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AM-16-15 Identifying the Root Cause of Afterburn in Fluidized Catalytic Crackers

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Identifying the Root Cause of Afterburn in Fluidized Catalytic Crackers

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Introduction

The FCC unit has a long history of upgrading low valued feed stocks into much higher valued LPG olefins and motor fuels. One notable reason for the long term success of this technology has been its stability in spite of high catalyst circulation rates. One common exception to this rule is the presence of afterburn which continues to plague many FCC units.

Afterburn is defined as any increase in temperature after the dense bed. Afterburn occurs in the regenerator dilute phase, cyclones, plenum, or in the most severe cases, in the flue gas handling system[1]. The point at which afterburn is observed is directly related to temperature. Higher temperature operations tend to observe afterburn in the dilute phase or the cyclones. Low temperature operations tend to observe afterburn occurring in the plenum or in the flue gas line. Afterburn may occur both in full combustion or full burn and partial combustion regeneration operations, but is more typically observed in full combustion.

There are two types of afterburn observed in FCC units today which includes generalized or kinetically limited afterburn and localized afterburn. In both instances, combustion gases rich in carbon monoxide and gases rich in oxygen mix above the dense bed of the regenerator which will then begin to combust. Catalyst densities drop rapidly after the combustion gases exit from the dense bed. The combustion of carbon monoxide to carbon dioxide releases substantial energy resulting in temperature rise. The lower the catalyst density the greater the temperature rise will be. This is especially true after the primary cyclones. Small amounts of CO oxidation will result in large temperature increases.

Afterburning, at best, will limit feedstock selection and operating severity. At worst, afterburn may lead to reduced charge rates, and in the most severe situations, damage to regenerator internals.

The simplest, albeit expensive, solution to afterburn has been the injection of platinum or palladium-based additives to shift carbon monoxide oxidation from the dilute phase into the dense

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[1] The reader is directed to J.W. Wilson's excellent analysis of afterburning as presented in the 2003 NPRA Annual Meeting ("FCC Regenerator Afterburn Causes and Cures", AM-03-44)

bed. However, the very fact that afterburn has continued to exist in spite of all that has been learned through the decades indicates that root-cause analysis is often challenging.

Generalized Afterburn

Generalized afterburn is associated with temperatures which are evenly distributed across the cross-sectional area of the dilute phase. This afterburn may be continuous or intermittent. The two most common causes for generalized afterburn are operating too near the transition zone to partial burn operations and insufficient residence time within the dense bed to complete the carbon monoxide oxidation.

Full combustion regenerators operate with typically 1-3% excess oxygen in the flue gas on a dry basis[i]. The minimum oxygen necessary to prevent afterburn is a function of temperature, residence time and unit design. As the combustion air rate to the regenerator is reduced carbon monoxide production will increase. This will continue until carbon monoxide combustion within the dense bed has reached the maximum possible and carbon monoxide will begin to be emitted from the bed. At this point afterburning will occur due to mixing of O_2 rich & CO rich gases in the dilute phase leading to combustion.

This point at which afterburning occurs at minimum excess oxygen in the flue gas defines the beginning of the transition from full combustion to partial combustion in a full burn operation. This “transition zone” from full to partial combustion is unstable. A regenerator operating near this transition point will “mysteriously” begin to afterburn and then cease to afterburn seemingly without cause. The root cause for such afterburning events will likely be found in small changes in feedstock quality (CCR, % residue, etc.) or operating severity (riser outlet temperature, equilibrium catalyst activity, etc.).

The simplest solution for such a case is to move the operation well away from this transition zone. This will be achieved via increasing the combustion air rate to the regenerator. In the worst-case scenario, this may require a reduction in charge rate or conversion if the unit is operating at maximum air blower capacity. An alternative solution may be oxygen enrichment.

More frequently, generalized afterburn occurs when the regenerator is kinetically limited due to insufficient residence time in the dense bed such that the carbon monoxide to carbon dioxide reaction is unable to progress to completion. This may occur in a unit which has high superficial velocities and/or low bed levels and is frequently observed in units which have low dense bed temperatures.

Increasing temperature in such operations can be achieved via increases in delta coke. Delta coke may be increased by increasing riser outlet temperature, increasing equilibrium catalyst activity, reducing preheat temperature, etc. Where possible, the FCC operator experiencing kinetic limitations should also increase the regenerator dense bed level. Care must be exercised to avoid exceeding the transport disengaging height leading to increased catalyst losses.

The simplest, albeit most expensive, solution to thermodynamic limitations is the injection of CO promoter[ii]. These additives are expensive but very effective in eliminating afterburn. CO promoters are most effective at controlling generalized afterburn. For most operations, an initial target of one ppm platinum in the circulating inventory is initially chosen with subsequent optimization for determining the minimum addition rate to achieve the desired reduction in afterburn.

One caveat for FCC operators utilizing CO promoters is to exercise caution when injecting antimony for nickel passivation. Antimony effectively deactivates platinum. Injection of antimony will deactivate approximately 50% or more of the platinum in the circulating inventory. The FCC operator choosing to inject antimony should make adjustments in the CO promoter injections accordingly.

In partial burn operations, an increase in air rate will increase the CO_2-to-CO ratio and the regenerator temperature. Continued increases in the air rate will reach a point at which insufficient residence time in the dense bed exists such that oxygen begins to break through the dense bed into the dilute phase. Afterburn will begin at this point. This is similar to a full combustion operation in which the air rate is being systematically reduced to minimum levels leading to carbon monoxide break through which also results in afterburn. The solution in the partial burn case is to reduce the air rate while the solution in the full combustion operation is to increase air rates. In both cases, the need is to move the unit well away from the transition zone solidly into the respective partial or full burn operation.

Localized Afterburn

Localized afterburn is identified by a quadrant or region of the regenerator experiencing afterburn while the remainder of the cross-sectional area continues to operate at near normal temperatures. Localized afterburn is usually due to damage to the regenerator internals or issues in the initial regenerator design or subsequent modifications.

A regenerator which has been operating in a stable manner which "suddenly" begins to afterburn is typically due to mechanical damage. This damage will often result in a corresponding change in the particle size distribution as measured in the first bin of an electrostatic precipitator hopper or third stage separator fines. Eventually, changes in the 0-40 µm, and in severe cases, the 40-60 µm fraction in the circulating inventory will be observed.

If the damage is related to the air distributor a reduction in the differential pressure across the distributor and an increase in control valve position will likely be observed. Additionally, the FCC operator will often observe a step change increase in NOx emissions. NOx emissions are extremely sensitive to maldistribution. Damage to regenerator internals sufficient to introduce afterburn will in most cases also result in severe maldistribution.

It is suggested that step tests in combustion air injection be carried out if the air distributor configuration permits air rate adjustment via quadrants or segments of the cross sectional area. The goal is to initiate incremental step change increases in the combustion air rate in the quadrant or region with the highest temperatures while closely monitoring for temperature reductions in the afterburn zone and as well as reductions in NOx emissions. Additionally, the process engineer is advised to closely monitor the catalyst losses during this exercise.

Transient localized temperatures in time or position are generally due to operating too close to the transition zone to partial burn for a full combustion operation or too close to the full burn zone for a partial combustion regenerator. It is recommended that the operator of the partial burn regenerator move deeper into partial burn by reducing air rate while the operator of the full combustion regenerator increase air rate to operate more solidly within the stable zone of full combustion.

As described above, the two best short-term solutions include increasing combustion air injection rates in the quadrant or zone experiencing afterburn where possible and the use of CO promoter. CO promoters will be less effective in regenerators experiencing localized afterburn. The best practice for optimizing CO promoter injections requires a gradual increase in promoter concentration in the circulating inventory while closely monitoring the temperature within the afterburning zone. The temperature in this zone will continue to drop until the available oxygen has been consumed. Further injections beyond this point are far less effective. In some cases, it may be possible to continue injections such that the temperatures in the zones not experiencing afterburn will drop somewhat below the average temperature.

Radioactive Studies

Valuable insight may be achieved by initiating a tracer study in the unit which had been operating in a stable manner and which suddenly begins to afterburn. This study may assist the refiner to pinpoint the root cause of the afterburn and whether it is related to the air distributor or spent catalyst distributor. This test will enable the refiner to have the most likely fix prepared before the unit is shut down. These tracer studies are typically carried out in two steps using a radioactive isotope of argon with a very short half-life to study the gas flows within the regenerator while a radioactive isotope of sodium with a very short half-life is used to monitor the catalyst flows.

It is strongly recommended that the process engineer overseeing the tracer study ensure that he or she understands and agrees with the placement of the radioactive detectors. It is important that the detectors are placed such that there will be no interference from internal structures such as cyclone diplegs.

Radioactive tracer studies are very effective at identifying damage within regenerators. Such studies are much less effective at identifying root cause for design issues.

Regenerator Fluid Flow Uniformity

CPFD Software has developed a quantitative measure of the regenerator fluid flow uniformity[iii]. The goal of this calculation is to quantify the uniformity of fluid flow within the cross-section of a fluidized bed. The purpose of this calculation is to enable a quantitative comparison of the uniformity of gas flow mixing between various modifications under consideration. The definition of uniformity adopted here is:

$$U = \frac{Cross\text{−}sectional\ area\ being\ used\ for\ fluid\ flow}{Total\ cross\text{−}sectional\ area} = \frac{A_{flow}}{A_{total}} \qquad (1)$$

To calculate the value of A_{flow}, two definitions of time-averaged flux are introduced: the first is the conventional area weighted flux and the second is a flux weighted by the mass flow. This is shown below where F_i and a_i are the fluid mass flux and cross-sectional area of cell i.

Average flux weighted by area:

$$F_{\mathrm{area}} = \frac{\int \mathrm{Fda}}{\int \mathrm{da}} = \frac{\sum_{\mathrm{i}} \mathrm{a_i F_i}}{\sum_{\mathrm{i}} \mathrm{a_i}} = \frac{m}{A_{total}} \tag{2}$$

Average flux weighted by mass flow rate:

$$F_{wt} = \frac{\int F dm}{\int dm} = \frac{\sum_i m_i F_i}{\sum_i m_i} = \frac{\sum_i a_i F_i^2}{\sum_i a_i F_i} \tag{3}$$

The difference between the average flux definitions is that F_{area} gives the average flux across the entire cross-section whereas F_{wt} is the average flux where the gas is actively flowing. Both flow definitions are related to the total mass flow in the cross-section by multiplication of the appropriate flow area. This provides a definition of A_{flow}:

$$m = A_{total} F_{area} = A_{flow} F_{wt} \tag{4}$$

Therefore, the definition of gas flow uniformity is:

$$U = \frac{A_{flow}}{A_{total}} = \frac{F_{area}}{F_{wt}} = \frac{\sum_i a_i F_i}{\sum_i a_i} \left(\frac{\sum_i a_i F_i^2}{\sum_i a_i F_i} \right)^{-1} = \frac{(\sum_i a_i F_i)^2}{\sum_i a_i F_i^2 \sum_i a_i} \tag{5}$$

This measure of regenerator gas flow uniformity has been applied to examples presented later in the paper. This uniformity calculation is then averaged across the region spanning the regenerator beginning from the spent catalyst distributor to the primary cyclone inlets.

Chart #1 presents a typical gas phase uniformity versus height for an FCC regenerator. Most regenerators equipped with pipe grids or air rings typically display a gas phase uniformity of approximately 30-40% above the distributor itself. This is due to the combustion air entering the dense bed via jets through specific nozzles. As the combustion air continues its journey through the bed and into the dilute phase the air quickly begins to distribute itself across the cross-sectional area leading to the improved gas uniformity.

Efficiencies of 80% or greater are observed where the gas is entering the primary cyclone inlets even in units experiencing strong maldistribution. The gas phase uniformity is defined as the averaged value from the spent catalyst entry to the primary cyclone inlets. This value is very close to that which is observed at the point midway to the cyclones.

Regenerator Design

The most difficult cases to troubleshoot are those related to the design of the regenerator. These regenerators typically afterburn continuously for years without solution. The authors have observed regenerators which have experienced afterburn for decades of continuous operation. This is in spite of multiple attempts to eliminate afterburn by modification of the regenerator internals. The very fact that such cases continue to afterburn in spite of the refiner's best attempts to eliminate the root cause points to the difficulty in actually identifying root cause.

The use of Computational Particle Fluid Dynamics (CPFD®) represents a radical new tool available to the refiner for determining root cause for design issues leading to long-term afterburn. CPFD is able to track the fluid dynamics of both gas molecules (O_2, N_2, CO, CO_2, SO_2, etc.) and catalyst particles as they pass through the regenerator. CPFD is also able to accurately track coke combustion on the spent catalyst as it enters the dense bed. This enables, for the first time ever, the refiner to quantitatively analyze the effectiveness of the regenerator.

The process engineer will be able to determine precisely where the majority of coke combustion occurs and the extent to which it is completed. Carbon monoxide and oxygen gases may be monitored for where bed breakthrough is occurring and where the afterburn begins. The bed and dilute phase temperatures are calculated based on the kinetics of carbon or carbon monoxide combustion. Afterburn is frequently observed to be more extensive than expected due to the lack of thermocouples in the operating unit. Furthermore, it is possible to observe short circuiting of spent catalyst directly into the regenerated catalyst standpipe leading to the so-called "salt & pepper" regeneration.

The computational model is constructed based on the actual configuration and orientation of the air distributor design, the spent catalyst distributor design, the cyclone body and diplegs and any other significant hardware present within the regenerator. This enables the FCC operator to customize the model according to their specific unit configuration.

The CPFD simulation is then "loaded" with the catalyst present within the regenerator dense bed and dilute phase. The combustion air rates, temperatures and pressures plus the spent catalyst flow rate, temperature and pressure are defined as the boundary conditions. The model is then "launched" and is run until steady state has been achieved.

Model accuracy is typically verified via "backcasting" a previous operation and checking for model consistency with respect to bed temperatures, cyclone inlet temperatures and flue gas composition (O_2, N_2, CO, CO_2, SO_2, etc.).

CPFD has been successfully used on several commercially operating FCC units to identify the root cause for long-term afterburn. In each case, identification of root cause has been clearly evident. CPFD Software highly recommends that the refiner cooperate closely with CPFD Software and their chosen engineering company. This entails discussions with the engineering company such that they understand the root cause for the afterburn and that the proposed solution may then be verified via CPFD simulation to ensure that the afterburn has actually been eliminated.

Furthermore, since these modifications are frequently significant, it is recommended that attention be paid to potential erosion points resulting from the hardware modifications. If present, these can also be addressed by the engineering company for elimination. This will ensure a long subsequent operating cycle without unplanned shutdowns due to internal damage and/or high catalyst losses.

The following examples are presented to demonstrate how CPFD is used to identify the root cause of afterburn. The final example provides a case in which the refiner formed a team between themselves, CPFD Software and their selected engineering company to successfully identify the root cause and then to evaluate the proposed solution for effectiveness.

Side-entry spent catalyst injection. Side entry spent catalyst delivery is a common design feature of many regenerators. In this particular case, the spent catalyst enters the side of the regenerator which has been equipped with a steel plate at a 45° angle to the catalyst entry in order to utilize the momentum of the catalyst to deliver the catalyst as close to the center of the regenerator as possible.

After passing into the regenerator the catalyst is observed to be quickly swept upward by the combustion gases (Image #1). This image portrays the spent catalyst vertical distribution for the first 15 seconds after entry into the regenerator. Image #2 demonstrates the degree of horizontal mixing of the spent catalyst. Very little horizontal mixing occurs after the catalyst enters the regenerator vessel. The addition of the 45° angled plate ("ski jump") has had limited effectiveness in this unit.

Image #3 demonstrates that the poor spent catalyst distribution has resulted in substantial afterburn. The region of the regenerator receiving little or no carbon (southwest hemisphere) will produce substantial excess oxygen while the region rich in carbon (northeast hemisphere) will be in partial burn producing large amounts of carbon monoxide. These gases begin to mix immediately above the dense bed with temperatures increasing up the regenerator. Please note that the dilute phase temperature exceeds 1380°F in the region above the cyclone inlets near the exterior of the plenum.

Image #4 indicates the distribution of carbon rich particles entering the regenerator. It is evident that the intention to distribute the spent catalyst across the cross-sectional area of the dense bed has not been successful.

Images #5-7 portray oxygen, carbon monoxide and carbon dioxide distribution in the regenerator. Image #5 demonstrates that the oxygen is well distributed by the combustion air distributor but is quickly consumed on the east side above the spent catalyst entry. Image #6 also indicates that the majority of the carbon monoxide is formed in the region above the spent catalyst entry point. The presence of carbon monoxide extends up the regenerator well into the dilute phase on the side of the spent catalyst entry. The side opposite rapidly oxidizes the carbon monoxide to carbon dioxide leaving excess oxygen present. Image #7 clearly indicates that the majority of the carbon dioxide is formed in the dilute phase well above the dense bed.

Chart #1 presents the flow uniformity of this regenerator versus height above the spent distributor. Please note that the average gas phase uniformity of the combustor is at 58%.

The use of CPFD clearly illustrates the shortcomings of this design. A solution for this refiner would include the delivery of the spent catalyst across the cross-sectional area of the regenerator perhaps via a system of troughs. This refiner would be greatly benefited by bringing these simulation results to their chosen engineering company prior to preparing their proposed modifications. In the meantime, optimization of the air distribution is strongly advised if possible.

Center entry catalyst injection. Center entry spent catalyst distribution also frequently results in afterburn. This is especially true for very large diameter regenerators. The following case presents an 18-foot diameter vessel with center entry which demonstrates substantial afterburn in the annular space surrounding the core of the regenerator.

Center entry regenerators that are not equipped with advanced spent catalyst distributors for effective distribution across the cross-sectional area of the vessel will often result in a cloud of carbon-rich spent catalyst remaining in the center of the regenerator dense bed. This region will typically be in partial burn while the annular region is in full combustion. The carbon monoxide being emitted from the center section mixes with the oxygen emitted from the annular space resulting in afterburn.

Images #8-14 and Chart #2 illustrate a regenerator equipped with center entry spent catalyst delivery but with limited horizontal distribution. Unlike the previous case, Images #8-9 demonstrate that the spent catalyst distribution is better than might be expected.

Image #10 portrays the temperatures observed within the regenerator both vertically and horizontally at various elevations. The center or core of the regenerator is at approximately 1340-1345°F while the annular space is approximately 30°F warmer. This annular space is clearly in afterburn. The three cyclone sets in the northern hemisphere of the regenerator will register approximately 30°F of afterburn with the combustion likely extending into the cyclones and possibly the plenum. The average width of the afterburning region is 2.4 feet. This represents 44% of the regenerator cross-sectional area. Image #11 supports this observation by indicating that the majority of the carbon rich particles remain in the center region of the dense bed.

These trends are confirmed in Images #12-14 which presents the oxygen, carbon monoxide and carbon dioxide levels. Images #12 and #13 indicate that the vast majority of oxygen and carbon monoxide production is in the center region of the regenerator while Image #14 indicates that the carbon dioxide is being primarily formed in the regions which are in afterburn. These regions contain lower levels of oxygen due to the oxidation of carbon monoxide to carbon dioxide.

Chart #2 presents the flow uniformity versus height above the spent distributor. Please note that the average gas phase uniformity of the regenerator is 66%.

The modification required to eliminate afterburn in this regenerator will be significantly easier than for the previous case equipped with side entry. In this case, retrofitting the current spent cat distributor with a high-efficiency distributor will likely fully eliminate the afterburn.

This case is particularly interesting in that it demonstrates annular afterburn. This annular portion of the regenerator has an average width of approximately 2.4 feet and is 4.5 feet wide at the largest point. This is a non-intuitive observation which would be difficult to anticipate without the use of Computational Particle Fluid Dynamics. The use of CPFD will enable the refiner to easily retrofit the regenerator for improved efficiency.

<u>Poor spent catalyst distribution.</u> This last case represents a refiner exhibiting 45-50°F of afterburn due to a poor spent catalyst distributor design leading to significant maldistribution. Images #15-18 and Chart #3 provide a qualitative indication of the degree of maldistribution. Image #15 portrays the full regenerator image with a second image presenting a vertical plane centered on the

spent catalyst distributor. This image demonstrates that the carrier gas used to pneumatically transport the spent catalyst into the regenerator combines with the combustion air from the air rings with the resulting gas jetting directly out of the dense bed into the dilute phase at the point of spent catalyst entry. Image #16 demonstrates the spent catalyst is making a nearly instantaneous 180° directional change after exiting the spent catalyst distributor and is being swept out of the dense bed prior to significant combustion.

Image #17 contains three images representing temperature, oxygen and carbon monoxide respectively. The temperature image indicates substantial maldistribution. Approximately 33% of the dense bed is operating at a temperature 50°F cooler than the remainder of the bed. The second image indicates that the majority the oxygen flows directly up the center of the regenerator while the third image indicates that the cooler zone of the regenerator is producing large volumes of carbon monoxide. The carbon monoxide subsequently mixes with the excess oxygen resulting in afterburn. The 50°F lower bed temperature (1320°F) dramatically reduces carbon monoxide combustion reaction rates. In this case, the homogeneous carbon monoxide combustion reaction rate is reduced by 63%.

This refinery utilized the CPFD simulation to assist their chosen engineering company in designing a new spent catalyst distributor. After the proposed modification was agreed upon this modified design was then verified using CPFD Software. Nearly 100% of the gas channeling and spent catalyst bypassing out of the bed was eliminated as observed in Image #18. An analysis of the gas uniformity indicates that this revamp has indeed achieved its goal. Prior to the modification the gas uniformity measured 65% while with the proposed modification the uniformity has increased to 83% (Chart #3).

This refinery has subsequently installed the modification and has been operating the regenerator stably for several months. Please note that the modification has been blacked out in Image #18 as the engineering company deems this technology proprietary. (At the time of the writing of this paper the refiner has not yet reported the results of the revamp.) This is an excellent example of a collaboration between a refiner, their engineering company and CPFD to analyze, troubleshoot and eliminate a long-standing issue of afterburn.

Conclusion

Afterburn has been experienced for decades within the industry. This is especially true after zeolites were incorporated into the FCC catalyst leading to the use of riser-based reactors and high temperature regenerators. Experience has led to many techniques capable of controlling afterburn such that the refiner is able to continue to operate with minimum constraints. Most often, this includes the injection of platinum or palladium-based CO promoters. These promoters are very effective but also represent a significant increase in the variable cost in the operation of an FCC unit.

CPFD is a new tool which will enable the refiner experiencing long-term afterburn to identify the root cause with high confidence. Furthermore, final engineering solutions may be verified via CPFD to ensure that the proposed modification(s) will be successful. This represents a step change improvement in the ability of the refiner to identify and eliminate the root cause for design related afterburn in the FCC regenerator.

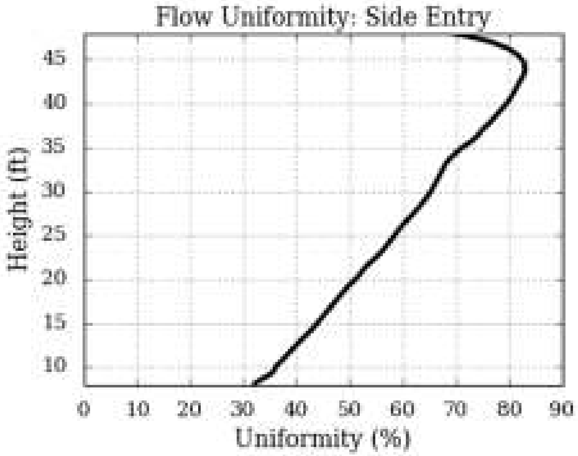


Chart #1: Side entry regenerator uniformity

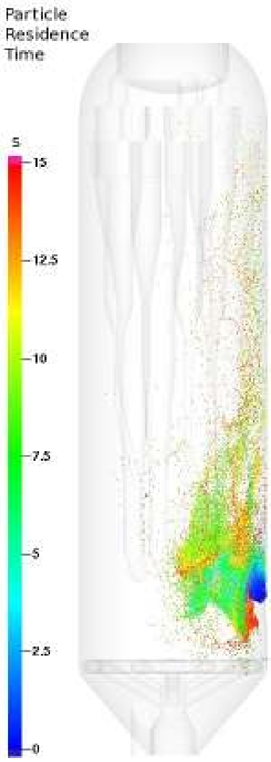


Image #1: Spent catalyst side entry with ski jump (side view)

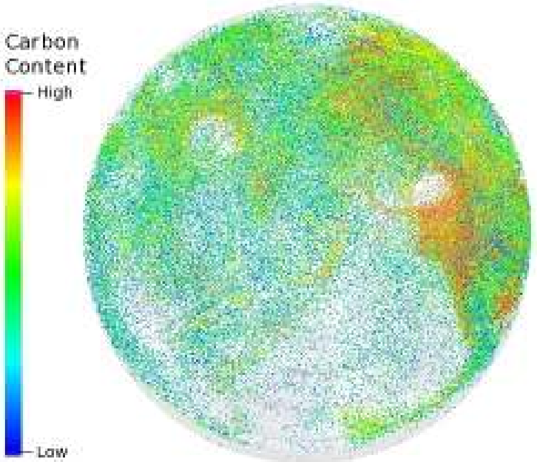


Image #2: Spent catalyst side entry (top down view)

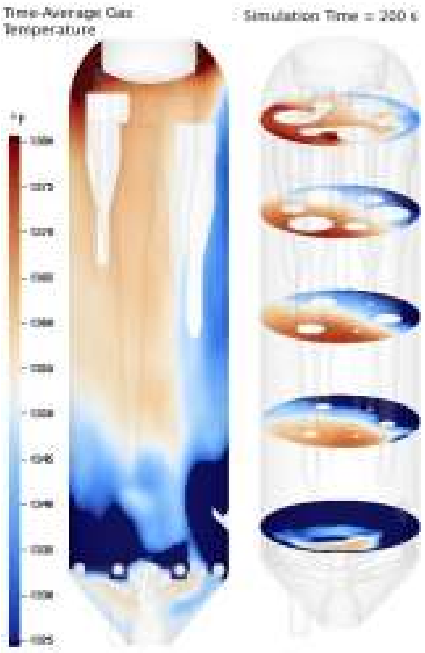


Image #3: Side entry temperature profile

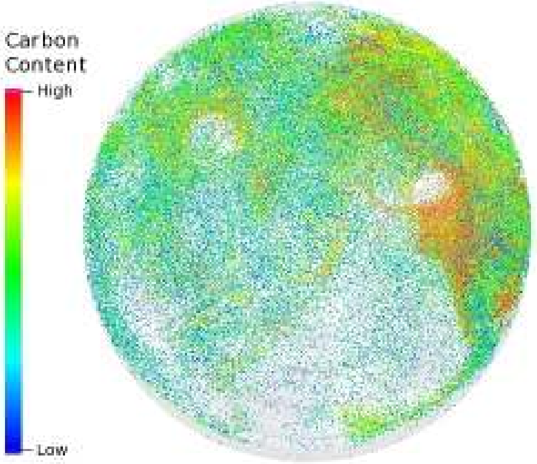


Image #4: Side entry carbon distribution

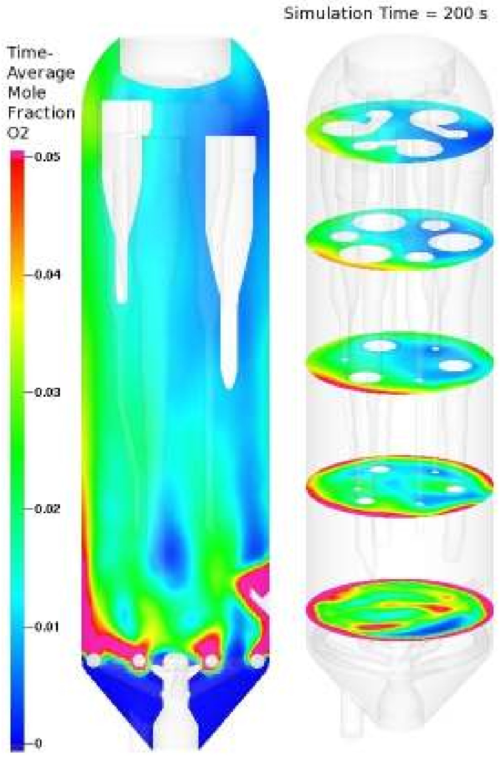


Image #5: Side entry O_2 distribution

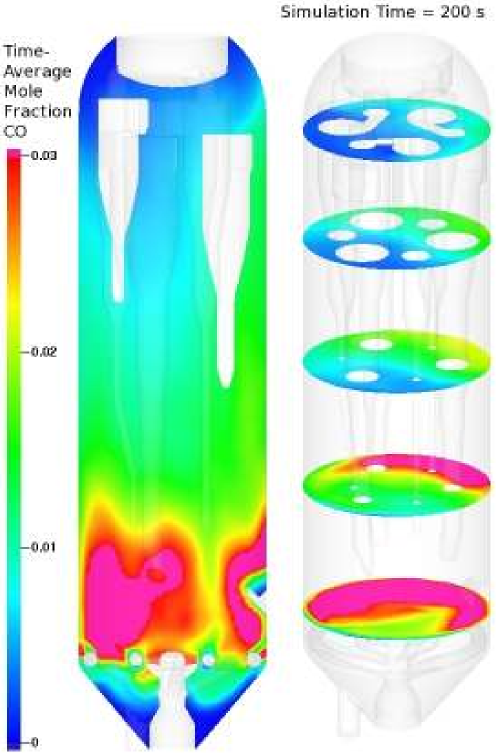


Image #6: Side entry CO distribution

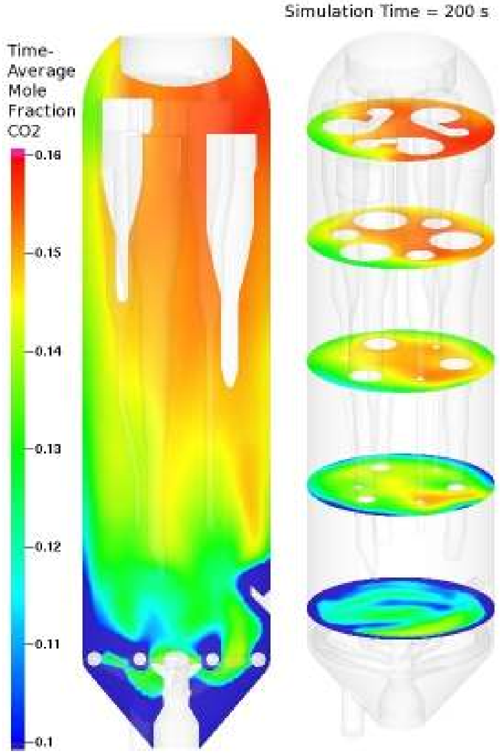
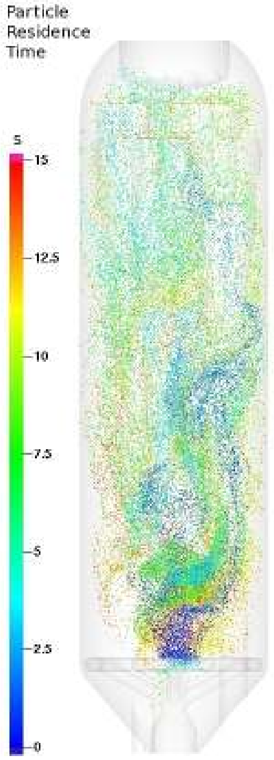


Image #7: Side entry CO_2 distribution



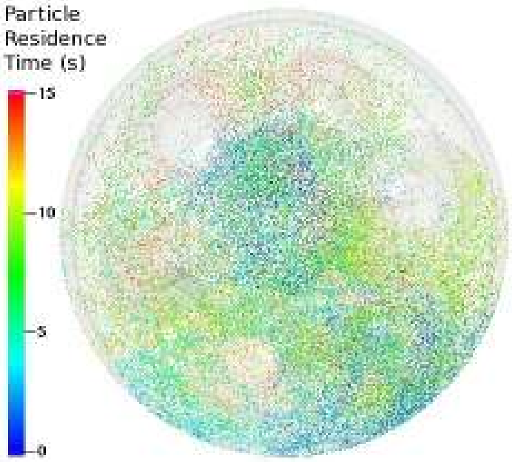
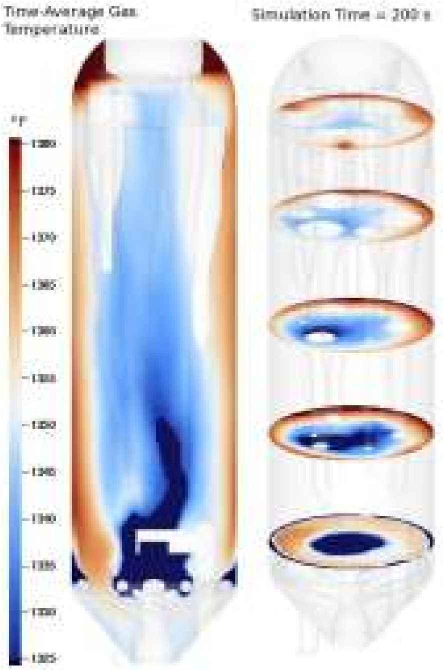


Image #9: Spent catalyst center entry

Image #8: Spent catalyst center entry



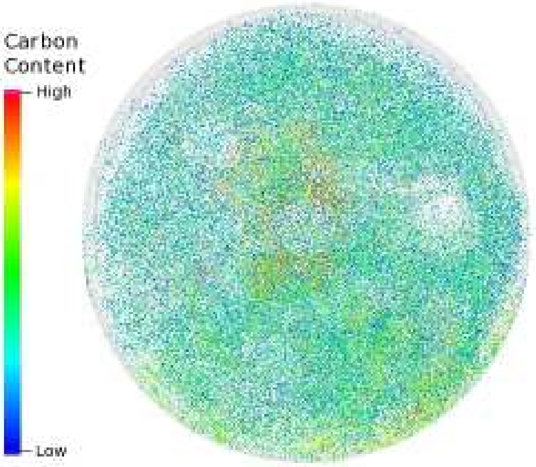


Image #11: Center entry carbon profile

Image #10: Center entry temperature profile

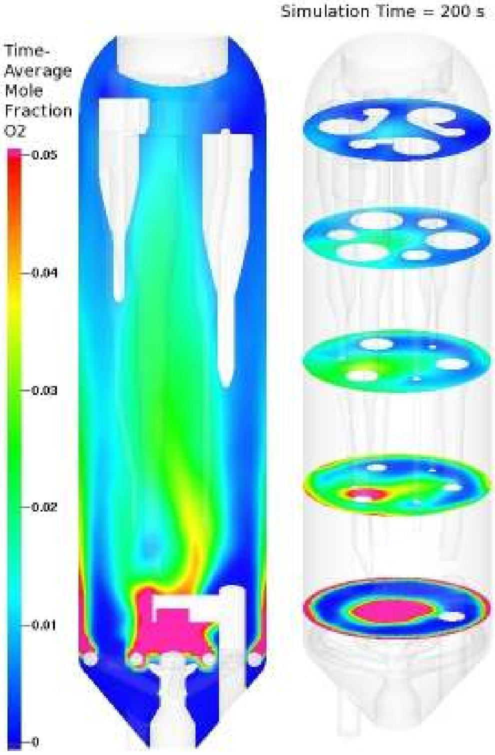


Image #12: Center entry O_2 distribution

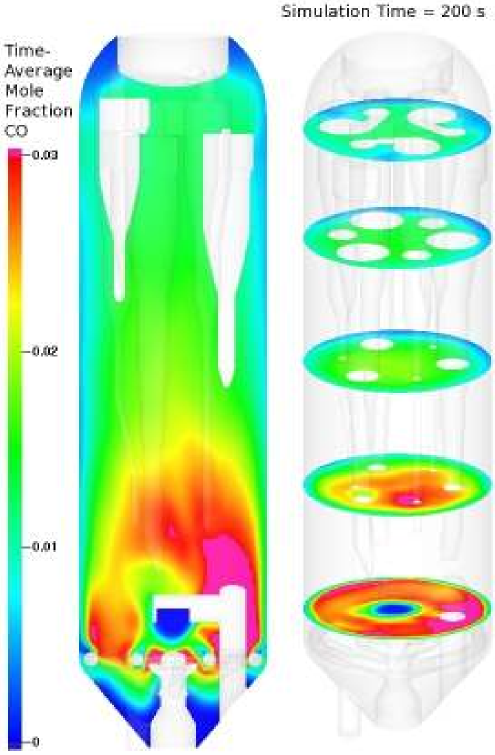


Image #13: Center entry CO distribution

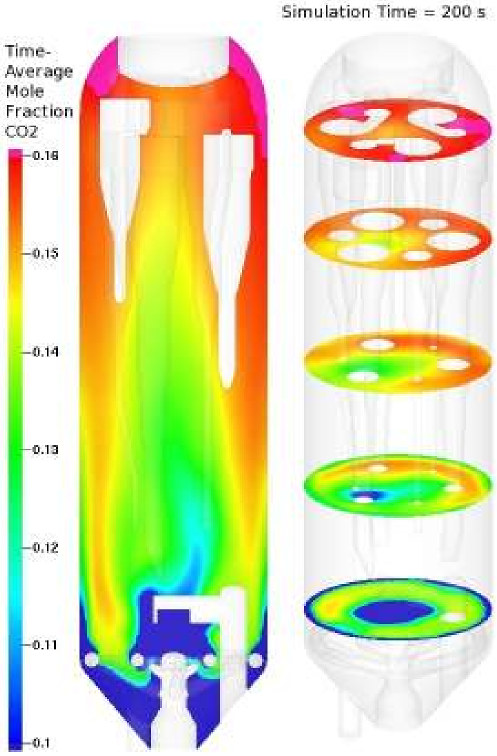


Image #14: Center entry CO_2 distribution

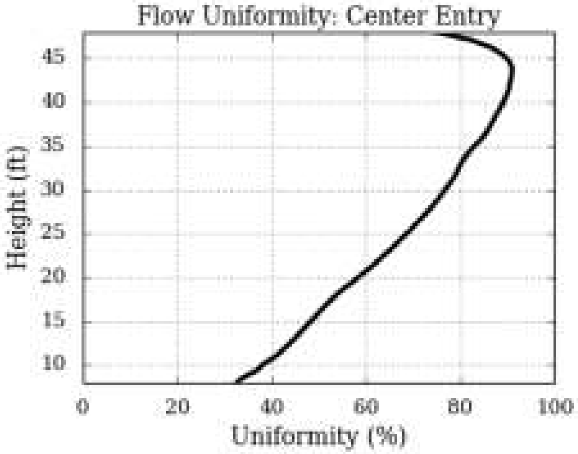


Chart #2: Center entry regenerator efficiency

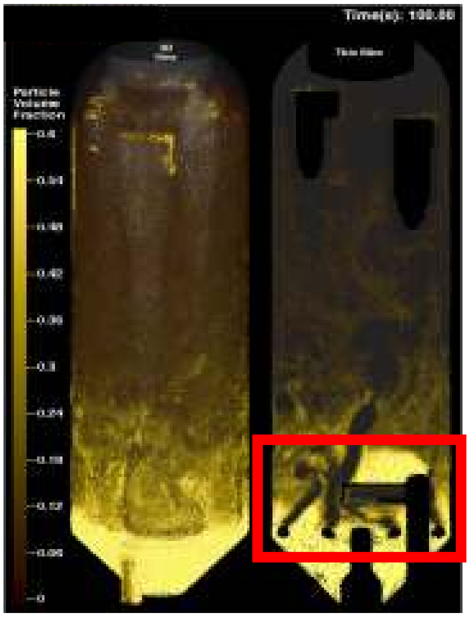


Image #15: Particle volume fraction

Image #16: Spent catalyst distributor detail

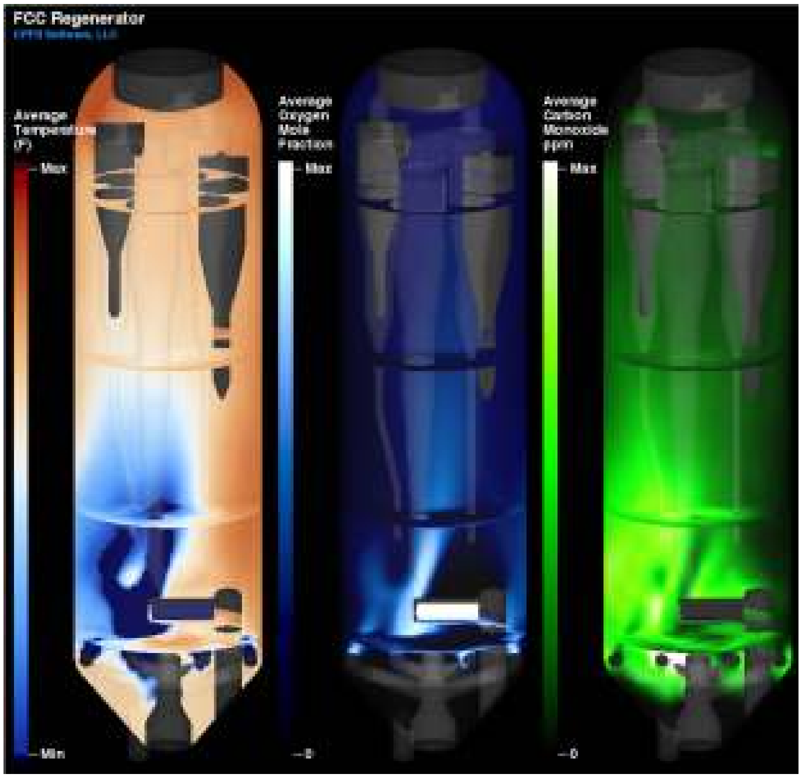


Image 17: Temperature, O_2 & CO profiles

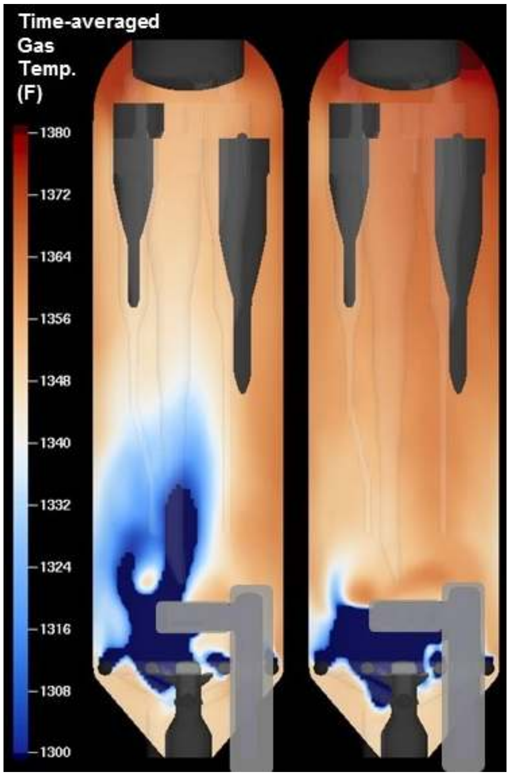


Image #18: Before & after temperature profiles

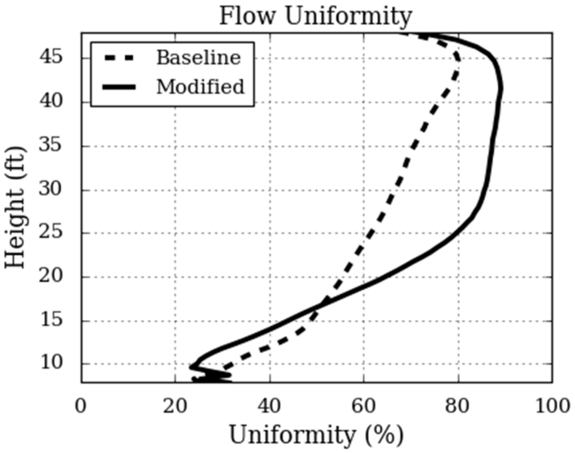


Chart #3: before & after gas distribution uniformity

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[i] W. Wilson, "FCC Regenerator Afterburn Causes & Cures", 2003 NPRA Annual Meeting, AM-03-44

[ii] R. Fletcher, M. Evans, "Optimizing & Troubleshooting the FCC Regenerator for Reduced Emissions", 2010 NPRA Annual Meeting, AM-10-173

[iii] Developed by James Parker, Principal Chemical Engineer, CPFD Software