2005 Q&A AND TECHNOLGY FORUM

FCCU

Process

- 1. What are your plans for FCC feed selection and treatment to meet the upcoming ULSD regulations? Specifically, are you planning or considering atmospheric resid hydrotreaters?
- 2. Are you processing unhydrotreated heavy coker gas oil (HCGO) in the FCC? What are the impacts on yields, product qualities and heat balance?
- 3. What types of slops streams are charged to FCC's? Are there any limits for the various slops streams, and why? What contaminants could be present that affect FCC catalyst additives as well as the cracking catalyst?
- 4. How can oxygen contaminated FCC gasoline be reprocessed to prevent problems in downstream units?
- 5. What options are available to maintain the heat balance on full or partial burn units as they process more severely hydrotreated feeds? As an extreme case, how would a two-stage regenerator resid FCC unit run with 100% hydrocracker bottoms as the feed?
- 6. What is your recent experience with catalyst fines removal from FCC main column bottoms product, either using a mechanical device or a chemical? If a backflush system is employed, where is the backflush material routed? If routed to the FCC riser, what is the impact on regenerator emissions?
- 7. To what extent does LCO cloud point impact your distillate blending? What changes in feed properties, catalyst formulation, riser/reactor conditions, product fractionation and/or FCC equipment technology will impact LCO cloud point? By how much?
- 8. Have you seen FCC equipment degradation over a 5-year run that has affected LCO quality (gravity, cetane, sulfur, nitrogen)? What changes are needed to maintain product quality specifications?
- 9. What FCC unit feedstock, operating, equipment and catalyst factors affect gasoline olefin production? What steps do you take to increase or decrease FCC gasoline olefins content? Will a lower FCC gasoline olefins level help preserve octane through a gasoline hydrotreater?
- 10. What factors influence the ratio of C3 olefins to C4 olefins in the FCC? What could cause a reduction in the propylene yield at constant butylenes yield? We have seen this with no apparent increase in propylene loss to the fuel gas system.
- 11. What are the options for processing or reducing LCO yield from the FCC?

Environmental

- 12. When considering the addition of a wet gas scrubber to the flue gas system, how important is the flue gas piping arrangement for inlet gas distribution to the scrubber? Has the liquid spray distribution ever been the cause of a scrubber performance problem?
- 13. Have you quantified the SO2 loss associated with a condensing drying system for FCC stack analyzer sample conditioning? For drying our sample, we have a cooling/condensing drying system followed by a reverse osmosis drying system. We are concerned that at 20ppm SO2 we may be losing a significant amount of SO2 in the condensing coolers (v. the amount lost at 150ppm SO2) and that this is possibly related to ammonia (NH3) slip rates. Is anyone using a different sample conditioning system without these issues?
- 14. What ratios of SO2 to SO3 have you observed in the FCCU regenerator flue gas? What are the key process variables impacting this ratio? Does SOx reduction additive affect the ratio? We have seen changes from 10% SO3 in SOx to 40% but don't know why. Have others seen these high SO3/SOx ratios at very low SO2? Could there be issues with analysis related to sampling and/or sample moisture levels?
- 15. NH3 can be added at several locations in the flue gas system upstream of the electrostatic precipitator (ESP), upstream of the CO boiler for selective non-catalytic reduction (SNCR), or upstream of a selective catalytic reduction (SCR) unit. Where and how are you monitoring the NH3 slip? Do you have experience with continuous NH3 slip monitoring? What do you consider to be state-of-the-art? Have you monitored NH3 at the wet gas scrubber (WGS) stack and what would impact NH3 slip through the WGS?
- 16. What are the FCC equipment capabilities and analytical measurement concerns for meeting PM10 (particulate matter, $<10\mu$) from the FCC flue gas stack? What levels of PM10 have been measured from tertiary cyclones or ESPs? How do the measurement method and NH3 affect the determination of PM10 from precipitation of salts and/or inclusion of condensable particulate matter?

Equipment

- 17. How is the run length or reliability of a FCC feed fired heater affected if it is used to control reactor temperature versus supplying a constant temperature?
- 18. Have you used computational fluid dynamics (CFD) modeling to study vapor-catalyst flows in FCC risers (sloped riser, new feed nozzles, etc)? How did you validate the models?
- 19. What practices do you use for online cleaning of air blower turbine surface condensers? What problems have been encountered? How do you address energy control to allow cleaning half of a split-box condenser?

- 20. What could cause a gradual (months long) localized reduction in the regenerator dense bed temperature to less than 1200°F? The other two bed temperature indicators remained above 1250°F. There has been no step change in air grid pressure differential (dP) and a profile gamma scan of the bed shows relatively even fluidization, though a grid tracer study indicates that more air is passing through the cooler side of the bed.
- 21. What are the coking mechanisms and ways that coke formation has been controlled in the FCC main fractionator bottoms system? Have you experienced coke laydown in the fractionator bottoms system piping? What analytical monitoring can help make adjustments to reduce coking tendency?
- 22. More severe hydrotreating of FCC feed reduces H2S in the main column overhead system. What changes have you made in your wash water scheme to avoid higher pH water and potential carbonate stress corrosion cracking in the overhead carbon steel piping?
- 23. Our FCC emergency shutdown systems include feed block valves and diverter valves which dump gas oil feed to the main fractionator. The dump valves protect the feed pumps and charge heater from loss of flow. Our emergency procedures shut down the FCC feed pumps within minutes. Leaking diverter valves may put gas oil into decant oil during normal operation, which is a significant economic penalty. Do you divert feed back to the feed drum instead? Is there a risk of losing main fractionator bottoms circulation in this case?

Catalyst

- 24. Have you used a ZSM-5 additive and seen no apparent effect on FCC gasoline octane? What would be a possible explanation?
- 25. Will the use of ZSM-5 additives influence the effectiveness of a gasoline sulfur reduction catalyst or additive? Do high amounts of ZSM-5 additive (>10% of fresh catalyst makeup) have more influence than lower (more typical) concentrations of ZSM-5?
- 26. The resid FCC generates spent catalyst with metals content of about 10,000 to 12,000 ppm nickel plus vanadium. We have not found a suitable disposal option to either the cement or clay manufacturing industries. Are there viable options such as metals recovery that could make this spent catalyst suitable for landfill and prevent leaching of the metals to soil?

GASOLINE QUESTIONS

Alkylation

- 27. What is the minimum acid consumption achievable in a hydrofluoric (HF) or sulfuric alkylation unit? Please specify feed type and alkylation technology. What operating practices and technologies are available to reduce acid consumption?
- 28. What are the "best practices" for monitoring and combating corrosion in alkylation units (both HF and sulfuric)?
- 29. What has been your experience with online acid analyzers in HF and/or sulfuric alkylation units? How have you resolved the differences between laboratory and online analyzers results? What reduction in frequency of sample collection (if any) have you observed when online acid analyzers are installed in sulfuric acid and HF units?
- 30. Do you analyze your sulfuric acid alkylation unit's spent acid for water content? Is there an optimum water content for HF or sulfuric acid with respect to octane response? Is there an online analyzer available that will measure acid strength and water content for sulfuric acid?
- 31. In sulfuric acid alkylation units, do you direct the olefin feeds segregated by carbon number to separate points in the reactor or to separate reactors? Are the separate reactors running at conditions optimized for the feed carbon number? What are the advantages of doing this?
- 32. Please share your commercial experience with alkylation contactor tube inserts. What increase in apparent heat transfer coefficient have you observed? Did adding inserts allow you to increase unit capacity?
- 33. Do you alkylate amylene? If so, why are you doing so and what technology are you using?

Gasoline Post-Treating

- 34. Are you doing alkylation unit API RP-751 audits and how often? Please estimate how many refiners are doing these audits. What kinds of things are you finding?
- 35. As of January 1, 2005 each refinery's annual average sulfur content in finished gasoline may not exceed 30 ppm (credits can be used) and beginning January 1, 2006 sulfur content may not exceed 80 ppm on a per gallon basis (except for refineries that have temporary exemptions). How will you ensure that the FCC gasoline desulfurization units meet that specification? For example, will you consider producing a lighter gasoline cut from their prefractionator? Will you hydrotreat FCC feed and, if so, will you install a spare recycle hydrogen compressor to keep the unit on line in case of a compressor trip?

- 36. What has been your experience with silver strip corrosion testing of gasoline? What are the best proven means of avoiding failure of the silver strip test? Has the mechanism for silver strip test failure been determined definitively and, if so, what is it?
- 37. Additives, such as anti-oxidants, are currently added to the FCC gasoline. Are such additives required after hydrotreating of the FCC naphtha? What is current commercial practice?
- 38. Do you have experience with hydrocarbon emissions from the dust collectors in continuous reformers and, if so, how do you handle the emissions? What are typical benzene concentrations when opening the dust collectors?
- 39. Which gasoline streams have online analyzers installed for measuring low levels of sulfur? Have online sulfur analyzers been installed for severity control of FCC gasoline hydrotreaters?

Naphtha Hydrotreating

- 40. What are the important parameters to consider when designing and implementing a system to remove silica from naphtha? Please share your experiences with hydrotreating catalyst, silica guard beds for reformer feed, and sources of silica.
- 41. Have you experienced nitrogen breakthrough in naphtha hydrotreater (NHT) units, including ammonium salt formation in associated reformers, due to processing crudes containing higher concentrations of organic nitrogen? What solutions have been or could be developed to address this problem?

Naphtha Reforming

- 42. Due to upstream limitations, we often operate below the ammonium chloride sublimation point in the top of our reformer stabilizer. What strategies can be employed to mitigate the impact of salt formation (i.e. water wash, stabilizer feed chloride removal, process changes, etc.)? What problems or complications can result from these solutions and how can they be handled?
- 43. What experience do you have with sending platinum-group metals (PGM) catalyst offsite for screening and/regeneration? Under what conditions would a refiner send catalyst offsite for regeneration? Please address the impact of quantity of catalyst to be handled, ultimate catalyst destination (reload or send to metals recovery), hazardous material handling of unregenerated catalyst, distance to offsite facility and economic incentives. Have you quantified the difference in PGM fines recovery between on-site and offsite screening?
- 44. Which FCC naphtha cut points are acceptable for reformer feedstock? What are your experiences when straying from these cut-point limits? Do these cut-point limits change if you operate a resid FCC?

- 45. What advances have been made in naphtha reforming with respect to higher hydrogen production?
- 46. What are you doing (or plan to do) to reduce benzene in gasoline if regulations impose a cap of 0.95, 0.75, or 0.5 vol-%? How low can benzene be reduced by prefractionating the reformer feed?

Isomerization

- 47. What is the maximum concentration of benzene in light straight run (LSR) isomerization unit feed that refiners have demonstrated can be saturated within the safe operating envelope of the isomerization unit? What solutions have been, or could be, developed to increase this concentration?
- 48. Do you feed butanes from HF alkylation units to isomerization units? If so, how do you handle fluorides in the butane stream?

Blendstocks

- 49. What gasoline blending problems related to Driveability Index (DI) arise when replacing MTBE with ethanol?
- 50. What will you do with surplus pentanes that may result from lower RVP requirements and the use of ethanol?
- 51. Are there any catalyst alternatives for catalytic polymerization (cat poly) units other than solid phosphoric acid (SPA) catalyst? Are there any technical advances to oligomerization processes?
- 52. For refiners converting MTBE units to isooctene units, what are you doing (or plan to do) with the alcohol side stream?

CRUDE/VACUUM/COKING

Crude Oil Evaluation

- 53. It seems that treatment of crude cargoes with amine-based hydrogen sulfide scavenger chemicals is becoming more common. Which crudes are being treated with amines? What negative effects have been observed from processing these crudes? What are the effects on corrosion and wastewater quality?
- 54. What are the "best practice" techniques for analyzing the salt content of crude oils? Are there any compounds in the crude that will interfere with the salt content analysis' accuracy and what are they?
- 55. What chloride species are found in vacuum resids from heavy crude oil processing? Why are they not removed in the desalting process? What laboratory methods are used to identify these species? Is there an upper limit specification for chloride in delayed coker feedstocks?

Desalting

- 56. What technologies would you recommend for desalter level control instruments in heavy oil applications? What new technologies have been implemented or are being considered? What is your experience with these technologies with respect to reliability?
- 57. What operational, mechanical, or chemical approaches are being employed to increase removal of filterable solids in crude tankage or during desalting? Where is the most effective place to do this? Which method do you use to measure filterable solids?
- 58. What are you doing to prepare for the processing of high conductivity, high calcium, and high TAN (total acid number) crude types (such as Asian, African and North Sea crudes), especially with regard to desalter design improvements, chemical emulsion breakers and related corrosion control treatment? What impacts do you expect in the wastewater treatment plant (WWTP)?
- 59. We observe oil soluble organic chlorides that carry corrosive salts to downstream process units. What are the sources of these compounds and why are they showing up in downstream units? What are the preferred analytical techniques?
- 60. What have been your recent experiences using naphthenic acid corrosion inhibitor chemicals? Have they been cost effective?

Distillates

61. Do you experience thermal stability problems in your straight run kerosene and what may be the possible causes? Do you use chemical additives (stabilizers) or clay treat the product? What criteria are used to select the clay type?

- 62. What are the pros and cons of NaCl versus CaCl2 drying for middle distillate haze suppression?
- 63. Our refinery has been struggling with premature failures of clay treaters in jet fuel service. Our gauge for determining a failure is whether we pass a JFTOT test downstream of the clay treater. We used to run for several years without a clay changeout and now we are lucky to make three months. Are you seeing the same trend? If so, what are the possible causes?

General

- 64. What cutpoint can be achieved in an atmospheric crude tower running heavy crudes? What is limiting heater outlet temperature, atmospheric tower pressure, or something else? What are your "best practices" to minimize diesel to the vacuum unit?
- 65. What is the average energy consumption (MMBTU per barrel of crude oil) of your crude/vacuum units? What is currently being monitored to optimize energy recovery? What is being done to improve the energy efficiency of your crude/vacuum units?
- 66. What parameters are used to control corrosion in the naphtha section of a crude tower? Do you have packing in the naphtha section of the tower and are you experiencing any problems with corrosion? What metallurgy is being used with success?
- 67. What layers of protection do you employ to minimize risk of a catastrophic pump seal failure in high vapor pressure streams, including streams such as unstabilized naphtha? Are you evaluating double seals, increased monitoring (vibration, lubrication), local hydrocarbon detectors, and/or pump operating criteria such as minimum flowrates?

Vacuum Distillation

- 68. Do you have any experience with high performance vapor horns in vacuum towers? If so, what improvements have you seen? What are the key design parameters to minimize entrainment?
- 69. What parameters do you use to optimize the wash oil rate in vacuum towers?

Coking

- 70. Have you analyzed coker heater deposits for percentages of organics v. inorganics and speciated these deposits to determine possible causes for accelerated coke deposition? Is sodium or iron an issue?
- 71. Have you seen the exact same coker furnace spalling procedure work one time and not another? Are there differences in the coker feed or heater deposits which prevent effective spalling?

- 72. What is your experience with coker 3-way switching valves? What type are you using? What is their maintenance history and what are you doing to improve their reliability?
- 73. Is there a "best practice" to minimize/eliminate hot spot formation in the coke beds of delayed cokers?
- 74. What type of coke drum unheading devices are you using? Are you satisfied with their safety and performance?
- 75. What is the minimum outage that can be run without risk of foamover that you have experienced? What is the drum reference point for the measured outage?
- 76. Please provide your "best practice" guidelines for antifoam usage in the coker drums. Specifically, please answer these questions:
 - a. What is your as-delivered strength of silicone? What is the strength of diluted silicone as injected into the drum?
 - b. At what drum level should you start adding antifoam? When should one end?
 - c. What is a reasonable amount of antifoam to use in a complete cycle (pounds silicone per 1000 barrels of feed)?
 - d. What viscosity antifoam do you use?
 - e. What carrier for the silicone do you use?
 - f. What type of antifoam injection system do you have?
 - g. What silicon levels do you experience in coker product streams?
- 77. Have you used hollow cone sprays in the coker fractionator? What are the advantages and disadvantages of this application? How many levels of sprays do you recommend? What angle and pressure differential (dP) do you use?
- 78. How are you currently injecting sludge streams into your coker? What are the sludge sources? What limits the amount of sludge you can inject?

HYDROPROCESSING

Catalyst

- 79. Please share examples of problems that you have encountered and lessons learned as a result of dense loading techniques.
- 80. Please discuss quality assurance and "best practices" during catalyst loading. Please contrast inert atmosphere procedures with procedures used when air is present.
- 81. Will the increased severity anticipated for ULSD operations increase the probability of runaway reaction conditions occurring? What mitigation strategy are you planning to reduce the probability of runaway reactions? What additional operating training is planned? How does the presence of LCO impact the probability of a runaway reaction?
- 82. How have recent molybdenum price increases impacted your strategy for managing spent hydroprocessing catalyst?
- 83. Hydrotreating catalyst availability has been very tight in 2005. How are you managing the current long lead time requirements for catalysts, associated materials, and services? What is the outlook for availability in the next 6 months, 12 months, 18 months, and beyond? Are there plans for increasing catalyst production?
- 84. Are hydrotreating catalyst vendors and/or refiners planning to maintain catalyst in inventory for emergency requirements?

Process

- 85. How do you manage cracked stock introduction during start-up of new catalyst, especially in light of new low-sulfur fuels specifications?
- 86. Have you had success in producing ULSD as a side cut from a cat feed hydrotreater (CFHU or FCC Pretreater) fractionator? Describe what was done to the fractionator and other considerations.
- 87. Why does light naphtha produced from mild hydrocracking contain more than 1% benzene? What can you do to reduce the benzene content?
- 88. Please discuss "best practices" for the location and number of thermocouples within hydrotreating reactors for assessing temperature distribution in the catalyst beds.
- 89. Please comment on how existing CFHU's are being utilized in the production of ULSD. Are they part of the solution?

- 90. Are you designing ULSD hydrotreating units to operate in trickle flow during the entire catalyst cycle or allowing 100% vapor operation at some point in the cycle? Please discuss actual experience.
- 91. What crudes are presenting the greatest challenges for hydroprocessing catalysts with respect to contaminants? How are you managing these crudes and/or protecting the catalysts?
- 92. Are there "best practices" for predicting hydrogen consumption when designing a make-up hydrogen compressor? If you rely on pilot plant data, how do you obtain the most accurate hydrogen consumption information (flow meters, carbon/hydrogen balance, etc.)?
- 93. How are you dealing with increased loading in amine systems due to increasing hydrotreating severity and increasing crude oil sulfur content?
- 94. How are you dealing with increased hydrogen demand/consumption resulting from low-sulfur fuels regulations and lower quality feedstocks?

Quality

- 95. Have you observed that new ULSD hydrotreaters generate a by-product naphtha stream with high benzene content? Is this causing problems within your gasoline pool and how do you plan to handle it?
- 96. Why does light naphtha produced from mild hydrocracking contain more than 1% benzene? How can you reduce the benzene content?
- 97. Remembering the issues that occurred with low-sulfur diesel (500 ppm max) in 1993 with respect to lubricity additives, are there similar concerns associated with the introduction of ULSD regarding lubricity, conductivity, and/or thermal stability, etc.?

Safety

- 98. Please discuss pros and cons and your criteria for using independent shut-down valves in hydrocarbon and sour water lines between the high pressure and low pressure separators in terms of safety.
- 99. Are you planning to use any non-traditional heat exchanger designs in ULSD units (e.g. plate-type exchangers, etc.)?
- 100. What are your "best practices" for inspection of hydrogen steam reformer furnace tubes by non-destructive techniques? How will these practices change as a result of the critical need for on-stream reliability in ULSD units?
- 101. What is your experience with high pressure testing of process units with media other than hydrogen?

- 102. For your hydroprocessing personnel training, are you outsourcing or developing/using your own in-house training? How are the training approaches different for training operators and engineers?
- 103. How are you planning to communicate and mitigate the effects of transient upstream operations to downstream ULSD hydrotreaters?