



## Controlling Fe Catalyst Contamination, Shifting Yields, Coke Selectivity, PM Reduction in FCC Operations

The recent NPRA Q&A and Technology Conference held in Baltimore, Maryland (USA) included a compendium of topics relevant to FCC and hydroprocessing technology, including the following responses to NPRA questions by Grace Davison engineers

**NPRA Question #85:** *What are typical ranges employed for iron (Fe) content on FCC E-cat. What methods are available to determine how Fe is accumulated on the catalyst surface? How does the distribution of Fe on the catalyst surface impact the FCC operation, yield structure and emissions?*

**David Hunt, FCC Technical Service Manager, david.hunt@grace.com:** Grace receives equilibrium catalyst (E-cat) samples for most of the FCC units operating worldwide. These samples show a distribution of average E-cat iron (Fe) levels for all FCC units that have provided E-cat samples to Grace in 2010. Mean Fe levels are 0.57 wt% and the highest Fe level in one unit is 1.36 wt%. Iron can be detrimental to the unit in many ways including bottoms conversion, catalyst circulation stability and SOx emissions.

Yaluris showed using an electron probe microanalysis (EMPA) technique that Fe from organic iron sources is primarily a catalyst surface contami-

nant.<sup>1</sup> Yaluris also used scanning electron microscopy (SEM) and optical microscopy techniques to confirm Fe is a surface contaminant. Figure 1 is an EMPA image of an FCC catalyst particle cross section. Warmer colors on the surface of the particle confirm that Fe and CaO are primarily surface contaminants.

Yaluris discussed how Fe contamination can lead to pore closure and nodule formation.<sup>1</sup> The presence of Na and CaO can act as fluxing agents, aggravating the effect of Fe. Figure 2 shows E-cat ABD vs. E-cat Fe levels. Decant oil also increases at the higher contaminant levels due to the damaged catalyst pore structure.

**NPRA Question #86:** *What are catalyst best practices to shift FCC yields rapidly between gasoline and diesel maximization and then back again? Many catalyst suppliers are recommending blending catalyst systems. Do you believe this catalyst/additive blending is the best approach?*

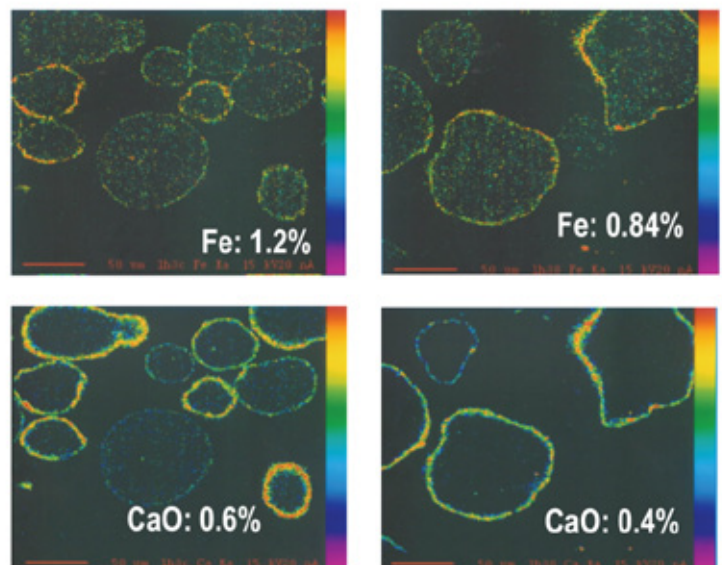


Figure 1. EMPA images of two FCC catalyst particles (Fe & CaO surface contaminants)

**Rosann Schiller, Product Manager, FCC Catalyst, rosann.schiller@grace.com:** In these challenging times, refiners

more than ever need flexibility. The GENESIS® catalyst system provides a means to maximize yield

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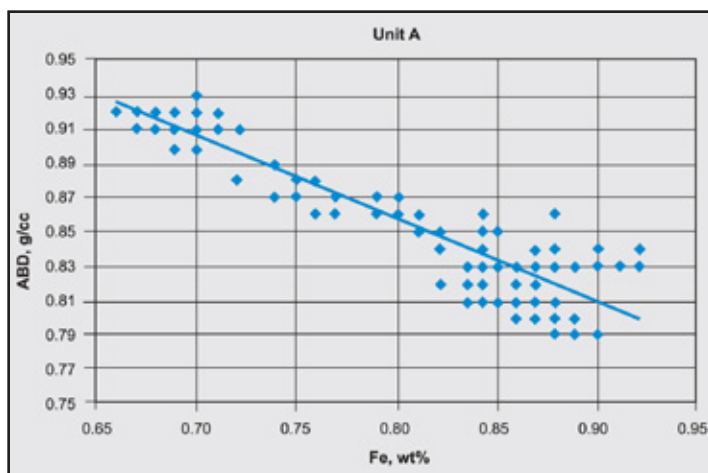


Figure 2. E-cat ABD vs. E-cat Fe levels

potential through the optimization of discrete cracking catalyst functionality.<sup>2</sup>

GENESIS systems offer refiners formulation flexibility and the ability to realize the desired yield shifts quickly in order to capture dynamic economic opportunities. 20% of the world's FCC capacity has utilized the technology.

For new applications, several scenarios (e.g. max gasoline or max LCO) are often prepared and presented to illustrate the flexibility and the power of GENESIS to change product slate. As product supply/demand balance shifts, GENESIS catalyst in the unit can be reformulated to maximize profitability and capture short term economic opportunities. To speed implementation, formulation adjustment often takes place in the fresh hopper, minimizing the delay

often associated with a catalyst change out. This catalyst system has also provided the flexibility to maximize profitability based on current supply/demand economics.

Since introduction to the unit, the refiner in Table 1 has reformulated GENESIS twice; first to maximize LCO and again to return to a gasoline operation. In the max LCO operation, the percentage of MIDAS was increased in the blend to maximize bottoms cracking and reduce Z/M. GENESIS 2, formulated for max LCO, delivered an additional 3.5 lv% yield for a net increase of 5.0 lv% LCO and 2.2 lv% reduction in slurry relative to the competitive base catalyst as shown in Table 1. When economics became favorable for gasoline, the refiner returned to the original formulation. Overall, these yield shifts were worth between \$0.45

and \$1.00/bbl, depending on the operating mode and the refining margins at the time.

For both catalyst reformulations, the blend ratio of MIDAS and IMPACT was adjusted to achieve the desired yield shift. Grace was able to reduce turnover time by working with the refiner to readjust the formulation within the fresh catalyst hopper.

A decision to reformulate within a GENESIS catalyst system typically happens 80% quicker than with a traditional catalyst because simply changing the blend ratio presents a lower risk option than a new catalyst or even a new additive. Catalyst Z/M ratio can be optimized to match the specific unit feedstock and operating constraints. In addition to optimizing the blend ratio, the activity levels of the individual components are carefully selected to match the operating mode and feed types. This formulation flexibility can deliver a significant selectivity change, allowing a refiner to accommodate a seasonal operation, manage a swing feedstock or even a hydrotreater outage, and most importantly, GENESIS catalyst systems allow refiners to capture short term economic opportunities.

**NPRA Question #87.** *In your experience how does catalyst activity affect the*

*catalyst's coke selectivity and the FCCU's delta coke? How are the coke selectivity and delta coke related? Lastly, discuss how to determine the proper activity to maximize conversion.*

**Rosann Schiller:** When designing an FCC catalyst, one must consider coke selectivity, delta coke and total coke yield. Coke selectivity is the relative coke-making tendency of the catalyst, or in other words, a catalyst with good coke selectivity produces higher conversion per unit of coke-make than the reference catalyst. Delta coke is, simply put, the difference between carbon on spent catalyst after stripping, and carbon on regenerated catalyst. Delta coke is expressed as a percentage of the catalyst. Generally, the delta coke is higher for catalysts with poor coke selectivity, but is also higher for more active catalysts and with heavier feeds. Higher delta coke translates to higher regenerator temperatures.

Total coke yield is the delta coke times the catalyst-to-oil ratio. In other words, total coke yield is the amount of coke burned in the regenerator, expressed as a percentage of the feed rate. Burning this coke, total coke, is responsible for fulfilling all the heat requirements, including the heat of reaction, in the FCC process. Total coke cannot change unless there is a change in these heat requirements. Consequently, if these heat requirements are held constant, a change in delta coke will cause an opposing change in cat/oil ratio to maintain the total coke yield constant.

**Table 1. GENESIS® provides flexibility to shift between gasoline and LCO modes.**

	Competitive Catalyst	GENESIS® 1 (Max. Gasoline) relative to base	GENESIS® 2 (Max. LCO) relative to base
Gasoline, lv%	Base	3	1
LCO, lv%	Base	1.5	5
Bottoms, lv%	Base	-1.5	-2.2

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There are four contributions to total coke: feed carbon, contaminant, stripping and catalytic. The feed coke can be approximated by the Conradson carbon level. Stripping or cat-to-oil coke results from the carry-over of occluded hydrocarbons after stripping. Stripping and feed coke are non-catalytic. Contaminant coke results from the metals in the feed, primarily nickel and vanadium. Lastly, catalytic coke is the intrinsic coke making tendency of the catalyst and feed. While both contaminant and catalytic coke appear to be controlled via catalyst, they are also dependent on the cat/oil ratio, which always adjusts to maintain the exact amount of total coke yield required for heat balance.

Catalyst design has a direct bearing on the formation of variable components of total coke. The needs for in-unit activity (catalytic coke) must be balanced against the contributions to coke from feed carbon and contaminant metals. For a resid application, a catalyst with “good coke selectivity” would typically have moderate activity and exhibit superior stability to metals deactivation as well as the ability to crack and convert coke precursors into liquid product. In this case, the effect of contaminant metals is minimized, and the catalytic activity is balanced against the contribution from feed carbon.

A heavily hydrotreated feed application, where there is minimal contribution to total coke from feed or metals, requires a higher catalyst activity to satisfy a given heat balance. If the catalyst is not active enough, torch oil or recycle must be utilized to achieve the equivalent

targeted coke yield per unit of feed, often to the detriment of the overall operation. For these hydrotreated feeds, the recommended catalyst still must possess excellent coke selectivity (that is achieve high conversion for a given coke yield) but have enough activity (delta coke) to deliver the prescribed total coke for the application. At Grace Davison, we strive to deliver the most coke selective catalyst for each application, in order to maximize liquid yield and profitability.

**NPRA Question #89:** *In shifting from partial burn to full burn in a side by side unit, what has been your observed impact on the NOx emissions? What is necessary to achieve 20 ppm NOx?*

**David Hunt:** Several Grace customers successfully operate with NOx emissions less than 20 ppm in full combustion without the use of NOx removal hardware in the flue gas circuit. These units have the following common theme:

- Regenerator flue gas excess O2 levels are less than 1.5 vol%
- If necessary, a non Pt combustion promoter like Grace’s CP® P is used to control afterburn and/or CO emissions. Additions of promoter are minimized since excessive additions of any CO combustion promoter can increase NOx
- Some of these units inject ammonia into the flue gas stream to meet NOx limits
- Some of these units use a NOx reduction additive such as Grace’s DENOX®
- The regenerator com-

bustion air and spent catalyst are extremely well mixed.

**Question# 91:** *Assuming the FCCU already has a third stage separator (TSS) what are the various options you consider for further reduction of particulate emissions (PM) and what is the expected level of pm to be achieved?*

**David Hunt:** Many FCC units which use third stage separators (TSS) operate with particulate limits <1 lb/1000 lb of coke burn. The absolute PM emission will depend, of course, on unit conditions such as the design characteristics, cyclone velocity, unit pressure and particulate loading of the TSS. To ensure low emissions from a TSS, an exhaustive review of the following FCC operations should be confirmed:

1. No excessive catalyst attrition sources are present:
  - a. Vapor velocities should be less than 300 fps and preferably less than 100 fps
  - b. Restriction orifices are present and the correct size
  - c. Torch is not being used
2. Regenerator cyclone velocities are within acceptable operating limits.
3. Regenerator bed level should provide the correct burial requirements for the cyclone dipleg valves and the transport disengaging zone should terminate below the cyclone inlet.
4. Secondary cyclone dipleg levels should terminate well below the top of the dipleg (3ft).
5. All steam sources are dry.
6. Regenerator superficial velocity is minimized.
7. Regenerator air and spent catalyst distribution is adequate to ensure the diplegs terminate in well

fluidized zones and each primary cyclone has similar catalyst entrainment. The catalyst design can also be optimized to minimize particulate entrainment to the TSS separators to ensure maximum third stage separator efficiency. Catalyst attrition is likely the most important catalyst property to consider. However, consideration of the amount of micron fines (<1 micron) generated during catalyst attrition is more important.

Cyclone efficiency falls by almost a factor of 10 for a 20 micron particle versus a 1 micron particle. As a result, two catalysts which have the same attrition index can have much different particulate emissions, depending on whether micro fines are generated during attrition versus particles in the 5 to 20 micron range.

The 0 to 20 micron and 0 to 40 micron content of the fresh catalyst is also critical to ensure low particulate emissions from a third stage separator. These particulate fractions should be minimized within the constraints of the catalyst circulation system. (Many units need higher fresh fines content to ensure stable catalyst circulation.)

A catalyst with a higher particle density, not necessarily higher apparent bulk density (ABD), will increase TSS efficiency. Al2O3 content can be used to increase the particle density.

An article entitled *Optimizing your FCC Regenerator Operation and Catalyst Design Can Minimize Catalyst Losses* provides a detailed review of many

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of the issues previously discussed.<sup>3</sup> Grace recommends our Al-Sol catalysts such as ALCYON®, IMPACT®, GENESIS®, AURORA®, and ADVANTA® for units which use TSS. Worldwide, Grace supplies more FCC units with third stage separators than any other catalyst supplier. ■

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Advanced Refining Technologies

## PROCESS OPERATIONS

# Low Capital Hydrogen Plant Retrofits

### Simple to Install Oxygen Enhanced Reforming Technology can Boost H2 Plant Capacity by 10-15%

Gregory J. Panuccio, Troy M. Raybold, James P. Meagher, Raymond F. Drnevich, V. "Jana" Janarthanan, Praxair, Inc.

The volume of low quality crudes needing to be upgraded to meet high quality product specifications has led to an increase in hydrogen (H2) demand. At the same time, costs associated with increasing H2 capacity have been escalating. The retrofit solution for increasing hydrogen production must also minimize plant

downtime and capital investment. Praxair's patented Oxygen Enhanced Reforming (OER) technology can efficiently and reliably expand H2 plant production capacity by enriching the steam methane reformer (SMR) combustion air with oxygen.

#### Debottlenecking SMR

Enrichment of combustion air with oxygen (O2) is a low-capital SMR debottlenecking strategy as opposed to other strategies, such as installation of a pre-reformer

(Table 1).<sup>1,2</sup> Enrichment of combustion air in the reformer with OER technology increases heat flux, radiant efficiency and furnace firing rate without increasing flue gas flow and maximum tube wall temperature.

The OER technology includes a simple-to-install lance or sparger to inject O2 directly into the burner flame (lance) or into the combustion air feed duct (sparger). An OER retrofit can typically be installed in most reformer types (can, terrace

wall, side fired, top fired) for a 10 to 15% H2 production increase, depending on current plant bottlenecks. Additional H2 production is achieved without increasing reformer tube wall temperatures, modifying the induced draft (ID) fan or convective section heat exchanger design, or appreciably affecting byproduct steam production rates. Further, an OER retrofit can be installed with very little plant downtime and capital investment. The characteristics of an OER retrofit are also shown in the previously mentioned Table 1.

A simplified schematic of the radiant section of an SMR furnace incorporating OER technology is shown in Figure 1. The combustion air is enriched with O2 by one of two means: either O2 is premixed with the air via sparger in the air feed ductwork or the O2 is injected directly into the burner flame via lance. For either delivery method, OER increases O2 concentration and decreases the concentration of inert nitrogen in the combustion air.

**Table 1. Comparison of common SMR retrofitting methods with Praxair's OER retrofit.1,2**

Method	H2 Rate	Cap Cost	Comments
Modify WGS Reactor	+3-5%	Medium	Single HTS reactor changed to 2-stage HTS, HTS + LTS, or MTS design
Upgrade Reformer	+5-15%	Medium-High	New catalyst; replace tubes with better metallurgy; modify pigtail/tunnel design; upgrade controls
Install Pre-reformer	+8-10%	Medium	Requires significant changes to reformer convection section; considerable drop in steam export
Install OER	+10-15%	Low	Simple installation, equipment and controls; non-invasive
Install Post-reformer	+20-30%	High	Large footprint; capital intensive

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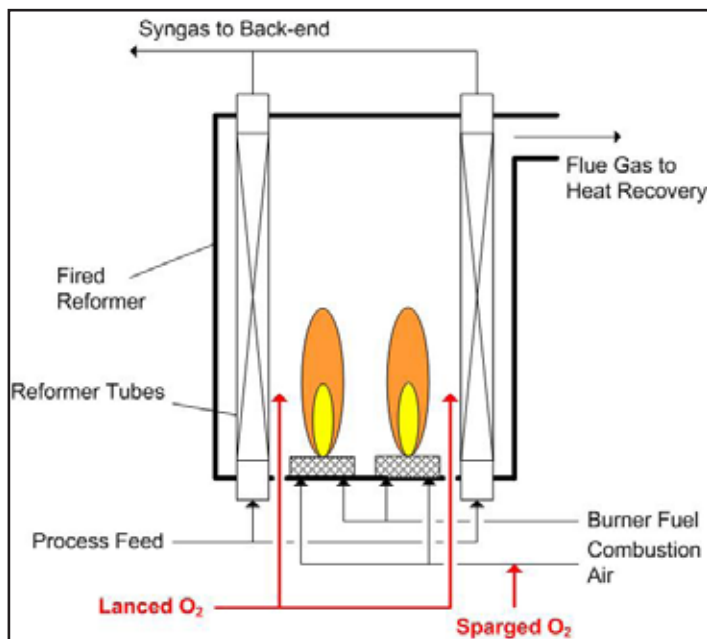


Figure 1: Simplified schematic of an SMR furnace radiant section with an OER retrofit

Since the O<sub>2</sub> concentration is higher than normal air, the furnace firing rate can be increased without increasing the volumetric flow rate of flue gas that is processed in the convective section of the reformer. Since the flue gas flow rate is unchanged, no modifications to the flue gas heat exchange equipment or the ID fan are required to maintain reformer performance. A secondary effect of increasing O<sub>2</sub> concentration in the combustion air is that the additional heat generated is released over the same distance or even over a shorter distance than with air. This results in an increase of the heat flux into the tubes

near the inlet of the reformer where the tubes are coldest. Process gas flow to the reformer tubes is increased to utilize the additional heat that becomes available and to maintain the maximum tube wall temperature at the desired value. Typical reformer tube heat flux and maximum tube wall temperature profiles with and without OER are shown in Figure 2.

The extent to which O<sub>2</sub> enrichment of combustion air can increase H<sub>2</sub> production capacity in an SMR will depend on many factors including whether other bottlenecks exist in the equipment upstream or downstream of the reformer furnace. Increasing

the O<sub>2</sub> concentration in the combustion air to between 22 and 23% can typically result in a 10 to 15% increase in H<sub>2</sub> production capacity. Field testing and simulation results show that between 15 and 20 tons of O<sub>2</sub> are typically required to produce 1.0 million scf (i.e., 1.0 million standard cubic feet at 60 °F and 14.7 psia) of incremental H<sub>2</sub> from a bottlenecked SMR. One of the other advantages of the OER technology is the operational flexibility inherent to the retrofit. If incremental H<sub>2</sub> production is not required for a period of time, the flow of oxygen can be turned off and the SMR will operate as it did prior to the retrofit.

### Oxygen Delivery: Lance v. Sparger

As previously mentioned, O<sub>2</sub> can be injected into the combustion air by either premixing it with the air via a sparger in the air feed ductwork or directly injecting the O<sub>2</sub> into the combustion zone within the furnace via a lance. There are advantages and disadvantages to both methods.

A sparger is simpler to install than lances. A sparger requires a single penetration into the air ductwork whereas lancing will require multiple penetrations into the SMR furnace near the

burners. It will be more difficult to install all the piping required to feed O<sub>2</sub> to multiple lances than the single pipe required to feed O<sub>2</sub> to a sparger. Furthermore, the lance nozzle orientation may have to be adjusted once it is installed to optimize operating conditions.

One disadvantage of the sparger is that nitrous oxides (NO<sub>x</sub>) production within the furnace will increase. The adiabatic flame temperature within the burner increases as the concentration of O<sub>2</sub> in the air increases, which in turn increases the production of thermal NO<sub>x</sub>. The extent to which NO<sub>x</sub> emissions will increase will depend on the design of the burners and the recirculation patterns within the furnace for the specific installation. Field testing has confirmed that lances can be installed such that the NO<sub>x</sub> emissions (on a lb/MMBtu fired basis) do not increase as O<sub>2</sub> is added to the SMR furnace. A lance installation can be NO<sub>x</sub> emission neutral because the lances can be designed to stage the O<sub>2</sub> consumption within the combustion zone and increase recirculation of cooler flue gases within the furnace.

Air ductwork materials incompatibility issues may limit the air enrichment level to 23.5% O<sub>2</sub> for the sparger case. According to CGA standards, air that has greater than 23.5% O<sub>2</sub> is subject to different safety standards than normal air. For lances, the enrichment is not limited to the equivalent of 23.5% O<sub>2</sub> in air because the O<sub>2</sub> is added to the furnace separately from the air supply. Therefore, there are no air duct materials incompatibility issues because the air duct is

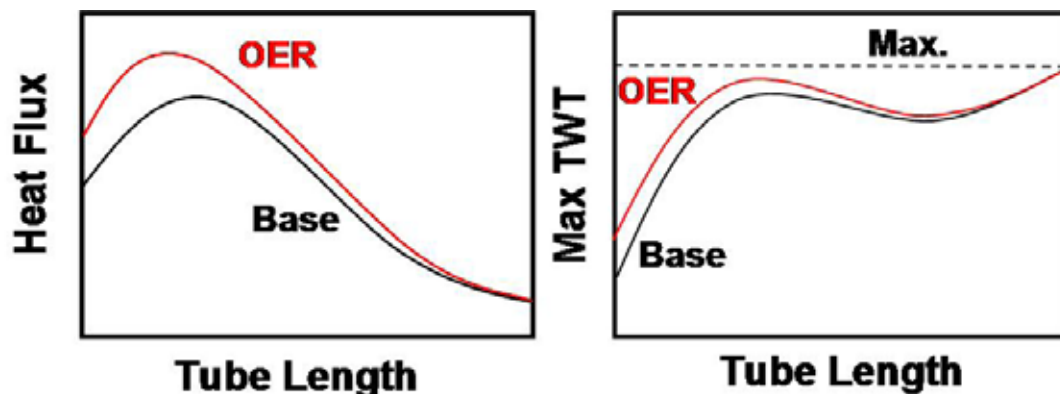


Figure 2: Approximate profiles of radiant zone reformer tube heat flux and maximum TWT with and without OER. With OER, H<sub>2</sub> production can be increased without increasing Max TWT and decreasing tube lifetimes

only exposed to ordinary air. Hydrogen production capacity can usually be increased to desired levels without increasing the concentration of O<sub>2</sub> in air beyond 23.5%, so either a sparger or lances would be suitable.

The O<sub>2</sub> injection method is custom designed for each retrofit. Though a sparger is much easier to install than lances, NO<sub>x</sub> emissions or O<sub>2</sub> enrichment limits may dictate that lances are the best option.

## OER Implementation

Praxair's OER technology supplements a growing portfolio of proven oxygen enhancement technologies for refinery applications. Today, Praxair supplies more than 40% of the US refineries using oxygen in their FCCUs and SRUs to improve performance and increase capacity. Praxair's oxy-fuel combustion technology is also used in process heaters to reduce NO<sub>x</sub> emissions while increasing throughput and efficiency. Praxair is best in class from a safety perspective, maintains excellence in project execution, and has proven world class plant reliability. Praxair leverages this collective experience for executing OER retrofit projects.

OER technology is a low capital cost solution because, unlike most other reformer retrofitting solutions, there is no new expensive equipment to install (e.g. catalytic reactors) and no significant modifications to the existing reformer furnace are required as part of the installation. OER retrofit equipment is simple, safe, and reliable. New equipment to be installed includes an O<sub>2</sub> supply

**Table 2. Summary of OER field testing results.**

Operating Condition	Base	OER	OER
O <sub>2</sub> Injection Device	None	Lances	Sparger
H <sub>2</sub> Production Rate	100%	111%	110%
O <sub>2</sub> in Air <sup>1</sup>	20.80%	21.90%	22.10%
O <sub>2</sub> /H <sub>2</sub> , 2 ton/mmescf	N/A	22	20
Natural Gas Feed + Fuel	100%	109%	108%
ΔMaximum TWT, <sup>3</sup> °F	Base	-1	+2
ΔReformer Outlet Temp., °F	Base	-1	+4
PSA Feed CH <sub>4</sub>	4.90%	5.60%	5.40%
NO <sub>x</sub> Emissions, <sup>2</sup> lb/mmBtu	100%	88%	120%

1 Equivalent O<sub>2</sub> enrichment level for OER cases with lances  
 2 Corrected for equivalent flue gas flowrate and flue gas O<sub>2</sub> concentration  
 3 Calculated (not measured)

system, an O<sub>2</sub> flow control skid, and an O<sub>2</sub> injection device (i.e. a sparger or lances).

The O<sub>2</sub> flow control skid is sized for the required O<sub>2</sub> flow rate and may be integrated with the facility's control system if desired. The flow skid can be installed in nearly any convenient location as it has a small footprint and can be built for compliance with most electrical classifications. The nature of the O<sub>2</sub> supply system will depend on the size of the application and location of the refinery. If the refinery does not currently have O<sub>2</sub> available in bulk on-site, a liquid O<sub>2</sub> storage tank or an O<sub>2</sub> generation plant may be installed. Depending on the refinery location, it may be possible to draw product from a nearby O<sub>2</sub> pipeline network. The O<sub>2</sub> supply system and O<sub>2</sub> flow control skid can typically be installed without shutting down H<sub>2</sub> plant operations. Installation of the sparger or lances could take up to one day of SMR outage.

Safety and environmental reviews of the proposed

design will be conducted before construction begins. Standards and procedures from both Praxair and the refinery will be applied such that the OER retrofit is installed and operated safely. New interlocks and alarms will be programmed into the control system to monitor critical operating parameters. The flow of O<sub>2</sub> to the furnace will automatically be shut down if design limits are exceeded. Praxair will also train refinery personnel as to the safe handling of oxygen and oxygen cleaning requirements.

An OER retrofit with a liquid oxygen supply system can be installed and commissioned within six-to-twelve months from contract completion. Detailed SMR design and operating data is required to engineer the retrofit since each OER installation is custom configured for the SMR in which it will be used. To expedite the project schedule, a comprehensive assessment of OER retrofit performance can be performed prior to contracting and the results can be reviewed along with the first

draft of the contract.

## OER Demonstration

The oxygen enhanced reforming technology was field tested at one of Praxair's cylindrical, up-fired, up-flow SMRs that utilizes a PSA for H<sub>2</sub> purification. Both the pre-mixed (sparger) and lanced O<sub>2</sub> delivery methods were tested. Most of the OER equipment and controls were installed over a period of several weeks. Only a single day outage was required to make the final oxygen connections: the sparger into the air duct and the lances into the furnace floor. Praxair standards, procedures, and training facilitated the safe installation and use of oxygen even though no pure oxygen systems had been used in the facility prior to the testing.

The results of the testing are summarized in Table 2. The results for each operating condition are from experiments representative of those operating conditions. Each of the values reported is given from a heat and mass balance process simulation of the SMR that was reconciled to

the experimental plant data. Some of the values that are reported in Table 2 (e.g. NO<sub>x</sub> emissions in lb/MMBtu fired) are not directly measured but are determined from a combination of direct measurements and calculations made in the plant process simulation.

When practical, observed and calculated values were renormalized to equivalent operating conditions within the corresponding process model for

the executed experiment as it was much easier to hold key operating parameters constant in a process simulation than it was during actual SMR operation. Note that these results may not reflect achievable outcomes for other OER installations. Actual OER operating conditions will vary dependent on the SMR design and the way in which the SMR is operated, but the results shown here should be fairly representative. ■

*Note:* This article was prepared from a more detailed Praxair paper (paper # AM-10-142) presented at the 2010 Annual Meeting in Phoenix, Arizona: "Oxygen Enhanced Reforming: A Low Capital Cost Retrofit Solution to Debottleneck Hydrogen Plant Production Capacity." For more information on Praxair's patented OER Technology contact Jana Janarthanan, Sr. Global Business Development Manager at +1 281 872 2197 ([v\\_janarthanan@praxair.com](mailto:v_janarthanan@praxair.com)).

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## INDUSTRY Q&A

### FCC Operations

#### Responses from Refinery FCC Consultants Bob Ludolph and Ken A. Peccatiello

*In troubleshooting catalyst losses, can you describe any cases where a unit shutdown was imminent (e.g., severe cyclone failure) if the losses could not be stopped quickly? What is your recommendation for avoiding shutdowns due to excessive catalyst losses?*



**Bob Ludolph:** There are a number of scenarios that can lead to a unit shutdown due to excessive catalyst losses.

Generally, inability to maintain regenerator bed level leads to an imminent unit shutdown. Since the stripper bed level is controlled with the spent catalyst valve any catalyst loss from the reactor or the regenerator is reflected in a loss of regenerator level. Refiners will face the decision to shut down whenever the catalyst loss is so high that:

- Not enough make-up catalyst (fresh or equilibrium) is available to restore the catalyst lost
- Catalyst loading via loader or pressuring from the hopper falls short of the required make-up rate
- Cost of replacing the lost catalyst becomes prohibitive
- Slurry oil ash or BS&W specifications cannot be met, leading to severe product discounts and loss of sales

- Wet gas scrubber (WGS) purge solids separation/containment inventory is inadequate
- Electrostatic precipitator fines collection rate exceeds the number of rolloff bins available
- Stack opacity/particulate emission limit compliance is difficult to achieve
- Slurry oil pump reliability and mechanical availability is unacceptable leading to significant feedrate reductions.
- Pressure bumping to possibly dislodge an obstruction or aerate a de-fluidized zone
- Adjusting the fresh catalyst attrition resistance or fines content
- Making up with equilibrium catalyst versus fresh catalyst
- Adjusting air/steam rates, as well as the distribution if multiple grids/rings are available
- Lowering/raising bed levels to check impact on cyclone operation
- Lowering/raising operating temperature to lower/raise velocities
- Lowering/raising operating pressure to raise/lower velocities
- Conducting diagnostic studies to help identify what equipment needs repair.

There may be opportunities to mitigate the catalyst loss and delaying the need for shutdown. The delay would allow the refiner to troubleshoot and develop corrective action plans for staying on-line and keeping operating costs down. The refiner could consider:

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**K. A. Peccatiello:** There have been circumstances where catalyst losses have been very severe and a shut-down was imminent. However, it is very unusual for the cause of an immediate/emergency shutdown to be cyclone damage due to normal “wear-and-tear.” The normal “wear-and-tear” damage can usually be observed, monitored, and anticipated well in advance by operations and technical personnel, thus avoiding an emergency outage; a good monitoring program will allow operations and technical personnel to work with planning and scheduling to plan an outage as the damage and losses become unsustainable.

The rapid and imminent causes are usually the result of a significant event or a catastrophic failure. The usual causes are refractory failure/loss following an upset or a thermal cycle which plugs or restricts one or more cyclone diplegs leading to massive catalyst carry-over. A second example is the use of “smear-coating” or “butter-coating” the refractory in the cyclones. “Smear-coats” or “butter-coats” do not adhere to the base refractory and spall off almost immediately upon start-up. Since the secondary cyclones are relatively small in diameter to most units (usually 8-10 inches), a major spall of this

type can easily plug (and has) the dipleg. An example unique for the reactor side, would be coke spalling from reactor cyclone gas outlet tubes following a thermal cycle and again plugging or restricting the cyclone dipleg (see figure 1 & 2). These situations can be observed in several manners:

- A rapid loss in catalyst level or inventory, usually in the regenerator as the reactor/stripper level is typically in level control and the regenerator level/inventory “takes the swing”
- Significant increase in the catalyst content in the main fractionator bottoms (MFB) slurry loop sample (IF it is a reactor cyclone)
- Significant increase in the catalyst content in the flue gas scrubber (FGS) effluent loop sample (IF it is a regenerator cyclone)
- Significant increase in the catalyst being dumped to the electro-static precipitator (ESP) bins (IF it is a regenerator cyclone)
- Significant increase in flue gas stack opacity if there is an electro-static precipitator (ESP) in service (IF it is a regenerator cyclone).

The failure mentioned previously may not be easily observed upon the restart / dry-circulation period when catalyst circulation rates are generally very low and the catalyst loadings to the cyclones are extremely low (generally less than 10% of operating catalyst circulation rates). The situation will manifest itself once feed has



Figure 1: Coke deposit on outer portion of reactor cyclone vapor tube. Note area of coke spalling.



Figure 2: Picture of erosion in cyclone dipleg.

been introduced into the unit and catalyst circulation rates, and thus catalyst loadings to the cyclones, are increased.

A more unusual, but still possible (possible because it has occurred) circumstance is the loss of a cyclone. A loss in this case means the cyclone failed or dropped from its supports. This can happen following an extreme thermal excursion (usually in the regenerator) or following some seismic activity for either or both the reactor and/or the regenerator sides (usually discovered upon a restart as the seismic activity most likely took the unit off-line). Again, the same five previously mentioned items

will be key indicators of a problem or issue. An FCCU/RFCCU process engineer should know the following critical pieces of information for their unit:

1. At what rate would catalyst be lost from the unit if a regenerator primary cyclone were to plug?
  - a) At normal catalyst circulation rates?
  - b) At minimum feed rate catalyst circulation rates (minimum feed rate is usually the point required for main fractionator operational and product yield stability)
2. At what rate would catalyst be lost from the unit



if a regenerator secondary cyclone were to plug?

a) At normal catalyst circulation rates?

b) At minimum feed rate catalyst circulation rates?

3. At what rate would catalyst be lost from the unit if a reactor primary/rough-cut cyclone were to plug?

a) At normal catalyst circulation rates?

b) At minimum feed rate catalyst circulation rates (minimum feed rate is usually the point required for main fractionator operational and product yield stability)?

4. At what rate would catalyst be lost from the unit if a reactor secondary cyclone were to plug?

a) At normal catalyst circulation rates?

b) At minimum feed rate catalyst circulation rates?

The ability of process personnel to quickly analyze and respond to any of these is the difference between a short five-to-eight day disruption or two-to-three week outage.

*What defines FCC under-utilization and where do you look for profit improvement in such situations?*

**Bob Ludolph:** In many respects, what defines under-utilization applies to when FCC feedrates are down or when operations are normal; the difference is a matter of degree. In general, under-utilization can be defined whenever:

- Pumps & compressors are unloaded (feed, liquid & vapor products, combustion air)
- Catalyst loading equipment has unused capacity

- Emissions control equipment is unloaded

- Regenerated/spent slide or plug valve  $\Delta$ Ps are exceptionally high, or

- The unit pressure balance has wider range-ability.

Where to look for profit improvement? Three places should be evaluated:

1. The sources and types of feed components that are cracked
2. The technology, formulation and blend of catalyst and additives cracking the feed
3. The operation of the cracking, combustion, flue gas and product recovery equipment.

Let's discuss the opportunities that come with each of these as well as potential obstacles hindering your success in pursuing them.

## Feed Opportunities

Crudes or purchased feedstocks with lower qualities than what are normally cracked offer the opportunity to improve profitability. Higher sulfur, acid number, carbon, and/or metal feeds can be economically attractive while being processed at levels that minimize your risk. Conversely, some refiners introduce feedstocks with better than normal quality in order to fill out their recovery sections while cracking less feed. Internally to the refinery there are incremental feedstocks, like atmospheric or vacuum resid, that can be cracked to raise overall volume gain for the facility. Also, FCC products can be recycled to obtain more valuable yield distributions, like gasoline

re-cracked to generate more olefins or heavy cycle oil re-cracked to more valuable liquid products.

Be mindful that an opportunity feedstock may be less crackable than what its reported bulk properties suggest. Excessive yields of fuel gas and coke could result, negatively impacting the heat balance and reducing the feedstock profitability. If the hydrothermal stability of the catalyst is insufficient, then the catalyst may not be able to tolerance additional metals. Additional or new process chemicals for mitigating fouling or corrosion may be needed when cracking more difficult feedstocks.

## Catalyst Opportunities

Optimization of catalyst selectivities, activity or both is worth reviewing with your supplier. Through reformulation or blending ratio changes, the yield structure or metals tolerance can be shifted in a favorable direction. Introduce cracking additive technology (e.g. ZSM-5, bottoms reducer) to shift the yield structure quicker or respond to feed quality changes better. Consider trialing new catalyst or catalyst additive technologies to pursue further product distribution improvement. Lowering catalyst additions would reduce your expenses. Raising catalyst additions may improve cracking selectivities. Trial each to determine what fits your operation better. Also consider adding equilibrium catalyst on a regular basis to reduce your expenses.

Adjusting catalyst technology or formulation could result in physical property changes of the circulating inventory. Monitor the

fluidization parameters since fines retention or catalyst attrition may be less. If catalyst additions are reduced, monitor the particle size distribution (PSD) of the inventory...you may have to adjust the fresh catalyst size grade. Standpipes may be over- or under-aerated depending on the operating conditions...adjust aeration rates as necessary for proper pressure build. Closely review the properties of any equilibrium catalyst under consideration for purchase...incompatibility with the fresh catalyst technology could lead to under-performance.

## Equipment Operation Opportunities

It is likely that the reduced rate operation will free up combustion air. This opens up the opportunity to operate differently and consume the unused coke burn capacity. Pertaining to the riser operation, lowering or removing feed preheat will increase catalyst circulation, conversion and volume gain. Feed dispersion steam can be conserved to reduce sour water production, or increasing the steam/feed ratio may actually improve feed/catalyst contacting. Being too aggressive with dispersion steam conservation can lead to poor feedstock atomization, feed nozzle plugging, or "wetted" spent catalyst going to the regenerator. Conduct steam/feed trials to determine what works better. Also consider taking feed nozzles out-of-service to improve overall atomization – review the design and procedures before trying this.

By introducing or increasing riser lift gas you may reduce the net dry gas production

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by “conditioning” the metals on the regenerated catalyst. You can also introduce or increase cracked naphtha injection to promote light olefin production. Under reduced feed rate conditions there will be more riser contact time, which should promote bottoms cracking. You may realize higher slurry ash content as a result, which may impact product blending or increase the erosion rate of system piping. Also, the riser velocity may get too low, which promotes backmixing, resulting in higher fuel gas and coke yields, gasoline overcracking to LPG and other selectivity shifts.

In the reactor section, with the air available, reactor temperature can be raised for more conversion and volume gain. Lowering the reactor pressure will result in less hydrogen transfer (better octane, olefin yield), better stripping, and reduced rotating equipment cost. Longer reactor residence time could also lead to product mix deterioration and vessel coking. Potentially higher butadiene yield may impact the alkylation plant. Slurry fouling rate may accelerate from higher conversion operations – you may need an antifoulant program. LCO properties will shift and may impact distillate blending for cetane, sulfur, and gravity.

In the stripper section, longer stripper residence time (from lower catalyst circulation) can lead to better stripping efficiency, product recovery, and lower coke hydrogen content, especially if reactor temperature is increased. Conserving stripping steam may help with sour water management but be careful of going too low. Like the feed nozzles, getting

too aggressive with stripping steam conservation can result in steam distributor nozzle plugging and lower actual stripper bed level, which may uncover cyclone diplegs. Operating at lower feed rate can also result in higher density spent catalyst, leading to higher slide/plug valve differentials – this presents the opportunity to shift the pressure balance in a positive way by lowering the reactor pressure.

In the product recovery section, generally the lower feed rate condition opens up wet gas capacity. This means you can handle lower suction pressure or lower molecular weight gas streams – this flexibility may expand your feedstock and catalyst options. Downstream recovery sections are likely to be under-loaded, resulting in better liquid/vapor product separations, product purities and improved treating conditions.

When it comes to the regenerator, combustion air will likely be available. You could continue to conserve in the interest of compressor energy savings or apply the excess for higher coke burns. You could also reduce or eliminate the cost of oxygen enrichment if it is part of your base operation. If the refinery needs steam and you have a catalyst cooler increase the coke burn to produce extra steam. If superficial velocities are down and there is less regenerator afterburn then your feedstock and catalyst options grow. You can also save on combustion promoter which may also result in lower emissions. Too low of a combustion air rate can lead to air distributor nozzle erosion and lower regenerator bed penetration. The burn will

become uneven with the radial temperature differences growing. The catalyst regeneration will be less uniform resulting in a “salt & pepper” appearance that could impact the catalyst cracking selectivities. The fluidized density will also vary throughout the bed, potentially impacting the stability of the catalyst circulation returning to the riser. Consider plugging off “extra” air distributor nozzles during the next outage if the operation is expected to last a very long time.

In the flue gas system, turboexpander vibrations from fines deposits could be reduced or eliminated. Less or no walnut shelling would be required. However, turboexpander power generation may be lost if the regenerator pressure is lower than the normal operation. Fuel to fired boilers could be reduced or burners modified to reduce emissions. Lower fines accumulation on boiler internals may mean less opacity spiking during sootblowing cycles. Lower chemical cost would be expected for NO<sub>x</sub> and SO<sub>x</sub> reduction equipment technologies.

Realize that lower vapor and flue gas rates may result in the loss of cyclone efficiency and less reactor/regenerator catalyst retention. Larger particle sizes may be preferentially lost. Consider sealing off “unnecessary” cyclone pairs during an outage if efficiencies are expected to be low for a very long time. Lowering operating pressure should help in this situation. High slide/plug valve differentials may also lead to high valve erosion rates. See if the pressure balance could be adjusted to address this. Process control valves may perform with less stability since

they may be operating near the low end of their range. Retuning may be necessary.

## Additional Opportunities

Consider riser, reactor, stripper, recovery, regenerator and flue gas system modifications. Alter or upgrade equipment to address plant constraints and reliability issues. Add new equipment/technology to expand processing capabilities and maximize profitability under reduced rate conditions.

Lastly, take the opportunity to improve your LP vectors for better representations of feed quality and operating condition changes. Also develop various business scenarios of interest and assemble the model projections for each. Conduct plant trials that simulate the cases and provide the necessary data. Update the LP as necessary.

**K. A. Peccatiello:** I would classify an FCCU or an RFCCU as under-utilized with two very different and distinct definitions. The first definition of an under-utilized FCCU/RFCCU is based upon the unit as a stand-alone entity. I do not necessarily consider the unit under-utilized if it is not at maximum feed throughput/rate or at maximum conversion. The true test of the definition for an under-utilized unit is if the unit is constrained? Is the unit operating or being allowed to operate within parameters within the control of the FCCU/RFCCU operations and/or technical team? Is the unit up against one or more major constraints? Is the unit limited by: main air blower

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(MAB); wet gas compressor (WGC); hydraulically on catalyst circulation or slide valve; main fractionator bottoms (MFB) heat removal capacity; main fractionator overhead (MFO) cooling/condensing capacity; hydraulically in the vapor recovery unit (VRU) area? Is the unit constrained singularly or with multiple constraints?

If the unit is not constrained, then the unit can be considered under-utilized unless it comes into conflict with the second definition. The second definition is if the refinery is constrained in such a manner that the FCCU/RFCCU is not operating at one or more of its constraints. If the refinery is operating in such a manner that it is uneconomical or unable to push the FCCU/RFCCU to a constraint, then I do not “punish” the FCCU/RFCCU, as this condition is beyond the control on the FCCU/RFCCU operations and/or technical team. There have been many circumstances where the refinery has cut crude runs either for economical reasons or due to one or more processing unit problems or issues. Anything that is “beyond the control” of the FCCU/RFCCU team should not count against them.

It is the duty of the FCCU/RFCCU

operations and technical team to always look for ideas/solutions in order to maximize the profitability of their unit; which usually means push the unit to multiple constraints. However, the team also needs to understand the place that their unit has in the over-all scheme of the refinery. There may be times when the FCCU/RFCCU may need to be under-utilized for the greater economic good of the entire refining complex. ■

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## EDITORIALLY SPEAKING

# Opportunity Crudes Conference Draws International Attendance

The recent Opportunity Crudes Conference in Houston sponsored by Hydrocarbon Publishing Company included a compendium of presentations [www.opportunitycrudes.com](http://www.opportunitycrudes.com) discussing the impact of heavy crudes on refinery operations. The well-attended conference included delegates from refineries throughout the world, indicative of the level of importance being placed on these high-fouling crudes.

Fouling and corrosion that occurs in fractionation equipment and heat exchangers when processing opportunity crudes were discussed at length throughout the

conference. Optimal processing of opportunity crudes directly impacts crude unit performance. At higher conversions (e.g., 80%), fouling in reactors is also noticeable. Opportunity crudes are, in most cases, higher acid (high TAN) crudes that predicate the need for processing assets with upgraded metallurgy and more frequent inspection programs.

To be sure, the potential margins associated with processing “opportunity crudes” need to be weighed against the costs of processing these types of crudes (typically from Canada,

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Venezuela, Africa and other areas). Considering that in late 2007, opportunity crude processing margins exceeded \$14 per barrel as compared to less than \$1.50 per barrel in late 2009.

Another important consideration when evaluating the economics of processing opportunity crudes is the increase in hydrogen consumption. To be sure, there are many other parameters to take into consideration on an enterprise-wide level (e.g., supply and distribution network) and on a unit level (e.g., determining

thickness of wash bed in crude/vacuum tower).

However, there are technical solutions that were not available until recently. For example, trying to understand the impact (fouling rate) before and after chemical treatment programs to prevent fouling in crude units processing opportunity crudes can be made more economical and effective with multiple regression analysis (MRA). Although MRA-based modeling is nothing new, its application in the mitigation of opportunity crude fouling is

to provide a relationship between inlet and outlet flows (i.e., better determination of fouling rates).

Most fouling and corrosion programs are focused on overhead systems (e.g., FCC main fractionator overhead system). However, significant discussion and exhibited demos at the conference focused on heat exchanger anti-foulant programs.

In any event, opportunity crude focused refiners want to “engineer” fouling out of their crude processing systems. The fouling propensity of Canadian-based

opportunity crudes can become even higher when combined with other types of crudes. These issues are very unit specific, such that an effective fouling program at one facility may not yield the same results at another facility. Closely associated with fouling and corrosion control imperatives with opportunity crude processing are the energy efficiency improvements in crude unit operations and other processing assets, including visbreakers, cokers and ebullated bed hydrocrackers. ■

## CALENDAR OF EVENTS

### NOVEMBER

7-12, AIChE Annual Meeting, Salt Lake City, Utah, [www.aiche.org](http://www.aiche.org)

15-17, API Fall Refining & Equipment Meeting, Nashville, TN, [www.api.org](http://www.api.org).

29 Nov- 1Dec. *ERTC 15<sup>th</sup> Annual Meeting*, Istanbul, +44 (0) 207 484 9700, [www.gtforum.com](http://www.gtforum.com).

### MARCH

20-22, NPRA Annual Meeting, San Antonio, Texas, +1 202 457 0480, [www.npra.org](http://www.npra.org)

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