) and operation to produce a total liquid product with very low sulfur (<500 ppm). The amount of undercutting required will be inversely related to the sulfur content in the total liquid product.

Dr. Tai-Sheng Chou (Haldor Topsoe, Inc.)
FCC pretreat units provide very specific HDS and/or HDN functions for maximizing FCC product value. It is possible to make ULSD in a FCC pretreat unit. However, this requires severe hydrotreating of the VGO down to 400-700 wt ppm sulfur, which will lead to more cracking, higher catalyst deactivation rate, and significantly higher hydrogen consumption, due to a higher operating temperature.

The refinery can obviously compensate by adding more reactor volume to the FCC pretreat unit and return to more conventional operating conditions, while obtaining a ULSD fraction from the FCC unit.

Topsoe has licensed FCC pretreat units to operate at a total liquid product sulfur that results in the ULSD cutoff the FCC unit being below 10 wt ppm.

Technology

Question 21
What fuel specification changes do you anticipate for kerosene, diesel, and fuel oil?

David Rapavi (HOVENSA)
We are anticipating that heating oil will have individual state regulation reductions rather than a federal change in sulfur levels and are using a 2012 - 2013 time frame for when the first reductions will be made from 2000-wt-ppm to 500-wt-ppm sulfur with the expectation that the sulfur level will eventually be reduced to ULSD levels. We also anticipate jet fuel and kerosene will eventually go down to USLD levels in the next 5 to 10 years. We anticipate sulfur levels in marine diesel oil and marine bunker fuels can be reduced to 0.1-wt% and 1.0 to 1.5-wt%, respectively, in the next 5 to 10 years, and this may be state regulated, or port specific, rather than nationwide.

Rich Rossi (UOP)
With regards to kerosene, there have been discussions regarding possible changes aimed at reducing sulfur content, but to date, no changes to qualities such as sulfur content have been agreed upon, and none are currently forthcoming. This may change as the EU is requesting airlines to reduce emissions, but issues of fuel performance reliability have to be addressed. At the same time, efforts have been underway to certify alternative sources of kerosene such as those derived from Fischer-Tropsch gas-to-liquids, coal-to-liquids, and biomass-to-liquids processes and other renewable sources.

Diesel fuel standards are changing at different rates across the world, with countries are moving towards essentially sulfur-free (15 ppm S) fuel. EU countries, with Sweden leading the way, have by in large implemented 10 ppm sulfur Euro IV diesel fuel (almost 100% compliance by 2009), while the U.S. has recently implemented the ultra-low sulfur diesel standards (15 ppm) for on-road diesel, with some off-road diesel to conform in 2010, but all to be in compliance by 2014. Many other countries are adopting Euro specs, although at different rates - Australia, Hong Kong, Japan, New Zealand, Singapore, South Korea, Taiwan are moving from Euro 3/4 towards Euro 4/5 requirements, and China, India, Indonesia, Philippines, Thailand, Vietnam are moving from Euro 2 towards Euro 3/4 requirements. The EU is currently debating the specifications for Euro V diesel, with timing of implementation not currently finalized. Proposals are currently being entertained to reduce poly-aromatics from 11% to 6%, as well as to bring all diesel fuels/gasoils (off-road) into compliance with the on-road diesel fuel specs. Carbon neutrality is also becoming important, though it is not clear exactly what the final mechanism will be.

If by fuel oil, you mean RSFO (bunker fuels), there is much discussion taking place, with the desire to reduce sulfur levels significantly. Governments have the ability to define special marine emission control areas (ECA's), which are essentially coastal areas such as the Mediterranean, North Sea, or off the U.S. coast. Current marine fuels can contain a maximum of 4.5 % in the open seas and 1.5% in the ECA's. Proposals have been put forward to reduce the sulfur content of ECA fuels to 1.0% in 2012, and 0.1% by 2015, and to reduce the open seas marine bunker fuel sulfur level to 3.5% by 2012, and 0.5% by 2020. This last specification could require refiners to install significant hydrotreating and hydrocracking capacity since it will likely be more cost-effective to convert bunker fuel to distillate rather than desulfurize to 0.5%. However, this would have adverse effects on CO_2 emissions due to the significant demand for hydrogen associated with this level of treatment.

Question 22

Describe your experiences with variable frequency (VF) electric drivers for recycle compressors and compare them to steam turbine drivers. What are the advantages of each type of driver?

Edwin Yuh (UOP)

UOP has had discussions with several customers during the design of their unit regarding the use of a VF electric driver for the recycle gas compressor. As of yet, the cost of a VF drive does not appear to be competitive with respect to a fixed two-speed motor. In other words, the power savings of a VF driver have not yet offset the extra cost. As the cost for a VF driver comes down, we should see more of them applied to hydroprocessing unit recycle gas compressors.

The operating characteristics of a VF driver are similar to a variable speed steam turbine driver. As far as whether a motor driver or steam turbine should be used, the individual refiner's steam balance usually determines the basic driver selection, i.e. motor or steam. Therefore, the economics of VF motor versus steam turbine don't usually come into play. The advantages of a motor driver are mainly related to the lower installed cost, particularly for a fixed speed motor. A motor driver also has the potential for being more energy efficient if the steam that would be used to drive a turbine driver is used to generate power instead and further heat recovery is utilized for the low level turbine exhaust steam.

The main advantage for a steam turbine is that recycle gas is generally not lost during a power failure. This has the potential of avoiding a temperature excursion and the need to depressure the unit during a power failure.

Question 23

What is your experience with and acceptance of high efficiency plate exchangers in high pressure hydrotreating service?

Edwin Yuh (UOP)

Very few, if any, plate and frame or all welded plate exchangers are available for high pressure service. UOP does not have any experience with this type of equipment in hydroprocessing. Therefore, as of yet we have not applied this technology to distillate or heavier hydrotreating service. The main issue is the inability to clean the exchanger should it become fouled. In order to design a unit with this type of exchanger, there must be a reasonable assurance that, over the life of the exchanger, fouling will not occur. For most units fouling can not be absolutely ruled out due to feedstock variations, mis-operation, or operational upsets.

Torkil Ottesen Hansen (Haldor Topsoe)

Topsoe has design and operating experience with plate heat exchangers in revamped diesel units. The units were modified with new high pressure plate exchangers which replaced old plate exchangers. Careful design, reactor loading and cleaning can avoid the typical problems with fouling, plugging and leaks. Commercial experience confirms that this approach is working.

The thermal efficiency is high, and the approach between hot inlet and cold outlet has been 4-20°F.

Question 24

New regulations on reducing total sulfur levels in refinery fuel gas present what challenges for conventional treating processes such as mercaptan extraction, amine, etc.? What hydroprocessing technologies can reduce sulfur to less than 40 ppm as required by the California South Coast Air Quality Management District (SCAQMD) regulations?

Luigi Laricchia (UOP)

Some refineries in California are successfully using the Extraction Merox™ process to comply with the SCAQMD sulfur regulations. The Merox unit typically installed downstream of an amine unit, reduces the hydrogen sulfide and mercaptans to very low levels below 40 ppm. Carbon dioxide is also removed in the pre-treatment section of the Merox unit.

Hydrocracking

Question 25
If you want to maximize diesel production, what vacuum gas oil (VGO) hydrocracking unit configuration do you recommend for maximizing conversion to diesel? What are the technical hurdles? Alternatively, can you maximize distillate yield just with a catalyst change? What are the strategic considerations and potential pitfalls of converting from naphtha to diesel-selective operation?

Edwin Yuh (UOP)
This question is difficult to answer in a brief form because they are short simple questions requiring long and complex answers. Having said that, there are a lot of factors one needs to consider when designing a cost-effective VGO hydrocracking unit to maximize diesel production.

Selection of the hydrocracking configuration to maximize diesel product from VGO cracking requires consideration of several factors as listed below.

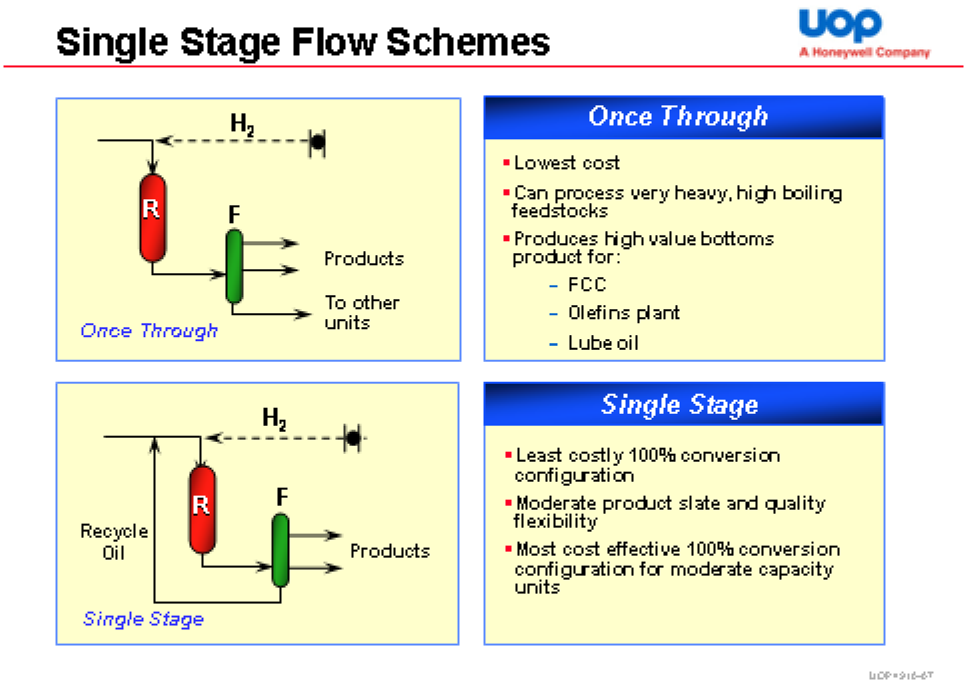
- VGO feed quality; complex feed components
- Product quality objectives (e.g. cetane, cold flow properties); disposition of unconverted oil
- Conversion severity, i.e. full conversion of VGO or partial conversion of VGO desired
- Throughput of the unit

There are several hydrocracking flow scheme configurations one could consider depending upon the factors listed. The UOP Unicracking™ Process flow scheme options include

- Once through hydrocracking
- Single-stage Hydrocracking configuration for high conversion
- Two-Stage Hydrocracking configuration
- Separate Hydrotreat configuration (variation of two-stage)

The operating environment in these configurations can be very different and catalysts that can operate at high selectivity to diesel in different environments are critical to maximizing diesel production. Each of these flow schemes have their own features to offer depending on processing objectives.

The following figure gives a high-level view of some features of each option.



Single Stage Flow Schemes

Once Through

- Lowest cost
- Can process very heavy, high boiling feedstocks
- Produces high value bottoms product for:
  - FCC
  - Olefins plant
  - Lube oil

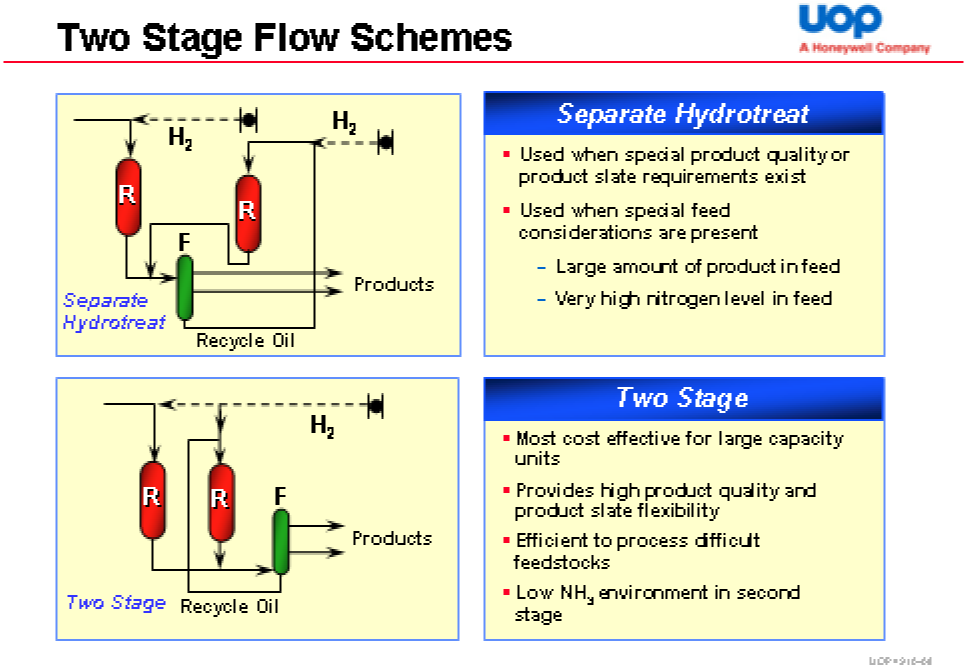
Single Stage

- Least costly 100% conversion configuration
- Moderate product slate and quality flexibility
- Most cost effective 100% conversion configuration for moderate capacity units

Single-stage flow schemes can be once-through or recycle depending upon the desired level of conversion of VGO to diesel. As indicated for partial conversion units once through flow configuration can be adequate and cost effective to produce good quality products. Once through hydrocracking is desired if unconverted oil is desired for down stream processing e.g. FCC feed, steam cracker feed or lube base oils. The once through flow scheme is simple and less expensive relative to recycle flow schemes.

When higher conversion of VGO is desired, the single-stage recycle flow scheme offers full conversion capability for moderate size capacity and typical VGO feedstock.

As feeds are becoming more difficult to process, it will contain increasing amounts of contaminants, such as higher sulfur and higher nitrogen. In order to handle these difficult feedstocks, the two-stage flow scheme offers an advantage. These flow schemes can also handle higher capacity than single-stage as there are multiple reactors. Typical two-stage flow scheme features are shown in the figure below.



Two Stage Flow Schemes

Separate Hydrotreat

- Used when special product quality or product slate requirements exist
- Used when special feed considerations are present
  - Large amount of product in feed
  - Very high nitrogen level in feed

Two Stage

- Most cost effective for large capacity units
- Provides high product quality and product slate flexibility
- Efficient to process difficult feedstocks
- Low NH_3 environment in second stage

The two-stage flow scheme basically comes in two flavors. (1) Separate hydrotreat flow scheme and (2) Two-stage

In the Separate hydrotreat flow scheme, the first stage performs only hydrotreating of feed so that feed contaminants are reduced and feed is hydrogenated. The H_2S and NH_3 are removed as well as any product formed or present in the feed is separated before going to the hydrocracking stage.

In a two-stage hydrocracking flow scheme, the first stage performs hydrotreating as well as hydrocracking. Thus, the two-stage flow scheme as defined here has hydrocracking catalyst in both stages.

As described above the recommendation of configuration needs to take into account several factors to maximize diesel production from VGO conversion. In order to maximize diesel product besides flow scheme selection, catalyst is also as important as flow scheme to maximize selectivity towards diesel production. Hydrocracking catalysts span a range of cracking activity and selectivity. Distillate or diesel selective catalysts usually are amorphous or low zeolite containing catalysts. UOP offers a wide range of distillate selective catalyst portfolio, HC™-215, HC-120, HC-115, DHC™-32, DHC-2 or DHC-8 to maximize diesel typically. Recent catalyst like HC-120 and HC-215 also give better cold flow properties for diesel thus diesel yields can be maximized by increasing back end cut point while meeting cold flow properties such as pour point or cloud point requirement.

Conversion of a naphtha selective hydrocracking unit to a diesel selective hydrocracking unit requires several considerations - catalyst selection, balancing pretreat and cracking catalyst activities, feed component selection, and shutdown equipment operability check. Diesel yield can certainly be increased through a catalyst change but not likely maximized. There are trade-off's and technical hurdles to be considered if an existing unit switches to a much more diesel selective catalyst. Since diesel-selective hydrocracking catalyst tends to have lower activity, cycle length will be impacted and the pretreating and hydrocracking reactors will need to be rebalanced. Fractionation equipment will probably present constraints. In addition, stability considerations like heavy polynuclear aromatics (HPNA) behavior would need to be addressed.

The refiner may want to consider a flexible catalyst for this operation change since this will allow swing operation between naphtha and diesel mode, if desired. There will be some compromise in loss of selectivity with flexible catalyst. Typically, the operating pressure of a naphtha unit is in the range of 1000 to 1400 psig. This will make it challenging to meet diesel aromatics and sulfur targets and proper selection of catalysts becomes critical. Refiners should consider catalysts that improve diesel cold flow properties while hydrocracking.

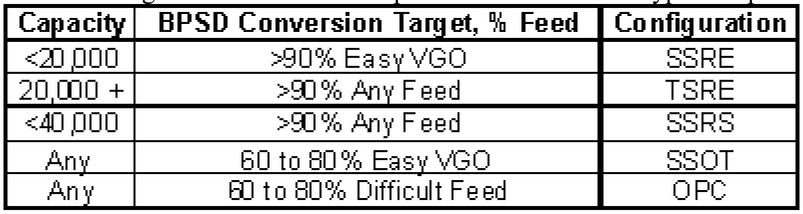
As indicated earlier, the answers can be complex. A licensor with a wide range catalyst portfolio and experience with designing units with different configurations can optimize the design of the hydrocracking unit to meet the refiner's objective in a cost effective manner.

Steven Souers (Chevron)
If you want to maximize diesel production, what vacuum gas oil (VGO) hydrocracking unit configuration do you recommend for maximizing conversion to diesel? What are the technical hurdles? Alternatively, can you maximize distillate yield just with a catalyst change? What are the strategic considerations and potential pitfalls of converting from naphtha to diesel-selective operation?

For maximizing diesel production that meets stringent Euro diesel specifications, the two-stage with recycle configuration ("TSRE") is by far the best option for full-conversion units with world-scale capacities. This is especially true with the difficult feedstocks of today that often have a significant refractory component such as Heavy Coker Gas Oil boiling in the VGO range. For easier vacuum gas oils when only partial conversion is required because of other factors such as the need to feed an FCC, petrochemicals or lube oils complex with the unconverted oil from the hydrocracker, a single stage once through ("SSOT") configuration is often used for conversions less than ~80%. For very high nitrogen, and refractory feedstocks, an optimized partial conversion ("OPC") configuration will provide the highest diesel yields and quality at minimum reactor volume and hydrogen conversion for units that require conversion in the 60 to 80% range. The optimized partial conversion configuartaion minimizes conversion in a first reaction stage to the level required to prepare the feed for a subsequent second stage that operates in a "clean" environment free of ammonia and hydrogen sulfide. For units in the 25,000 to 40,000 BPSD range, the CLG configuration Single Stage Reactor Sequenced ("SSRS") configuration will provide diesel yields comparable to a two-stage with recycle configuration but at considerable savings in capital. The scheme involves feeding the raw VGO stream in between the second and first reactors, with all the second hydrocracking reactor effluent mingling with the raw VGO.

The second reactor effluent provides most of the treat gas requirement for the downstream reactor where the raw VGO is hydrotreated and partially converted. The liquid effluent from the upstream reactor acts as a heat sink for the downstream raw VGO processing reactor. Substantial savings in exchanger, recycle gas compressor, and pipe sizing is realized. Realtively small, high-conversion units, can use a single stage with recycle ("SSRE") configuration in maximum diesel service because the added cost of some equipment required in the TSRE configutaion may not justify the diesel yield advantage of this configuration at such small capacities.

The following table summarizes the potential schemes with typical capacities:



Capacity	BPSD Conversion Target, % Feed	Configuration
<20,000	>90% Easy VGO	SSRE
20,000 +	>90% Any Feed	TSRE
<40,000	>90% Any Feed	SSRS
Any	60 to 80% Easy VGO	SSOT
Any	60 to 80% Difficult Feed	OPC

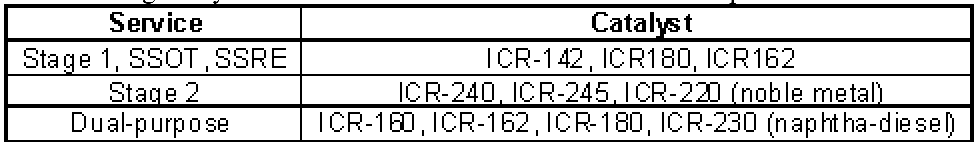
(Note: An SSOT configuration can be used for conversions as low as 30% with integrated distillates upgrading facility to make high quality diesel)

The most diesel selective catalysts are not as active as naphtha selective catalyst systems. One of the major technical hurdle is the necessity of keeping reactor size and weights within local limits and providing two to four years of catalyst run cycles even as feeds become more difficult.

Diesel selectivity can be increased by catalyst replacement if the units were originally designed for diesel service. In units originally designed for naphtha service, available catalyst volumes are lower and the diesel selective catalyst will suffer from reduced run lengths unless the net conversion from the unit is dropped. This is especially true when the refiner increases the end point of the feed gas oil from the HAGO/LVGO range typical for naphtha service to the VGO range that is is more typical for diesel service. The problem becomes more severe when the hydrocracker for naphtha service was designed for lower pressure (~1500 psig) with the intent of hydrocracking a lower end point material such as HAGO to napaphtha using very active hydrocracking catalysts; the lower pressure will impact the catalyst run length especially in the lead reaction stage as feeds get heavier in diesel service.Aromatic saturation will be lower and the refiner will find it difficult to meet diesel gravity, and cetane specifications.

A refiner interested in producing increased naphtha in summer and increased diesel in winter will be well served by the use of one of CLG's moderate activity catalyst systems that can swing between the relatively severe demands of naphtha service by possessing enough activity, and still retain the selectivity to diesel when operating in diesel mode. With a TSRE configuration the refiner can modulate Stage 1 conversion, Stage 2 conversion, the Recycle Cut Point (the TBP cut point between diesel and unconverted oil), and the conversion per pass in the second stage to meet the seasonal demand for naphtha or diesel. Very careful attention has to be given to the fractionation section (including the gas plant) to build in enough flexibility to swing between the naphtha and diesel modes.

The following catalysts are available from CLG to maximize diesel production:



Service	Catalyst
Stage 1, SSOT ,SSRE	ICR-142 , ICR180, ICR162
Stage 2	ICR-240, ICR-245, ICR-220 (noble metal)
Dual-purpose	ICR-160 , ICR-162 , ICR-180, ICR-230 (naphtha-diesel)

Dr. Tai-Sheng Chou, Principal Hydroprocessing Engineer, Haldor Topsoe, Inc.

Diesel selectivity can be maximized by using diesel selective hydrocracking catalysts and/or optimized process flow configuration. Process flow scheme optimization can improve the potential diesel selectivity significantly. In order to maximize diesel yield, one may consider a two-stage full conversion hydrocracker. The first stage has the pretreat catalysts for reducing the sulfur and nitrogen concentration to the second stage where cracking/conversion takes place. Inter-stage fractionation allows recovery of the diesel cut product from the pretreat stage without further hydrocracking to naphtha and lighter. This diesel cut from the pretreat stage results from any diesel boiling range material in the feed blend or resulting from boiling point shift from hydrotreating reactions. Since the second stage is essentially free from nitrogen and H_2S inhibition, it can be operated at a lower temperature compared to that of a single-stage hydrocracker. Per pass conversion for the second stage has to be limited in order to maximize the diesel yield.

Other Issues:

a) HPNA mitigation for full conversion hydrocracker: Coronenes and Ovalenes tend to accumulate in the unconverted oil recycle loop for the full conversion hydrocracker causing fouling of the catalysts and in the reactor effluent cooling train. One may elect sufficient bleeding for the unconverted oil, hot high pressure separator, and/or high hydrogenation function catalysts to mitigate HPNA issues. Feed management, if possible, may be another option for dealing with HPNA's.

b) Reactor reliability and control for a full conversion hydrocracker: Reactor quench zone design will become increasingly important for the full conversion diesel selective hydrocracker. Reactor temperature needs to be controlled precisely to avoid excess cracking to naphtha. Quench zone temperature control should eliminate any temperature wave propagation from one bed to another. A precise reactor temperature control via an improved quench zone design helps to avoid a temperature excursion or runaway.

c) Catalyst changeout to diesel selective catalysts is a cost-effective means to maximize diesel yield. However, one needs to evaluate process equipment to ensure that the fractionation section can handle the anticipated yield shift.

d) It is also feasible to revamp the existing naphtha hydrocracker to a diesel selective hydrocracker. If the feed is in diesel boiling range, one can use the first stage (pretreat stage) to treat the feed to satisfy ULSD spec. If the scope of revamp is to convert the existing naphtha hydrocracker to VGO to diesel hydrocracker, one needs to check the following equipment to ensure the revamp feasibility.

Sour water separation in the pretreat stage: Due to the small specific gravity difference between the hydrocarbon and the sour water, it may be a challenge to remove sour water completely from the hydrocarbon phase in the high pressure separator (without a hot separator).

Metallurgy in the hydrocracking stage: For many naphtha hydrocracker units, due to the sweet service in the second stage, the second stage reactor may be Chrome-Moly without Stainless Steel overlay. VGO to diesel hydrocracker may require sulfidation protection in the hydrocracking stage reactor and hot feed/effluent exchanger shells due to a higher H2S concentration.

It would also be advisable to check fractionation section for product recovery.

Question 26

What catalytic solutions are available for cold flow property improvement in a high conversion and/or mild hydrocracker?

Hemant Gala/Don B. Ackelson (UOP)

Cold flow property improvement is possible by either selectively cracking long-chain n-paraffins to lower molecular weight n-paraffins or by hydroisomerization of n-paraffins to i-paraffins. In both high-conversion hydrocracking and mild hydrocracking the reactor environment is sour. In this environment, hydroisomerization catalysts that use noble metals for hydrogenation cannot operate optimally. The refiner is then left with the option of using the selective cracking catalysts. Hydroisomerization of diesel in a separate reactor is possible, but becomes rather expensive. UOP has developed a new line of hydrocracking catalysts that do a significant amount of hydroisomerization while cracking the larger VGO molecules to diesel range molecules all within the sour reaction environment. This enables conversion of VGO while producing a higher ratio of iso-to-normal paraffin products. The resulting diesel has significantly improved cold flow properties.

Peter Nymann and Per Zeuthen (Haldor Topsoe)

Topsoe has introduced a new series of hydrocracking catalysts for the maximum middle distillate segment. These catalysts not only provide higher middle distillate yields and excellent hydrogenation, but also target cold flow improvement of all fractions.

The catalysts are based on a combination of tried and proven hydrocracking catalyst technology and special modifications to the carrier material that boost the isomerization activity of the catalyst.

Cloud point improvements of as much as 45ºF of the typical diesel fraction can be achieved when using these catalysts.

The improvement in cold flow properties increases with increasing conversion and unit pressure. Applying these types of catalysts reduces the requirement for dumping kerosene into the diesel pool and even enables increasing the end point of the diesel, resulting in further increasing the diesel yield.

These new catalysts can either be used as the main bulk catalysts or as post-treatment catalyst in the bottom part of the hydrocracker. As opposed to installing conventional isomerization catalysts, due to the high selectivity to diesel and high hydrogenation activity, drawbacks like extensive light ends production and lack of hydrotreating activity are avoided.

Question 27

What technologies are available to upgrade light cycle oil (LCO) and/or heavy cycle oil (HCO) in hydrocrackers? What are the processing conditions for these feeds (catalyst type, hydrogen partial pressure, temperature and/or pressure)? What product yields and product qualities have you realized?

Edwin Yuh (UOP)

Light Cycle Oil (LCO) has become an orphan stream in the refinery with stricter specifications for diesel. LCO requires severe hydrotreating to produce ultra low levels of sulfur and still has low cetane quality. With LCO having lower cetane quality and higher density, blending of it in the diesel pool is limited by the pool quality.

UOP has done considerable amount of work in upgrading LCO.

LCO can also be upgraded in a low pressure, 1000-1400 psig, partial conversion mode so that hydrocracked product is a high octane gasoline blend stock and the unconverted portion of LCO will be ULSD with better cetane than just hydrotreating of LCO. UOP has provided technology to refiners utilizing catalysts which are designed to selectively add hydrogen to boiling ranges other than the naphtha. In some commercial applications, the Unicracking unit can process 100% LCO making heavy naphtha product that can be directly blended into the gasoline pool. The UOP HC-53, HC-24 and HC-190 catalysts are examples of catalysts with this characteristic.

Depending on the objectives of the refiner, LCO can also be co-processed with VGO in a medium-pressure 1400-1800 psig hydrocracker to produce high-quality ULSD. In units processing Heavy Cycle Oil as a co-feed, it is important to be aware of the potential for negative stability impacts when processing such a refractive stream. A HCO stream requires proper selection of catalyst and operating conditions. The end boiling characteristics should be controlled at levels which optimize the benefits of processing the heavier feeds, while limiting the potential deactivation due to heavy polynuclear aromatics (HPNA) compounds. The UOP HPNA RM™ System can be applied to maximize conversion.

In addition to traditional Unicracking units which process significant quantities of LCO and HCO, UOP also offers the UOP LCO-X™ Process which has been specifically designed to provide an aromatic-rich feedstock for a petrochemical complex. These units use specific catalysts and tend to operate at somewhat lower pressure levels, approximately 1000 psig. The process is currently commercialized with one licensed unit. Please refer to NPRA paper AM-07-40 from the 2007 Annual Meeting.

Dr. Tai-Sheng Chou (Haldor Topsoe, Inc.)
LCO and HCO are refractory feed streams. In a conventional process scheme, a hydrocracker is used to upgrade these to naphtha. However, this strategy for converting LCO to naphtha will have to be adjusted in view of the higher profit margins for the diesel range product. A conventional LCO hydrotreater with high aromatic saturation may help to maximize ULSD production in the refinery. Cetane improvement through LCO hydrotreater alone may not be sufficient to satisfy the diesel cetane requirement. However, the debit in cetane from LCO hydrotreating may be compensated for after blending with other ULSD streams in the refinery to satisfy the pool cetane requirement. Further improvement in LCO cetane may be attained through ring opening.

Alternating LCO hydrocracking is a potential scheme to produce aromatic gasoline and ULSD by partially saturating multi-ring aromatics followed by cracking. The unconverted LCO will have reduced aromatics (or concentrated paraffins) to attain a boost in cetane compared to the feed.

Process Conditions	Conventional Hydrocracker	LCO Hydrotreater	LCO Hydrocracker
Conversion %	>98	Minimal	40-60
Catalyst	Hydrotreating/ Hydrocracking	Hydrotreating	Hydrotreating/ Hydrocracking
Hydrogen PP, psi Temperature, F	2500/1700 600-780	1000-1500 650-750	600-1200 650-750
Product	Naphtha to Reformer	ULSD	ULSD/gasoline

Upgrading HCO containing streams requires hydrocracking. Hydrotreating alone is insufficient for the back-end cracking to satisfy diesel product spec.

FCC

Safety

Question 28
Following a shutdown from a power or utility loss, what are your general guidelines and recommended practices for:

- *a. unloading coked or oil-soaked catalyst from the reactor;*
- *b. unloading partially regenerated catalyst from the regenerator?*

Kevin Burton (HOVENSA LLC)
HOVENSA has not experienced a shutdown from power or utility loss in which the reactor had to be unloaded to remove coked or oil soaked catalyst. However, we have experienced similar emergency shutdowns where we have had oil soaked catalyst in the reactor. During these events, we utilize an operating procedure to regenerate the oil soaked catalyst from the reactor. To summarize, the spent and regenerated catalyst slide valves are closed, while riser and stripping steam are maximized to maintain fluidization and assist with stripping of the hydrocarbon. Air flow to the regenerator combustor is slowly increased while monitoring the temperature. If necessary, the air heater is fired and once the regenerator combustor temperature approaches 1300^{o}F, the spent catalyst slide valve is slowly opened to introduce the oil soaked catalyst to the regenerator. The air flow and catalyst circulation from the reactor are adjusted accordingly to maintain the combustor temperature near 1300^{o}F and prevent temperature excursions. As the reactor level starts to decrease, the regenerated slide valve is slowly opened to establish catalyst circulation. Catalyst circulation is maintained until the oil on the catalyst has been burned off.

It should be noted that extreme caution should be taken anytime an emergency shutdown occurs and oil soaked catalyst is suspected. During the unit restart, careful monitoring of reactor/stripper temperature distribution, reactor/regen levels, and catalyst losses should be evaluated, among other variables. We had the unfortunate and costly experience of a significant catalyst carryover event during a restart two years ago which resulted in a three-week shutdown. The primary cause was attributed to the reactor cyclone diplegs being submerged in oil soaked catalyst for an extended period of time during the shutdown, which most likely resulted in defluidized catalyst in the reactor cyclone diplegs and/or stripper. Although we did not have to remove oil soaked catalyst from the reactor, we had to remove it from the overhead reactor vapor line, Main Fractionator, slurry bottoms circuit, exchangers, and run down lines. During the shutdown, we had to hydroblast, vacuum into portable bins, and shovel into drums to remove the oil soaked catalyst.

We never had to unload partially regenerated catalyst into our hoppers. We have always been able to restore circulation and regenerate the catalyst before deinventorying the regenerator.

Scott Flathouse (ConoocoPhillips)
While unloading catalyst from the regenerator after a shutdown, at least one FCC unit within ConocoPhillips has implemented the practice of maintaining steam flow to the flue gas line to minimize the risk of stirring up pockets of unregenerated catalyst and carrying it over to the ESPs.

Question 29
What start-up precautions do you take to avoid water vapor over-pressure events in the slurry circuit of the main fractionator bottoms?

Kevin Burton (HOVENSA LLC)
The key to eliminating over pressure events in the slurry circuit during start-up is to drain all low points frequently and heat up slowly. Draining of low point bleeds is conducted throughout the initial unit steam out, pressure testing, and fuel gas pressurization step of the Main Column before flush or start-up oil is introduced to inventory the unit. Once the Main Column Bottom (MCB) and slurry circuits are inventoried with raw cold oil (about 175-200^{o}F), we start circulation of the MCB circulation and product pumps. During circulation, we continue to drain low points from the slurry circuit, heat exchangers, bottoms pumps, etc., to displace water. It is important to open exchanger bypasses and switch between the spare MCB circulation and product pumps periodically to remove accumulated water. The same procedure is used to inventory, flush, and remove water from the HCO, LCO, and Naphtha sections of the tower. In addition, we also utilize our water wash draw tray in the upper column to aid in water removal.

One half of the MCB Steam Generators are put in heat-up service, and the steam flow is adjusted to maintain an outlet temperature of 220°F. We always maintain outlet temperatures below 250°F until MCB are water free; approximately 2 - 4 hours. Heat-up of the MCB continues at 25°F per hour, holding for one hour at each step until a temperature of 300°F is reached. During the heat-up we continually drain LCO, HCO, and MCB circuit low points until no water is observed and product is draining. Once all the circuits are drained, the MCB temperature is slowly heated up to 500°F at a rate of 100°F per hour. When final instrument and level checks are performed and the Reactor/Regenerator/Gas Con are ready, feed is charged to the unit. This procedure has worked quite well for us, and we have not experienced water vapor over pressure events which caused damage to the slurry circuit or internals of the Main Column.

Question 30

What are the benefits of reactor vapor line sampling and what safety issues have to be considered?

Kevin Burton (HOVENSA LLC)

The benefits of reactor vapor line sampling primarily result from the fact that the FCC reaction mixture samples are collected before entering the FCC Main Fractionator. This allows for isolation of FCC total product before streams from other units can be co-mingled in the FCC recovery section. Also, when there are significant problems with FCC mass balance, the results of overhead line sampling can be used to both determine accurate unit yields and to diagnose the source of the mass balance inaccuracies. Reactor vapor line sampling provides the ability to complete an FCC unit variable study in one day, which eliminates the need for fractionator line-out (unless there is some form of recycle) and minimizes the potential for feed quality shifts during the variable study. Reactor vapor line sampling, also known as Reaction Mix Sampling, is an effective tool for tuning process models and for determining the potential benefits of various unit upgrades.

At HOVENSA, we sampled from the Main Fractionator inlet to identify the degree of post-riser cracking that was occurring on our unit. This test was completed to determine the amount of conversion loss that would result if we modified our riser termination from the original vented riser design to an alternate reactor termination device. Test results from the vapor line sampling significantly altered the economic justification, as the conversion differential across the reactor overhead line was determined to be just half of what was originally projected.

Reactor vapor line sampling requires the availability of an appropriate tap with double valves. At the end of the second valve, a flange with a welded packing gland is mated to the probe assembly and provides the seal between the unit and probe. In order to insert the sample probe it is usually necessary to drill out the coke deposits which fill the sample tap from the reactor vapor line to the first valve. First, a flanged coke drill assembly with a packing gland is used to clear the sample port. After the sample port is cleared, a small diameter sample pipe is inserted through the flanged probe assembly into the sample tap for sample collection. A needle control valve is used to control the flow of reactor vapor out of the probe and through an air-cooled coil. The reaction products are collected in special sample bags. After the sample bags are equilibrated, the liquid and vapor portions of the sample are separated and collected for analysis. Just as with any sampling of hot hydrocarbons, the operator must be outfitted with thermal gloves and a face shield, in addition to standard PPE. The sample taps are often located in difficult to access places, so it is critical that there is sufficient space for quick egress from the sample site if necessary. We recommend that the samples be collected by someone experienced in the techniques, since small differences in technique can influence the results. When we last performed this type of testing, we placed a plug of insulating fiber in the sample tap near the Main Fractionator entrance so that the amount of coke formed in-between samplings would be held to a minimum, and could be safely and easily cleared for sampling on the run if desired.

Catalyst

Question 31

For refiners who do not have in-house catalyst evaluation capabilities, how are catalyst selections made? Discuss: frequency of evaluations, use of testing results from catalyst suppliers or third party laboratories, back-to -ack unit trials, and catalyst change post-audit practices.

Scott Flathouse (ConoocoPhillips)

ConocoPhillips does perform in-house catalyst evaluations. For catalyst selection, we do not solely rely upon the methods of catalyst vendors because of lack of standardization in the testing. We generally do not perform back-to-back unit trials due to the significant time involved in changing the catalyst inventory. ConocoPhillips does conduct post-change audits.

Question 32

When would you consider using a catalyst additive to address fluidization problems?

Question 33

How much gasoline sulfur reduction can be achieved with the use of additives? Have you seen sulfur reduction in the LCO fraction? How well do these additives perform? Where does the sulfur end up?

Environmental

Question 34

On some older FCC units' designs, relief valves on the reactor and main fractionator discharged to the atmosphere.

a. What are the current design practices?

b. What are the drivers and economic implications of modifying an older system to be consistent with these current design practices?

Scott Flathouse (ConoocoPhillips)

A. Current design practices for relieving the reactor include relieving to a flare system, relieving back to a feed surge drum (which in turn relieves to a flare system), or installation of a High Integrity Pressure Protection System.

B. ConocoPhillips does have some refineries with atmospheric relief devices on the reactor or main fractionator. There is an effort underway within ConocoPhillips' downstream operations to review all atmospheric relief devices and develop mitigation plans to continue to reduce risk. Recent process safety incidents in the industry are driving this effort.

Process Technology

Question 35

What is the minimum information with regard to feed properties required to predict FCC yields?

Ed MacNeel (Aspen Technology, Inc.)

Feed properties required to calibrate FCC yield models are:

- Feed source (VGO, HT VGO, resid, coker, syn crude)
- Gravity
- Distillation (e.g. D2887, D86, or D1160)
- Sulfur content
- Total nitrogen
- Feed carbon – Conradson or Ramsbottom
- Metals (Cu, Fe, Na, Ni, V),

It is strongly recommended that some indicator of aromaticity of the feed be included in addition to the above analyses. Possible properties include refractive index or aniline point. While these may be estimated using gravity

and distillation correlations, a direct measurement is always preferable. Viscosity is also useful if accurate data is available.
Aromatics (di, tri, tetra) are important to predict coke yield, close the regen heat balance, estimate conversion levels and the over-crack point. In multi-lump yield models this information can be helpful in predicting LCO and heavier yields. Higher aromaticity pushes the over crack point (riser temperature) to the left (lower temperature).

Conradson carbon is used as a part of the coke calculation in the risers, reactor, and regenerator. Nitrogen and the metals are used to calculate catalyst activities and catalyst deactivation rates.

Including other feed properties help to predict additional helpful FCC information:

- HPLC – more commonly used; can help in determining feed aromaticity
- GC/MS
- NMR
- NIR

Question 36
What are the key parameters that determine coking and fouling tendencies of the main fractionator bottoms circuit? How have you established the target values for these key parameters? What are typical values for these key parameters?

Question 37
What are the typical sulfur contents of FCC products for various FCC feed types and sulfur levels?

Ed MacNeel (Aspen Technology, Inc.)
When predicting FCC feed sulfur distribution to products two key feed types include:

- Hydrotreated gas oils (HT GO)
- Un-hydrotreated gas oils (GO)

Virgin gas oil feed sulfur will typically crack to H_2S. Hydrotreated gas oil feed typically has the easily-crackable sulfur already removed by the hydrotreater and the remaining refractory sulfur will pass through the FCC and appear in cycle oil cuts. Sulfides tend to crack to H_2S while thiophenes remain in high molecular weight structures that concentrate in the cycle oils. Benzothiophenes and di-benzothiophenes tend to concentrate in the LCO, bottoms and coke. Mercaptans are found in the feed, but can also be produced from other sulfur species as a result of cracking reactions.

Typical product sulfur levels (wt% sulfur basis feed):

	HT GO	**GO**	Comments
Dry gas	30-40	40-60	as H_2S
LPG (C3/4)	<1	<1	mercaptans, sulfides
Gasoline (C5+)	2-5	3-8	all sulfur types
LCO	20-30	15-25	Benzothiophenes
Bottoms	25-35	20-30	Di-benzothiophenes
Coke	6-12	3-8	

For residual oil feeds, generally less of the sulfur will exit as H_2S and more will go to cycle oils and coke. This is because a higher percentage of the feed sulfur is typically thiophenic. This may not be the case, however, for some highly paraffinic resids.

Scott Flathouse (ConoocoPhillips)

	Refinery A	Refinery B	Refinery C	Refinery D
Feed Type	100% Hydrotreated GO	Hydrotreated GO	0% Hydrotreated 25% 1050+ 75% SWEET RESID	50% Hydrotreated GO 50% ATM Resid
Feed Sulfur Content	45 ppmw	2400 ppmw	4600 ppmw	180,000 ppmw
Dry Gas	0.03 mol% H_2S			1.2 mol %/1.8 wt% H_2S
Naphtha	5 ppmw	240 ppmw	470 ppmw	Heavy - 240 ppmw Light - 120 ppmw
LCO	180 ppm	4500 ppmw	4300 ppmw	200,000 ppmw
HCO	-	-	6100 ppmw	-
Slurry	-	10,000 ppmw	7700 ppmw	430,000 ppmw

Question 38

How often do you evaluate upgrading the FCC's process technology versus a maintenance-only turnaround? Is this considered every turnaround cycle?

Scott Flathouse (ConoocoPhillips)

ConocoPhillips' unit review process is designed to evaluate technology upgrades for every turnaround. This program requires getting started on FEL-0/1 conceptual studies early following the most recent turnaround (within 6-12 months) so that sufficient time is available for FEL studies and turnaround planning. ConocoPhillips has a centralized Refinery Technical Services group that leads the unit reviews. Participation in the unit reviews includes process engineering, planning and economics, environmental, maintenance, reliability, and operations personnel. Individuals from other refineries are called upon to participate as well.

Question 39

What energy key performance indicators (KPIs) do you monitor for the FCC?

Scott Flathouse (ConoocoPhillips)

Some of the KPIs related to energy in the FCC are as follows:

- Total pressure drop (air blower discharge to flue gas stack)
- Excess O2. We try to keep this under 3%, and around 1% is the target. Too much air wastes energy at the air blower driver.
- Overall steam balance; energy consumed (coke burn) vs. energy produced (steam make).
- Flue Gas Boiler outlet temperature. A fouled flue gas boiler results in poor heat transfer and excessive heat loss out the stack.
- Feed temperature. From an energy standpoint, it is best to receive feed hot directly from upstream units. FCC feed that is sent to intermediate storage is often cooled, then re-heated before it is charged into the FCC.
- Main fractionator gasoline and LCO 5% - 95% points. Using too much reflux can cause excessive heat loss to air.
- Slurry boiler U factors. The slurry boilers should be monitored to determine the need for cleaning.

Here are some energy KPIs that are related to specific equipment that could be in FCC service:

- If a surface condenser turbine is used, then vacuum on the condenser should be monitored for leaks and poor cooling.
- Efficiency of expanders should be monitored for spalling opportunities.
- Furnace efficiencies. Preheat furnaces, superheaters, or fired reboilers should be monitored for stack temperature, excess O2, and overall efficiency as part of an energy management program.

Question 40

What are the options for increasing capacity of the main air blower?

Scott Flathouse (ConoocoPhillips)

If the air blower is a constraint for the FCC, then some simple evaluations should be performed first to identify low-cost improvements. If the blower has inlet dampers, then they should be checked to make sure that they are fully open when the controller output calls for 100%. One ConocoPhillips engineer cites an example where he was able to gain 5% capacity on the air blower by unbolting the actuator and manually opening the damper further. If there is an inlet air filter, it should be checked for cleanliness. Also, the air filter and inlet dampers could be changed out to a lower dP design. A pressure survey on the air blower discharge line will reveal losses due to fittings and pipe runs. Check valves on the air lines should be properly (not excessively) weighted.

If the air blower is driven by a turbine, the steam supply and discharge conditions should be monitored to ensure that they are close to design conditions. It is not unusual to find the turbine designed at steam header pressure but the line loss from header to turbine inlet is large enough to have an effect. In this case tweaking up the header pressure and maybe putting in a parallel steam feed line to reduce pressure loss can help. If the turbine is a condensing turbine consider putting a small refrigeration unit on the water to the condenser. In the summer this can improve power significantly.

Operationally, if there is no cyclone or regenerator velocity constraints the pressure of the regenerator could be lowered thus increasing the capacity of the blower. Also, the reactor/regenerator pressure balance could be evaluated to see if lower slide valve dPs could be used, thus reducing the regen-reactor pressure differential. Improving regenerated catalyst standpipe fluidization to allow lower dP is not always an obvious solution, but it is an option.

Capital improvement options include upgrading the blower itself. Sometimes the blowers rotating assembly can be replace with an upgraded design or the rotor speed can be changed. Most times these changes would mean upgrades or replacement of the gearbox and driver since more horsepower is required. Another option would be to use oxygen enrichment up to 27% O2.

ConocoPhillips has demonstrated success in increasing the capacity of the main air blower by installing chillers on the air inlet of the blower. In July, 2001, an inlet cooling system was installed at the blower suction at a COP FCC Unit with a blower constraint. Operational results delivered an average charge increase of 5% over prior throughput. Aggreko North America designed and provided a system capable of cooling FCC regenerator air from 97°F to 55°F. This system was designed to provide delivery of up to 8.5% more air mass to the FCC during the heat of summer.

Based on the success of this chiller system, another FCC unit at a different refinery installed Aggreko chillers in 2007 and gained approximately 5% capacity on the air blower. They also saw benefits in cooling of the regenerator bed. Lowering the bed temperature helped alleviate their afterburn constraint.

Reliability

Question 41
Both blinds and valves have been used to isolate the reactor from the main fractionator. What has been your experience with each?

Scott Flathouse (ConoocoPhillips)
Several FCCs within ConocoPhillips use gate valves which are opened during start-up. One of the FCC units at Sweeny and both units at the Ponca City refinery have Zimmerman & Jansen, Inc. double-disk isolation devices. In contrast to a conventional gate valve, the double-disk blinding device is not susceptible to coke build-up, and generally can be opened or closed after start-up. The device consists of two disks with a steam purge between them. The primary incentive for installation of the double-disk blinding device is a reduction of risk compared to pulling a blind during start-up. There is an additional advantage in that the time required for start-up can be reduced with the double-disk blinding device, particularly if there is a problem and the main fractionator needs to be isolated from the reactor.

At one of our refineries, shortly after start-up after they installed the Zimmerman & Jansen double-disk isolation device, they lost both unstablized gasoline pumps and had to take the charge out and go on circulation. After circulating for an hour they closed the blinding device, therefore keeping the steam out of the fractionator section. Without the blinding device, all the steam from the reactor would have ended up in the fractionator section and the operators would have to drain water for hours prior to re-introducing charge. With the blinding device they had very little water and were able to put the charge back in sooner. Another big advantage was being able to pre-load the fractionator section with gas-oil and start heating up the fractionator section while heat soaking the regenerator & reactor section. They estimated a reduction of 3 to 4 days from charge in to on-test product compared to the prior practice of pulling a large isolation blind.

Question 42
The use of hydrogen induced cracking (HIC) resistant carbon steel has successfully mitigated hydrogen blistering and wet H_2S cracking over the last few years. We have been running about six years without any internal surface blistering. What future inspection requirements should be put in place? How often should the equipment be inspected and which inspection practice should be followed?

Kevin Burton (HOVENSA LLC)
HOVENSA does not use HIC resistant carbon steel. We use a fine grain killed carbon steel, and after Post-Weld Heat Treatment (PWHT) is performed, a WFMPT inspection is conducted in the shop. Currently, we have 15 years of operation on our FCC and have not experienced cracking or blistering with any of our vessels. Cracking generally poses a bigger problem than blistering in most FCC units. However, with proper water wash and use of a promoted catalyst, the cyanides can be mitigated and the corrosion mechanisms which facilitate blistering can be significantly reduced.

While HIC resistant steels have been found to be resistant to wet H_2S damage in “mild” hydrogen charging services, the real concern is with “severe” charging environments. There have been cases where HIC resistant steels have been used in severe services and Stress Oriented Hydrogen Induced Cracking (SOHIC) developed, but it was not preceded by or associated with the telltale signs of blistering. This is not necessarily a good thing. Since blisters generally have no effect on structural integrity because there is no loss of hoop stress, it can be used as a warning sign that HIC/SOHIC damage may be present in a vessel. As such, we use the blisters as an early warning detection system to indicate that something is not right with our process conditions. This would trigger us to take corrective action with water wash or perform additional related NDE to look for more serious SOHIC problems. With the elimination of this early warning system we then run the risk of getting a false sense of security because the field inspectors do not see blisters so they do not incorporate the additional NDE.

Equipment inspection requirements and frequency should be evaluated on a case-by-case basis. We utilize an API Risk Based Inspection (RBI) Program and rely heavily on our past and current inspection records to determine the extent of NDE required based on the severity of the system. For severe hydrogen or wet H_2S services, the equipment should be inspected during each turnaround cycle or as dictated otherwise by RBI. We incorporate such NDE techniques as WFMPT, UT, or Automated Shear Wave on a percentage of the weld seams, shell, and heads per our RBI requirements. If discontinuities are found we will weld map the area and if warranted will provide external inspection during the run cycle.

In summary, there has been extensive testing and much debate over the last 20 years which indicate that there may not be a significant improvement in these ″resistant steels″ as compared to other standard fine grained killed carbon steels. We would recommend paying closer attention to the materials used, welding techniques, PWHT procedures, pre-welding Non-Destructive Examination (NDE), and water wash. This probably offers a better value than the selection and use of the HIC resistant carbon steel.

Question 43

What methods and best practices do you recommend for on-line cleaning of equipment in flue gas service (e.g. flue gas coolers, boilers, SCRs, ESPs, etc.)?

Scott Flathouse (ConoocoPhillips)

ConocoPhillips' FCC units typically use periodic injection of abrasive media to clean waste heat boilers (flue gas coolers). This media includes black slag (sandblasting sand), granulated clay absorbent (kitty litter), e-cat, or walnut shells. Expanders are cleaned on-line with walnut shells. Spalling is another technique utilized for cleaning expanders. For ESPs, rappers are typically used. Steam soot blowers have been used for CO boilers.

ConocoPhillips has had some less than favorable historical experience with sonic horns for cleaning flue gas boilers.

Question 44

What type(s) of isolation valves do you use for the wet gas compressor? How are they actuated?

Kevin Burton (HOVENSA LLC)

Currently, HOVENSA has KF Industries Series P Ball Valves installed in the 1st and 2nd stage suction, discharge, and spillback of the Wet Gas Compressor(s). There are a total of 18 valves with sizes ranging from 12 inch to 36 inch and they have been in service for 15 years. During this time, we have experienced good reliability with these valves and have had no major repairs or service conducted since installation. The valves have undergone our normal shop/field service during planned turnarounds. More recently, however, these valves have begun to show signs of deterioration in the valve seat and ball which has restricted the valve to fully seal and provide positive isolation. Due to the fact that rebuild/refurbish kits are unavailable and the valves are no longer supported by the vendor, we have decided to upgrade these valves with a different type during our next scheduled turnaround. The valve(s) that we have selected for replacement is the Cameron Trunnion Mounted Ball Valve and includes NACE MR-0175 trim. This valve was selected because it offers the following advantages over our current valves:

- Rotating Seat - The seat rotates 15^o each time the valve is operated, exposing a fresh sealing surface which greatly extends the life of the valve.
- Double Block and Bleed - The valve design allows for block and bleed of the body cavity with the ball in both the open and closed position. This is intended to test the valve integrity. If the valve does not blow down, this indicates that the seat is leaking.
- All Welded Construction - The fully welded ball valve eliminates body flanges and thus reduces overall size and potential leak paths.
- Secondary Seat Seal Injection System - The valve incorporates a secondary seat seal injection system that allows for the routine and/or emergency flushing of the seats.

We utilize both manual gear operated and motor operated isolation valves around our Wet Gas Compressors. For the valve sizes ranging from 12 inch to 16 inch, we use gear operated valves, and for the larger valve sizes ranging from 20 inch to 36 inch, we use remote-operated EIM Electric Motor Operated actuators.

Question 45

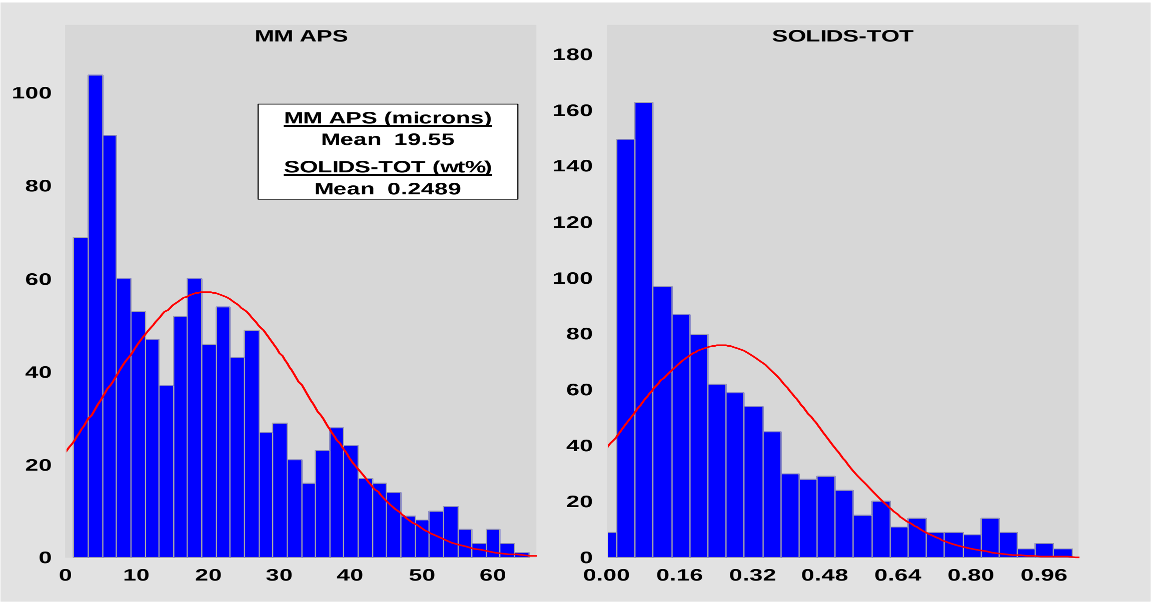
What is an acceptable range for wt% ash in the main column bottoms circuit, what values are typical, and what is the significance of particle size distribution (PSD)? What types of slurry pumps have proven reliable in this service?

Kevin Burton (HOVENSA LLC)

Typical "good" values for ash content in slurry run in the 0.10-0.25 wt% range. However, as units process more hydrotreated feed and the slurry yield drops, this can run up to 0.5 wt% due to the solids concentration increase in the bottoms circuit. Ultimately, slurry product specification and erosion of the slurry circuit hardware defines the acceptable upper limit; while erosion of pump internals, control valves and slurry exchanger tubes are the typical consequences of an overloaded slurry circuit. As ash increases, life expectancy of slurry circuit equipment will be shortened. This acceptable upper limit will vary from unit-to-unit depending on slurry circuit velocities and additives used; however, 0.5 wt% is a good benchmark for the acceptable upper limit of ash in slurry.

The Particle Size Distribution (PSD) of the ash will give indications of catalyst attrition problems and/or cyclone performance. When looking at the solid particles recovered from slurry, if a significant portion of the distribution is in the 0-5 micron range, an attrition source may be indicated. Alternatively, if the distribution contains an appreciable portion of >30 micron particles, this could indicate some compromise in cyclone performance. This can be observed slowly over the course of the run due to erosion of the cyclones or can happen quickly when the cyclones are run outside optimal velocities, become plugged/obstructed, or reactor levels change outside acceptable limits.

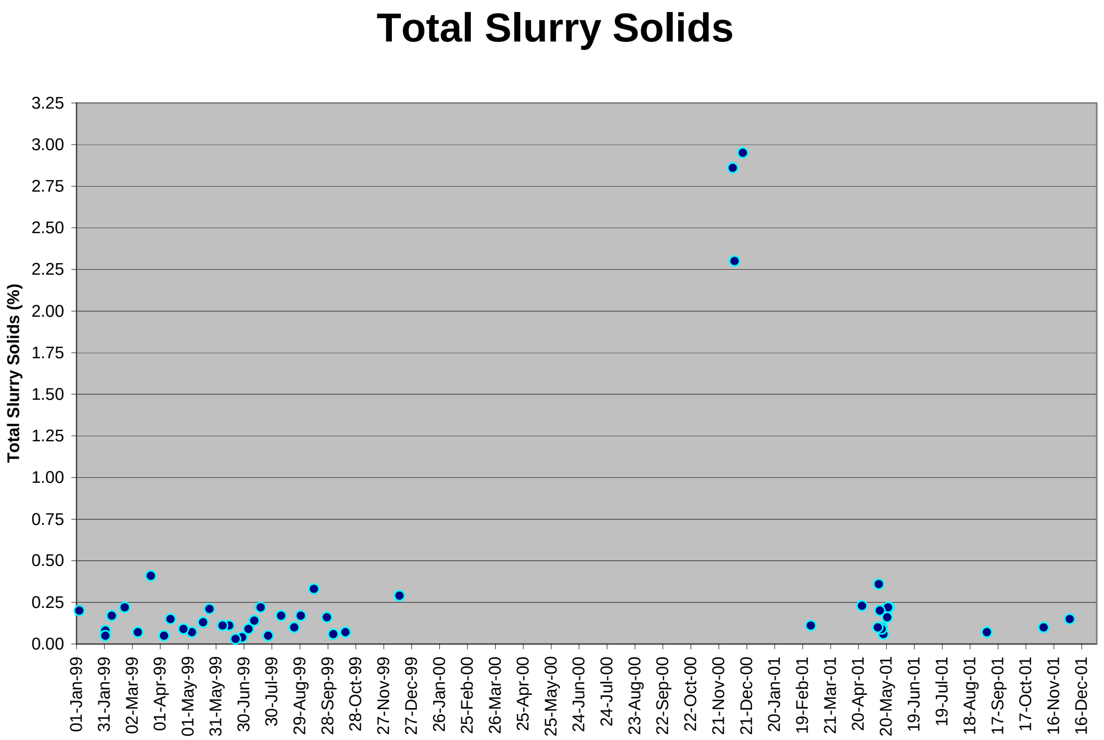
The following data was provided by GRACE Davison and is a representation of typical industry average showing the average particle size and total solids for slurry samples received. The data is a compilation of 800+ slurry samples analyzed by their lab in 2007 and 2008 YTD for North American refineries who submitted samples.



As shown in the figure, the average particle size was 20 microns and total solids content was 0.25 wt% for the slurry samples received. The y-axis is the number of samples which showed the corresponding result on the value axis. The average particle size plot shows indications of tri-nodal distribution. The first peak around 4-6 microns could represent units that are experiencing attrition problems. The second peak around 18-22 microns represents the typical normal distribution. The third peak around 38-40 microns and greater is an indication of units struggling with cyclone retention.

Scott Flathouse (ConoocoPhillips)
Slurry samples should be taken at least once a month to establish a good baseline PSD when everything is working well.

Some of ConocoPhillips's refineries have experienced a variety of slurry particulate loadings. When one of the FCC units experienced a plugged reactor cyclone dipleg, significant catalyst carryover into the main fractionator resulted. The total slurry solids were 2-3% for several weeks until turnaround. Upon inspection, there was no abnormal wear noted on the slurry pumps or circuit. This unit does not have the recommended low-speed slurry pumps. The chart below shows typical and high slurry solids loading for the unit.



Other ConocoPhillips FCC units have also experienced high concentrations of slurry solids for extended periods without detrimental effects. One unit had not seen erosion of the slurry pumps when they ran in the 0.5% range for close to a year. They continued to operate until the scheduled T/A.

For our slurry pumps, we use a Lawrence API 610 fully lined horizontal centrifugal pump. It contains a through-hardened HC-250 liner (25% Cr) inside a carbon steel case. This material is an ASTM 532 class III Type A white cast iron and has a hardness of 400-600 BHN, depending on if it is cast or annealed. They are designed for severe duty service, and although more expensive initially, they eliminate problems of erosion. With this type of pump, we have not experienced erosion in 15 years of service. These pumps are also used in our Wet Gas Scrubber circulating system, which has an equal or higher percentage of solids loading. The pumps are designed as a low speed, 880 RPM pump with total encapsulation of the slurry within the hardened material. We have experienced periods of extreme catalyst loading in the systems and they look brand new when opened. Since the material is hardened, it is inherently brittle and therefore, must be operated within a range of 50-75^{o}F/hour temperature change during startup or shutdown.

Question 46
What are the key parameters that influence your company's philosophy regarding replacement of refractory in a coking environment? Are these parameters different for cast, gunned, or packed refractories? Discuss recent developments in refractory that improve refractory service life in coking environments.

Scott Flathouse (ConoocoPhillips)
Concerning replacement of refractory in coking environments, it, of course, depends on the service environment. On disengager (or reactor) walls, spalling is usually the main problem, and the material has usually been gunned. We would replace anything that was less than 50% of full thickness, and often anything that has lost 1.5" out of an original 4" thickness. In a riser, pinch spalling and erosion are the main problems. These applications are usually, but not always, cast or gunned. Again, anything less than 50% - 65% of full thickness would be replaced. Infrared scans can be helpful in identifying areas that may be a problem prior to shutdown. Installing anchors on a tighter pattern has helped some plants reduce spalling of gunned or cast refractory.

On a riser, it seems to help if the refractory can be designed so that the shell stays cool enough to keep the refractory hot face in compression. If the shell gets too hot, grows too much, and then tends to put the refractory in tension, then cracking is more of a problem. Cracks may coke up and cause additional spalling problems.

In cyclones, if the refractory is worn down to the clinches or tabs of the anchors, we would recommend replacement. In cyclones in a coking environment, often the anchors wear down faster than the refractory. If the hex, flex, S-bar, Curl, or equivalent anchors are worn down by 50%, even though the refractory itself is still full thickness, we often would consider replacement. Some of the plants have had the anchors wear down enough that the refractory has come loose from the cyclone, even though it is still near full thickness. Some of our plants have had good success with using Resco AA-22 Brush Mix to coat an area where the anchors were worn, but the refractory was still near full thickness. This has tended to fill in the areas on the tops of the anchors and retard further wear. Please understand that it is not a cure-all or absolutely 100% effective, but it has been successful in several plants.

The main thing about using hex or flex in a coking environment is to ensure that it is welded in 100% of the cells, not just in every other cell. If not welded in every cell, the coke can tend to push it off the wall.

Question 47
For refiners who operate reactor strippers with structured packing, describe the mechanical condition of this equipment when inspected during turnarounds. Were any repairs or changes required?

Scott Flathouse (ConoocoPhillips)
ConocoPhillips has the structured packing at the FCC in one refinery with one 4-year TA completed. About 2 years into the run, the steam distributor directly under the stripper packing failed and jetted steam up at the bottom packing on one side. Upon inspection during the next turnaround the packing was found to be in nearly new condition on most of the layers except the bottom one or two layers directly above the steam jet. The packing support and one layer of packing were replaced only because of the steam problem. If there would have not been a steam distributor problem the packing would have been fine.

The structured packing was also installed in another ConocoPhillips refinery in 2006. There has been no inspection as of yet, but there have been no operational problems.

CRUDE & VACUUM DISTILLATION and COKING

Safety

Question 48
What precautions do you take when sampling hot streams such as reduced crude or streams which contain high concentrations of hydrogen sulfide?

Dennis Haynes (NALCO Energy)
In taking samples of hot hydrocarbon streams, such as a heavy gas oil or reduced crude, it is best to find a point in the rundown line where the samples has been cooled to below flash point conditions. If this is not possible, self-contained sample system or a cooling system would be recommended. Typically, due to viscosity issues when these stream temperatures are reduced, they are sampled at temperatures that have burn risks; therefore, persons taking the samples should have appropriate thermal protective clothing.

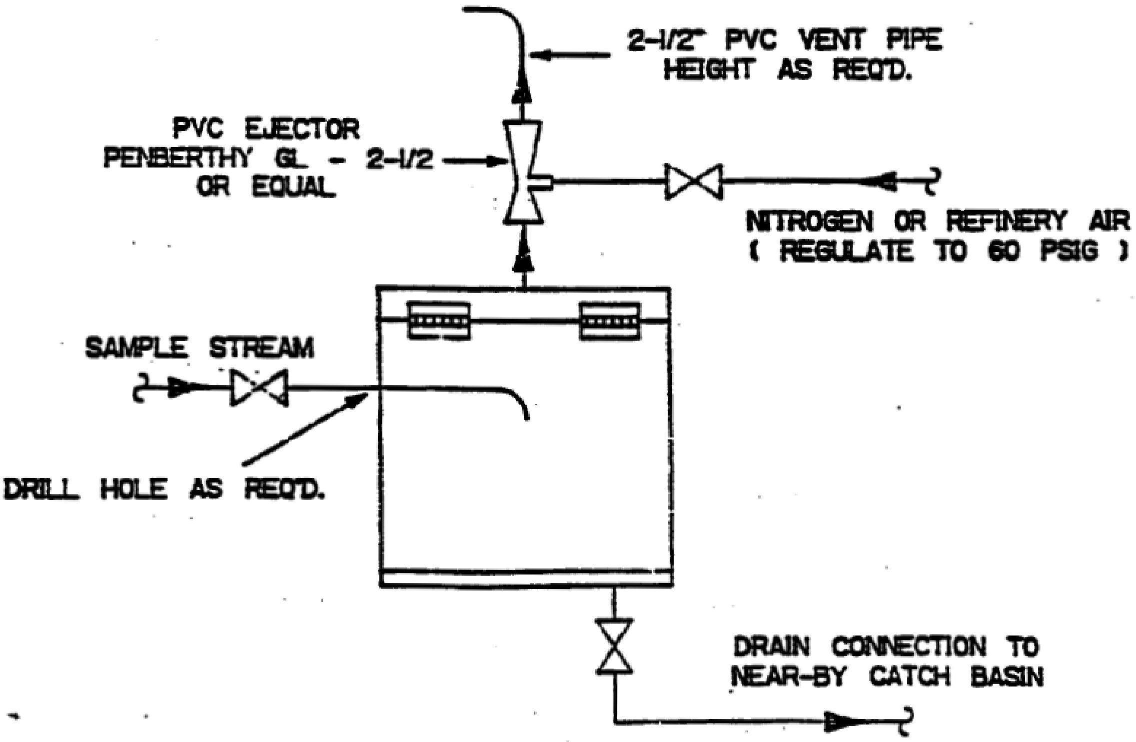
For a stream such as a desalted crude sample, a sample cooler is a requirement. There is a representative experience from one location without a cooler where multiple samples were taken at various flow rates through the samples point. The results of this provided a correlation that slower sample flow had less flashing and so more Basic Water in the crude obtained. This was the result of the crude being hotter than the vaporization temperature of water at this point. To eliminate this type of error, proper sample cooling is critical.

For many streams where hot hydrocarbon samples are taken frequently, sample continuous flow loops are put in place to reduce the amount of sample that needs to be drawn to purge the sampling line. The purpose is to improve how representative the sample is. The flow loops are then connected to sample cooling coils, which then flow into sampling vessels.

To eliminate hydrogen sulfide exposure and minimize hydrocarbon vapor release, a variety of systems are used. One strategy is to use the system described above with a continuous flow loop, sample cooler, and small diameter piping to minimize the total amount of sample required. An addition to this type of system is where the sample vessel is placed in a small, evacuated box to remove vapors and gasses emitted during the sampling process. Another version of this is to have the sample introduced into the sample vessel through a diaphragm with a purge line to enclose the entire sample within the sample vessel. Use of a personal hydrogen sulfide monitor is highly recommended whenever working in an area that may result in hydrogen sulfide exposure.

For a system like the desalters, where it is important to be able to visually inspect the quality of the tri-lines, larger forced-air sampling boxes, similar in appearance to small laboratory fume hoods have been put into place at some locations. [See drawing below] The air draft through the box minimizes exposure to hydrogen sulfide and hydrocarbon vapor while still allowing the operator to inspect the quality and properties of the interfacial layer in the desalter.

There are locations where the hydrocarbons or water samples to be taken are very sour, and the evolution of hydrogen sulfide is beyond acceptable. At these times, sampling requires either an enclosed sampling system or some locations have procedures in place that rely on SCBA PPE and a dedicated safety watch during sampling.



Mitch Moloney (ExxonMobil)

The main concern with sampling hot streams is exposure to flashed vapors, such as light hydrocarbon and H2S. Key features of a sampling system are:

- Use of a steam or tempered-water cooler to bring the temperature to less than 475°F if the process temperature is hotter than that; the cooler should be installed in the fast loop line rather than in a separate take-off line that requires flushing after each sample.
- Use of a Strahman or "Texas Sampling System" valve close-coupled to the sample line. A "regular" normal-body Strahman design be used in the fast-loop piping. Extended body Strahman valves used in heavy-wall-piping can distort and leak through the packing. It is also important to have the valve piping well supported to avoid any torque on the Strahman body.
- Installation of the sample valve as a take-off on a fast loop line installed in parallel with a flow control valve or other pressure drop device.
- Use of a globe valve downstream of the sample valve in the event the sample valve leaks and to allow throttling of the sample line flow.
- Use of steam tracing or jacketing and insulation to prevent line pluggage.
- Flushing connections and isolation valves around the sample valve to allow the sample valve to be taken out of service for maintenance (these would normally be provided on the fast loop sample line.
- The capability to fill one gallon (or 1 quart if desired), 5 gallon and 55 gallon sample containers.
- The sample container should be rated for the sample temperature and allow safe handling in the field and the laboratory.
- Proper shielding to protect the sample taker
- Adequate lighting and proper sample station ingress/egress

Question 49

How do you maintain availability and reliability of coke drum relief valves? What inspection frequency and mitigation strategies are adequate to minimize accumulation of coke in the relief valve inlets?

Mitch Moloney (ExxonMobil)

- The PRV’s should be installed on a dedicated coke drum nozzle or nozzles.
- Inlet nozzle(s) should be self-draining to avoid accumulation of material
- Block valves should have their gate stems oriented horizontally and should be car-sealed open.
- Proper steam purging on the suction (and sometimes discharge) sides is needed to prevent accumulation of foulant.
- Cleanout flanges should be provided in the discharge piping to allow inspection.
- Use at least two PRV's to allow staggered set points and contingency balancing
- Valves are usually large and require trolley rail chain hoist access for maintenance
- The PRV’s should be verified to have completely reseated should they have opened and released hydrocarbon. This can be done by doing a gas test, if there is sufficient pressure on the discharge side. If not the valves should be individually shopped and bench tested. If they opened during the cyclic steam test, reseated and coke drum pressure holds, no further verification is needed.
- If the valves opened as part of a coke drum foamover, cleaning and inspection of the inlet and outlet side is needed. Boroscopes or “crawler” cameras can be used.

Desalting

Question 50

What are some of the issues with respect to desalting bitumen-derived crude? Specifically, discuss BS&W and salt, and methods to enhance their removal.

Dennis Haynes (NALCO Energy)

There are specific challenges to processing bitumen-derived crudes. These challenges are gravity and viscosity of the hydrocarbon, asphaltene stability issues, and solids issues.

The heavier gravity and higher viscosity of the crudes can cause limitations on the desalter operational capacity. The relative velocity of a water droplet falling through a hydrocarbon system is proportional to the density difference between the water and hydrocarbon at temperature divided by the viscosity of the hydrocarbon. This is known as Stokes Law:

V=K(pw-po)/u
K = constant
pw = density of water at temperature
po = density of hydrocarbon at temperature
u = viscosity of hydrocarbon at temperature
An example of what this equation means is as follows:
“30 API” @ 100 °C (212 °F)
pw = 0.97, po = 0.85, u = 3.8
“22 API” @ 100 °C (212 °F)
pw = 0.97, po = 0.88, u = 11 %3861002230=×*VV*
So, settling time difference at an equivalent temperature for differing hydrocarbon densities and viscosities can be significant.

Due to this, many of the bitumen-derived crudes are blended with solvents to improve their transportation and processability. Examples of these solvents would be condensates, conventional crudes, synthetic crudes, and naphtha streams. The challenge with this is that the choice of and quantity of diluent potentially may adversely impact the stability of the asphaltenes in the bitumen matrix. Changes in solubility of these asphaltenes are a driving force for agglomeration, which would result in formation of asphaltene particulate in the hydrocarbon feedstock. This may result in challenges regarding processing in the desalter and also fouling in the crude unit preheat and furnaces. The following is a representation of asphaltenic build-up on the surface of a water droplet:

It can be seen how particulate on the surface of the water droplet can serve as a barrier layer around the droplet. Some of the bitumen-derived hydrocarbons are dried of production water via a thermal flashing process. This reduces the amount of water in the heavy hydrocarbon; however, as the brine water is driven off, some of the residual salt will remain as hydrocarbon coated crystals. This crystalline material is more difficult to contact with wash water in the desalting process and may result in increased chlorides in the atmospheric distillation overhead system or result in increased caustic usage for chloride scavenging.

In some of the bitumen-derived crudes, there are high amounts of solids with small average particle sizes. In some cases, the solids loading has been reported as many hundreds of pounds per thousand barrels of crude. A large portion of these solids are so small that they will not be retained by the typical sized filter paper (i.e. <0.45um) used in many of the filterable solids tests. These solids going into the water phase at larger quantities may result in darkening of the desalter effluent. It is important to differentiate if the discoloration of the effluent is solids or hydrocarbon or a combination. In some cases, it may only be related to solids removal and not oil under carry. With the increase in solids loading, it is important to optimize mud-washing practices. This includes confirming correct flow rate of mud wash water to the headers, optimization of mud wash duration and increased frequency. In some cases, it has been found to be beneficial to add break tanks to accept the mud wash effluent. The purpose of the break tanks is for settling of solids and resolution of entrained hydrocarbons in order to protect the waste-water treatment facilities. This is due to the oil-laden solids and increased mixing of the desalter water phase required to remove the heavy sludge from the desalters.

It has been found that increasing the wash water rate to the desalters has been beneficial when processing bitumen-derived crudes. In some cases, the wash water rates have been found to be optimal at levels near or greater than 10%. However, when employing this strategy, it is critical to define that the desalter vessel has adequate residence time in the aqueous phase for resolution of entrained hydrocarbons. Also, for desalter operations, it is critical that the appropriate emulsion breaking strategy be put in place. This may include primary (oil phase) and secondary (water phase) chemistries, yet may also include crude preconditioning in the tank farm, crude dewatering, and other appropriate chemistries.

Todd Sandifer (Marathon Petroleum Company)
Bitumen-derived crudes processed at one of our refineries contain 1 to 1.5 times the level of filterable solids that we typically observe and we have experienced problems associated with asphaltene destabilization which results in oil under carry and high oil and solids loading in the effluent water.

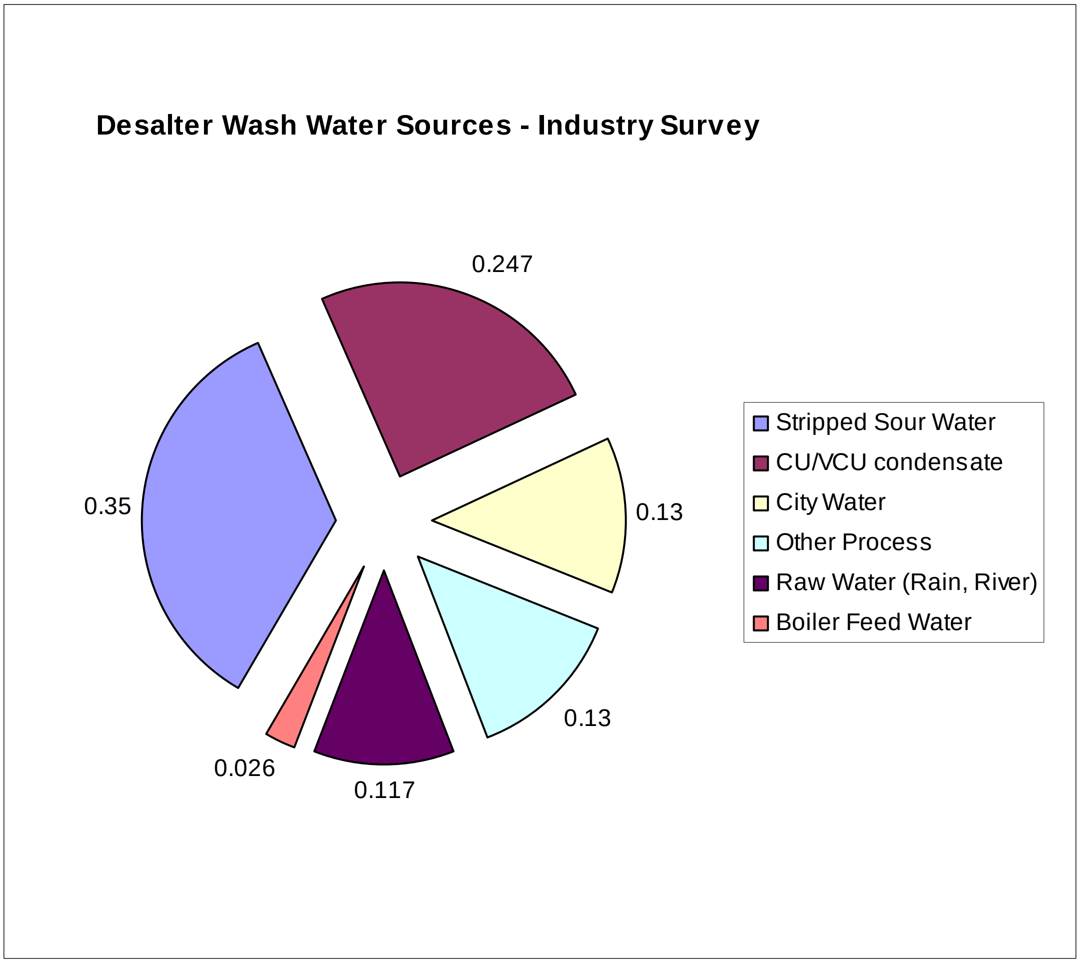
Through the combined use of an asphaltene stabilizer and demulsifier on crude receipts we have reduced oil and solids loading to our WWTP by around 50%. The demulsifier aids in oil water separation, allowing non organic solids to drop out cleanly without carrying oil or causing a large rag layer. The asphaltene stabilizer reduces destabilization of the asphaltenes as crudes are blended and heated, resulting in reduced preheat fouling and organic solids settling.

Scott Bieber (Baker Petrolite)
This topic is covered at length in a Baker Petrolite technical paper delivered at the 2008 NPRA Annual Meeting, “Strategies for Desalting Heavy Western Canadian Feedstocks” (AM-08-36). Copies are available on the NPRA web site, or from your Baker Petrolite representative. An article based on this paper, “Rethink desalting strategies when handling heavy feedstocks” can also be found in the September 2008 issue of Hydrocarbon Processing, page 113.

Briefly, these feedstocks can be problematic due to their high solids and asphaltene contents, and in some cases the presence of non-desaltable chlorides. Refiners can improve their ability to handle these feedstocks by increasing wash water rates, and by optimizing desalter mixing energy, desalter temperatures, and mud wash practices. Successful processing of these feedstocks can require significant changes in the crude oil chemical treatment program used. For example, crude tank pretreatment, solids wetting agent, and wash water polymer programs have all been used to improve bitumen-derived crude processing capabilities. Bench top screening tests can be used to predict feedstock incompatibilities, and to select the most effective chemical treatment program for particular crude blends and specific plant desalter operating conditions.

Question 51
List the sources that you use for desalter wash water and the advantages and disadvantages of each water source.

Todd Sandifer (Marathon Petroleum Company)
A variety of wash water sources are used for desalter wash water. The figure below is a survey of industry practices; approximately 60% of desalter units operate using stripped sour water, crude unit (CDU) condensate, vacuum column unit (VCU) condensate, or a combination of these water sources. Another 25% of desalter units use either city water or raw water. Some examples of raw water are rainwater, river water, and well water. Less than 5% of desalter units use boiler feed water.



Stripped Sour Water Advantages: Low Cost, available at higher than ambient temperature and in large quantities, NH3 content typically very low, low hardness, some of the organic neutralizing amines in treated condensate are stripped out. PH less than 8.5
Ammonia less than 30 ppm,

Stripped Sour Water Disadvantages: pH is generally higher than other sources and can fluctuate causing desalter performance issues, typically has some un-stripped organic amines that can partition to crude and form salts in the crude tower, and poor desalter operation resulting in high NH3 can partition to crude and from NH4Cl salts in crude tower.

CU/VCU condensate Advantages: Low Cost and available at the crude unit, saves SWS capacity, and usually consistent and low pH for better desalter operation; low hardness.

CU/VCU condensate Disadvantages: Organic neutralizing amines are not stripped out and can partition in crude at desalter resulting in salting and corrosion of tower top or ovhd line ahead of water wash injection, NH3 can be high relative to SSW since it is not stripped, usually not enough available to meet wash water requirements, can contain high concentration of iron sulfide and oil, vacuum leaks can result in high oxygen concentrations.

City Water/Well water Advantages: pH is neutral to basic and typically consistent

City Water/Well water Disadvantages: Pretreatment of city water and raw water by ion exchange, filtration, etc. may be needed to improve the quality of these water sources. Untreated water has high hardness and can result in salts precipitating in desalter at higher pH; typically have high dissolved oxygen concentrations and should be de-aerated before use.

Boiler Feed Water Advantages: Relatively pure with possibly small amounts of residual boiler treatment amine, pH neutral to acidic and typically consistent.

Boiler Feed Water Disadvantages: Usually limited by supply and expensive relative to other alternatives. No buffering capacity.

Preferred sources are Stripped Sour Water, Atmospheric Tower Overhead Condensate, and Vacuum Tower Process Overhead. Oxygenated or mineral containing waters, such as city, raw surface, and well waters, are not recommended without treatment to remove dissolved oxygen, calcium ions, etc.

75% of the fresh wash water should be injected into the Raw Crude for single stage desalters and into the Second Stage crude inlet piping for Double Stage Desalters. The remaining 25% should be injected into the Raw Crude ahead of the preheat exchangers
Total rate of wash water injection should be 4 to 6 vol% of the crude charge rate for crudes with API >22°. For heavier crudes with API <22° the minimum injection rate should be 6 to 8 vol% of the crude charge rate. The maximum wash water rate in all cases should not exceed 12 vol% on the above basis.

Brine Recycle can be used to increase effective wash water rate, but the ratio of recycle to fresh wash water should not exceed 1:1 on a volume basis.

Species	**Value**	**Comments**
Chloride	100 ppmw max.	Assure effective salt removal and reduce corrosion and salt potential in Crude Distillation Unit (CDU)
Calcium	150 ppmw (as $CaCO_3$) max	Reduce scaling potential in brine system
pH	6 min., 8 max.	Reduce aqueous corrosion and improve demulsification
Total Ammonia	150 ppmw max.	Reduce potential for salt formation in CDU
Dissolved Oxygen	50 ppb max.	Reduce corrosion in hot brine and CDU
Fluorides	1 ppm max.	Reduce corrosion and fouling potential in CDU
Total Hydrogen Sulfide	50 ppmw max.	Reduce potential for wet H_2S cracking of carbon steel
Surfactants	“Low”	Usually indicated by oil content or foaminess of fresh wash water

Dennis Haynes (NALCO Energy)
There are various sources that may be used as desalter wash water. These include atmospheric overhead condensate water, vacuum overhead condensate water, stripped sour water, condensate waters from downstream processes (such as FCC, HDS, Coker, etc), industrial/city/well waters, boiler feed water, or recycle brine. These are the main sources.

Atmospheric overhead condensate water tends to be a very good source as the pH is normally in an acceptable range and it typically contains low levels of materials that would be considered contaminants (such as ammonia and hardness).

Vacuum overhead condensate water is used quite a bit as a wash water source, but care needs to be taken to confirm that the pH is not controlled to too high a level. Many vacuum overhead systems can operate with a pH target of 5.0-5.5, which is also beneficial to emulsion resolution in the desalting process. If the pH of the vacuum overhead system is controlled to a high level, then there is the potential for entrained hydrocarbon in the hot well aqueous condensate, and this may lead to emulsion stability in the desalter.

Stripped sour water is very common as a desalter wash water source, but it can also be problematic. Many of the sour water strippers have multiple feed sources causing potential variability and contamination. Variability of quality may be regarding pH control for desalter wash waters. Contamination may be due to ammonia from downstream processes, cyanides from upgrading unit effluents, and possibly entrained hydrocarbons with surfactant capabilities. If stripped sour water is used, the quality must be controlled to be consistent and the pH needs to be less than 8.5. Minimization of any entrained hydrocarbons or surfactant material is very important.

Industrial/city/well waters are sometimes used; however, there are concerns with these sources due to the possibility of oxygen entrainment leading to elevated corrosion concerns at the crude unit, some sources may have high levels of fine particulate leading to increased emulsion stability, and some of these water sources may have high levels of carbonates and hardness leading to scaling problems in the desalter. Scaling may result from temperature change, hardness concentration shift on washing the crude, and pH changes in the cases of using multiple wash water sources. Since some of these streams may come into the process at ambient or reduced temperature, the ability to preheat them for introduction to the desalters is limited in some cases. Due to this, there is the potential for thermal shocking the crude oil feed. This results in increased emulsion stability due to elevated viscosity and potential wax issues at the interface and also lower desalter temperatures.

Boiler feed water has been used, and it is a very clean water source for the desalters; however, in most cases where there are alternative water sources, it is found to be a costly alternative. It is important that if boiler feed water is used, that it be de-aerated in order to minimize oxygen-induced corrosion at the crude unit.

Recycle brine is sometimes used as a portion of the wash water charge to increase the total wash water to the desalter. For systems that are water limited or effluent processing capability limited, this strategy can be beneficial; however, caution is required due to the fact that if there is entrained hydrocarbon in the water phase in the desalter, a recycle brine would draw this oil-in-water emulsion from the vessel, bring it through a recycle pump causing further emulsification and then send it to the wash water inlet to the crude oil. This will result in a problematic emulsion being formed. If there are high solids loading, and these are drawn from the crude into the desalter water phase, a recycle brine will also bring these back into the charge to the desalter. Use of a recycle brine can be a good strategy to increase wash water rate for better emulsion resolution in the hydrocarbon phase and better washing of the crude oil, but care must be taken to ensure that the water being returned to the process is of a quality that it will not be problematic.

The use of different waters can be checked to some degree by working with your desalter chemical supplier to have them evaluate the impact on emulsion formation of the new water sources by means of laboratory testing.

Atmospheric Distillation

Question 52
How do you design hot-end crude preheat exchangers (crude vs. gasoil or resid) that stay clean between turnarounds? What fouling factors are calculated in these services for well-designed exchangers? Is crude oil typically on the tube or shell side? What were the important design criteria: high velocity/pressure drop; unconventional exchanger types (spiral or twisted tube bundles); or something else?

Eric Hutchins (Process Consulting Services)
Refineries are often built and revamped with a keen eye on capital cost while operating cost/reliability take a back seat. By installing the preheat exchanger surface with parallel trains and lower velocities, capital savings can be had in lower exchanger costs, reduced piping costs due to line classification, and smaller charge pumps. This results in preheat trains that cannot operate for full turnaround cycles without cleaning, particularly as crudes get heavier and higher in contaminant loads. The unfortunate "solution" to this has often been to add MORE surface in parallel to provide opportunities to remove trains from service to allow for cleaning without significant rate reduction. However this lowers velocity, increases fouling rates and lowers heat transfer coefficients due to reduced turbulence. It is not uncommon for these type of revamps to come on line with worse preheat performance than pre-revamp.

When designing a new or revamped Crude Unit, a balance must be struck in the preheat train between capital and operating expense. As refiners continue to extend run-lengths between turnarounds and charge heaters are pushed to limits, it is essential that steps be taken to reduce preheat train fouling. High head charge pumps, piping and exchanger upgrades, reconfiguration, and mid-train PSV installations all should be considered as tools to solve the fouling problem and improve heat transfer performance.

While fouling rates will all vary based on feed type and operating conditions, increasing velocity is always a critical tool that must be considered to minimize fouling rate. However, increasing velocity has the consequence of increased delta P. The design engineer must evaluate breakpoints in exchanger design, line classification and pumping requirements in order to optimize the design as a minimum, preheat exchanger velocities should be kept above 7 ft/s and often far higher than that depending on the service.

Selecting design fouling factors is a key component of preheat system design. Under predicting fouling factors leads to designs that are incapable of meeting run-length targets, over predicting fouling factors leads to excessive capital costs and suboptimal and/or potentially unstable operation when exchangers are clean. Fouling factors are highly dependent on crude type and operating conditions and it would be inappropriate to recommend values without knowing detailed information regarding the particular unit.

The material with the highest fouling tendency is typically placed on the tube side for ease of cleaning. This places crude on the tube side with some notable exceptions.

1. At the front end of cold preheat trains, crude viscosity and low temperatures often mandates that crude be on the shell side to maximize heat transfer coefficient and control pressure drop.
2. High viscosity resid will often be placed on the shell side with accommodations made for effective flushing and isolation.
3. At the hot end of a preheat train if flashing is anticipated the crude might be switched back to the shell side.

Unconventional exchanger types such as helical baffle and twisted tube exchangers are gaining broad industry acceptance. Helical baffle exchangers improve shell side flow patterns without impacting pressure drop reducing dead zones typically found in conventional exchangers. Twisted tube exchangers, while far higher in cost, pack far more surface area in to a shell than a conventional bundle. Upgrades to these types of bundles in some cases allow refineries to minimize revamp costs by reusing existing shells and piping. This also minimizes shutdown time which is often the largest economic driver.

Question 53

What are you doing to mitigate the impacts of processing bitumen-derived crudes on preheat train fouling, furnace operation, and fractionation performance?

Eric Hutchins (Process Consulting Services)

Production upgrader experience proves oil sand bitumen is even more difficult to refine than conventional heavy crudes. However, the industry's casual attitude of "it doesn't matter which crudes will be processed; they all have about a 20° API gravity," remains. On-stream factors of months versus years or very low HVGO product yield, much higher coker charge rate than expected and higher incremental coke production of 1 wt% or more are what should be expected when processing bitumen. Today these major economic consequences tend to be ignored because price discounts are high. Few refiners have any experience processing high blend percentages of ultra heavy crudes with a true deepcut vacuum unit, or have experienced the challenges of high percentages of oil sands bitumen.

Most heavy crude revamp projects require a complete new vacuum unit because these feedstocks are so difficult to vaporize. Oil sands bitumen presents the greatest challenge by far. Realizing heavy vacuum gas oil (HVGO) product TBP cutpoints of only 950°F and meeting probable 4-6 year run length requires the best available vacuum unit technology when processing oil sands bitumen crudes. One thing is certain: *low capital cost dry vacuum units will suffer poor reliability and extremely low HVGO cutpoints – and very likely both*.

Oil sands bitumen requires special process and equipment design that incorporate low oil residence time double-fired heaters, properly designed preheat exchanger trains, residue stripping and ejector systems capable of handling extremely large amounts of cracked gas. Without residue stripping, HVGO product cutpoint will be limited by practical heater outlet temperatures and this cutpoint will be very low even with the best heater technology and coil steam to reduce oil residence time. And ejector systems sized for typical cracked gas production of 0.2-0.3 wt % feed will not be large enough even with a very low residence time heater.

The controlling parameter regarding preheat train exchanger fouling when processing oil sands bitumen is velocity. Ironically heavy crude and bitumen related revamps which add surface area often lower velocity and impact both heat transfer coefficients and fouling tendency. A holistic look at the entire CDU/VDU energy balance and preheat train hydraulics is required for maximum heat recovery reliability. In addition, these crudes will negatively impact desalter performance increasing the fouling potential on the hot preheat train. Optimizing the desalter inlet temperature, limiting centerline velocities, having sufficient power to the grids, and having the best possible chemical program all will reduce foulant load on the downstream exchangers.

The designer/operator of a Crude and Vacuum Unit processing oil sands bitumen must be aware of the type and quantity of diluent used and understand its impact on the atmospheric tower operation. For example, a bitumen with naphtha boiling range material used as a diluent, could easily overwhelm the upper section of an atmospheric column that was designed or revamped of typical heavy crude processing. The preheat train may also be affected because there is less heat available to recover in the middle distillates potentially impacting raw crude preheat and desalter temperature.

Oil Sands Characteristics

Specific oil sands production determines particular processing characteristics and challenges. Some deposits contain very high quantities of naphthenic acids and chlorides whereas others do not. Furthermore, bitumen is often produced by mining or SAGD. Which method is used influences the amount of clay and sand in the finished product. Nonetheless, all oil sands bitumen deposits do have some similarities. Relative to other crude oils, all oil sands bitumen have poor thermal stability and contain large quantities of asphaltenes with varying stability. It is imperative that the crude/vacuum unit be designed keeping these realties in mind. Many oil sands bitumen generate significant amounts of cracked gas at 680°F heater outlet even with a well designed double-fired heater. Maximum heater outlet temperatures are likely to reach only 710-715°F even with a fully optimized heater design. Moreover, asphaltenes precipitate and coat the inside of the heater tubes causing skin temperatures to rise.

Recently one US refiner processing oils sands bitumen through a dry vacuum unit quickly found the heater outlet temperature had to be reduced to 690°F to prevent overloading the ejector system. Although a larger ejector system would have allowed higher heater outlet temperature, there is a practical upper limit to cracked gas production because of the rate of coke laydown in the heater tubes. Furthermore, asphaltenes precipitate at a rate related to temperature and radiant section fluid velocity. Higher velocity slows the rate of asphalt laydown but there is an upper limit due to tube bend erosion from solids.

Processing oil sands bitumen will severely limit heater outlet temperature compared to conventional heavy crudes. This results in low HVGO product cutpoints even with best vacuum unit technology. Once maximum heater outlet temperature is reached incremental increases in HVGO cutpoint will be achieved through residue stripping and low column operating pressure. The former can increase HVGO product cutpoint by up to 80°F depending on steam rate and stripping section efficiency. When processing oil sands bitumen, therefore, the vacuum unit should be designed with a residue stripping section.

HVGO product cutpoint is used to assess vacuum unit performance with 1050°F often cited as the benchmark or design basis for new units. In reality actual vacuum unit cutpoints vary from below 900°F on extra heavy crude to over 1100°F for light crudes with the majority operating well below 1000°F even on moderately heavy 26-28°API gravity feeds. Feed characteristics control potential cutpoint. Maximum cutpoint is determined by vacuum unit type and design. For example, a fully optimized vacuum unit with heater coil and stripping steam processing 100% 22° API gravity Maya or similar Venezuelan crude can theoretically achieve cutpoints up to 1085°F because the vacuum heater can be operated at 800-805°F. In reality, however, to our knowledge no refiner has yet to actually meet this target. Interestingly, several announced Canadian heavy projects are being touted as designed to meet a 1050°F HVGO product TBP cutpoint or even higher. Meeting this mystical cutpoint goal is challenging enough with conventional heavy crudes. *It is simply impossible when significant amounts of oil sands bitumen are processed.*

Heater run length depends on the rate of coke formation which is a function of oil residence time and peak oil film temperature for a given feedstock. The lower the oil thermal stability the lower the peak oil film temperature before excessive thermal cracking occurs. Thermal cracking causes coke to accumulate on the inside of the heater tube. Once the metal temperature reaches its allowable maximum the coke must be removed. Vacuum heaters designed without steam often have radiant section oil residence time of more than 1 minute. Inexperienced designers will attempt to compensate for high film temperature by specifying radiant section average heat flux of 8,000 Btu/hr-ft^2 or lower. Even though this decreases peak film temperature compared with a heater designed for 10,000 Btu/hr-ft^2, it also increases the oil residence time by 25%. But the rate of coke formation depends on both peak oil film temperature *and* oil residence time. Moreover, most designers continue to specify single-fired heater tubes because they are cheaper even though they dramatically increase peak oil film temperature. Single-fired tube peak heat flux is approximately 1.8 times the average for the tube compared with a double-fired tube which is only 1.15 times its average. Single-fired, dry vacuum heaters are thus a very poor selection when the feedstock is not thermally stable.

Coil steam reduces the radiant section oil residence time from over 60 seconds to much lower, depending on the specific heater design. An ultra-low residence time heater has only 10-20 seconds in the radiant section depending on steam rate and design. An optimized double-fired heater should be designed for higher average radiant section heat flux of 10-12,000 Btu/hr-ft^2 to take advantage of the more uniform heat distribution around the tube in order to lower residence time. The higher heat flux heater will thereby have a lower oil residence time than the lower heat flux heater. The double-fired design allows a much higher average flux than a single-fired design assuming the same limiting oil film temperature.

The three types of vacuum units are dry, wet (damp) without residue stripping and wet (damp) with residue stripping. Wet (or damp) units with coil steam only achieve higher cutpoints than dry designs because the heater outlet temperature can be operated 20-30°F higher due to reduced radiant section oil residence time. Coil steam also reduces column flash zone oil partial pressure raising HVGO product cutpoint. Heater coil steam increases the column size because it increases vapor traffic and reduces vapor molecular weight. It also increases ejector system size. Wet units with heater coil steam and residue stripping produce the highest HVGO product cutpoint, and best HVGO quality, for a given HVGO product cutpoint. Wet designs with residue stripping will permit maximum HVGO product cutpoint of 950°F when using the best technology to process 100% oils sands bitumen.

Residue stripping produces the highest HVGO product TBP cutpoint and lowest metals. It maximizes refinery liquid volume yield, reduces the size of the coker unit and achieves the longest run length. Residue stripping increases cutpoint by reducing the oil partial pressure as the oils flows down through the stripping section. It produces a much higher HVGO product TBP cutpoint for same flash zone oil partial pressure as in a unit designed with coil steam only. Importantly HVGO product metals are much lower because the HVGO product distillation 95% to endpoint tail is reduced since stripping vaporizes a lower boiling range material as compared with the heater only case. Vacuum units designed with only coil steam have lower HVGO yield and higher metals.

A fully optimized vacuum unit will be able to reach approximately 950°F HVGO product TBP cutpoint on whole bitumen using coil steam to reduce oil residence time, double fired heater, residue stripping, low column operating pressure and other design considerations. Refiners assuming their new vacuum units will meet a 1050°F cutpoint will be surprised by an 8 wt% higher coker charge rate on whole bitumen. Compared with a 1050°F design, a conventional dry vacuum unit will achieve cutpoints well below 900°F producing as much as 15% higher coker charge rate compared with a 1050°F design.

Question 54

Given current diesel margins, how are you modifying crude and vacuum tower operation to maximize distillate yields and minimize "650°F minus" give away to FCC feed? Discuss the impact on atmospheric gas oil (AGO) and vacuum gas oil (VGO) recovery.

Todd Sandifer (Marathon Petroleum Company)
The biggest handle available to increase diesel yields is to shift heat balance to increase the diesel endpoint and to increase use of stripping steam in AGO and Reduced Crude. AGO and VGO recoveries will obviously drop as diesel end points are increased.

Diesel endpoint targets should be adjusted to manage to finished diesel 90% point target specifications while at the same time minimizing naphtha endpoint targets to meet flash specifications on kerosene.

In at least one scenario, we have been able to increase distillate yields by lowering total crude rate to allow increased crude heater outlet temperatures; however this has been at the expense of reduced crude and naphtha yields.

Eric Hutchins (Process Consulting Services)
When targeting to improve diesel recovery in existing Crude and Vacuum Units refiners often first look to improve the atmospheric column performance. Fractionation, of course, requires theoretical stages and L/V (liquid to vapor ratio), increasing these, albeit with diminishing returns, leads to improved fractionation.

Good diesel-AGO product fractionation requires adequate reflux rate (liquid-vapor ratio), 8-10 trays, and good tray efficiency. Most atmospheric columns wider than 16ft in diameter will use 4-pass trays. These large diameter towers will have low weir loadings (gpm/in of weir) and the tray efficiencies can be low. Low reflux and tray efficiency dramatically reduce diesel yield.

Depending on existing heat removal capacity, revamp modifications often include increasing upper pumparound heat removal capability and allowing more vapor traffic up the column. These changes along with internals modification if required to handle the increased traffic, can increase distillate yield.

However, when evaluating a unit for maximum diesel recovery the Crude and Vacuum units should be looked at as one system. Improving distillate recovery in the atmospheric column directionally reduces the flash zone stripping/partial pressure effect of that material and reduces VGO recovery from vacuum resid. Unless this can be compensated for in the Vacuum unit with increased heater coil outlet temperature, improved steam stripping, or reduced flash zone pressure, the gain in diesel yield in the atmospheric tower may be offset by the loss of VGO recovery in the Vacuum Column. Due to the fact that the majority of refinery modifications have been driven by increasing throughput, many vacuum columns are already pushed up to C-factor limits. Once the C-factor limits are reached, attempting to increase lift results in sharp reductions in VGO quality due to entrainment.

Producing diesel from the vacuum unit always maximizes overall diesel recovery. In some instance yield increases of 5% or more on whole crude have been realized. Diesel boiling range material is produced as the top product from the vacuum column. This requires installation of a fractionation bed in between the top pumparound and the VGO product. With sufficient theoretical stages and proper distribution it is possible to produce a diesel product with a small 95%-EP distillation tail freeing up FCC capacity for more appropriate feedstocks. In order to achieve good fractionation proper liquid distribution is essential. While attempts have been made to use spray headers in this application, trough style distributors are essential for good performance.

Question 55

When maximizing distillate production, the temperature profile in the atmospheric crude tower changes. How do you determine a lower limit for the overhead temperature? What criteria are most important? What do you do to mitigate salt deposition and corrosion inside the tower and under external insulation?

Todd Sandifer (Marathon Petroleum Company)

The lower limit for overhead temperature is determined by the aqueous dew point or the amine hydrochloride or ammonium chloride salt point, whichever comes first. As a rule of thumb, best practice is to maintain the tower overhead temperature at least 25 oF above the dew point or salt point. Tray metallurgy, overhead line metallurgy, and reflux/top PA temperature may also be factors when determining the minimum operating temperature.

The best mitigation strategies for internal corrosion are:
Reduction of chloride, amine, and ammonium chloride levels to move the salt point to an acceptable location.

Properly designed and operated water wash, appropriate metallurgy, and effective use of corrosion inhibitors and dispersants are key to a successful corrosion control program.

At typical operating temperatures for a crude fractionator, we have not seen problems with corrosion underneath the outer insulation. Application of an acceptable epoxy coating to the exterior of the tower prior to insulating would mitigate external corrosion concerns.

Eric Hutchins (Process Consulting Services)

It is typical for refiners to attempt to calculate the dewpoint in the top of the atmospheric column and then operate with a certain delta margin above that temperature in hopes that they can avoid free water formation in the column. The success of this technique is spotty for a variety of reasons the first of which is it is obviously highly dependent in the quality of the data used in the calculation. In addition if pumparound return temperature or top reflux temperatures are low enough it is possible to have areas of localized or “shock” condensation.

While tools like dewpoint calculation can give you guidance, there is no better indicator than the unit operation itself. If your tower top is salting up, pressure drop increases and indications of flooding occur such as high overhead product endpoint. Additionally during shutdowns you will see heavily corroded and/or fouled trays, vessel shell corrosion, and in downstream saturate gas plant equipment you will see evidence of corrosion products deposition (depending on metallurgy).

The chemical suppliers all offer dispersants which can be used to help keep the salts and corrosion products “moving’, however you need to always be aware where those salts and corrosion products are going to move to, and be certain that you are not just relocating a problem to an even more critical part of your operation.

In order to minimize corrosion in the top of the column, it is necessary to operate with top pumparound and reflux temperatures far above dewpoint and above that required for formation of the heavily corrosive salts formed at temperature at or above 275 F. For example Hamaca crude is known to generate salts at elevated temperatures causing severe fouling and corrosion. H_2S amine scavengers and other contaminants in the crude are also major contributors. With some crudes very high crude column overhead temperatures are needed to prevent salt formation inside the column.

If this is not feasible, it is possible to design an effective tower top water wash system that allows you to remove the salts on line with only moderate impact on unit operation; these designs along with good metallurgy choices can yield acceptable performance in relatively low tower top operation.

With regards to corrosion under insulation (CUI) any steel operating in the range where CUI is a potential risk should be primed as a minimum and coated if possible. We are aware of Crude Unit main columns with low operating temperatures that have, in fact, corroded through-wall from CUI.

Dennis Haynes (NALCO Energy)

One approach would be to first identify what the temperature target is required to maximize your distillate production. This would then be compared to the salt (amine and NH_3) formation and water dew point temperatures.

Once the dew point for the system is calculated, some refiners operate the top pumparound/reflux combined return or independent reflux return, which ever is coolest (design dependant) at the dew point plus some temperature (experience has been in the range of dew point plus 25-55F for various locations). Since salt formation is predicated on the product of the partial pressures amine/ammonia and chloride, the important criteria are:

- Minimize the amount of stripping steam that is being used (this impacts the water dew point)
- Minimize the amount of hydrolysable chlorides thru improvement of desalter operation and use of caustic
- Minimize the amount of ammonia containing streams to the crude tower, such as wild naphtha's, Coker off gas, etc
- Minimize the amount of "Tramp Amines" by means of the desalter (water selection, acidification, etc.)
- Minimize atmospheric tower overhead pressure where possible
- Minimize the wetness of the reflux naphtha by adjusting operating levels in the atmospheric overhead accumulator, using the filmer that has good WISM (MSEP) properties, use a demulsifier in the reflux drum

Some locations that operate the atmospheric column top pumparound/reflux combined return or reflux independent return consistently at or below dew point have chosen to add a water draw tray below the point of shock condensation in order to remove the condensed water from the system.

George Duggan (Baker Petrolite)

The concerns that arise with decreasing tower top temperature are two-fold: 1) risk that the tower top will operate at or near water dew point and 2) risk that the tower top will operate at or near the temperature at which corrosive salts can deposit.

The term "approach temperature" is used to evaluate this risk, where approach temperature is defined as tower top temperature minus the appropriate phase temperature (water dew point or salt formation temperature). When this approach temperature value becomes small, the risk of shock cooling (e.g., from cold reflux return) increases and may produce a local, corrosive phase. When this approach temperature becomes negative, the tower is certain to be operating with a corrosive condition present. Baker Petrolite's experience suggests that a minimum approach temperature of 25°F should be maintained under all operating conditions.

Determining the tower temperature limit requires that the phase temperatures for dew point and salt formation be determined. These values are then compared to the tower top temperature to determine the approach and, consequently, the risk. Baker Petrolite's Ionic Model is a proven tool for making these determinations.

Mitigating salt corrosion in a tower is best achieved by defining an operating envelope to avoid deposition of the salts. If this is proven to be infeasible, other options such as intermittent tower washing and metallurgy upgrades can be considered, but these methods all have limitations.

Question 56

What practices do you employ, both operational and mechanical, to limit or avoid liquid carryover in the overhead of the atmospheric crude tower?

Todd Sandifer (Marathon Petroleum Company)

We have not observed any issues of this sort at our facilities.

Liquid carryover (entrainment) in the overhead of an atmospheric tower is likely caused by high vapor velocity. If there is significant liquid carryover, then the trays are at or near flood and installation of a higher capacity tray should be considered.

Tray fouling can also cause entrainment; fouling causes high localized vapor velocities which generate small liquid droplets that do not disengage and result in liquid carry over. If tray fouling or salting is occurring, water washing the top section of the tower is an effective means of removing salts.

We have discontinued the use of demister pads due to issues with iron chloride scale formation and safe removal of such during turnaround/maintenance on the tower.

A good reference for calculating flood points and understanding the impact of various tray design parameters on flooding is Kister, Henry Z., *Distillation Design,* McGraw-Hill, Inc., 1992.

Eric Hutchins (Process Consulting Services)

We can think of no circumstances in which the installation of a de-entrainment device makes sense for the top of an atmospheric column. Our first comment to the author of this question would be how do they know they have liquid carryover?

The amount of liquid entrainment in the atmospheric column overhead vapor will be a function of the vapor velocity (C-factor), the design and mechanical condition of the top reflux/pumparound distributor, and the % of flood on the top tray.

If they are actually experiencing gross liquid carryover there is something fundamentally wrong that will not be corrected with the installation of a de-entrainment device.

Don’t operate the tower in flood, and address the fouling issues that cause flooding.

Question 57

Traditionally, total acid number (TAN) has been used to indicate the corrosion potential of crude oils and product streams. What other indicators are you using and what operating windows, with and without chemical treatment, have you established for these indicators?

Eric Hutchins (Process Consulting Services)

In addition to the total acid number, typical indicators of the corrosion potential of a particular crude include salt, sulfur, nitrogen and amine contents.

Given that every desalter design is limited to a certain percentage removal of incoming contaminants, higher contaminant levels in the crude charge result in higher contaminant levels being fed to the process. Salt compounds of various forms hydrolyze in the charge furnace resulting in free chloride load on the system. Free chloride at the initial water condensation point results in strong acid, highly corrosive environments if left unchecked. However, limits to inlet salt content are dependent on desalting capability, downstream equipment design and metallurgy, and adequacy of corrosion control program.

Higher sulfur crudes obviously result in higher sulfur concentrations in the various products and pumparounds. High sulfur content coupled with high process temperature result in accelerated corrosion rates, which are in turn aggravated by high velocity. For carbon steel in high sulfur crude service, breakpoint design temperatures are typically in the 500º F range. However, the recommended break point will be dependent on the speciation of sulfur contaminants in the stream.

McConomy curves can be used to asses the relationship of sulfur concentration and temperature on corrosion rates. Typically refiners will establish maximum allowable corrosion rates that will allow for safe run lengths of at least one turnaround cycle. The elevated temperatures of these streams make it challenging to get accurate inspection data online and often require shutdowns to determine the actual rate of corrosion. Therefore, good practical judgment suggests that the minimum predicted life should exceed two turnaround cycles whenever possible.

Nitrogen containing compounds including amines in the feed will result in the formation of salts which lay down in a variety of locations in the process units dependent on molecular weight and operating temperature. The deposition of these salts leads to a phenomenon known as under deposit corrosion, which can be a significant portion of a refinery's internal corrosions challenges.

The use of annual RT inspection at suspect corrosion locations with high velocity and temperature such as control valves, heater outlet thermowells and pump discharge piping can assist in identifying areas of concern. In addition, in some instances salt formation in top pumparound systems has corroded pumparound pump suction line piping where velocities are less than 3 ft/s.

Randy Rechtien (Baker Petrolite)
There are several references in the literature which suggest that crudes below TAN = 1 or side-cut streams below TAN = 1.5 are "safe". While TAN is certainly important, it must be noted that TAN includes the measurement of some non-naphthenic acids which do not contribute to naphthenic acid corrosion. Baker Petrolite has developed an analytical method called SCAN (specific carboxylic acid number) which determines a stream's naphthenic acid content independent of other acidic species. Our experience indicates that SCAN is a better predictor of naphthenic acid corrosion potential than TAN.

Factors such as TAN, sulfur, temperature, shear stress and metallurgy are all inter-related in their effect on naphthenic acid corrosion potential. Therefore, all factors must be considered. However, our field experience suggests there are no hard and fast safe limits of operation. Instead, a complex assessment where each of these factors is accounted for is required to establish the operating window and guide the treat/no treat decision.

Question 58
The old rule of thumb for gas velocity through air cooled fin fans of 20 fps was a limit specifically for hydrocrackers. What is the allowable gas velocity through fin fans in other wet services such as crude units and cokers? How did you determine this limit and how do you monitor it?

Mitch Moloney (ExxonMobil)
Delayed Cokers are more concerned with trading off proper turbulence for heat exchange (surface area) and system pressure drop, to optimize coke drum operating pressure. A typical spec is 2 psi DP with a process side fouling factor coefficient of 0.002 hr-ft^2-°F/Btu (0.0004 m^2-°C/W).

Eric Hutchins (Process Consulting Services)
The 20 fps guideline was for carbon steel tubes only and not specific to hydrocrackers but any system with high ammonium bisulfide concentrations, as can be found in hydroprocessing units. For crude units that have low ammonia contents, velocities can be higher and often are. Typical guidelines suggest that with concentrations of less 2 % ammonium bisulfide in the water, velocities of 30 fps have acceptable corrosion rates.

Rigorous process simulation can be used to calculate, and thereby monitor, velocities in the operating unit.

Question 59
How is jet fuel processed downstream of the crude unit? If it is caustic treated, have you experienced color or low conductivity issues? Is there potential for stratification in the finished product tank?

Vacuum Distillation

Question 60
What are some proven design practices and operating guidelines to minimize vacuum tower wash bed coking? What are the most reliable methods for calculating the true over flash in the vacuum tower?

Eric Hutchins (Process Consulting Services)
Optimizing the design and operation of a vacuum tower wash zone requires striking an appropriate balance between clean HVGO and coking mitigation/run length. Feed type and rate vs tower diameter, cut point targets, and product quality requirements all play roles in this optimization. For example a grass roots design of a unit running 30 API "clean" crude with an HVGO cutpoint of 1050 F, will have a completely different design than a unit processing 21 API "high metals" crude with a 975 F cutpoint. In addition the optimum metals and CCR contaminant levels of the HVGO that is used for feed to an internal FCC may be different that the product sales requirement for that stream to the market.

Ideally the vacuum column wash zone should remove nearly all the entrained residue in the vapor leaving the flash zone minimizing heavy vacuum gas oil (HVGO) product contaminants. However, when the wash zone cokes, HVGO product metals and micro carbon increase with the magnitude being a function of the vacuum residue metals and micro carbon content. With crude oils such as Merey, Maya and others with high contaminants levels, small amounts of entrainment have a large influence on HVGO product metals. Preventing coke formation is critical. Once coke forms inside the packing it reduces the cross sectional area increasing vapor velocity which prevents the packing and the wash liquid from doing its job of residue removal.

The design and operation of a well designed wash bed can be broken into three key areas;

1. Vapor Distribution

Proper vapor distribution is critical to insuring uniform wash bed temperatures and wetting. If the distribution is poor there will be wash bed zones with varying amounts of vapor and liquid flow. The low liquid flow areas can lead to long residence times resulting in coke formation reducing the vapor flow in that area.
Keys to success include;

- Transfer line design - The length, Diameter (velocity), and straight run prior to tower entry are all important.
- Vapor distributor design - There are many proprietary vapor distributor designs available in the market, with all levels of complexity. The design of this distributor becomes more critical as the C-Factor increases. If the C-Factor is less than .3 ft/s and there is enough free space below the wash bed, even poorly designed vapor distributors have little impact on tower performance. However push those Vacuum towers up to C-Factor limits and you will see the impact of poorly designed vapor distributors.
- Overflash collector tray - A well designed overflash collector tray needs to generate sufficient pressure drop to aid in distribution without creating excessive column pressure drop.

2. Liquid Distribution

The keys to successful liquid distribution include:

- Type - What type of distributor is installed, if it is a trough WHY? If it is a spray header, how many nozzles, what is the spray pattern, angle, cone, full-cone, droplet size (mist and carryover)? Ideally the top of the wash bed is uniformly covered with a liquid flow of droplets of wash, the closer you can approach this ideal the better.

- Wash Rate - How much wash is being used, how is the rate determined, have you done testing? Be aware of the wash rate impact on spray header/nozzle performance. Too little wash and the middle of the bed will dry out and coke, too much wash and you are downgrading gasoil to Vacuum Resid.
- Construction - Internal flange leakage? We have seen "cost saving" measures applied to spray distributor headers which result in gross leakage and poor distribution.

- Strainers - Install external strainers that are suited for the open area of the spray nozzles. Be careful not to revamp your spray header with new nozzles but not check the external strainer to be sure that they will protect the nozzles from plugging. Be sure that the strainers are maintained, that the baskets are intact, and not bypassed.

3. Wash Bed Mechanical Design

The type of grid/packing to use is dependent on the operating conditions, feed type, and the efficiency required. The designer needs to be careful to avoid the more-is-better fallacy here. The depth of the bed should be the minimum required to effectively do the job, more packing simply adds to tower delta P and provides excess surface area for coke formation. Vacuum units processing low metals crude at flash zone temperatures of 720°F or lower may only require 3 feet of grid packing to produce acceptable quality VGO. The required bed depth increases to up to 6 feet as the metals content and flashzone temperatures increase.

Column Modeling

During a revamp or a new unit design the correct amount of wash oil flow rate must be determined. Unfortunately most designers under-predict wash oil flow rate by 100-200%. The root cause is incorrect process flow sheet modeling. Vacuum units are often modeled assuming that the liquid and vapor in the flash zone are in equilibrium. This assumption determines the vapor composition and the temperature to the wash bed. For a given amount of wash oil flow rate, the vapor temperature and composition have a large impact on the overflash rate.

The dryout rate (wash oil flow/overflash flow) is calculated assuming the flash zone is an equilibrium stage and one theoretical stage in the wash zone is about 3 to 1 (dryout rate) In reality the flash zone is not an equilibrium stage, therefore the dryout rate is much higher than the 3 to 1 calculated for a single stage. For instance, if the actual dryout rate is 6 to 1 rather that 3 to1, then the wash oil flow rate will need to be doubled for the same overflash. Wash oil flow rates on several units we are familiar with have had to be increased by over 200 percent of the design flow rate to avoid coking

Improperly defined computer models assume ideality therefore the models calculate liquid rates which are often too low to avoid coking. Low liquid rate to the packing causes high oil residence time in the middle of the packed bed. This causes coke formation on the packing. The true minimum liquid rate (overflash) required to avoid coking depends on the transfer line flow regime, vapor distribution, quantity of residue entrainment from the flash zone, packing type, packed bed depth, and liquid distribution.
The vacuum column wash zone minimum flow rate is also highly dependent on a number of specific equipment design issues. Simple statements like "the minimum liquid rate to avoid coking is .05 GPM/ft2 of cross sectional area" have no practical significance.

Mitch Moloney (ExxonMobil)
Tray designs and structured packing designs are typically in place to achieve good fractionation of the vacuum resid. To minimize coking, it is essential to have reliable pumpdown wash flow into the fractionation zone, and it is essential to cover the entire zone with refluxed liquid. Lack of coverage will lead to coking, maldistribution in the fractionation zone and loss of quality control.
Sprays above the fractionation zone should be the low point in the piping to facilitate self draining of the HKGO from the system if flow is lost.

- Auto Steam injection is required if the HKGO wash flow to the sprays is low/lost. Would prefer that this steam is injected automatically, rather than relying on an
- The piping should eliminate low points where coking can occur.

- Strainers (one in standby) should be installed upstream of the headers (at grade) to remove any solid material that could plug the minimum opening of the spray.
- Sprays should be tack welded in several places to prevent them from coming loose in service.
- Experience suggest that the wash piping from grade to the spray headers be boroscoped every 5 - 10 years to check that coke has not built up in the piping downstream of the strainers.
- For good monitoring of this system, recommend that the header pressure and flow be recorded/trended by the TDC to monitor spray performance
- Double nut the internal wash header flange bolts to keep them from vibrating loose.
- Plan to disassemble the internal hot wash header piping on turnarounds to confirm cleanliness especially of the nozzles.
- Set a minimum hot wash flow control valve % open to ensure good minimum hot wash rate even if the flow meter is lying to you.

XOM has had good experience trapping out the overflash, removing from the tower, and returning it via a pump through an orifice flow meter. The orifice meter leads need to be properly sized, traced, insulated and oriented to provide good reliability. We have also trapped out the liquid and gravity flowed it to the stripper section distribution tray via a gravity head low meter.

Question 61

What types of instrumentation, analysis, and controls are needed for monitoring the vacuum tower wash bed to ensure maximum run lengths and yields?

Eric Hutchins (Process Consulting Services)

Unfortunately monitoring wash section performance is problematic. The goal is to supply sufficient wash oil flow to prevent coking during the run without downgrading vacuum gas oil to resid. The amount of wash oil flow required to prevent coking is difficult to determine precisely and it will always be, at best, an estimate. But one thing is certain, process modeling alone cannot be used to determine minimum wash oil flow rate. Once a unit is operating, minimum wash oil flow rate can be estimated by doing a material and component balance around the wash section.

Wash beds almost always coke in the middle of the packing because the middle has the lowest liquid rate. Wash oil is distributed to the top of the packing where it contacts the rising vapor. It vaporizes as it flows through the packed bed. Residue entrainment is removed in the bottom of the packed bed thus it keeps this area wet which suppresses coking. The middle section has the lowest liquid rate and it is the area where coke initially forms.

Wash oil is distributed to the top of the wash section packing and most of it vaporizes before leaving the bottom of the packing. Wash rate must be high enough to keep the middle of the packed bed wetted. The slop wax/HHVGO/Dirty gas oil leaving the wash section consists of overflash plus residue entrainment. Overflash is the wash oil that is not re-vaporized. A simple material balance is slop wax= residue entrainment + overflash. Slop wax must be metered while the overflash and entrainment are unknown.

A component balance must also be performed. Asphaltenes are normally used. The quantity of asphaltenes in the slop wax are equal to the asphaltenes in overflash + asphaltenes in the vacuum residue (entrainment). Asphaltenes do not vaporize hence the overflash has none. To perform the balance, samples of the slop wax and vacuum residue are needed with the asphaltene content measured in the laboratory. Overflash and entrainment are calculated from the two equations. The rate of overflash must be high enough to prevent coking. The wash oil flow is adjusted to meet the targeted overflash rate.

Ultimately the refiner must determine how low an overflash rate is needed to prevent coking. Assuming the wash liquid and vapor distributions are good then the required wash oil flow rate is between 0.05-0.1 gpm/ft^2. Since wash oil and vapor distribution are often poor the amount of overflash needed to prevent coking is typically much higher than the minimum. Because many refiners operate at low flash zone temperature the rate of coke formation is low, thus coke formation is not a problem. But refiners operating at high temperature will coke if the wash section design is poor and operation is not monitored.

Todd Sandifer (Marathon Petroleum Company)
Controls: At one of our facilities we have developed an inferred property controller based on correlations of MCRT to bed inlet and outlet temperature that calculates the overflash continuously so that operators don't have to wait on lab samples to correct an operational problem. The overflash calculation is shown below.

$$\text{Overflash} = \frac{\text{SW rate (Em-SWm)}}{\text{Em} - \text{Ofm}}$$

SW rate = Slop wax flow rate
Em = Entrainment metals or MCRT (Vac Bottoms)
SWm = Slop wax metals or MCRT
OFm = Overflash metals or MCRT (HVGO)

Question 62
What are some common causes for reduced vacuum system performance? Wax? Elemental sulfur? What do you do to predict, detect, and prevent performance degradation?

Todd Sandifer (Marathon Petroleum Company)
Diagnosis of vacuum system problems needs to begin with a baseline performance test. This performance test should be done when the vacuum system is performing well, such as after a turnaround. The performance test should include analysis of the vacuum tail gas, a pressure and temperature survey of the ejectors and condensers, a pressure survey of the motive steam supply to the ejectors, and a cooling water temperature and flow survey of the condensers. Baseline data are extremely valuable if problems arise because they serve as a source of comparison.

Deterioration of vacuum system performance is usually caused by overloading the vacuum system. There are many sources of overloading, but air leakage, excessive velocity and/or stripping steam, and cracked gas are the most common. If air leakage is present, analysis of the vacuum tower tail gas will help to pinpoint its location. A high O2 concentration means that the air leakage is the cooler sections of the vacuum tower, e.g., the vacuum jets, condensers, seal legs, overhead piping, LVGO. If CO and/or CO2 are present then the transfer line and flash zone sections are suspect. Also, if air leakage is present in a pump suction piping flange then the pump will cavitate.

If a vacuum system is designed to handle velocity and stripping steam (damp operation) then the vacuum could be adversely affected if too much steam is used. The first stage intercondenser is designed to condense this steam, as well as the first stage motive steam and any condensable hydrocarbons. An increase in duty load will raise the first stage intercondenser vapor outlet temperature and increase the first stage ejector discharge pressure. Any steam that is not condensed in the first stage intercondenser will carry to the second stage ejector, increasing its gas load and suction pressure. An increase in suction pressure will then raise the discharge pressure. Depending on the amount of steam and the second stage intercondenser performance the gas load could then be increased to the third stage ejector. If any ejector discharge pressure exceeds its design maximum discharge pressure (MDP) then the ejector will break.

If a vacuum system has a precondenser, the lowest top tower pressure obtainable is set by the vapor pressure of water at the precondenser outlet temperature. If the precondenser becomes overloaded then the same problems can occur as previously described.

Cracked gas can be generated in the vacuum heater or in the bottom of the vacuum tower. Too much cracked gas will increase the gas load and could overload the ejectors. Decreasing heater outlet temperature will reduced the cracked gas make. Also, if a vacuum tower has a bottoms quench then decreasing the vacuum tower bottoms temperature by adjusting quench circulating rate may also reduce cracked gas volume.

Plugged seal legs can cause vacuum problems because the condensed water and hydrocarbons will not be able to drain into the hot well. This liquid will then back up into the condenser and increase the condenser pressure drop. This can lead to higher tower pressures and ejector break. Plugged seal legs can be caused by wax buildup, which can occur in cold climates.

If a condenser does not drain liquid properly, then the effect will resemble that of plugged seal legs. One reason can be due to improper condenser baffle design. A Marathon Petroleum refinery experienced high vacuum tower pressure because liquid could not drain from the first stage intercondensers. The bundles were TEMA E-shell with horizontal and vertical baffles. It was discovered that the horizontal baffles had small drain holes which prevented liquid from draining. This caused liquid carryover to the second stage ejectors, which reduced their capacity and raised the first stage ejector discharge pressure. The E-shell bundles were replaced with X-type design and the problem was resolved.

Wet motive steam can adversely affect vacuum because it can erode a jet nozzle over time. It is important to make sure that the steam is dry. Ejector steam nozzles should be inspected for wear every turnaround. Also, if the motive steam pressure is too high, too much steam can enter the ejector and cause the ejector to choke resulting in poor vacuum.

Eric Hutchins (Process Consulting Services)
Wax and elemental sulfur build up are not common in vacuum crude unit ejector systems; however the following are common causes for reduced vacuum system performance;

Fouled condensers - Shell side fouling can be particularly problematic if proper fouling resistances were not specified for initial design of the system.
Plugged dip legs - Dip legs which plug from corrosion products, salt, or wax formation can lead to flooding the condensers which reduces available surface area for condensing, increases pressure drop through the condensers, and overloads the ejectors.
Improper steam pressure/temperature- Delivered steam pressure lower than design, higher temperature than design, wet steam (extremely detrimental from performance and erosion stand point).
Overloaded cooling water systems - Results in higher than design cooling water temperatures to the condensers reducing LMTD and increasing vent saturation temperature, so load to the next stage increases.
Low cooling water pressure (no booster pump) - Results in lower than design cooling water flow rates and higher cooling water delta T which reduces LMTD and increases vent saturation temperature, so load to the next stage increases.
Eroded ejector throat – Dimensional changes in the ejector nozzle and diffuser throats move the jet off of its design curve. If cross-sectional area of throats wear by more than 7% they should be replaced. If nozzle or diffuser throats are out of round or not smooth they should be replaced.
Plugged Check Valve – Some designs have located check valves in the vent gas line which has a high potential for plugging.

In addition to loss of performance of the ejector system it is critical not to ignore the possibility that lower tower vacuum (higher absolute pressure) may be the result of changes in the load which exceed the capacity of the ejector system.

Excessive stripping or coil steam
Increasing unit charge rate
Higher than anticipated non-condensable gas load – This could come from cracked gas production from heavier crude processing, furnace coil outlet changes, and air in-leakage.

Any of the above conditions except even throat wear may result in what is know in the industry as a "break" in performance of a critical ejector. When a vacuum system "breaks" there is a sudden rapid increase in pressure (loss of vacuum) resulting in unstable operations. Resulting break pressures can be 3 to 5 times higher than design. The system is no longer operating on its curve so performance under a break condition cannot be predicted.

Nothing beats getting out of your air conditioned office, getting up on the structure and taking real readings on temperature, pressure and flow. Often the instrumentation on these systems is neglected, if installed at all. Identify all locations in which temperature and pressure can be read. If necessary, use skin temperatures to approximate actual process values. Accurate pressure readings by electronic gauge at the suction and discharge of each ejector in a multi stage system are the most critical trouble shooting data points. A complete pressure profile of the system (not just suction at 1st stage and hotwell pressure) provides the necessary information for system performance analysis. Taps are not always present at ejector discharge or condenser inlets, but interstage pressures are critical to analysis of system performance, so taps should be installed at shutdowns if not available.

Learn what the ejector performance curves look like; evaluate loads and match performance to curves. If it's not on the curve what is wrong? Calculate duties on condensers and compare to design. By performing these types of fundamental process engineering follow-ups routinely, a unit engineer can often detect deviations in performance before they become unit limiting.

Dennis Haynes (NALCO Energy)
There is a report of a Vacuum Distillation Tower that during a turnaround removed a demister pad that was in place in the tower. Due to this, there was an increase in carry through of some heavier hydrocarbons. During winter, plugging of the overhead coolers was experienced. The plugging was identified as wax fouling. The solution put in place was to control the temperature of the cooling water to the exchangers to above the flow point temperature measured for the heavier gas oil. Reoccurrence of the problem has not been reported.

Coking

Question 63
What crude and/or resid properties and plant operating parameters predict delayed coke quality, e.g. volatile combustible material, shot coke, Hargrove Index, or others?

Mitch Moloney (ExxonMobil)
Response - All are independent functions of feed properties, coke drum operating conditions and coke drum coking time. Operating variables are given in prioritized order from most important to least.

<u>VCM</u> is a strong function of basic resid type, crude source, operating severity and position in the coke bed.
<u>Basic resid type</u> means atmospheric resid or vacuum resid. Atm resid will tend to have a higher VCM due to the higher level of gas oil in the feed.
<u>Crudes</u> with high levels of heavy resins (e.g., multi-ring aromatics) will coke more slowly and yield a higher average VCM.
<u>Operating severity</u> refers to temperature, pressure, % natural recycle, % distillate recycle, and steam rate. Higher temperature, lower pressure, lower natural recycle, higher distillate recycle and higher steam rates increase coking severity in that they liberate more product from the coke bed, which translates into less VCM remaining with the coke.
<u>Position in the coke bed</u> means that coke higher in the coke bed will have higher VCM, given that it has been cooking longer than the coke beneath. This has been well documented by Great Lakes Carbon pilot plant studies. Increasing temperature near the end of cycle can help lower VCM.

<u>Shot Coke</u> is function of crude type, molecular composition, operating severity, basic resid type, and coke drum hydrodynamics.
<u>Crudes</u> with high levels of asphaltenes (nC7 insolubles are the best correlator) will be more prone to shot coke, given that they will be more prone to link and precipitate from solution. Ratio of CCR (or MCR) to asphaltenes, as noted in the literature is a good indicator of shot coke tendency.
<u>Molecular Composition</u> is another key factor. The presence of heavy aromatic molecules, like those found in FCC heavy gas oil or bottoms, can solubilize the asphaltenes, preventing their crosslinking and resultant precipitation. The presence of indigenous heavy resins (e.g., multi-ring aromatics), as mentioned for VCM, will coke more slowly and also affect coke morphology. Correlations can be developed that take into account compositional variables to predict shot coke.

Operating severity refers to variables mentioned for VCM. Increase coking severity and its effect on shot coke tendency, is well documented by Lieberman in the literature. Higher severity liberates more product from the coke bed, which translates into less asphaltene solubilizing material in the cracking liquid.
Basic resid type, as defined above, can affect shot coke tendency. Atmospheric resids consume heat of vaporization in the furnace at constant operating temperature, which will leave more material to solubilize and bind asphaltenes, reducing the tendency for shot coke.
Coke Drum hydrodynamics means that sufficient turbulence is needed to form the shot coke BB's. This turbulence threshold is typically well below commercial operating conditions, but can be a factor when unit feed rate are 50% of normal.

HGI, or Hardgrove Grindibility Index, is inversely proportional to coke hardness. Lower HGI indicates a harder coke, in that a fixed amount of energy is applied to a standard sample, the amount of crushed material passing through a filter is compared to a standard. Less material per kg of coke indicates a harder, more difficult to grind, coke. HGI is inversely analogous in behavior to VCM, being a strong function of basic resid type, crude source, operating severity, coking time and position in the coke bed.
Basic resid type - Atm resid will tend to have a lower VCM due to the higher level of gas oil in the feed. Such resids can have HGI's 20 to 30 index units above vac resid for the same crude.
Crudes with high levels of asphaltenes will have lower HGI's.
Operating severity – Higher severity will reduce HGI.
Coking Time – Longer cycle times will translate into harder coke, given the increased cooking time. Typically cokers that have gone to 12 hour cycles, have seen average bed HGI's increase.
Position in the coke bed – As with VCM, the coke at the top of the bed has less time at temperature and will have higher HGI.

Question 64
What operating practices have you used to minimize vapor emissions (i.e., light hydrocarbons) when opening coke drums to the atmosphere?

Mitch Moloney (ExxonMobil)
Safety is more concerned with H2S level and environmental performance is more concerned with VOC's (Volatile Organic Carbon). Key factors are crude type, unheading pressure, steam stripping, quench procedure, PRV closure integrity, and isolation valve closure integrity.
Crude type – Low sulfur crude will yield lower H2S emissions, with little effect on VOC's.
Unheading Pressure – Unheading at $\leq$1 psig will yield less emissions to the vent than at 10 psig by simple thermodynamic equilibrium.
Steam Stripping – The rate of steam and the duration of stripping to the Main Fractionator and Blowdown will help displace coke bed voids.
Quench Procedure – Higher water rates and longer times will help displace voids. Cokers that "water over," overflow the coke bed with water to the pit or pad, will have reduced top head emissions, but will still have possible release of light HC to the environment. The EPA has recently promulgated a New Source Performance Standard setting a limit of 5 psig for opening the coke drum to the atmosphere.
PRV Closure Integrity – if the PRV is not completely closed, vapors from the discharge side of the PRV can back flow to the coke drum. Some cokers close the discharge block valve using a lock and tag procedure or an automated valve with PLC-interlock to mitigate this risk.
Isolation Valve Closure Integrity – Use of double block and steam barrier isolation on all valves linked to hydrocarbon sources greatly reduce the risk of leakage to the coke drum. Lock and tag procedures or automated valves with PLC interlock are encouraged.

Question 65

How do you predict whether a delayed coker drum has hot spots or is ready for a blowout?

Mitch Moloney (ExxonMobil)

Hot drums typically occur because partially coked resid at the top of the coke bed collapses after drum switch and encases 800°F coke. This resid glassifies on cooling with water and prevents quenching of the coke within. When high pressure cutting water hits the area, the water explosively vaporizes, pressurizing the coke drum and lifting coke out of the coke drum. Hot drums can also occur in the lower reaches of the coke bed, if coke drum warm-up was poor or if resid is poorly coked due low temperatures or high aromatic feed content.

Hot drums occurring in the top of the coke bed can be "predicted" by one proactive method, namely by developing crude blend correlations , which relate resid compositional variables to coke morphology. The idea is to create blends that are relatively "fast coking," reducing the amount of partially-coked resid in the coke bed. The frequency and severity of hot drums can be reduced by the following:

Increase coke bed temperature neat end of cycle – This will help reduce quantity of uncoked resid.

Maintain Minimum Steam Stripping – The rate of steam and the duration of stripping to the Main Fractionator and Blowdown will allow the coking reactions to complete since steam does not greatly cool the coke bed (it actually is heated as it moves through the bed). Higher steam rates will keep flow channels open and reduce the amount of coking resid slumping back into the coke bed.

The presence of hot drums can be deduced by the following:

Correlating the amount of quench water collected in the blowdown system – Less then normal quench water normalized for the amount of feed can indicate that water did not penetrate portions of the coke bed. Precautions like partial drain and fill, water over or soaking can then be employed.

Install and Monitor Skin Thermocouples on the Coke Drum walls – This is less effective than totalizing water recovered in blowdown, but can indicate maldistribution or channeling in the coke bed. Again additional cooling steps can be taken and precautions during coke cutting can be used.

Question 66

What are your current experiences with coke drum life and how do you measure and monitor their condition? What on-line inspection techniques do you use? What improvements have been made to coke drum design and what techniques are used to replace them? What parameters are specified for drum cycle management to optimize unit production and drum life?

Mitch Moloney (ExxonMobil)

Coke drums are unique pressure vessels in that they undergo significant cyclic thermal fatigue over their life. As many know, cycle times in the last 20+ years have been reduced from 24 hours to between 12 to 16 hours on many units, greatly increasing the number of thermal fatigue cycles per year. Reduced cycle times result in inadequate warm-up of the coke drum prior to feed introduction and cause refiners to reduce steam stripping and speed bed quenching. In addition, the processing of heavier coker feeds has increased the prevalence of bonded shot coke beds, which are more prone to maldistribution when water quenched, creating more severe drum metal stress peaks. All these factors increase the likelihood of developing coke drum cracks.

Our typical coke drum life is 30 to >40 years. As the drums age, we increase monitoring using stress/strain measurements and inspection of known high-stress weldments, like the drum-to-skirt and outage welds.

On-line inspection techniques include use of removable insulation panels at weld seams to allow visual inspection via rope access or platforms, or the use of more sophisticated techniques like UT Shear Wave, Phased Array and Time of Flight Detection.

Coke drum design features include proper dimensioning of skirt height-to-diameter ratio using Finite Element Analysis, use of a skirt hot box, use of skirt slots, minimization of course panel thickness changes, strict weld quality control, proper nozzle designs and minimization of attachments to the coke drum. Skirt slots can be retrofit on-line via planned panel replacements.

Controllable parameters are coke drum warm-up temperatures measured with skin thermocouples and optimized steaming and quenching to meet cycle time requirements while minimizing metal stresses measure with strain gauges or other techniques.

Utilities

Question 67

Recovery of heat from overhead condensing systems is typically limited by temperature difference and available cold sinks. A good sink is treated, demineralized water to feed water to deaerators. Discuss:

- *a. Current temperature of deaerator feed water.*
- *b. Experience with existing waste heat recovery systems to preheat deaerator feed water.*
- *c. Economic payouts to further increase deaerator feed water temperature by recovering heat from overhead condensing systems.*
- *d. Rebalancing the steam system to utilize steam backed out of the deaerators.*

Todd Sandifer (Marathon Petroleum Company)

- a) Ambient to 120 Deg. F.
- b) Waste heat exchangers used to increase the make up water temperature can often fail due to oxygen corrosion. With the use of demineralized water make up as opposed to softened water make up the potential for oxygen corrosion is reduced, however it is still recommended that exchangers be constructed of Duplex 2205 or stainless steel. The only successful application we have required Duplex 2205 bundle metallurgy.
- c) The economic payout is related to the reduction in steam required to heat the water to the operating temperature of the deaerator. This is only a valid savings if a facility does not have excess low pressure steam that is vented to the atmosphere. In addition, it is necessary for the deaerator to maintain a minimum level of steam; otherwise it will not effectively remove dissolved oxygen. For most tray type deaerators there must be at least a 20 to 30 degree F increase in the temperature of the inlet water for there to be enough scrubbing steam to effectively remove dissolved oxygen. For scrubber type deaerators, the required temperature increase is 50 to 60 deg. F. Designs should consider the catastrophic impact of leaking hydrocarbon into the boiler feed water system where steam is used for stripping, blanketing, purging, etc.
- d) Turbine drive economics can be considered at current electrical vs fuel values. In certain cases it is more cost effective to eliminate turbine drives to reduce low pressure steam production. There are typically few alternatives for use of low pressure waste steam other than deaerators.

Mitch Moloney (ExxonMobil)

The National Environment Agency (NEA) has developed a Code of Practice for the Control of Legionella bacteria in Cooling Towers. Here is a link to the web site => http://app.nea.gov.sg/cms/htdocs/category_sub.asp?cid=227

ExxonMobil has developed a corporate practice that addresses the microbiological control of open loop recirculating cooling water systems. Key aspects of the program are

Written documentation. The microbiological control program for each Cooling Water System shall include written documentation for the control of microbiological growth and
for personnel exposure to mist. The program shall include plans and procedures for responding to cooling system operations when outside the normal operating range.

Monitoring of key performance parameters: Key system parameters shall be maintained within specified control limits. The monitoring program shall include:

- Free halogen residual (recorded as ppm free chlorine)
- Total Viable Colonies
- Adenosine Triphosphate (ATP), bacteria dip slide method, or equivalent
- Legionella
- Hydrocarbon Level (if the system is susceptible to hydrocarbon contamination)

The monitoring program should include trend analysis to develop a baseline on which to assess ongoing system performance.

Key water quality parameters. The water treatment program shall include measurement of required parameters through either the use of analyzers or via sampling and lab analysis on a regular basis.

<u>Free chlorine</u> - Free chlorine residual shall be measured at least once a day to ensure that a minimum free chlorine residual of 0.3 ppm is maintained continuously throughout the system.

<u>Microbiological Level</u> - Weekly testing: Cooling water shall be tested weekly for microbiological activity using adenosine triphosphate (ATP), bacteria dip slide methods or an equivalent method. The testing frequency should be increased to twice a week if the hydrocarbon level increases above a predetermined limit, see Paragraph 3.4.3.

<u>Microbiological Level</u> - Twice monthly testing: Cooling water shall be tested at least twice monthly for total bacteria counts using a total viable (plate) count method. If weekly plate counts are conducted, ATP or dip slide testing is not required as this is an equivalent method.

<u>Microbiological Level</u> - Legionella: Legionella test frequency shall be once per quarter using a plate counting method.

<u>Hydrocarbon Concentration</u> - Systems susceptible to process contamination shall also incorporate hydrocarbon monitoring and control procedures into their microbiological control procedures.

<u>Oxidizing Biocide Addition</u>: Continuous sodium hypochlorite injection is preferred. However, site specific circumstances may result in the selection of gaseous chlorine or bromine based biocides. Calcium hypochlorite is acceptable where the increased calcium is compatible with the treatment. The selected halogen-based-oxidizing biocide shall provide a free halogen residual and shall be calculated as free chlorine residual to meet the control levels.

<u>Use of a Biodispersant</u>: A biodispersant should be considered, as necessary, to control bacteria which adhere to the internal surfaces of the cooling system. The biodispersant should be injected gradually to control sloughing and to minimize foaming.

Additional recommendations:
- Minimize cooling water dead legs
- Keep external components of the tower free from moss and algae
- Contain water droplets within the tower where possible
- Fix basin leaks
- Maintain the drift eliminators in good condition.

Question 68

If you were adding new boilers to the refinery, what boiler design criteria would you consider and how do they relate to water quality requirements? What quality measurement do you use and what water preparation process would you recommend, e.g., softener, reverse osmosis (RO), demineralizer, etc.?

Dennis Haynes (NALCO Energy)

Nalco is not involved in the design of boilers; however, the following are some comments based on experience as a water treatment company.

A refinery needs to decide what type of steam temperature and pressure are needed for the particular process. With that said there are definitely some "design considerations" that will impact corrosion and fouling in the steam circuit.

Steam Purity

1. Units need to be designed with an adequate steam drum size. Small steam drums result in more carryover.
2. Units need to have adequate steam separation equipment in the drum. (cyclones, chevrons, demisters, etc.)
3. Attemperation water needs to be ideally a "sweet water condenser" of condensate (preferably polished). RO water is not acceptable.
4. Demineralized water or NaZ RO water makeup plus condensate return will produce a boiler water that is low in TDS, allow high cycles and low silica levels.

Boiler Internals

Boilers internal issues are predominately iron and hardness precipitation issues in non-demineralized systems. If softened water is used, on-line chemical treatment that is automated to demand is required. Softened water can have substantial variability and would not be preferred. High purity RO or demineralized water should be the choice in new facilities. Corrosion is the major issue in high purity water systems.

1. RO systems are very popular for < 1000 psig systems. RO systems make very low TDS water, which is easily handled in the < 1000 psig systems. However, RO systems require a total dedication to having low suspended solids and microbiological control or the system will fail. This means "best in class" suspended solids monitoring and removal (filtering and ultrafiltration) and chlorination. The systems need on-line monitoring and automated control of all of the applied chemistry. Without that dedication, demineralization including polished condensate should be used instead of RO.
2. Demineralized water is excellent for all boilers < 1000 psig. If the system is high pressure > 1000 psig the systems should include polished condensate.
3. Low pressure condensate should be collected in a tank and then pumped to the deaerator system. A tank provides a "wide spot in the line" so hydrocarbon contamination can be separated out. Pumping condensate will also stabilize de-aerator operation.
4. High pressure systems need to have condensate polished and have activated carbon filtration for "suspect condensate" with hydrocarbon or organics.
5. On-line monitoring and automated chemistry control is needed to provide "best in class" corrosion and scale protection.

Deaeration

1. Critical to use a source of steam and a control system that will deliver proper mechanical oxygen removal.
2. Chemical oxygen scavengers need to be fed to the storage section of the deaerator process. Feed after the deaerator is not recommended.
3. On-line oxygen monitoring and pH is recommended downstream of the BFW pumps.

Sampling

The most encountered failing in refinery boiler systems is hot steam and water sampling.

Uncooled samples are dangerous and provide unreliable data. All sample coolers in the steam system should have a sample cooling system not just a sample cooler. Sample cooling system includes flow and temperature control with dual coolers in parallel.

Steam sampling must be done with an isokinetic sampling system. Saturated steam is generally the steam sampled in a refinery system.

Economizers should have water outlet sample points that are routinely sampled to insure no active corrosion is taking place.

Todd Sandifer (Marathon Petroleum Company)

When adding a new boiler it is important to first assess what the steam requirements are: quantity and variability, pressure, temperature and purity. These factors all depend on steam use. If the boiler will produce superheated steam to drive a steam turbine, the turbine manufacturer's steam specifications should be identified. These specifications will normally be the most stringent requirement for steam purity so if they are met, then the steam will probably be suitable for other uses. If the boiler will not produce superheated steam to drive a turbine then you need to assess what process requires the purest steam and establish that level. ASTM isokinetic steam samplers should be included in design scope to monitor conductivity and sodium. The fewest number of boilers required for reliability and inspection should be constructed and should be designed for highest efficiency without getting into flue gas corrosion issues

Once the steam purity requirements are established, they need to be compared to the boiler manufacturer's guarantee of fractional carryover of boiler water into the steam. This will enable you to determine the maximum permissible solids (often related to sodium for ease of measurement) and silica levels in the boiler water. We require design criteria that include adequate disengaging space to meet 0.5 TDS in steam.

The next step is to assess which types of external treating equipment will allow you to maintain the boiler water total solids and silica levels at, or below, the "maximum permissible" levels at a reasonable boiler blow-down rate. Do not forget to include the condensate return in this assessment.

When the water treatment systems that will produce water with satisfactory levels of solids and silica have been identified they should all be assessed with respect to their ability to reduce potential deposit forming substances such as calcium, magnesium and iron to acceptable levels for the boiler being considered. The ASME "Consensus on Operating Practices for the Control of Feed water and Boiler Water Chemistry in Modern Industrial Boilers" suggested water chemistry limits provide suitable recommendations on these contaminants for most fired boilers

After identifying those systems that still meet these criteria, the rest of the evaluation should focus on economics, equipment and installation costs, operating and maintenance costs, water treatment costs and expected system reliability.

The chemical costs vary with the pretreatment scheme. Acid, salt, and caustic chemical costs (for regeneration) have risen dramatically over the last few years and must be considered in the economics.

Membrane technologies can be built with minimal footprint and lower initial costs, but are limited to approximately 98% rejection of dissolved solids; a secondary treatment scheme is necessary to consistently achieve ASME hardness limits.

For high hardness surface waters, the favored scheme is zeolite followed by RO. This allows the scaling chemicals (calcium, magnesium) to be removed prior to the RO via the least expensive regenerant (salt). The use of expensive antiscalants can be minimized by this method, high recovery rates can be achieved, lower boiler and afterboiler chemical costs are gained, and energy cost reduction by increased boiler cycles can be obtained.

For well waters with no suspended solids and low hardness (less than 100 ppm), it is likely that the most economical scheme would be to treat with RO initially, then polish with a zeolite to ensure that hardness was consistently acceptable. This scheme would allow minimal regeneration chemical costs, and the low hardness would reduce the RO scaling concerns.

Question 69

How do you evaluate and control the risk of Legionnaires' disease in your facility?

Dennis Haynes (NALCO Energy)

Generally, there are 5 steps to be taken in sequenced order to implement a “Best In Class” Legionella Risk Management program. The first step is to define a Corporate Policy for Waterborne Pathogens.

After creating this policy, the second action is to complete a physical assessment of risks at the individual sites, in conjunction with standards created in the corporate policy. These assessments will generate site-specific waterborne pathogen risk management plans.

The third phase is the execution and implementation of these site-specific plans. The execution phase includes, but is not limited to, adhering to the recommended projects to physically reduce risks, as well as the implementation of routine risk reduction programs, such as pathogen analytical testing.

The fourth step is the execution of potentially non-routine action items. These items would include responses to documented risks and the subsequent remedial follow up action projects, as defined by the corporate policy and risk assessments.

Lastly, the documentation and due diligence review of the risk management program is completed and set up as an ongoing oversight project. This includes oversight from the responsible parties at each site and the oversight from the responsible corporate entities to ensure the risk reduction programs are properly followed to reduce overall corporate liability.

Specifically, many refiners are addressing this. There have been incidents (major ones) occur in refineries. These incidents have led to the process above. Many refineries are testing, and they typically test frequently due to either process or biological control concerns, among others.

Sid Dunn (Baker Petrolite)
Baker Petrolite is fully committed to helping hydrocarbon processors effectively and efficiently deal with the various HSE complications Legionella populations can create. We have developed a position paper on how we engage with our customers to help them comply with industry guidelines as appropriate. We are happy to share this paper with any hydrocarbon processor facing such potential issues. Specifically, we have particular expertise in the application of certain biocide treatments cited by industry guidelines as appropriate for the control of Legionella numbers.

GASOLINE PROCESSES

Safety

Question 70
How frequently do you have fires on reformer reactor flanges? What bolting techniques and gasket types do you use to prevent leaks? What other fixes, such as flange resurfacing, have you employed? Do you use steam rings as a temporary fix?

Rick Grubb (Chevron USA)
We have experienced several fires in the past but recently this has been greatly reduced. We've developed a Best Practice for gasket selection and bolting techniques. Following these Best Practice Guidelines has been successful. Areas were we've seen problems in the past we have installed steam rings and employed techniques such as chicken wire to make detecting a leak easier.

We use Kamprofile gaskets for any raised face flange over 24 inches. These gaskets are robust, easy to handle, provide a very reliable seal and the gasket core can be reused after replacement of the facing materials. A modified star pattern bolting technique is employed where 4 nuts are torqued to 100% in a star pattern and the rest are torqued to 100% in a clock-wise pattern for two passes on each nut. After insulators are finished with the piping someone needs to verify that the flanges (studs) are not insulated to ensure the studs maintain their integrity.

Flange surface finish should be 125 RMS to 250 RMS, which is a pretty standard finish. (Pipe flanges are typically 250 RMS.) A high quality graphite material must be used for the Kamprofile gasket covering. We specify APX-2 graphite as it has the highest oxidation temperature. Stud loads should be set to obtain a 20,000 to 25,000 psi gasket stress. Steam rings should never be needed if the right gasket is used and assembled correctly. They should only be used in emergencies and never as a temporary fix.

Question 71
Is your company planning to install modified HF acid capability (usage of a volatility suppressing additive)? What are the incentives for doing this? What alternatives have you considered?

Javier Quintana (Valero Energy)
Vapor suppression additives represent only one possible feature for consideration as part of a comprehensive HF acid Process Safety Management (PSM) program. Industry recommendations to take into consideration are outlined in API RP 751 – "Safe Operation of HF Acid Alkylation Units". An effective program will comprise recommendations emphasizing leak prevention and monitoring along with mitigation systems to be used in case of a leak event. There are various elements recommended under API 751 for consideration:

- HAZOP assessment of existing unit equipment & controls
  - per API RP 750 – Management of Process Hazards
- Management of Change program to address controls, instrumentation, metallurgy, procedures, relief system
- Thorough emergency response and control plan
- Regular and thorough unit audits to address:
  - Unit specific & industry incidents and risk exposure in the unit
  - Inspection, maintenance & training records
  - Mechanical & procedural changes since previous audit

  - Testing & maintenance of detection, monitoring, control systems
  - Testing & maintenance of mitigation systems in case of a leak
  - Procedure compliance, understanding via observation, interviews
- Technology developments that further reduce accident risk
- Regular and rigorous equipment inspections to confirm integrity of unit equipment, especially acid containing equipment
- Use of correct metallurgy – per NACE 5A171
  - Confirmation with Positive Material Identification program, especially in case of repairs or changes to equipment, piping
- Tracking mechanism to ensure resolution, close-out of identified issues – design tracking system to facilitate next audit
- Reliable level instrumentation systems less prone to fouling, such as nuclear, radar, ultrasonic or magnetic
- Minimum acid inventory
- Mitigation systems

Mitigation systems can include active and/or passive elements, as well as tell-tale components, such as HF detectors (point, open path or imaging systems, deployed as deemed necessary in the unit risk envelope) and HF-sensitive paint on flanges, pump seals, etc. Active mitigation systems will often include water deluge and/or water curtain systems, remote video monitoring and remote activation / isolation systems, and a rapid dump system to contain the acid inventory and limit the impact and quantity of any release event. Passive systems may include barriers and catch pans to contain any acid release, minimum acid inventory control and staging in the plant equipment, or vapor suppression additives.

Each facility should determine their location-specific risk factors, and assess the appropriate combination of active and/or passive mitigation systems needed to minimize risks involved in operating the unit. Any PSM program should also be verified to be in compliance with relevant local, state, and/or federal regulations.

Alkylation

Question 72

What feed contaminants can lead to metal corrosion in both sulfuric acid and HF alkylation units? What operating conditions promote corrosion? What do you do to reduce corrosion and/or remove contaminants?

Rick Grubb (Chevron USA)

I've consulted others within Chevron and this answer has been provided by Gary Ash from Pascagoula and Steve Mathur from Corporate. The biggest corrosion problem in the reactor section of the alky unit is acid. Feed contaminants don't really cause significant corrosion by themselves, but they can potentially make the acid more corrosive. Water is the worst and corrosion rates can increase very dramatically if water contamination results in diluting acid below 92% strength. Alcohols (present in MTBE unit raffinate) can also increase acid corrosion. Most other feed contaminants can spend acid but will not greatly accelerate corrosion at normal acid strengths.

The above being said a good deal can be done to minimize sulfuric acid corrosion by controlling temperature and velocity. For acid services we generally limit temperatures to <100 F (max) and try to minimize velocity and turbulence in acid piping by using long radius elbows, carefully controlling the use of throttling valves or flow orifices, etc. Also critical is to avoid potential dead legs in pipe where acid could potentially settle out and then sit. And our most important control is metallurgy. In general we do not use carbon steel pipe for acid service.

Allen Kaiser (Delek Refining)

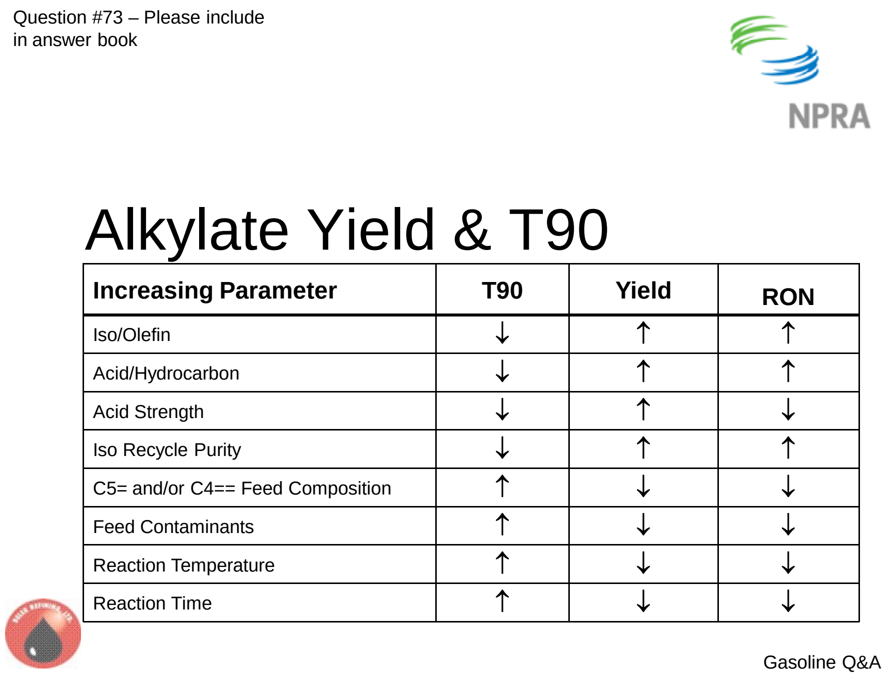
There are several good practices that all refiners should follow in the operation of their alkylation units – 1) closely monitor the acid strength and water content in the case of HF; 2) for HF units, carefully monitor the acid regeneration operations to ensure both good rejection of acid-soluble oils and retention of acid; 3) for sulfuric units, maintain good operations in the effluent treating section (acid/caustic wash followed by a 120ºF+ water wash); 4) monitor the equipment and piping that is susceptible to excessive corrosion with a good mechanical integrity program. NACE papers 04645 "The Effect of Operating Conditions on Corrosion in HF Alkylation Units" and 07570 "The Top Ten Corrosion Issues Affecting HF Alkylation Units" contain good references for metal corrosion in HF alkylation units (with some applicable items for sulfuric units).

Question 73

Does alkylate volume yield decrease if T90 increases? Have you quantified the costs and benefits of reducing T90 by changing reaction conditions?

Allen Kaiser (Delek Refining)

Each of the variables that a refiner can directly and easily effect changes to in the alkylation unit has a particular impact on the alkylate distillation end point (EP) and 90% boiling point (T90), but few have a direct impact on the T90 itself without indirectly affecting it by creating more or less polymer material. Most refiners are already running near an optimal point to minimize polymer production in their units – which directionally improves alkylate yield and reduces alkylate T90. Monitoring the primary reaction variables and performing a cost/benefit analysis on significant changes to those variables, with some limited test runs to determine particular equipment and processing limitations, can likely provide a clear indication on any gains to be made.

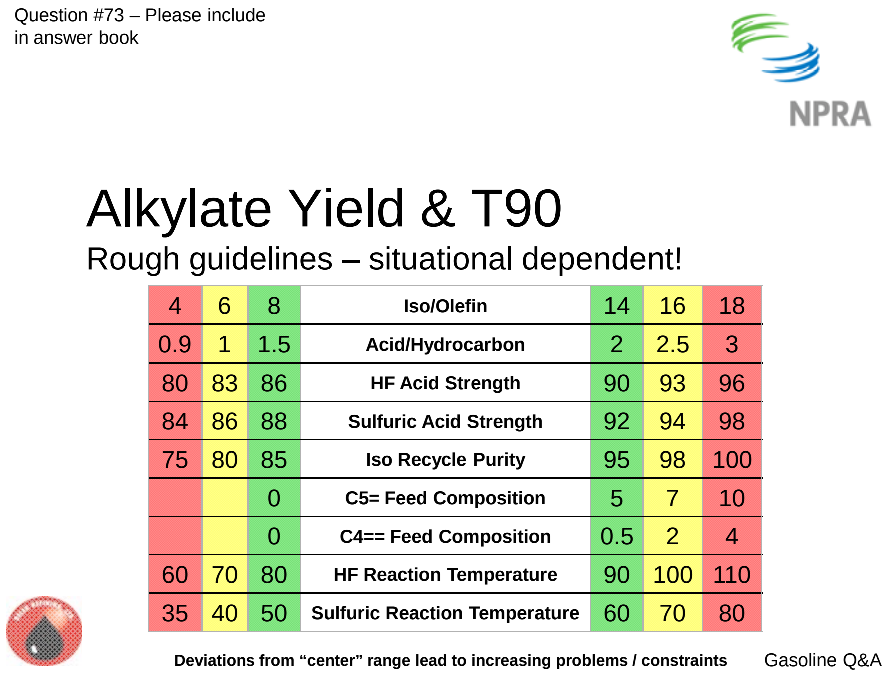


Question #73 – Please include
in answer book

Alkylate Yield & T90

Increasing Parameter	T90	Yield	RON
Iso/Olefin	↓	↑	↑
Acid/Hydrocarbon	↓	↑	↑
Acid Strength	↓	↑	↓
Iso Recycle Purity	↓	↑	↑
C5= and/or C4== Feed Composition	↑	↓	↓
Feed Contaminants	↑	↓	↓
Reaction Temperature	↑	↓	↓
Reaction Time	↑	↓	↓

Gasoline Q&A



Question #73 – Please include
in answer book

NPRA

Alkylate Yield & T90

Rough guidelines – situational dependent!

4	6	8	**Iso/Olefin**	14	16	18
0.9	1	1.5	**Acid/Hydrocarbon**	2	2.5	3
80	83	86	**HF Acid Strength**	90	93	96
84	86	88	**Sulfuric Acid Strength**	92	94	98
75	80	85	**Iso Recycle Purity**	95	98	100
		0	**C5= Feed Composition**	5	7	10
		0	**C4== Feed Composition**	0.5	2	4
60	70	80	**HF Reaction Temperature**	90	100	110
35	40	50	**Sulfuric Reaction Temperature**	60	70	80

Deviations from "center" range lead to increasing problems / constraints

Gasoline Q&A

Kurt Detrick/Joe Zmich (UOP LLC)

Olefin feed composition probably has the greatest effect on T90 – especially the C5 olefin content.

For a given olefin feed composition, changing the process variables within the normal range of operation would typically not have a strong effect on T90 and the effect on the alkylate volume yield will also be limited. If the T90 increases the specific gravity of the alkylate would also be expected to increase and since the alkylate weight yield would remain about the same, the volume yield would be expected to be slightly lower. If the T90 is increased by decreasing the isobutene/olefin ratio, then the octane of the alkylate would be expected to decrease – this effect could be significant.

UOP has not quantified the costs and benefits of reducing T90 by changing reaction conditions.

Question 74

Have you experienced a shortage of KOH supply for your HF alkylation unit? Are you concerned about KOH availability? What are your alternatives if KOH is unavailable?

Question 75

The butane stream from a catalytic polymerization (cat poly) unit which contains 69% isobutane, 14% butylenes, and 17% normal butane would appear to be an excellent alkylation unit feedstock, especially if isobutane is in short supply. In the case where the cat poly unit uses solid phosphoric acid (SPA) catalyst, what are the consequences of having trace amounts of phosphoric acid in the alkylation feed? Do you have a rule of thumb for estimating the increase in acid consumption based on phosphoric acid concentration in the feed? Are you aware of any refiner which has fed a cat poly butane stream to an alkylation unit?

Kurt Detrick/Joe Zmich (UOP LLC)

UOP does not have experience with traces of phosphoric acid coming into the HF Alkylation unit. However, we strongly recommend avoiding this possibility because in most cases, combinations of two or more strong mineral acids result in a much more aggressive corrosion situation than either of the individual acids alone.

UOP is aware of at least one refiner that feeds a Cat Poly product stream to the HF Alky unit. The product stream goes through a water wash, sand tower (coalescer), and a UOP Merox™unit along with the olefin feed from the FCC unit before going to the Alky unit.

Question 76

The regeneration of feed dryers/sulfur guard beds on butane isomerization units generates a butane slop stream. Will processing this butane slop stream in an HF or sulfuric acid alkylation unit cause any problems? If so, what else may be done with this slop stream?

Javier Quintana (Valero Energy)

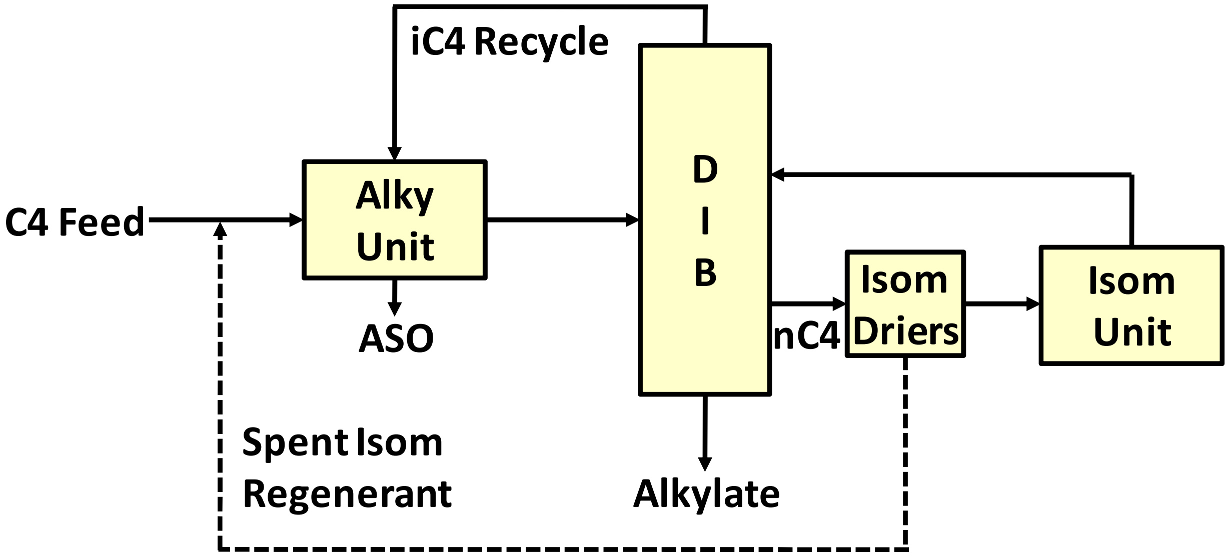
The spent drier regenerant stream from a butane isomerization unit contains a substantial amount of butanes which are attractive to recover. The composition of these butanes depends on the regenerant source, and can be primarily n-butane, i-butane, or a mix of the two. However, this stream also contains the various impurities which the drier adsorption cycle managed to accumulate and remove from the isomerization unit charge stream. These impurities include water, sulfur and oxygenate compounds which are primarily nC4 co-boilers, which must be considered in determining optimal routing of this stream. These impurities will also be contained at relatively high concentrations in the regenerant stream; only excess water is removed to any extent in the regeneration system via the regenerant coalescer, but the final regenerant slop stream is saturated when leaving the isomerization unit.

If the spent regenerant is sent to an alkylation unit for recovery of the butanes, then the alkylation unit feed driers will remove water, but not necessarily the sulfur or oxygenate impurities, generally with three consequences:

- Sulfur compounds and oxygenates will consume acid, but are not necessarily completely converted in the alkylation unit.
- Acid consumption byproducts will increase load on the acid regenerator
- The unconverted portions of sulfur and oxygenates will typically end up the nC4 stream from the fractionation section, recycling back to the isomerization unit feed

Acid consumption levels due to these impurities can be significant, in the range of 8-12 pounds of acid per pound of contaminant in sulfuric acid units. Oxygenates can particularly problematic in HF units, where lighter boiling range contaminants are made, often reducing the initial boiling point of the acid soluble oil stream by more than 100°F, forcing a reduction of temperature in the acid regenerator, thereby increasing physical losses of acid.

The following sketch illustrates the impact that such unconverted sulfur and oxygenate species will have, in that they will add to the level of impurities that were introduced via the fresh the alky butane feed, resulting in a “wind-up” of sulfur and oxygenate levels in isomerization unit feed, possibly breaking through the feed driers and deactivating isomerization catalyst.



The tolerance of a particular unit to this wind-up effect depends in large part on the amount of sulfur in the refinery fresh butane stream to the alkylation-isomerization section and the available slack capacity in the isomerization unit feed driers. If there is little slack capacity in the driers, then any such wind-up presents risk of break-through and catalyst deactivation.

Alternatives to sending the spent regenerant to the alkylation unit involve finding a location where either the contaminant species are converted to a greater extent than in the alkylation unit, resulting in a lower extent of wind-up, or where the residual impurities do not recycle at all to the alkylation or isomerization units, thereby eliminating the wind-up effect. The ideal solution is usually to co-process the spent regenerant in a hydrotreating unit (generally the naphtha treater is used), with the treated refinery butanes pooled and sent to the alkylation / isomerization section.

Depending on the refinery fuel balance, some dispose of the spent regenerant by vaporizing the stream into the fuel system, although the sulfur level of the stream may present a concern with SOx levels in heater flue gases. Another alternative is to send the stream to a FCC butanes sweetening unit, although sulfur removal occurs to a lesser extent than in the hydrotreater.

Question 77

What is your experience with cooling water exchangers in an HF alkylation unit? How long do you go between cleanings? Do you have a special water treatment program for cooling towers dedicated to the alkylation unit?

Allen Kaiser (Delek Refining)

Cooling water exchangers in an HF alkylation plant are no more problematic than any other exchanger in the plant when considering the water side of the bundle. In the HF unit where I have experience, the HF coolers were generally able to maintain acceptable performance for 2-3 years. Nearly all of the leaks in the water cooler exchangers I've had to deal with were due to process side corrosion. Both alkylation units that I have direct experience with have their own dedicated cooling towers. The type of treatment program for an alkylation cooling tower is not necessarily significantly different than any other tower in the refinery. Rapid pin-pointing of the leaking exchanger is critical to minimizing corrosion damage to other exchangers and to the cooling water distribution piping.

Kurt Detrick/Joe Zmich (UOP LLC)

We have seen corrosion in cooling water exchangers in HF alkylation units on both the process and water side.

Typically the corrosion rate on the process side of the reactor bundles and the acid cooler bundles is relatively low at normal operating conditions. Excessive temperature or high %water in the circulating acid can cause corrosion and plugging on the process side of these exchangers.

Refiners have reported higher corrosion rates on the process side of water-cooled condensers – especially if the water content of the circulating acid is high.

Corrosion on the cooling water side of the exchangers is often due to low cooling water flow rate. The low water flow rate can lead to fouling of the tubes due to biological growth or calcium scaling – both of which can lead to under-deposit corrosion. Inadequate treatment or blowdown of the cooling water can also cause corrosion on the water side of these exchangers.

HF acid leaks into the circulating cooling water can cause tube failures in multiple exchangers if the leak is not detected quickly. UOP recommends conducting both fluoride and hydrocarbon tests on cooling water tower to check for tube leaks due to the presence of LPG and HF acid.

UOP strongly recommends a separate cooling water tower for the HF Alky unit, but I do not believe that we require it in our typical new unit specifications.

There is new unit activity for HF units. Current permitting requirements do not prohibit installation of new HF Alky units. However, in many cases, it is necessary to evaluate the risk of installing an HF Alkylation unit, and to show the permitting authorities that this risk is acceptable. Probably the best way to do this is to perform a Quantitative Risk Assessment (QRA) for the HF Alky unit.

Question 78

For HF alkylation units, have you changed your criteria for materials given the low availability of low carbon/non-recycled steel? Are you heat treating welds? Can you control Brinell Hardness with welding procedures? For small bore pipe, do you recommend using flanges or threaded pipe?

Allen Kaiser (Delek Refining)

I would not recommend a materials specification change for HF services. API RP 751 does recommend post-weld heat treating (PWHT) of all welds in HF service. The upper recommendation on Brinell Hardness (BH) is 200 BH. The overall hardness of a weld can be (at least partially) controlled by weld procedures. Most weld procedures are not sufficient, in and of themselves, to guarantee repeatability in meeting the 200 BH spec. Small bore piping should also use socket-weld flanged connections. NACE papers 03651 “Specification for Carbon Steel Materials for HF Acid Alkylation Units” and 5A171 “Materials for Receiving, Handling, and Storing Hydrofluoric Acid” both contain good references for materials selection in HF alkylation units.

Blending

Question 79

It has been reported that di-isobutylene (isooctene) causes a stability problem when blended in gasoline. Do you have experience blending di-isobutylene in gasoline and, if so, were there stability or other problems?

Rick Grubb (Chevron USA)

I’ve consulted others within Chevron and this answer is based on information provided by Shenggao Liu and Dave Kohler. There is no intrinsic, chemical reason to expect this olefinic stream to be more susceptible to stability issues than other highly olefinic streams. As with other olefins, isooctene isomers are subject to easier oxidation than the corresponding saturated C8 isoparaffins/isooctanes. If unchecked, the oxidation to hydroperoxides may promote further molecular condensation to form higher molecular weight species which may lead to insoluble gum residues in the fuel. This tendency can be mitigated effectively by the addition of a low level of appropriate antioxidant chemical, either phenylenediamine or hindered phenol type chemistries. As with the addition of antioxidants to other process streams, it is always most effective to add the antioxidant as soon as the product exits the process unit in the rundown line to storage.

Chevron has installed two units with the ion exchange resin type catalyst technology for isooctene production. These were a conversions of former MTBE plants. To the best of our knowledge, the blending of their isooctene has not caused any measurable decrease in gasoline stability, at least as assessed by existent or potential gum contents.

We also have experience with two solid phosphoric acid distributed on a solid support type oligomerization processes. The olefin oligomer streams cause no stability issues with the refinery’s motor gasolines and would be stabilized with a minimum amount of an appropriate antioxidant.

In addition we have experience with Dimersol type of olefin oligomerization units. They dimerize propylene into highly branched isohexenes which may be blended to premium gasolines as high as 25 volume %. We have seen no stability issues blending this material. In any case, these Chevron gasolines would contain at least some minimum level of an appropriate antioxidant.

Depending upon the source of the C4 olefins, the feed stream may also contain measurable amounts of diolefins, such as 1,3-butadiene, or, if the distillation range is broad enough perhaps even isoprene (2-methyl-1,3-butadiene). Conjugated diolefins such as these two species are generally much easier to peroxidize than the corresponding monoolefins of the same carbon number. This tendency can be mitigated effectively by the addition of a low level of appropriate antioxidant chemical.

Again, depending upon the source of the C4 olefins, the feed stream may also contain measurable amounts of reactive sulfur compounds such as ethyl- or propyl mercaptan. These mercaptan species are notorious for being easy to peroxidize. This tendency can be mitigated effectively by the addition of a low level of appropriate antioxidant chemical.

Javier Quintana (Valero Energy)
Valero Energy has several iso-octene units in operation, and has experienced no issues with stability of the iso-octene product or the gasoline into which it is blended. The key is to inject the stabilizing antioxidant chemical into the product rundown line at the appropriate dosage rate. This is consistent with A stability test, such as ASTM D525, on the iso-octene product can be used to optimize the dosage rate for a particular antioxidant. Your chemical treatment vendor should be consulted for specific product and dosage recommendations.

Isomerization

Question 80
Where in the isomerization reactor catalyst bed does the hydrogenation of benzene (exothermic) occur? How does this affect the other isomerization reactions? What concentration of benzene in the isomerization feed is acceptable?

Richard Rosin/Joe Zmich (UOP LLC)
Benzene saturation occurs at the inlet of the reactor. In order to assure maximum octane and yield from a light naphtha isomerization reactor it is necessary to saturate benzene. Benzene will adsorb on acid sites making these sites unavailable for paraffin isomerization. If benzene is not immediately saturated in the front of the reactor, the benzene will tie up acid sites effectively increasing the space velocity for paraffin isomerization reactions.

The main effect of benzene in a light naphtha isomerization reactor is thermodynamic rather than kinetic. The very high heat of saturation of benzene will increase the temperature of the reactants. The maximum achievable concentration of high-octane iso-paraffins is limited by equilibrium. The equilibrium level of iso-paraffin decreases with increasing temperature. The effect of benzene on isomerization reactions is to raise the temperature to a point where the shift in thermodynamic equilibrium lowers the maximum attainable octane. Multiple reactors, with inter-reactor cooling, may be required to process feedstock with benzene levels greater than 3 lv%.

For most purposes the maximum allowable concentration of benzene in isomerization feed is 5 vol%. Higher feed levels of benzene are possible with a benzene saturation reactor in front of the isomerization reactor(s), e.g., UOP Penex Plus^{TM} process.

Javier Quintana (Valero Energy)
Valero Energy has experience with processing isomerization feeds as high as 5 lv% benzene content, with a substantial resulting exotherm in the lead reactor. The inter-reactor cooling capacity of the unit, and the resulting temperature that can be maintained at the lag reactor inlet, will determine the isomerate product quality that can be achieved relative to the same feed with lower benzene levels.

Question 81
Has the optimum feed for light naphtha isomerization units changed given that: 1) ethanol blending reduces the octane value of other blendstocks; 2) the demand for premium gasoline is down; and 3) ethanol blending increases RVP compliance costs? Are you removing pentane from the isomerization unit feed stream or shutting down the unit? Or, are the units still valuable for isomerizing normal hexane and saturating benzene?

Allen Kaiser (Delek Refining)
Each refiner will make one of the following three moves when introducing ethanol into the gasoline blend pool – shut the isomerization unit down, change the isomerization feed makeup by dropping most hexanes into the reformer feed, or keeping the isomerization unit up at previous rates and feed composition, but off-setting the increase in pool octane by lowering reformer (or other unit) octane severity. The specifics of that choice depend on refinery site economics and regulations.

In the first case, the refiner's isomerate stream can be offset by the ethanol introduction and the cost of importing the ethanol is lower than the cost of processing the isomerization feed. In the second case, moving the hexanes into the reformer feed likely provides better overall gasoline pool RON and RVP balance and is favored by economics. The isomerization of the pentane molecules is still likely favored due to the increase in octane. In the third case, the refiner is probably operating the isomerization unit for benzene control and has no other palatable options for isomerization feed.

Javier Quintana (Valero Energy)

The Renewable Fuels Mandate has impacted isomerization unit economics due to reduced octane requirements to produce CBOB (Conventional Blendstock for Oxygenate Blending) gasoline streams, increased vapor pressure constraints, as RVP specifications must be met after ethanol splash blending at the distribution rack, and flat gasoline demand from US refineries after accounting for volume impact of ethanol blending and finished gasoline imports.

While the economics for isomerization unit operation may vary with each refinery's unique situation, in general the impact expected is to render C5 isomerization economics marginal to negative, with C6 economics slightly better than C5 economics due to the difference in RVP of the products. However, most refineries do not separate the C5 naphtha fraction from the C6 fraction, and therefore, additional equipment and operating cost may be necessary to selectively process a C6 cut – this may be difficult to justify. This is especially the case when the C6 isomerization function is provided by the naphtha reforming unit. Furthermore, if the isomerization unit is shut down due to economics, the light naphtha stream will likely contain some benzene that was previously saturated in the isomerization reactor, which may lead to a reduction of the light naphtha / heavy naphtha cutpoint as part of a refinery's MSAT II compliance strategy. This situation is likely to occur if a post-treat strategy is adopted on the reformer, thereby containing all benzene to be treated in a light reformate stream. This approach can spare the isomerization unit to be deployed for saturation only, so as to achieve compliance without aggravating the tighter RVP constraint that will prevail in a CBOB blending environment.

Question 82

In light of coming benzene regulations, are you using (or planning to use) the isomerization unit for benzene conversion? How does this affect isomerization catalyst performance and unit operation? How does this affect the gasoline pool? How does benzene saturation in an isomerization unit compare to a dedicated benzene saturation reactor/catalyst?

Richard Rosin/Joe Zmich (UOP LLC)

This question relates well with question #80. Light naphtha isomerization units are extremely flexible in their ability to handle increasing amounts of benzene in the feed. A UOP Penex^{TM} process unit operating with <5 vol% benzene in a straight run light naphtha feed can in most cases be easily revamped to a Penex-Plus^{TM} process unit capable of handling over 30 vol % benzene in the feed.

Saturation of benzene with isomerization of light paraffins in a new isomerization unit leads to an octane gain as opposed to an octane loss in a stand-alone benzene saturation unit.

Allen Kaiser (Delek Refining)

There are several options for dealing with the benzene production in each of our facilities – precursor reduction, post-treatment "destruction", and extraction.

First, extraction relies on having an outlet for the benzene stream. If this outlet is not available, or the economics do not support the additional capital costs of this solution path, then it will not be a fit for the refinery. Second, post-treatment destruction via a saturation unit is likely to be a popular choice if the refinery either does not have assets to reuse, revamp, or capacity available in existing units. The final options are pre-treating and post-treating in an isomerization unit. The unit must be able to handle the designated feed stream, the unit yield shift must fit into the refinery gasoline blend pool, and the scheme must meet the benzene reduction requirements.

Each refiner is going to need to take a look at the assets and outlets they have and make an engineering call. Couple all the above issues with 40+ week delivery times for major equipment (towers, heaters, compressors), and the need to decide NOW what you're going to do should be apparent.

Petrochemicals

Question 83

Since Sulfolane-based aromatic recovery units are experiencing corrosion related problems, are there alternative solvents available? What are the advantages and disadvantages of these alternatives?

Javier Quintana (Valero Energy)

Virtually all solvent extraction solvents suffer from oxidative decomposition mechanisms, and as such most extraction units are at risk of corrosion related issues. This is certainly not unique to Sulfolane, and since it is generally expensive to consider a solvent change for an extraction unit, due to differences in operating temperatures and heat integration issues for different solvents, it usually best to undertake solutions to address the root cause of the corrosion, which is oxygen ingress into the extraction unit.

The best defense against such corrosion is to eliminate oxygen entry via the feed stream, especially if it passes through tankage as opposed to entering directly from upstream fractionation, or via leaking flanges, pump seals or fittings in the vacuum sections of the unit. Among the recommended steps to limit the potential for oxygen entry via the feed stream are:

- Ensure feed runs direct from upstream fractionation
- Any import from tankage is stripped of oxygen
- Ensure feeds do not go through tankage, but rather bypass tank inlet, float on tank outlet to charge pump
- Ensure feed tank is nitrogen blanketed, verify the sizing basis of the blanketing system
- Confirm tanks seals are in good condition, and that any rubber shrouds on gauging hatches have not deteriorated
- Ideally, dissolved oxygen in feed should be <0.5 ppm

It should be noted that conventional liquid-liquid extraction units tend to have a higher risk of corrosion issues from feed oxygen ingress than extractive distillation units, as with the latter systems any feed oxygen tends to be stripped to the extractive stripper column overhead system, and generally is not contained in the solvent phase circulating in the unit.

Oxygen ingress in the vacuum sections of the unit can often occur from deteriorated or improperly placed gaskets, or from improper piping alignment that can result from inserting plate blinds during periods of equipment maintenance; use of permanent spectacle blinds or spacers can largely eliminate such alignment issues. Over time, flange faces can be scratched and deteriorated sufficiently to allow air ingress, and may have to be refaced to eliminate such leaks. Helium leak detection systems can be used to identify the location of such leaks such that appropriate maintenance work can be undertaken to fix the root cause.

Question 84

What is your experience with cleaning multi-upcomer trays in aromatics extraction service? What cleaning methods are most effective?

Javier Quintana (Valero Energy)

While we have multiple upcomer trays installed in one of our extraction units, we have not yet had to clean these trays. We have in the past had to clean conventional raindeck extraction trays, and we would expect similar techniques to be applicable to MU tray systems. Generally, we have found that a steam out of the extractor column from the bottom of the column, followed by a hot condensate wash from the top down, is an effective way of loosening bulk deposits, and washing them down the extractor, removing the majority via the condensate outlet from the bottom outlet piping.

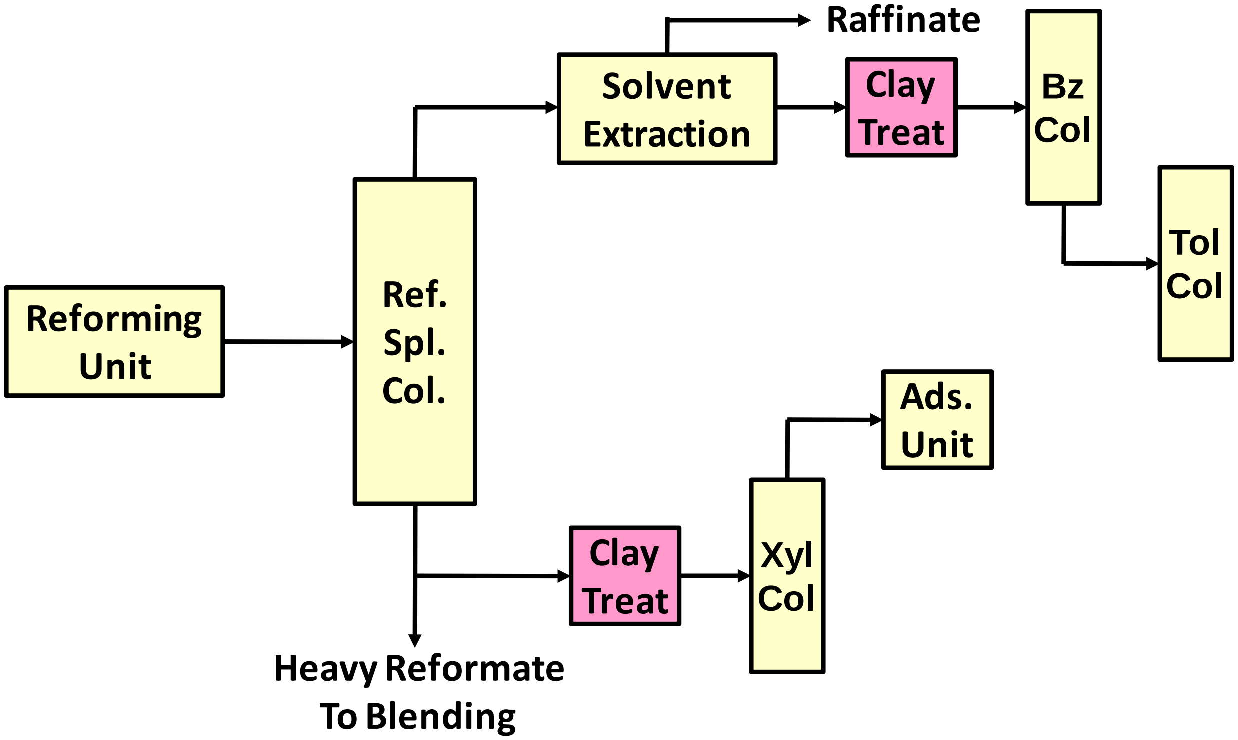
For extremely dirty trays, this initial wash can be followed up with chemical cleaning, usually with an inhibited citric acid solution. A chemical cleaning contractor should be able to recommend a cleaning system and treatment program that can achieve this additional cleaning. However, care should be taken to ensure that the cleaning program does not attack the tray metallurgy, as the tray efficiency depends on maintaining the design hole diameter on the trays. This suggests that there is greater risk associated with using more aggressive mineral acids, although some refiners may have used these in the past.

Question 85

Olefins that are formed in the catalytic reforming process must be removed or converted when the reformate is processed in an aromatics extraction unit. Historically, what unit operations have been used to remove/convert the olefins in the reformate? Are there any good alternatives to clay treating? How do the alternatives compare to clay treating with respect to capital cost, maintenance, operating cost, environmental impact, and effectiveness of olefin removal? What can you do in the reformer to reduce olefin production?

Javier Quintana (Valero Energy)

The olefin species formed in the reforming unit are determined by the reaction thermodynamics in that reaction system. The reformate olefin content is a function of the reforming unit feed quality and the operating severity of the reformer as determined by the pressure, temperature and hydrogen content at the last reactor. Higher severity operation will yield higher level of olefins, as will leaner feedstocks that contain higher paraffin content. However, the olefin content of reformate is usually an incidental consequence of the target severity as determined by the reforming economics rather than by downstream extraction considerations. The following sketch illustrates two potential locations of clay treating systems downstream of a reforming unit.



Whether these olefins must be removed or not depends on the type of aromatics extraction unit at issue. With conventional solvent extraction systems producing BTX aromatics products, no olefin removal is necessary, as the process can be managed to reject the majority of olefins to the raffinate stream, where the olefins contribute to the octane value. With newer, higher severity reforming operations, where the extraction feedstock is progressively lighter, the olefin content in the extraction feed tends to be higher, as most reformate olefins are distributed towards the lighter fraction, and the total olefin content of the higher severity operation tends to be higher as well. The feed olefin content is often in the 1-3 vol% range, but can be even higher in extreme cases. In the extraction unit, these olefins can wind up in concentration in the internal extractor recycle stream, sometimes in excess of 10 vol%, affecting unit capacity, reliability and performance. Unit optimization techniques can be used to directly manage this olefin wind-up and improve unit performance with significant feed olefin levels.

The residual amount of olefins that end up in the aromatic extract (~250-500 wt ppm) usually represents less than 1% of the feed olefins, and to prevent these trace levels from affecting final BTX product specifications, clay treating is the most effective option to maintain final product quality. These beds function by alkylating the olefin molecule with an aromatic molecule, producing a heavy aromatic component that is separated by fractionation. This is the primary reason why clay treating is usually found on the feed to a fractionation column.

If the reformer severity is sufficiently high that the reformate splitter column lifts a BT cut to the solvent extraction unit, and the xylenes and heavier fraction is sent to a xylene column and an adsorptive separation unit for para-xylene production, then the olefin content of the heavy reformate becomes a potential issue for the adsorption media, as these species will usually foul the pores of the adsorbent, and reduce unit capacity over time. In this case, the olefin content can be as high as 0.2-0.5 wt% of the heavy reformate stream, while treating the stream can present a challenge. The clay treating byproduct in this case represents even heavier molecules which can foul the clay pores, resulting in rapid deactivation. Using the highest activity clays, which are commonly used in the BTX extract service, can lead to xylene losses via transalkylation reactions, representing a significant economic penalty. Clay lives in this service have been known to be as short as 4-8 weeks per bed, creating a significant maintenance load.

Recently, some alternative systems have been commercialized, intending to replace the heavy reformate clay treating application. Alternatives include more selective catalyst systems that continue to alkylate olefins, similar to the clay system but with less xylene loss, while others seek to selectively saturate the olefins while avoiding any aromatics saturation. As these are relatively new developments, we would suggest you contact the relevant technology licensors to understand their expectations of relative costs.

Rick Grubb (Chevron USA)
We don't have experience with the typical BTX processing but we do have experience with Benzene processing or Xylenes processing independently. For our Benzene Extractive Distillation Unit we use Selective-Hydrogenation (SHU) for di-olefins saturation only and allow the olefins to pass through. For the xylene's unit we have a clay treater that processes the C8+ reformate to remove olefins. We have had problems with the clay life and several years ago contemplated some other method of olefin removal. A SHU system was evaluated but was deemed too expensive since we would have had to pipe-in hydrogen and added equipment to remove vapors. We continue to just try to optimize our predictions on the clay treaters life and have implemented procedures that allow for a quicker response to the need for a clay treater changeout.

Catalytic Reforming

Question 86
The reformer's feed properties can be affected when the refinery is maximizing refinery diesel yield. How do these changes to reformer feed affect performance with respect to C5+ yield, hydrogen production, cycle length, and economics?

Michael Newton (Roddey Engineering)
The reformer's feed properties can be affected when the refinery is maximizing refinery diesel yield. How do these changes to reformer feed affect performance with respect to C5+ yield, hydrogen production, cycle length, and economics?

Answer
The heavy end of the reformer feed will be sent to the diesel stream, thus lowering the EP of the reformer feed. The effects of lower EP in reformer feed are as follows:
a. C5+ yield – typically decreases
b. H2 production – typically decreases, but there may be a little offset if the LHSV is lowered
c. Cycle length (semi-regen)– increases due to lower coke make
d. Heavier feed is easier to reform; lighter feed = higher inlet temp for same LHSV and severity, but most likely the LHSV will be lowered and thus the temperature lowered

Economics will vary from refinery to refinery, but it may be that what makes economic sense for the reformer itself doesn't make sense for the entire refinery's economics. H2 and RON demand along with turnaround schedules for other related units (i.e. hydrotreaters) will dictate the minimum requirements for the reformer.

Question 87

Iron contamination of CCR, cyclic, and semi-regen reformer catalyst is a common problem. What level of iron concentration typically justifies catalyst replacement due to poor catalyst performance?

Michael Windham/Joe Zmich (UOP LLC)

Iron contamination of catalytic reforming unit catalysts was a discussion topic in the 2000 NPRA Q&A.

It is common for catalytic reforming unit catalysts to accumulate iron, normally present as corrosion products adhering to the exterior surface of the catalyst pills. Levels of iron above 1 wt-% (> 10,000 wt-ppm) on catalyst have been observed without any apparent effect on catalyst performance. Normal methods of chloride adjustment should minimize any effect on performance. Iron has been detected on catalyst in both Fixed Bed and continuous reforming units, so it does not come exclusively from the Regenerator. Large quantities of corrosion products can affect flow distribution, but such cases are unusual.

Javier Quintana (Valero Energy)

Since the performance impact of iron on the reforming catalyst is indirect, it is difficult to define a specific level of iron at which a catalyst replacement is justified. Rather, the current level of catalyst performance due to diminished catalytic activity, whether from iron, catalyst phase change, or other impacts, should determine when the catalyst should be replaced. A significant impact of iron is the generation of water in the regeneration sequence. Iron on the catalyst will oxidize during the carbon burn step, and subsequently produce water during catalyst reduction. This release of water will manifest itself in different ways for different units. In a semi-regen unit, the additional reduction water will require a longer reduction step to dry down the unit; if the catalyst is put back on oil prematurely, the higher moisture level can lead to increased cracking and higher coke production, resulting in a shorter catalyst cycle. In a cyclic unit, this can have similar impact, with the catalyst being wetter when brought back on oil, similarly affecting product yield and prematurely coking, such that regeneration capabilities become more constrained. In a CCR unit, the continuous catalyst reduction results in a higher equilibrium moisture level in the recycle gas, which if sufficiently high, can similarly reduce reformate yield, and increase the coke level on spent catalyst.

Question 88

What is your experience with feed side fouling on combined feed/effluent (CFE) exchangers? What is the foulant? How often do you clean them and what cleaning techniques do you use? On Texas Towers (vertical shell & tube exchangers), how do you extract the bundle from the shell if it gets stuck?

Michael Newton (Roddey Engineering)

Many reformers have some if not significant feed side fouling of their CFE. Typically the foulant is a polymer plus corrosion products (iron sulfide/iron oxide) from upstream units and feed coming in from tankage. In addition to monitoring heat exchangers for fouling, fouling can be exhibited on fixed bed semi-regen units during the purge after oxidation. High SO2 readings and/or long purge times when purging out the compressor discharge indicate fouling in the feed/effluent exchanger and/or heater.

Cleaning of vertical feed/effluent (VFE) exchangers has typically been avoided by many refiners due to the extra work requirement of the tall exchangers. Some refiners try to chemically clean these exchangers, but our company's experience has shown that cleaning with a crane and lance/mole type device has been the most successful way of cleaning. Take cover plates off and let water flow out bottom

Our experience with refiners removing bundles is that they get stuck and a replacement exchanger must be built to replace it.

Javier Quintana (Valero Energy)

Valero Energy has had very limited experience with feed side fouling of CFE bundles, especially in the case of shell and tube exchangers, where the feed is usually on the tube side, and the velocities tend to be sufficiently high that it is difficult for foulants to deposit. Due to the typical construction methods to accommodate thermal expansion at the bottom end of vertical CFE bundles, it is usually very difficult to extract the bundle in place, and this should be attempted only as a last resort. In the extreme case that repairs are needed on the bottom tubesheet, pulling the bundle is best done in a shop environment, where the bottom channel cover can be removed without damaging the expansion joint attached to the internal floating end of the bundle. Often the vertical CFE bundles will be fabricated without the shell girth flange needed to extract the bundle, as it results in a lower exchanger cost, and eliminates a potential hydrogen leak point.

If cleaning is needed on the feed side, then removing the top channel cover and hydroblasting has been successfully used to clean the channels. Depending on the level of sulfur passivation used in a particular unit to avoid metal catalyzed coking, such hydroblasting could put the exchanger at risk of polythionic acid attack at the hot end of the bundle, where the passivating sulfide layer is laid down. In such a case, the hydroblasting can be performed with a soda ash solution so as to minimize the risk of polythionic acid formation.

If the CFE is a Packinox welded plate exchanger, then the feed spray bars can foul with salts carried in from the upstream hydrotreating unit, especially if water washing frequency is extended, and slugs of salts are washed through at one time. The feed filters in front of the spray bars usually can trap most particulates, but we have experienced salt fouling of the spray bars under certain conditions. If such plugging occurs, it can usually be cleared easily if a back-flush system is installed on the exchanger. If such a system is not available, then the unit will often require a shutdown for removal and cleaning of the spray bars. How long the fouling can be tolerated is a function of the maximum allowable pressure differentials for the exchanger system.

If the reforming unit is fed directly from storage, such as from a sweet naphtha tank, and if the hydrotreating step does not completely remove all olefins, then it is possible to experience polymer fouling on the feed side. This can usually be avoided by ensuring that any sweet naphtha feed from tankage is fed only to the stripper column in the upstream hydrotreating unit, so that any dissolved oxygen can be effectively stripped out before reaching the reforming unit. We maintain a minimum reflux guideline on these stripper columns of 0.2 v/v reflux/bottoms ratio in order to ensure there is sufficient stripping to remove oxygen, water and hydrogen sulfide from the hydrotreating effluent.

Ka Lok/Joe Zmich (UOP LLC)

Tube side (feed side) fouling has been due to feed contamination, typically overuse or misuse of a corrosion inhibitor, or charging feed from unblanketed intermediate storage to the unit. High rates of inhibitor injection, coupled with an inhibitor that is not highly hydrocarbon-soluble, result in the inhibitor dropping down the stripper and moving on to the reforming unit.

Charging feed from unblanketed intermediate storage or other oxygen contamination of the feed is can also cause vertical combined feed exchanger (VCFE) fouling. The resultant peroxide gums foul the tube side of the exchanger. UOP strongly recommends that reforming unit feed always be direct from the NHT whenever possible.

Cleaning of the tube side is typically successful using high-pressure (up to 10,000 psi) water blasting. This cleaning (hydroblasting) can be done without removing the bundle, as both ends can be made accessible. If the tubeside of the VCFE is plugged, remove the top flange and expose the tubes. The high-pressure water jet lance can be inserted in order to clean the tubes.

Shell side fouling can result from PNA (polynuclear aromatics) and/or ammonium chloride salt deposition. Typically the exchanger temperatures are not cool enough for salts to deposit on the shell side of the VCFE; rather the salts deposit further downstream, e.g., in the reformate stabilizer, fin fans, and recycle gas compressor. It is possible for PNA to deposit on the shell side. Trace amounts of PNA can be generated in a catalytic reforming unit, more likely at high severity. High feed endpoint increases the quantity of PNA in the reactor effluent. PNA’s are carcinogenic. Personnel involved with maintenance must wear proper PPE.

UOP has limited direct experience with a bundle becoming stuck. UOP does not recommend removing the bundle unless absolutely necessary. Attempting shellside chemical cleaning before or instead of bundle removal could prevent this. If the bundle is removed, it is imperative to maintain proper tube bundle support to prevent deformation which can lead to difficulty in extracting the bundle.

Question 89

What are the typical problem areas for CCR catalyst circulation loops? What are the most reliable valve types? How frequently do you conduct fines surveys and what is a reasonable range for fines make?

Rick Grubb (Chevron USA)

My experience is with designing a new unit and looking for ways to ensure it's reliable by consulting others within Chevron that have experience. With their input I've compiled this answer.

For valve reliability we use a soft seat "V" notch ball valve wherever catalyst flow must be stopped. We use double seated plug/globe "G" valves on the vents between two spring loaded "B" ball valves used to provide a gas tight seal in the catalyst transfer lines. We prefer valves that have a spline driver connecting the shaft to the ball. A very successful thing we've done is to change all 3 valves (B's and G) when we find one of them leaking. We maintain spares for immediate installation if needed. The valves are checked by surveys conducted by operations once per week.

As for problems with catalyst circulation loops, we closely monitor lift gas velocities to avoid excessive catalyst attrition or line erosion. We conduct surveys once per week and adjust the elutriation gas flowrate to target 20% whole pills. The disengaging hopper PSV's don't reseat well. In the dust collector the bags are sometimes holed through leading to wear on blowers, screens, and etc. These bags are checked about every year and we are installing DP meters to see if we can monitor for a hole.

Some things we do to prevent problems is to monitor the temperature on the catalyst transfer legs to ensure things are flowing freely. We watch the surge hopper purge rates to minimize damage and fines. When the regenerator is shutdown we bar over the blowers daily to avoid seizure. Also during shutdowns we move two batches of catalyst to relieve radial pressure inside the reactor. If we suspect the potential for plugging upon the startup we do 5 short 10 sec lifts to heat up the system to heat things up.

Javier Quintana (Valero Energy)

Typical catalyst circulation issues include mechanical problems, the state of the catalyst and process condition deviations. Mechanical issues include ball valve alignment, any lips or protrusions in the catalyst flow path that can increase catalyst attrition, and erosion of lift equipment or catalyst lines, resulting in rough edges promoting fines production. Catalyst that is excessively hot will have difficulty in lifting, as will any catalyst that is wet or dusty. Improper process conditions for elutriation, drying and lifting of the catalyst can all contribute to the catalyst becoming hot, wet or dusty. Additionally, higher catalyst circulation rates are more sensitive to these factors.

All licensor-approved valves can work effectively in a CCR unit. The essential part of a successful operation is the development and application of a rigorous quality control and assurance program for all aspects of maintenance and inspection of the valves. Each valve that is removed for service must be undergo a thorough inspection and adjustment to ensure good alignment prior to reinstallation in the unit.

In the absence of any excessive fines production, we recommend to our operating units either monthly or quarterly fines surveys. However, if fines make increases substantially relative to historical average, then the frequency is increased while troubleshooting is underway until the root cause of the increased catalyst attrition is identified and corrected. A good benchmark for what fines production level is reasonable is the licensor's original fines production guarantee level when the unit was new. The actual quantity of fines expected varies with the configuration of the regeneration system, and with the size of the unit.

Question 90

What determines the minimum feedrate for a fixed bed reformer? What process indicators would tell you that the feedrate is too low?

Rick Grubb (Chevron USA)

Besides mechanical limitations, such as pump capacities, flowmeter ranges, control valve sizes, etc., the process factors that determine the minimum feed rate of a fixed-bed reformer are:

- Flow distribution in the reactors
- Heat of reaction dissipation in reactors
- Flow distribution in furnaces
- Phase separation in exchangers

Most refineries set the feed rate minimum at 40% of design (liquid hourly space velocity of 0.6 volumes of feed per volume of catalyst per hour). The minimum space velocity for continuous operation is 0.8 v/v/hr.

At low feed rates, the most critical issue is free radical cracking. When flow through a catalyst bed is low, the heat is generated by hydrocracking faster than it can be carried away. At a certain temperature, the hydrocracking changes from normal hydrocracking to free radical cracking, also called demethylation. Free radical cracking is essentially thermal hydrocracking in which feed molecules are totally cracked to methane with a huge heat release. This is the most important effect of low feed rate to watch for, because at such high temperatures, catalyst can fuse and destroy reactor internals in internally insulated (cold wall) reactors. In a hot wall reactor, such an excursion could result in a reactor outlet piping rupture if not caught soon enough.

The first signs of free radical cracking in one or more reactors (usually not the first one) are:

- Recycle specific gravity starts to rise
- Reactor DT's start to drop and may go positive in the last and next to last reactors
- C_1/C_2 ratio in the recycle gas starts to rise above the normal 1.2-1.4:1
- Reformate color turns to a darker yellow
- Net hydrogen yield per barrel of feed starts to drop off

For normal hydrocracking, the total DT is 200-250°F. For demethylation the DT can be as high as 1200-1400°F. So, a significant drop in individual reactor DT's can be an indication of free radical cracking.

Russ Weinhammer/Joe Zmich (UOP LLC)

UOP has traditionally used a minimum liquid hourly space velocity (LHSV) of 0.75 hr-1 or 50% design feedrate whichever is greater. For units with lower design LHSV UOP advises maintaining the combined feed mass flow above 50% of the design value. The main process implication with low LHSV is an increase in cracking reactions. The increase in cracking leads to decreased reformate and hydrogen production, lower reactor delta T's, lower recycle gas H2 purity, increased stabilizer off gas and LPG flow, and increased C1-C4 yield.

Javier Quintana (Valero Energy)

Valero has experience operating as low as 0.6 LHSV in a fixed bed reformer, although such operation was accompanied by an elevated H2/HC ratio in order to ensure good flow distribution through the catalyst beds.

Question 91

In a catalytic reformer with a given pressure, severity, and feed quality (N+2A), what are the major factors that determine the C5+ yield? How do you optimize yield? Have you quantified the impact of pentane and/or hexane content in the feed?

Michael Newton (Roddey Engineering)

Setting pressure, severity, and feed quality limits you on any significant "knobs to turn" in determining the C5+ yield. If you assume that LHSV is also fixed, there are two factors that can impact C5+ yield.

Reactor Inlet Temperature Profile – typically running a "downhill" profile will give you a slightly higher C5+ yield and will lower overall coke make in the unit.

Water Chloride balance – having an over-chlorided catalyst will result in more cracking and lower C5+ yields. Under-chlorided – higher deactivation, higher yield, higher temp required.

Yields can be optimized by maintaining a good water chloride balance and working with your technology supplier or consultant in determining the best temperature profile and recycle gas rate to obtain the desired cycle length or total coke make.

Rick Grubb (Chevron USA)

We've noticed that catalyst fouling and feed distillation have an effect on C5+ yield in addition to the items listed above. As the catalyst fouls the C5+ yield decreases. We've also seen that as the distillation gets heavier near the endpoint the C5+ yield also decreases. As the distillation gets heavier near the initial boiling point the C5+ yield increases slightly. With that said, we don't typically push for C5+ yield as much as we consider it a result from the other refinery optimizations. We target the crude distillations to maximize the product slate for optimum profits and octane blending between the chemical plants and the mogas blending demands. In other words, the short range planners take distillation and catalyst age into account when choosing distillations and octanes.

We do monitor the C5+ yield to ensure the unit is operating well. We've implemented process monitoring standards to ensure consistent overview between the different units and engineers. These standards allow for consistent monitoring techniques and help bridge gaps between personnel transfers.

Question 92

What criteria do you use to determine end of run (EOR) catalyst life for a CCR? How many regeneration cycles have you achieved between catalyst replacements?

Willie Morrissette/Joe Zmich (UOP LLC)

There are a number of considerations in determining the End of Run for a catalyst cycle in CCR operations. Refinery economics are typically the ultimate factor used for determining when to replace CCR Reforming catalysts. The useful life of a CCR catalyst is impacted by the operation of the unit and is a function of the ability to maintain the proper metal and acid function of the catalyst as well as the condition of the catalyst base. UOP's CCR Platforming^{TM} catalyst can achieve very long life because UOP reactor and regenerator operate at optimum conditions. A number of Platforming Unit operations have achieved in excess of 800 regeneration cycles prior to making a catalyst change out.

Key considerations for catalyst change out can include one or more of the following:

1. An inability for the catalyst to achieve optimal platinum dispersion through regeneration.

2. An increase in chloride injection requirements during regeneration resulting from a reduction in regenerated catalyst surface area as compared to fresh catalyst and leading to increased chloride loss in the reforming reactor section during normal operation.

3. An increase in catalyst fines production due to irreversible phase damage to the catalyst base resulting in decreased catalyst surface area, increased catalyst attrition, loss in catalyst activity, and fines-induced process equipment plugging problems.

4. A loss of catalytic metal and acid function of the catalyst due to accumulation of poisons such as metals on the catalyst eventually resulting in loss of catalyst activity, selectivity, or regenerability.

5. A loss of catalyst activity resulting in operations approaching the equipment or unit design constraints.

6. An advancement in catalyst technology resulting in sufficient economic benefit to replacing the catalyst before it otherwise reaches the end of its life.

7. A scheduled unit operating shut down providing a convenient opportunity for catalyst change out.

Javier Quintana (Valero Energy)
The EOR criterion for catalyst change out in a CCR is an economic optimization considering a number of factors, including:

- Ability to meet process objectives (rate, octane)
- Chloride consumption and treating costs
- Phase change content of catalyst inventory
- Level of accumulated contaminants (Fe, Si, etc)
- Ability to disperse platinum (activity, yield)

Valero's expectation for ultimate life of CCR catalysts is in excess of 600 cycles for early generation CCR units, and in excess of 700 cycles for recent generation units. Not all units reach these targets, but any such shortfall is normally directly attributable to operating issues that lead to the anomalies indicated in the list of factors above.

Question 93
On a CCR, what causes the regenerator chlorination zone to plug off before the regeneration zone?

Ka Lok/Joe Zmich (UOP LLC)
Assuming that the question relates to the inner screen of the chlorination zone of a UOP Atmospheric CCR regeneration section relative to the burn zone, the most likely cause of this is failing to operate the CCR regeneration section burn zone per the UOP General Operating Curve. If the catalyst circulation rate for given oxygen concentration exceeds the maximum indicated by the curve, it's likely that catalyst with higher than desired coke will enter to the chlorination zone leading to catalyst damage. The damaged catalyst can be smaller and fracture into dust and chips in the chlorination zone leading to plugging of the chlorination zone screen.

Some licensees have observed an increased slot width in the chlorination zone after a long time in operation. An increase in slot width increases the tendency of the screen to foul with catalyst chips or smaller diameter catalyst.

Question 94
In monitoring catalytic reformer operation, how often do you perform a feed/product analysis and what analytical methods do you use? How often do you perform a mass balance and what is the acceptable mass balance closure? What is a typical mass balance closure?

Michael Newton (Roddey Engineering)
Units were the feed properties are relatively constant need to be monitored much less than those were the properties change often.

For material balances during performance evaluation, accuracy should be within +/-1%. For daily monitoring, +/-2% is acceptable. All balances and monitoring require good data from the lab and making sure that meter data is input and calculations performed correctly.

A typical "routine" schedule is shown in the table:

SAMPLES	SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY	SATURDAY		Weekly/Monthly
REFORMER CHARGE	API D86 Sulfur	API D86 PONA GC Sulfur	API D86 Nitrogen Sulfur	API D86 PONA GC Sulfur	API D86 PONA GC Sulfur	API D86 PONA GC Sulfur	API D86 Sulfur		Contaminants (Si) Heavy HC GC (C9-)
REFORMER STABILIZER BOTTOMS	API D86 RVP RON	API D86 RVP RON	API D86 RVP RON	API D86 RVP RON	API D86 RVP RON PONA GC	API D86 RVP RON	API D86 RVP RON		Heavy HC GC (C9-)
REFORMER SEPARATOR GAS	HCl H2S	HCl H2S GC	HCl H2S GC	HCl H2S GC	HCl H2S GC	HCl H2S GC	HCl H2S		Some do GC 1-2 times a week
STABILIZER OVERHEAD VAPORS									GC - weekly
STABILIZER OVERHEAD LIQUID									GC - weekly

Question 95

How often do you perform CCR and cyclic reformer turnarounds? What determines the turnaround interval? What actions can you take to extend the turnaround cycle?

Javier Quintana (Valero Energy)

Valero's best practice guideline for reformer turnarounds is currently 4-6 years, but eventually we will target 10 years. With the longer turnaround horizon, catalyst condition in a CCR unit can be managed with on-the-fly change out, which has been demonstrated several times in practice, while in cyclic units, a reactor can be changed out while the remainder of the unit is operating.

In CCR units, the primary determinant of turnaround timing is plugging of the lead reactor center screen with catalyst fines, due to incomplete elutriation or misoperation in the regeneration section, leading to fines generation downstream of the elutriation system. Ultimately, regulatory requirements related to inspection frequency will govern the turnaround timing if the catalyst condition is maintained such that no such reactor fouling occurs. In the case of cyclic units, mechanical issues with motor-operated valves (MOVs) are key factors with turnaround timing, along with any regulatory inspection requirements.

Extending the turnaround frequency begins first and foremost with maintaining good catalyst quality. Units that operate with lower coke levels on spent catalyst (i.e., lower severity operation) generally have longer periods between turnarounds. Key factors to maintain include ensuring complete fines removal in the elutriation system, ensuring good mechanical condition of the catalyst piping such that there are no protruding lips or rough edges that can generate catalyst fines, proper drying and cooling of the catalyst in the regeneration equipment, and ensuring that the regenerator operating curve is followed to ensure complete combustion occurs in the burn zone, with no coke slip into the chlorination section. Episodes of coke slip lead to overheating of catalyst, with attendant phase change which is more susceptible to attrition.

Also essential is to maintain stable operation, with minimum number of emergency shutdowns. Thermal cycling of the reactors is associated with internals damage, although slow, regulated transfer of catalyst out of the reactors during cooldown can be used to largely eliminate bed pressure increases that are associated with internals damage. Additionally, it is important to monitor the reactor operation to ensure catalyst pinning does not occur, as pinning leads to rapid catalyst attrition and fouling of reactor centerpipes. Such events usually lead to the need to open the reactors for cleaning and repairs shortly after such events.

Chris Polaniecki/Joe Zmich (UOP LLC)
The frequency of a turnaround on a UOP CCR Platforming^{TM} unit depends largely on refinery and local government requirements. The reactor internals of the Platforming™ process should be thoroughly inspected on a routine basis. The first inspection should come after the initial two years of operation. Most licensees are increasing the time between turnarounds with some looking to go to more than an 8 year run time.

Although many factors contribute to long operational runs and unit safety, preventative maintenance is probably the most important. A proper and thorough unit inspection during scheduled turnarounds not only results in extended run lengths and maximum safety but also greatly reduces the probability of unscheduled shutdowns. UOP can provide a comprehensive checklist of all major unit equipment and piping recommended by UOP for inspection during a turnaround. This checklist includes recommendations for inspection and repair of piping, compressors, combined feed exchanger, fired heaters, and reactors.

Question 96
How do you manage sulfur in the feed to a catalytic reformer? What is the minimum allowable sulfur for CCR, semi-regen, and cyclic reformer feeds? What are your sampling frequencies and allowable ranges? What is your experience with carburization and/or metal-catalyzed coking?

Joe Zmich (UOP LLC)
UOP has extensively researched the tendency of metal surfaces to promote coke formation. UOP will provide specific recommendations on operating guidelines based on unit design and operating conditions. We are aware of two fixed bed units that have each operated with feed sulfur below 0.05 wppm and experienced coke growth in the reactors. Subsequent operation with a target of 0.15 wppm S successfully prevented repeat coke growth. Most fixed bed reforming catalyst systems must be properly sulfided following regeneration to attenuate the catalyst metal function. UOP has no direct experience with cyclic reforming unit operation as it relates to sulfur management. UOP's philosophy is to regulate feed sulfur concentration and perform regular feed analysis as well as sampling recycle gas and stabilizer off gas once per shift. In addition to reactor section metal surface passivation and prevention of metal catalyzed coke, sulfur also contributes to inhibiting heater tube carburization.

In general, reactor section coke is metal catalyzed that can be prevented by ensuring adequate sulfur in the feed to the unit. UOP would need to evaluate the specifics of the unit operating conditions and the history of the coke growth to determine the course of action that UOP would recommend to prevent future coke growth in a cost-effective manner.

Rick Grubb (Chevron USA)
We have experience with both carburization and metal-catalyzed coke. In the past, we have had a furnace develop a tube leak and we have collected stringy coke on occasion in other units. We currently manage sulfur in the reformer feeds by either adding DMDS or by removing the sulfur sorbers on the effluent of the NHT's. The spec is 0.3 to 0.5 ppmw in the feed. This spec is more critical in the lower pressure units and those units inject DMDS into the feed. Some of the older existing semi-regen units don't have sulfur control other than what is in the product from the NHT. We test the feed for sulfur daily and test the recycle gas for H2S each shift (every 12 hours). For the older higher pressure semi-regen units that depend on the NHT's, there are occasions were the feed sulfur is non-detectable. In those cases, we feel safe if we have some H2S in the recycle gas. If we don't detect anything in the recycle gas then we backdown the severity in the NHT's.

Javier Quintana (Valero Energy)
Sulfur management in reforming feed is essential to ensuring adequate protection from metal-catalyzed coking. However, this is not to suggest that it is acceptable to reduce hydrotreating severity in an attempt to control sulfur slip, as such a practice would generally be associated with slip of other impurities such as nitrogen and possibly metals. Rather, Valero's best practice is to ensure maximum hydrotreating to remove all feed impurities, sufficient reflux in the hydrotreater stripper to ensure complete stripping of all moisture and hydrogen sulfide, followed by a controlled injection of a sulfiding agent into the liquid feed to the unit.

Our minimum recommended injection rate is 0.3 wt ppm on feed, although higher levels may be necessary depending on unit-specific history. If a unit has evidence of metal-catalyzed coking, including trace levels of carbon build-up on reactor walls between scallops or in other low flow areas of the reactors, then that unit should increase the minimum target level of sulfur injection. Negative yield effects of sulfur are not expected until injection rates are in excess of 1.0 wt ppm, at which level most units (even those at extremely high severity) should be adequately protected. Injection rate should be confirmed with draw down of the level in the sightglass of the vessel or skid containing the sulfiding agent. All reforming units are at risk of metal catalyzed coking, with some units having higher risk than others – we have experienced such coking in relatively high pressure fixed bed units, as well as in moderate pressure CCR units.

If any maintenance work is done in the hot portions of the unit, such as retubing a furnace or even taking a tube sample for metallurgical testing, then the new furnace tubes will lack the necessary passivating layer of sulfur, and may be at higher risk of forming metal catalyzed coke. In such a case, an elevated level of sulfur injection is recommended on restart.

Question 97
What technologies and adsorbents are you using for net hydrogen off gas chloride traps and what operating problems have you experienced? What are the criteria for changing out the adsorbents and how often are the beds changed?

Javier Quintana (Valero Energy)
There are various adsorbents available for effective chloride treating of the hydrogen-rich net gas stream, including activated aluminas, promoted aluminas, and zeolites. Valero has moved away from the alumina products towards a best practice of using the zeolite products, not only for reasons of cost per quantity of chloride removed, but also for ease of changeout and completeness of chloride removal. The alumina products can present certain operating issues, such as:

- Green oil or red oil formation, which fouls downstream compressors, fuel gas system piping and burner tips
- Organic chloride breakthrough, which occurs long before HCl breakthrough, yet is difficult to detect
- Powdering of the adsorbent (disintegration), which can lead to significant compressor reliability and maintenance
- Hydrocarbon freeing requires an extended hot nitrogen strip, as steam out will leach chlorides from the bed, potentially causing corrosion in associated piping

The zeolite products generally do not form the green or red oils associated with polymerization reactions due to acid activity, and can be steamed out without leaching chlorides, which results in faster bed change-out. They are also more effective at removing both organic and inorganic chlorides, whereas the alumina beds pick up primarily inorganic HCl, while forming organic chlorides as the adsorbent chloride loading increases.

Adsorbent change-out timing is best estimated using a chloride uptake calculation, verifying the inlet gas HCl content on a daily basis, and with the gas rate, maintaining a running estimate of the total chloride loaded on the bed. When that estimated level reaches ~90% of the represented saturation capacity of the adsorbent. Since organic chlorides are present, yet are extremely difficult to measure, the uptake calculation is only an estimate. A cross-check of the estimated chloride loading at change-out with samples at different levels of the adsorbent bed can provide feedback as to the ratio of organic:inorganic species in the feed gas, which can be used to adjust the uptake calculation for future treater loads.

Question 98

What metallurgy are you using for mesh pads in reformer compressor suction knockout drums? How often are the mesh pads inspected and how often are they replaced? Are the same criteria used for mesh pads in product separators?

Rick Grubb (Chevron USA)

We typically use 304 SS demister pads in the refinery and inspect them every 10 years. In reforming service we have been using Tefzel demister pads and have been replacing them approximately every dump and screen due to separator internal inspections. If we go into the vessel we go ahead and inspect the mesh pad, but assume before opening the vessel that the pad will need replacing. The Tefzel pads have greatly increased the reliability such that we don’t find mesh pad pieces in the compressors anymore. We have been contemplating using co-knit pads (synthetic fiber inter-woven with a SS fiber), but have not done so yet.

NPRA

National Petrochemical & Refiners Association

1667 K Street, NW
Suite 700
Washington, DC
20006

202.457.0480
www.npra.org

© 2008 National Petrochemical &
Refiners Association