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Ye-Mon Chen
Shell Global Solutions

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EVOLUTION OF FCC – PAST PRESENT AND FUTURE – AND THE CHALLENGES OF OPERATING A HIGH-TEMPERATURE CFB SYSTEM

Ye-Mon Chen
Shell Global Solutions (US) Inc.

ABSTRACT

The fluid catalytic cracking (FCC) process is one of the most important circulating fluidized bed processes. Although the FCC process has been in commercial operation for over 60 years, the technology continues to evolve in order to meet new challenges, which include processing more difficult feedstock and meeting more stringent environmental regulations. This paper presents selected snap-shots of a few challenges (high temperature erosion, corrosion and emission control) that the FCC process faces today and the new challenges yet to come in the near future.

INTRODUCTION

The fluid catalytic cracking (FCC) process is one of the most important circulating fluidized bed processes, with more than 400 units in operation worldwide today. The FCC unit is the primary conversion unit in a refinery, which converts, or cracks, low value heavy ends of crude oil into a variety of higher-value, light products, such as gasoline and LPG. The unit consists of a reactor and a regenerator, as shown in Figure 1.

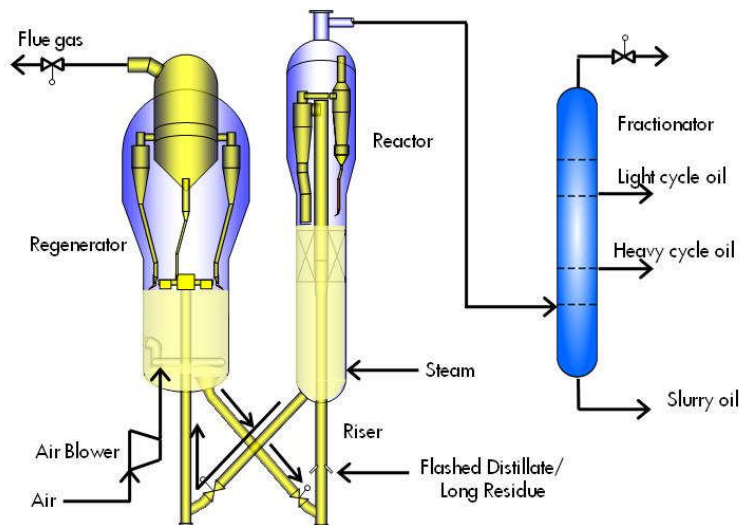


Figure 1: A typical FCCU configuration

Historically, the FCC unit and its downstream units, such as the alkylation unit, supply about 50% of the gasoline supply in the US. Although FCC is a mature process commercially deployed for over 60 years, the technology continues to evolve because of following unique capabilities:

- The FCC process is the only continuous catalytic process in the refinery business, which can adjust or replace catalyst on the run without a shutdown,
- The FCC catalyst is relatively robust to handle a wide variety of feedstock, and
- The FCC process can be operated over a wide range of conditions.

The focus of this paper is NOT on the historical evolution [1, 2, 3, 4] of FCC technology. Instead, the paper focuses on selected snap-shots of issues, such as high temperature erosion, corrosion and emission control, that exemplify the challenges that the FCC process faces today and the new challenges in the future.

EXAMPLES OF CHALLENGES THAT FCC FACES TODAY

It might sound strange at first that keeping an FCC unit running, without having the unit fall apart unexpectedly, is in fact the biggest challenge today for a process that has been around for over 60 years. To put this in the right perspective, the average run length between two scheduled maintenance shutdowns for an FCC unit was about 2 years in the 1970's/80's,

Examples of Today's Challenges

1. Cyclone reliability
 - A. Erosion
 - B. Corrosion
2. Emission Control – NOx reduction

whereas the current average run length is now being stretched to between 4 to 5 years. Considering the fact that an FCC unit, on average, circulates about 50 tons of catalyst per minute between the reactor and the regenerator; keeping an FCC unit running continuously for 4 or 5 years means that the equipment will experience the traffic of over 100 million tons of catalyst without falling apart, which is by no means a small task. On the other hand, the incentive of stretching the FCC run length is also enormous because the average costs of an FCC maintenance shutdown is on the order of 10's of millions of dollars.

Cyclone Reliability

The FCC unit relies on reactor and regenerator cyclones to keep the catalyst within the unit while circulating catalyst between the two vessels. Two recent industry surveys reveal the pervasive problems of cyclones used in FCC operation today. Table 1 summarizes the survey results from Grace Davison as presented at their 2002 Dublin FCC conference. The results indicate that catalyst losses from cyclones were the number 1 problem in FCC operation, identified by the participants of the meeting. The 2006 Solomon survey (Figure 2) again revealed that FCC cyclone reliability was the number 1 limitation of FCC unit run length today, with more than 41% of unscheduled shutdowns of FCC units in US caused by cyclone problems. Two common cyclone problems that challenge FCC units today, high-temperature cyclone erosion and corrosion will now be discussed.

Cyclone Reliability – Erosion Problem

Problem Statement

One major contributor to unscheduled FCC unit shutdowns is unexpected cyclone failure due to high temperature erosion. Figures 3a and 3b show two examples of high temperature cyclone erosion problems. Figure 3a shows a cyclone which was eroded

through, from inside out, with holes on the cyclone body. Figure 3b shows multiple cyclones that had severe erosion into the cyclone diplegs such that several diplegs were cut off and fell to the bottom of the vessel.

Table 1: Grace Davison 2002 Survey

Problem Areas in FCCU - Grace's Survey (2002 Dublin FCC Conference)	
Cat losses	15
Cat Circulation	12
Transfer line coking	11
Coking/slurry fouling	10
Low coke	6
High regenerator temperature	5
Poor stripping	5
High corrosion	5
High coke	4
Main fractionator fouling	4
Catalyst deactivation	4
Expander vibration	4
Excessive afterburn	3
Other	4

2006 Solomon FCC Survey Events Determining TAR Timing (Outside of Planned Maintenance)

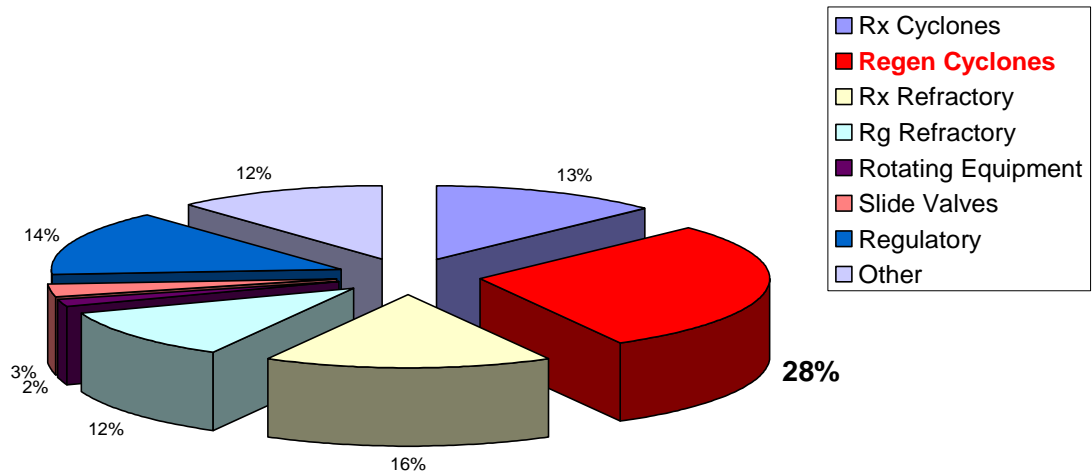


Figure 2: 2006 Solomon Survey Chart



(a)



(b)

Figure 3. FCC cyclone damage a) Inside out erosion; b) Diplegs cut off due to erosion

What is Happening in the Cyclone?

The most pervasive problem is high temperature erosion in the secondary cyclone, particularly in the lower cone and in the transition to the dipleg, which is the focus of the study.

There is a fundamental difference between erosion patterns in first and second stage FCC cyclones. Highly-loaded first stage cyclones normally experience little to no cone erosion, whereas the lightly-loaded second stage cyclones can have severe cone erosion. This seems to be counter-intuitive at first. However, the key difference in erosion pattern lies in the differences in the solids flow patterns and vortex formation, as shown in Figure 4. Due to high solids loading and low gas velocity in a typical FCC primary cyclone, the gravitational force plays a key role; as a result, the solids appear to drop (or fall) rapidly down into the cyclone cone and dipleg, as shown in the figure on the left side of Figure 4, taking only one to two full turns before exiting the cyclone bottom. The vortex length in the highly-loaded primary cyclone is much shorter because the high solids loading dampens the formation of a robust vortex. Therefore, the vortex does not “whip” the solids at a high velocity around the cone in the primary cyclone.

In a typical FCC second stage cyclone, the solids loading is approximately 1/1000 to 1/10,000 of the loading in the first stage cyclone. Due to the light solids loading and high gas velocity, the vortex is relatively long, energetic and, more importantly, moving asymmetrically about its axis. As the swirling solids in the outer vortex approach the cone in a second stage cyclone, the long, rapidly-rotating vortex accelerates the solids stream and causes it to intensify its rotation (i.e., the solids spin faster similar to the motion of a figure skater pulling inwards).

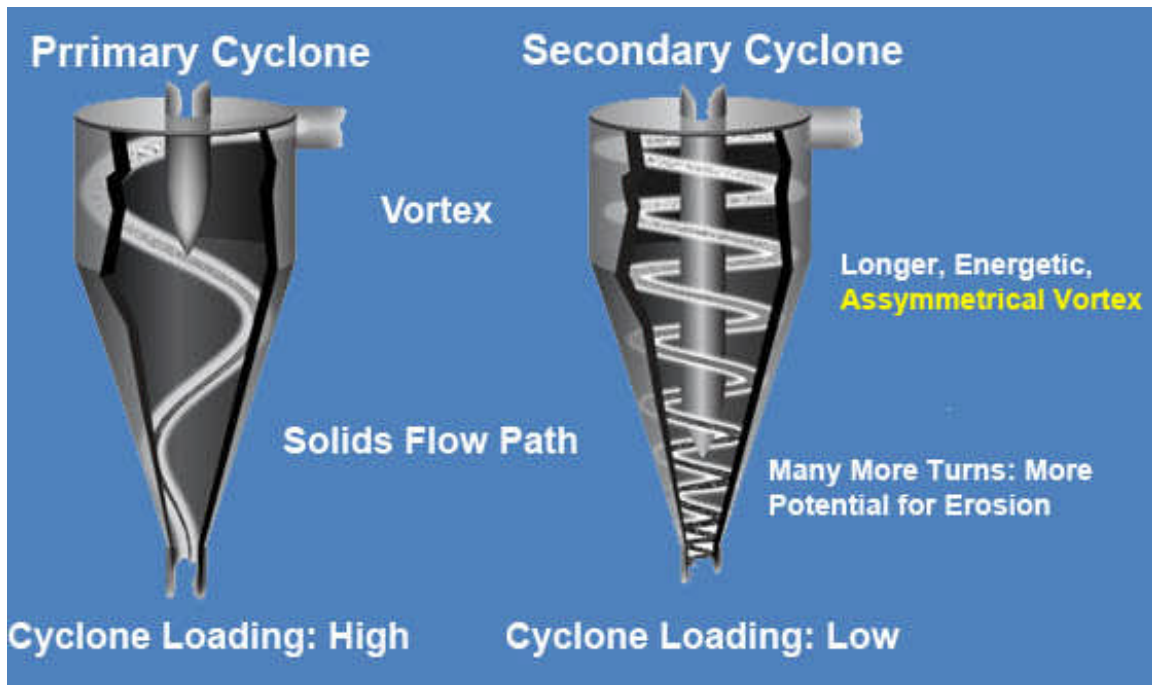


Figure 4: Schematic Depiction of First and Second-Stage Cyclone Operation

The outer vortex in a second-stage cyclone typically takes from four to six turns before exiting the bottom cone, as shown in the figure on the right in Figure 4, and the spinning continues into the top portion of the dipleg below the cone. The concentrated solids stream rotates at a high velocity, and the unstable, continuous movement of the vortex causes the significant erosion observed in the cone and the top of the dipleg of second-stage cyclones.

Solution to the Cyclone Erosion Problem

Most FCC units in US rely on cyclone vendors to provide cyclones for FCC applications, which will be categorized as “**conventional cyclones**” in this paper. Shell Global Solutions, on the other hand, has developed a cyclone technology, which is different from conventional cyclone in that it uses a vortex stabilizer.

Particulate Solids Research, Inc. (PSRI), an independent, industrial consortium, recently studied and benchmarked different FCC cyclone technologies [5], since high temperature cyclone erosion and cyclone reliability were highlighted as the major concerns of FCC operation for companies in recent surveys. The PSRI cyclone test program was structured to benchmark three different possible solutions to mitigate the damaging erosion occurring in FCC second-stage cyclones:

1. Increasing cyclone length (L/D) of a conventional cyclone
2. Increasing the angle of the cone of a conventional cyclone
3. Adding a vortex stabilizer to a conventional cyclone

Air was used as the conveying gas in the test unit. The solids used were equilibrium FCC catalyst with a median (D_{p50}) particle size of approximately 75 μm . The fines

(material <44 μm) concentration in the catalyst was approximately 8 wt.%. The particle density of the catalyst was 1488 kg/m^3 . Loadings to the second stage cyclone were varied between 0.001 to 0.16 kg/m^3 .

Multiple coatings of drywall joint compound were added to the inside of the cyclone before each test. The amount of erosion occurring in the cyclone was measured by the weight loss of the drywall compound occurring over a certain period of time.

Effect of Increased Cyclone Length

The study found that the erosion took place primarily in the bottom 1/3 of the cone of a secondary conventional cyclone. A photograph illustrating this effect is shown in Figure 5. This figure shows that the drywall coating was completely eroded from the bottom 1/3 of the cone, whereas the remaining drywall was mostly intact.

Cyclone lengths were increased by increasing the length of the conventional cyclone barrel with L/Ds of 3.1, 4.1 and 5.1. In these tests, the inlet gas velocity to the cyclone was 19.8 m/s and the outlet gas velocity was 26.8 m/s .

The results of the testing to determine the effect of cyclone length are shown in Figure 6. As can be seen, the erosion rate decreased with increasing cyclone length. The measured erosion rate at an L/D of 5.1 was about seventy percent (70%) of the erosion rate of the cyclone with an L/D of 3.1.

Barrel erosion rates were also measured in the tests and were found to be much lower than the erosion rates in the cone at the test conditions, as also shown in Figure 6. The measured barrel erosion ranged between 85 to 105 g/h , which is approximately fifteen percent (15%) of the cone erosion rate for the cyclone with an L/D of 3.1, and approximately twenty percent (20%) for the cyclone with an L/D of 5.1.

Effect of a Longer Cone Conventional Cyclone

The effect of a longer cone of a conventional cyclone on cyclone cone erosion was tested by adding a longer cone so that the cone angle from the horizontal increased from 79° to 84° . This increased the cone length from 0.8 m to 1.7 m . When comparing the two cone configurations, the overall length of the cyclone was held constant.

As shown in Figure 7, the longer cone had a higher erosion rate at lower gas velocities than the shorter cone (but longer barrel). However, the erosion rate became approximately equal to the erosion rate of the shorter cone at the highest gas velocity.

The trend of the two curves was exactly opposite. For the short cone, the erosion rate increased with gas velocity, whereas for the longer cone the erosion rate decreased with increasing gas velocity. For an outlet gas velocity of approximately 26.8 m/s , the erosion rate for the short cone was approximately 800 g/h , while the erosion rate for the longer cone was approximately 1800 g/h —a factor of 2.25. However, even at the highest gas velocities, which are outside typical operating conditions of the secondary cyclones, the longer cone did not have a significant advantage over the shorter cone in regard to cone erosion

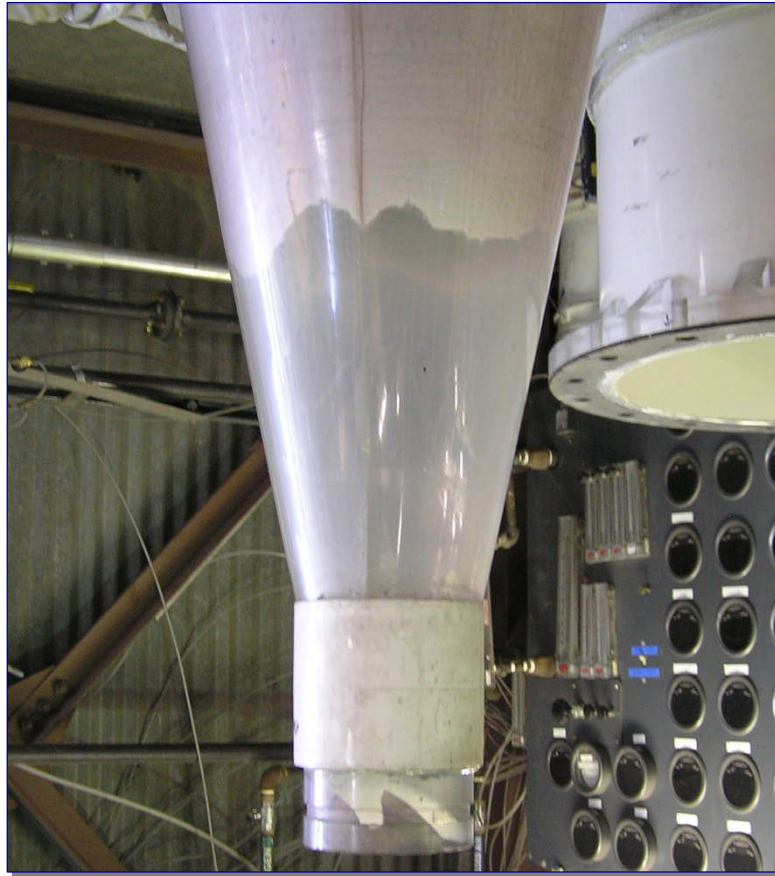


Figure 5: Photograph of Erosion of Drywall Joint Compound in the Cone of a Second Stage Cyclone

The Effect of Adding a Vortex Stabilizer to a Conventional Cyclone

To determine the effect of adding a vortex stabilizer to a conventional cyclone on cone erosion, a flat-disk vortex stabilizer was added to the cyclone, approximately 1/3 of the cone length up from its bottom to simulate the improved cyclone technology.

The effect of adding the vortex stabilizer disk to a conventional cyclone, simulating the improved cyclone technology, on cone erosion is shown in Figure 8 for cyclones with an L/D of 3.1. It was found that cone erosion for a cyclone with the vortex stabilizer was significantly lower than that for a conventional cyclone without a vortex stabilizer. Cone erosion increased linearly with increasing gas velocity for a conventional cyclone without a vortex stabilizer. However, cone erosion of a cyclone with a vortex stabilizer decreased slightly with increasing gas outlet velocity. The decrease in erosion is counter-intuitive at first; however, this can be explained by the fact that the vortex diameter is smaller when the diameter of the outlet tube is decreased to increase the gas outlet velocity. This increases the distance between the vortex and the cone wall, which then reduces the centrifugal force (and, therefore, the solids velocity) on the solids rotating in the cone. This reduction in force on the solids would explain the decrease of cone erosion vs. gas outlet velocity for a cyclone with the vortex stabilizer as shown in Figures 8.

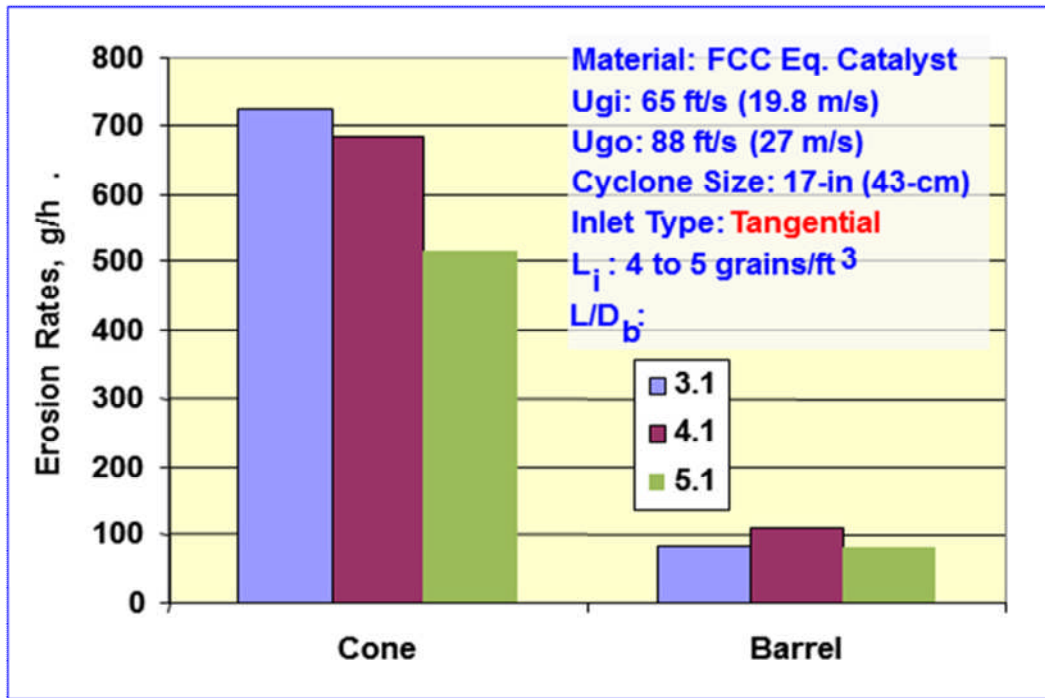
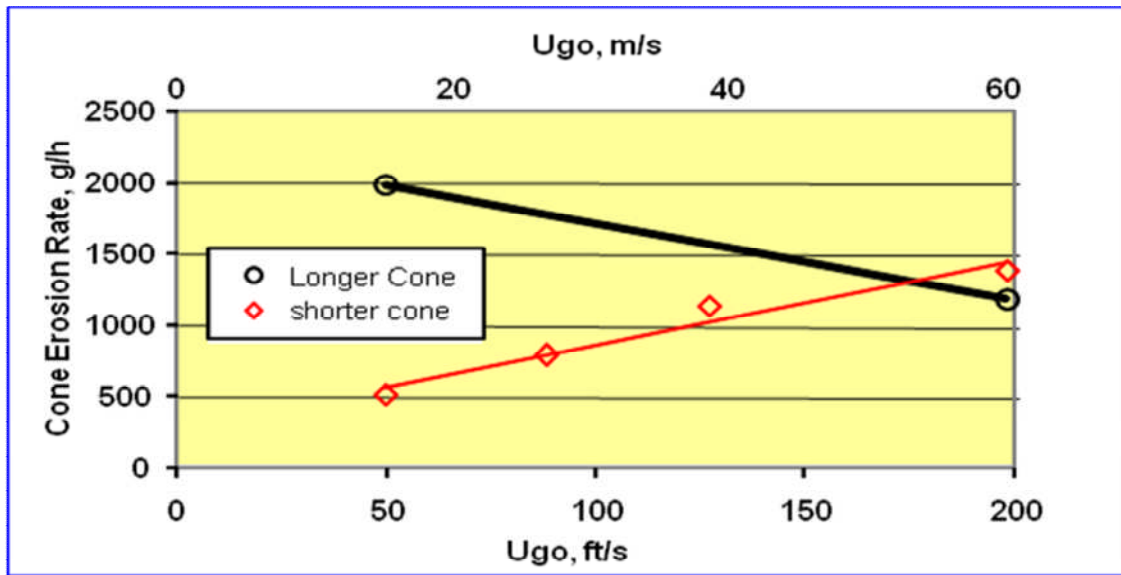


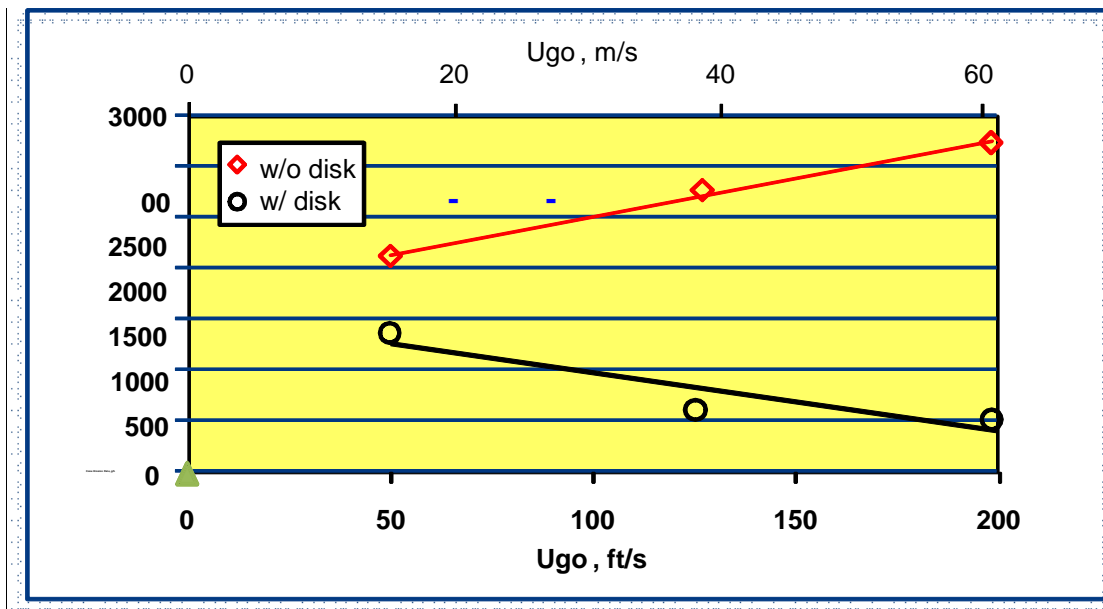
Figure 6: The Effect of Second-Stage Cyclone L/D on Cone Erosion and Barrel Erosion



Material: FCC Eq. Catalyst
 Ugi: 65 ft/s (19.8 m/s)
 Cyclone Size: 17 in (43 cm)

Inlet Type: Tangential Entry
 L/D_b : 5
 L_i : 14 grains/ft³

Figure 7: The Effect of Cone Length on Second-Stage Cyclone Cone Erosion



Material: FCC Eq. Catalyst **Inlet Type: Tangential**
Ugi: 65 ft/s (19.8 m/s) **L/D_b: 3**
Cyclone Size: 17-in (43 cm) **L_i: 14 grains/ft³**

Figure 8: The Effect of Gas Outlet Velocity on Second-Stage Cyclone Cone Erosion for Cyclones With and Without a Flat-Plate Vortex Stabilizer (Cyclone L/D = 3.1)

For the shorter cyclone, the cone erosion rate was approximately 2100 g/h for the conventional cyclone without a vortex stabilizer at a gas velocity in the outlet tube of 15.2 m/s. The corresponding cone erosion rate for the cyclone with a vortex stabilizer at the same gas velocity was about 1400 g/h. The cone erosion rate with the vortex stabilizer was about 67% of the cone erosion for the cyclone without the vortex stabilizer. However, at an outlet gas velocity closer to actual practice (~ 46 m/s), the cone erosion rate for a cyclone with the vortex stabilizer was only about 600 g/h. The corresponding cone erosion rate for the conventional cyclone without the vortex stabilizer was about 2900 g/h. This is a factor of about 5.

For the cyclone with an L/D of 5.1, the overall cone erosion rates were lower. This was to be expected because the tests with a longer cyclone described above gave lower cone erosion rates than shorter cyclones. As with the shorter cyclone, the trend lines of cone erosion rate vs. outlet gas velocity were linear. Similarly, the curve for the conventional cyclone erosion without a vortex stabilizer increased with increasing gas velocity, and the curve for the cyclone erosion with the vortex stabilizer decreased slightly with increasing gas velocity. However, as with the shorter cyclone, the cyclone with the vortex stabilizer was found to have much lower erosion rates than the conventional cyclone without the vortex stabilizer. Comparing the cone erosion rates at an outlet gas velocity of 46 m/s, the conventional cyclone without a vortex stabilizer had a cone erosion rate of approximately 1200 g/h, while the cyclone with the vortex stabilizer had a cone erosion rate of about 240 g/h. This is a factor of approximately five, which is similar to what was found for the shorter cyclone.

Why does the vortex stabilizer decrease cone erosion? It appears that the stabilizer prevents the vortex from "whipping" the solids around at high velocities below the stabilizer in the region where high cone erosion rates are experienced for a conventional cyclone. Below the stabilizer, the high-velocity central vortex does not really exist. Therefore, this reduction of spinning solid velocity in the outer vortex leads to significant reduction in erosion. A comparison of the cone erosion rates for various second-stage cyclone configurations is given in Table 2.

Table 2: Comparison of cone erosion rates for different cyclone configurations

	L/D (-)	Velocity Inlet, m/s	Velocity Outlet, m/s	Erosion Reduction Factor	Cone Erosion Rate, g/h
Short Cyclone	3.1	19.8	46	Base	2850
Long Cyclone	5.1	19.8	46	>2	1200
Long Cone	5.1	19.8	46	>2	1200
Vortex Stabilizer	3.1	19.8	46	>4	650
Vortex Stabilizer	5.1	19.8	46	>11	240

Drywall joint compound was also added to the disk to see if the upper surface of the vortex stabilizer would be eroded by the vortex. However, essentially no erosion was measured on the upper surface of the disk. No erosion was found on the supporting rods as well.

Commercial Bench-Marking

In the 1980's, Shell had over 30 FCC units within the system, mostly with Conventional Cyclones, which were found to be the number one cause of all FCC unscheduled shutdowns.

Shell made a conscious decision in developing improved cyclone technology, using the vortex stabilizer, and started the implementation of the technology in the early 90's. Figure 9 shows the result of how this improved cyclone technology reduced overall FCC unscheduled down time in Shell refineries. Using 1992 data as the base line, Figure 9 shows that the improved cyclone technology, with the vortex stabilizer, reduced the total unit down time of all FCC units in Shell system by a factor of 10.

Cyclone Reliability – Corrosion Problem

Problem Statement

In recent years, several FCC units have encountered unscheduled shutdowns due to high temperature corrosion failure of the cyclone refractory system. These refractory systems failed unexpectedly in some cases within only 4 to 5 years. Figure 10 (a) [6] shows examples of a failed refractory system which resulted in sheets of refractory

peeling off from the walls of the regenerator cyclones. Figure 10 (b) shows that the fallen refractory sheets were caught above the primary cyclone termination device.

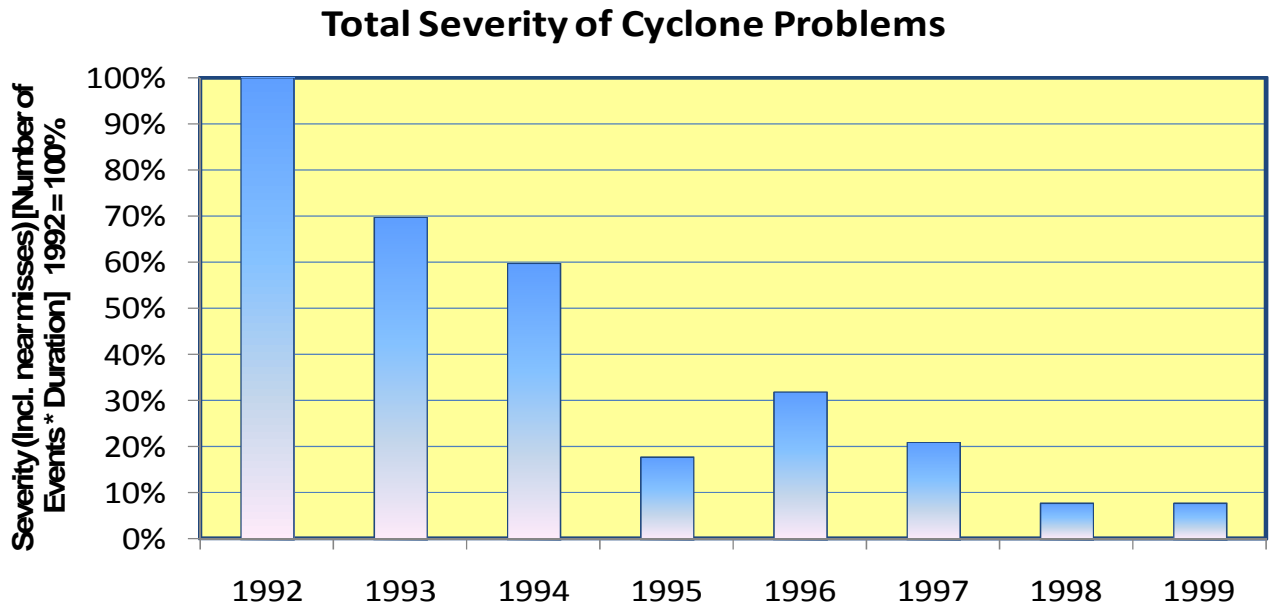


Figure 9: Severity of cyclone related issues in Shell FCCUs

Regenerator Hexmesh Corrosion



Figure 10. (a) Failed refractory, in sheets, due to Hex Mesh corrosion [6]; (b): fallen refract sheets caught above the primary cyclone termination device

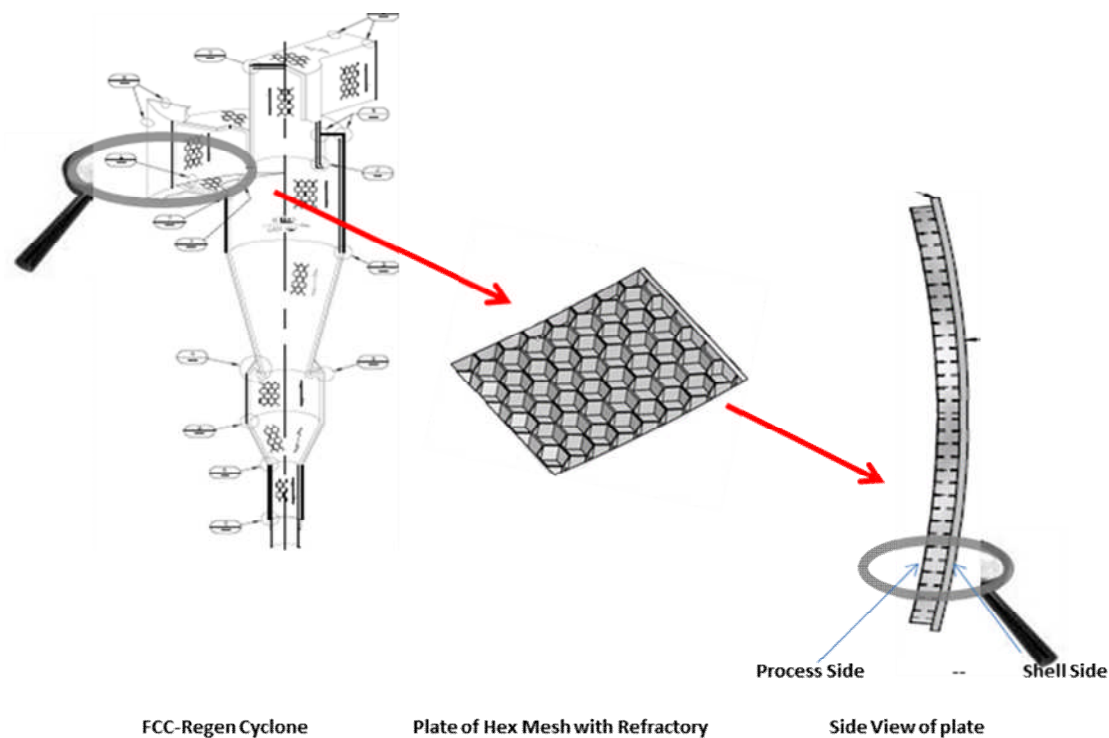


Figure 10: Hex Mesh Refractory Structure

What is Happening to the Cyclone Refractory System?

The FCC regenerator cyclones are typically made of SS 304H material for high temperature (~ 1400 °F) operation. In order to protect cyclones from high temperature erosion damage, as discussed previously, the regenerator cyclone internal surface is commonly lined with SS 304H hex mesh, approximately 2.5 cm deep which is welded on to the cyclone interior and packed with refractory within the hex mesh. The structure of the hex mesh/refractory looks like a honeycomb, as shown in Figure 11. The refractory is a concrete-like material which has high resistance to erosion.

Historically, the hex mesh/refractory system has served the FCC industry well in providing protection against high temperature erosion. However, a series of unexpected failures of the hex mesh/refractory system, due to corrosion of the SS304H hexmesh, has surfaced very recently as reported by a number of operating companies as well as FCC licensors [6, 7]. As shown in Table 3 and based on current known information, a common pattern involves the application of a “calcium-rich” refractory in the regenerator section of FCC units and failure appears to be related to a corrosion mechanism that attacks the SS304H hex mesh support system for this refractory. It is more prevalent in complete combustion mode (full burn).

Table 3: Summary of refractory analysis [7]

Refractory Analysis – Sample Summary
Effect of exposure to process conditions

	Refinery	Reported Refractory Type	Location	Installation Date	SO2 Level (ppm)	S	Na	Volatiles
Bad	Refinery X	Ca-rich binder	Dipleg - 1st stage cyclone	2005	2500	1.80	0.41	2.55
	Refinery Y	Ca-rich binder	Regen Primary Cyclone			1.34	0.21	1.38
	Refinery Z	Ca-rich binder	primary cyclone	1997		-	-	-
	Refinery U	Ca-rich binder				1.43	0.62	1.43
Good	Refinery X	Ca-rich binder	Regen cyclone	2002 (original)	2500	1.69	0.27	2.89
	Refinery T	Ca-rich binder	Regen Cyclone	2002	900	0.01	0.716	0.33
	Refinery H	phos-bonded	Regen Cyclone Dipleg		900	0.07	0.11	0.27
		?	Regen Cyclone			0.16	0.11	0.4
	Refinery Y	phos-bonded	flue gas expansion joint			1.12	0.07	5.66

- Both Ca-rich binder and phos-bonded materials appear to absorb sulfur from the process gas
- No clear relation between S, Na and volatile content and “good/bad” rating

Although there are some minor variations, this particular type of corrosion has very specific patterns that are strikingly similar from all reported failures:

- The attack of the 304H SS hex mesh was identified primarily as sulfidation/oxidation corrosion of the metal support structure.
- The corrosion occurs preferentially on the underside of the hexmesh metal lining where it is welded to the base steel, such as at the cyclone wall, whereas little corrosion is observed on the process side of the hexmesh lining where it is exposed to the bulk of flue gas, as shown in Figures 12 and 13
- The corrosion on the process side is mild oxidation with a well protected Cr-O layer, shown in Figure 14. The corrosion on the underside is a combination of oxidation, sulfidation and carburization where Cr in SS304H no longer forms a tight formation of Cr-O protection layer.
- The hexmesh/refractory detached from the wall in sheets, as shown in Figure 10, due to weakening of the corroded hexmesh.
- The corrosion can be very aggressive. Some units reported that newly installed regenerator cyclones could have total refractory system failure within 4 years.

flue gas side unattacked



wall plate side attacked

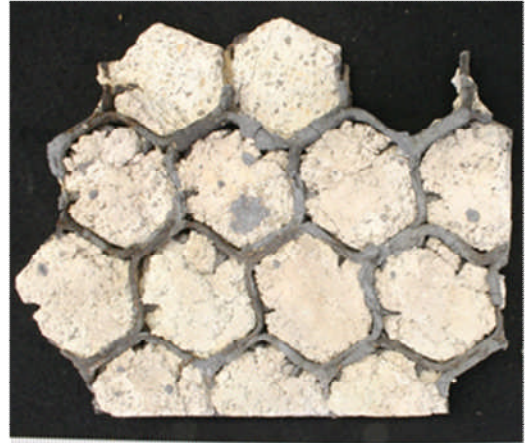
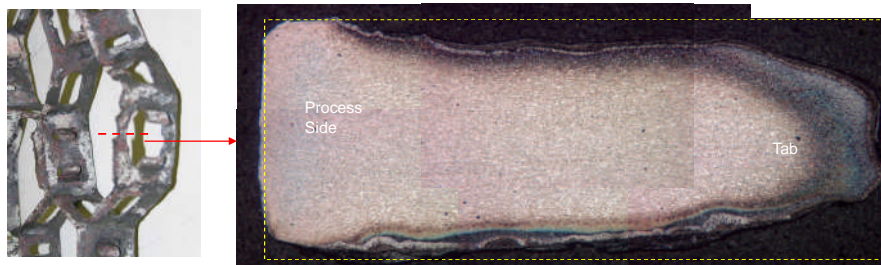


Figure 11: Refractory on process side vs. underside of the hex mesh lining

Corrosion Characterization *General Trends*



- **Process gas itself does not appear corrosive.**
 - Conditions are different within/behind refractory.
- **Accelerated corrosion seemingly always associated with carburization of base metal.**

Figure 12: Assessment of general trends in refractory corrosion characterization [7]

Regenerator Hexmesh Corrosion

- SEM/EDS analysis of a corroded hexmesh ligament
 - Exposed side – oxidation
 - Creviced region – carburization
 - Underside – carburization & sulfidation/oxidation

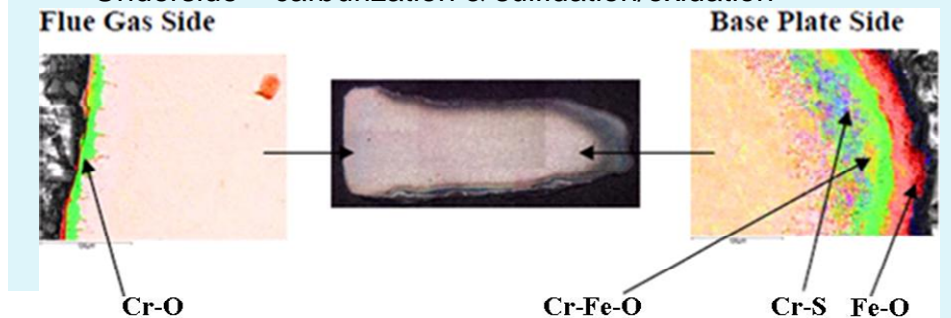


Figure 13: Possible corrosion mechanism: Process side vs. Underside [6]

Possible Solutions

The root cause of the high temperature corrosion to the refractory metal support structure is currently being discussed in the FCC industry. Several teams in the industry are actively working on the problem. The common belief is that the hexmesh on the underside is under a sub-environment that is more reducing than the bulk flue gas (more oxidizing), and hence more prone to sulfidation and carburization. However, the exact mechanism of how local reducing, sub-environment is formed is still being debated. Possible solutions are a work in progress at the moment.

Emission Control – NO_x Reduction

Problem Statement

The FCC regenerator is a major NO_x emission source from the US refineries. Several existing technologies are available to reduce NO_x emissions from an FCC regenerator, which include SCR, or selective catalytic reduction. Even though SCR is quite effective, it has several issues:

- It is quite expensive, on the order of 10's of millions of dollars, and even more so, on the order of hundred million dollars, when the CO boiler needs to be replaced due to the increase of back pressure caused by the catalyst bed of SCR.
- It requires a higher a residual flue gas temperature. Unless a second stage heat recovery system is included (which means additional cost), the unit loses energy efficiency

There is a potential cost-effective solution to this challenge.

What is Happening Inside the Regenerator?

Most of the NO_x emissions from FCC units comes from nitrogen in the feed. The contribution of direct oxidation of N_2 to NO_x is negligible, particularly for full combustion FCC regenerators. For partial combustion regenerators, the contribution of direct oxidation of N_2 to NO_x is relatively small if low- NO_x burner technology is applied in the CO boiler/incinerator.

A recent study [8] shows that about 50% of the nitrogen in the feed exits the FCC unit on the reactor side and the remaining 50% of nitrogen in the feed exits as coke on the spent catalyst sent to the regenerator. Of the 50% of the feed nitrogen exiting from the reactor, about 10% of the feed nitrogen ends up as ammonia, which is collected in sour water, and the other 40% of the feed nitrogen ends up in various streams of the reactor liquid products.

This section focuses on the remaining 50% of the feed nitrogen, which enters the regenerator in the form of coke on the spent catalyst. As the spent catalyst is regenerated and coke is burned off in the regenerator, the nitrogen species on the coke are released into the flue gas. Recent studies [8, 9] further show that only a small fraction, less than 10%, of the feed nitrogen on coke is released in the form of NO_x emissions in the flue gas. The majority, or more than 40%, of the feed nitrogen on coke is initially released in the form of NO_x or other intermediates, but is eventually converted in-situ to N_2 in the regenerator.

The recent study [9] of batch regeneration of spent FCC catalyst with oxygen and helium reveals a close interaction between the combustion of carbon and the release of nitrogen in the coke. Figure 15 shows the concentrations of CO, CO_2 , and O_2 in the flue gas as a function of time as coke on the catalyst is burned off in the batch regeneration experiment. The amount of coke on catalyst was not directly measured, but Figure 15 implies that coke on catalyst was removed continuously, converted to CO/ CO_2 , and became negligible after 26 minutes as both CO and CO_2 concentrations fell to negligible levels. For the first 9 minutes, the O_2 concentration remained low and the CO concentration was higher than CO_2 , indicating a reduction environment in this period of the batch regeneration. As O_2 broke through the unit around the 10-minute mark and its concentration continued to rise afterwards, coinciding with sharp drop of CO concentration and rise of CO_2 , the batch regeneration shifted gradually from a reduction environment to an oxidation environment.

Figure 16 shows the concentrations of NO, HCN, and N_2 in the flue gas as a function of time as coke nitrogen is released in the same batch regeneration experiment. Note that most of the coke nitrogen was released as N_2 , which peaked around the 13.5-minute mark at about 200 ppm, under a reducing or a slightly oxidizing environment. A fraction of the coke nitrogen was released as HCN, which peaked around the 10.5-minute mark at 35 ppm, under the same environment. Note that the NO concentration was below 20 ppm for the first 14 minutes under a reducing or a slightly oxidizing environment when both coke on catalyst and CO were present. The NO_x level increased sharply afterward, and peaked around the 18-minute mark at 190 ppm when the CO concentration fell sharply and the O_2 concentration increased beyond 1%, as shown in Figure 15.

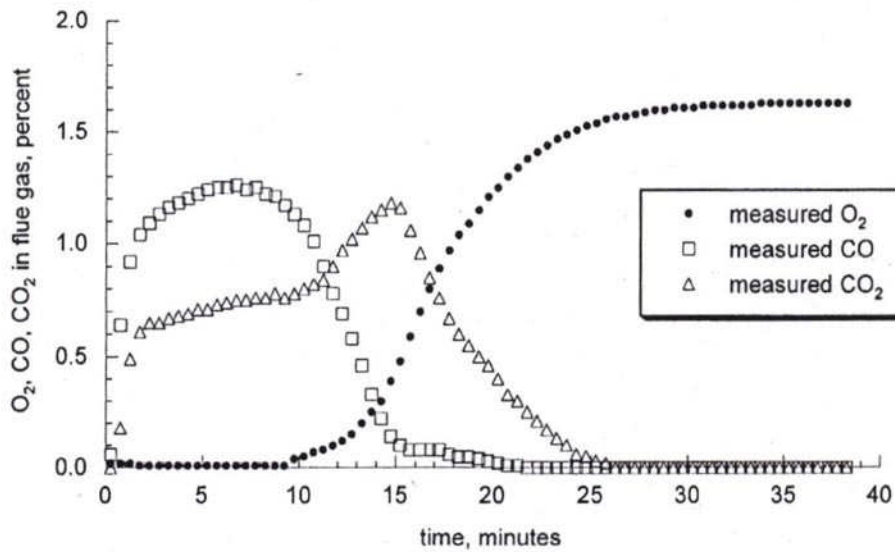


Figure 14: CO, CO₂ and O₂ in the Flue Gas as a Function of Time [9]

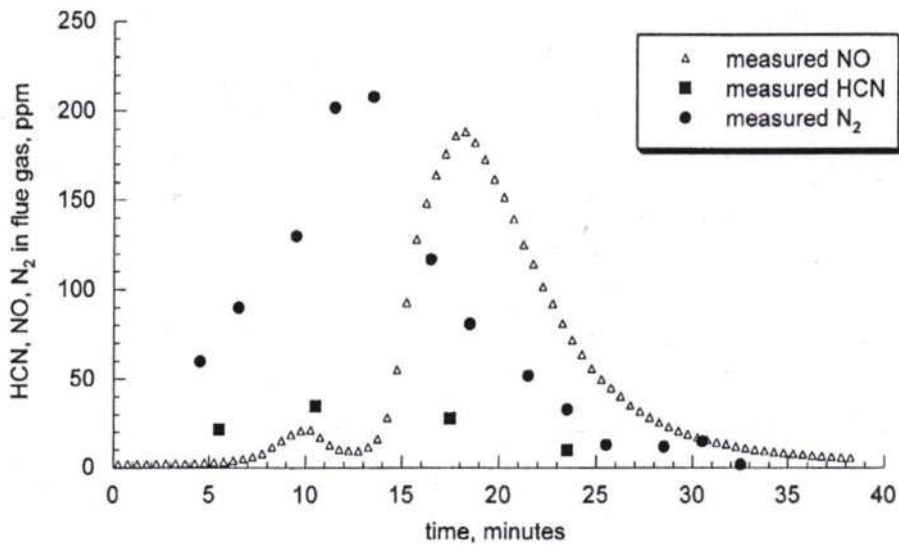


Figure 15: NO, HCN and N₂ in the Flue Gas as a Function of Time [9]

The proposed reaction kinetics [9] for the release of coke nitrogen in the FCC catalyst regeneration process involves initial volatilization of coke nitrogen as HCN, which could be hydrolyzed to another intermediate, NH₃. Both intermediates, HCN and NH₃, can be oxidized to NO, which can be reduced by the presence of CO or/and coke on catalyst to N₂.

Solution to the NO_x Emission Problem

The FCC regenerator design has a direct impact on the effectiveness of in-situ reduction of NO_x to N₂, and hence reduction of the final NO_x emissions in the flue gas. The new Shell Global Solutions' low NO_x regenerator technology [10] involves an improved process consisting of the strategic design of catalyst and air distributions, as shown in Figure 17, which enables the unit to operate in both full and partial combustion modes with low NO_x emission.

As shown in Figure 17, the regenerator system 1 includes a single regenerator vessel 10 having an upper end 12 and a lower end 14. The regenerator vessel 10 includes a dilute phase catalyst zone 16 above and a dense phase catalyst zone 18 below with a transition surface 20 between the two. The dense phase catalyst zone 18 further includes a high velocity central region 22, located in the central portion 26 of the dense phase catalyst zone 18, and a low velocity annular region 24, located in the annular portion 28 of the dense phase catalyst zone 18. It is a significant aspect of the new regenerator technology that the high velocity central region 22 and the low velocity annular region 24 are formed within the dense phase catalyst zone 18, without the use of a structural element such as a vertical baffle or a partition. The two fluidization regions are instead formed within the dense phase catalyst zone 18 by the introduction into the dense phase catalyst zone 18 of more than one fluidization gas stream, each of which is directed and controlled in such a manner as to cause the formation of multiple fluidization regions. Introduced into the central portion 26 of the dense phase catalyst zone 18 is a high velocity fluidization gas stream that passes through the fluidization gas distribution ring 32 near the bottom of the regenerator vessel 10. Introduced into the annular portion 28 of the dense phase catalyst zone 18 is a low velocity fluidization gas stream that passes through the fluidization gas distribution ring 38 located within the annular portion 28 near the bottom of the regenerator vessel 10.

The controlled introduction of the various fluidization gas streams at the different fluidization gas flow rates along with the directed introduction of the fluidization gas streams to desired locations induces a desired circulation of the FCC catalyst within the dense phase catalyst zone 18, as depicted in Figure 17 by the bold arrows 40 that show the general direction and circulation of the FCC catalyst within the dense phase catalyst zone 18. As shown by the bold arrows 40, catalyst particles in the high velocity central region move in a generally upward direction, and catalyst particles in the low velocity annular region move in a generally downward direction. Catalyst from the bottom end 42 of the low velocity annular region 24 flows into the high velocity central region 22 and most of catalyst from the top end 44 of the high velocity central region 22 flows into the low velocity annular region 24, thereby forming the catalyst circulation within the dense phase catalyst zone 18.

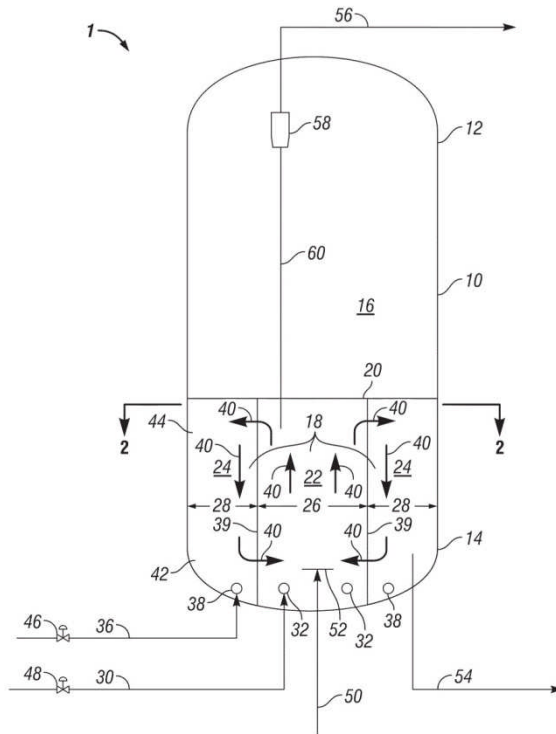


Figure 16: A Schematic Diagram of the Low NO_x Regenerator System

The regenerator system 1 further includes the introduction of spent catalytic cracking catalyst into the high velocity central region 22 through conduit 50, which can be a riser or a standpipe. Connected to the end of conduit 50 is a spent catalyst distributor 52 that introduces spent FCC catalyst into the high velocity central region 22 in a generally horizontal direction and mixes with catalyst circulating from the bottom end 42 of the low velocity annular region 24. The regenerated catalyst is removed from the low velocity annular region 24 by way of conduit 54, which removes regenerated catalyst from the annular portion 28 of the dense phase catalyst zone 18.

One advantage of the new regenerator system is that the induced catalyst circulation pattern distributes partially regenerated spent catalyst to the proximity of the surface 20, which results in reducing NO_x emissions from the regenerator. Another advantage of the new regenerator system is that the location and the spent catalyst distributor design induce intimate mixing between catalyst and transport air, thus preventing transport air or entrained hydrocarbon from breaking through the dense bed, and resulting in reduced afterburn.

Commercial Experience

The new low NO_x regenerator technology was implemented as an integrated part of a recent major FCC revamp, as presented in the case study below [10].

The original FCC unit was a large side-by-side unit with a regenerator diameter > 15 m, as shown to the left in Figure 18. The scope of the revamp, as shown to the right in Figure 18, included:

- A new stripper,
- Catalyst Circulation Enhancement Technology (CCET) [4] at the stripper outlet,
- A new, larger air blower,
- Additional pairs of regenerator cyclones for handling higher air flow, and
- The low NO_x regenerator technology, consisting of a new spent catalyst distributor, new regenerator outlets with CCET, new air distributors, and the controlled system.

The unit performance was measured before and after the revamp. Key performance improvements were observed:

The unit was able to operate in both full and partial combustion modes with low NO_x emission after the revamp. Figure 19 shows the NO_x level in partial combustion mode under 4 different air distribution conditions. As shown in the figure, NO_x emission is the lowest with Case D, with 40 ppm @ CO concentration of 2.4%. The unit can reach NO_x level lower than 40 ppm under either lower CO concentration or full combustion mode with O_2 concentration < 1% (not shown in the figure); however, partial combustion with CO concentration in the range of 2 to 3.5% is the preferred mode of operation because of its capability to increase the unit feed rate.

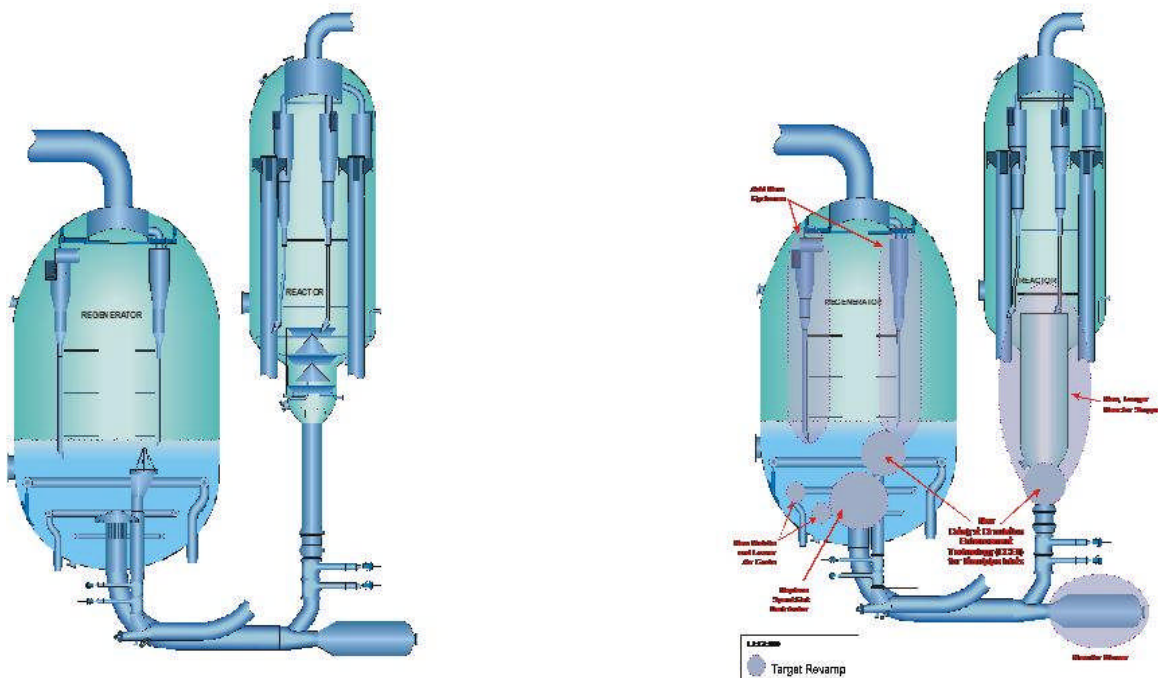


Figure 17: Scope of the FCC Revamp in the Case Study

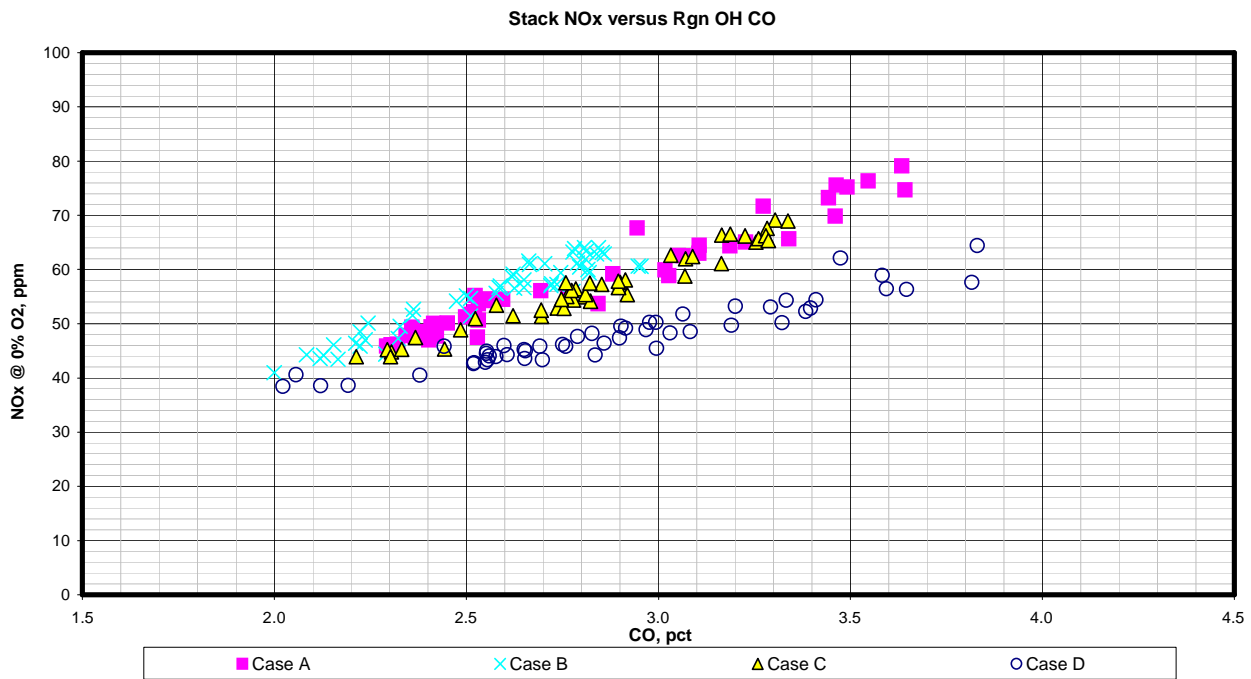


Figure 18: NOx emission in partial combustion under four cases of air distribution

What the Future of FCC Might Look Like

Shifts of Product Demands and Feedstock

Historically, the FCC unit and its downstream units provide the majority of gasoline supply in the world. However, the landscape of the demand from FCC products is shifting and is region-specific as shown in Figure 20.

The demand for propylene from FCC products has increased, and in some regions, the light olefins have become the premier products from FCC. In addition, in many regions the demand for diesel outpaces the demand for gasoline.

Figure 21 shows the demand shift in the US. The motor gasoline demand has reached a plateau and the long term projection is a decreasing demand trend. On the other hand, demand for gasoil and diesel is increasing. This shift from motor gasoline to gasoil/diesel follows a similar pattern as was seen in Europe 10 years ago. In parallel, the demand for propylene in the US is also growing so rapidly that the traditional source for propylene - steam cracking - cannot keep up with the demand. From the available technologies to bridge the gap, FCC is by far the best.

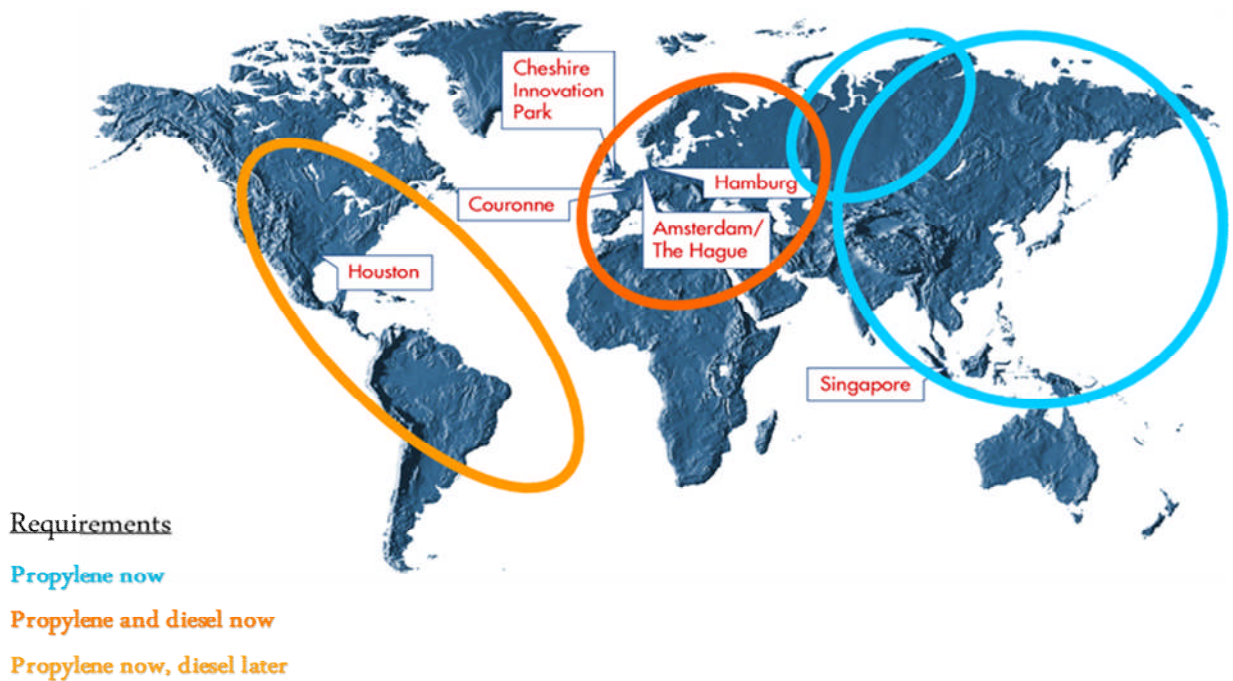


Figure 19: Current market demands of FCC products

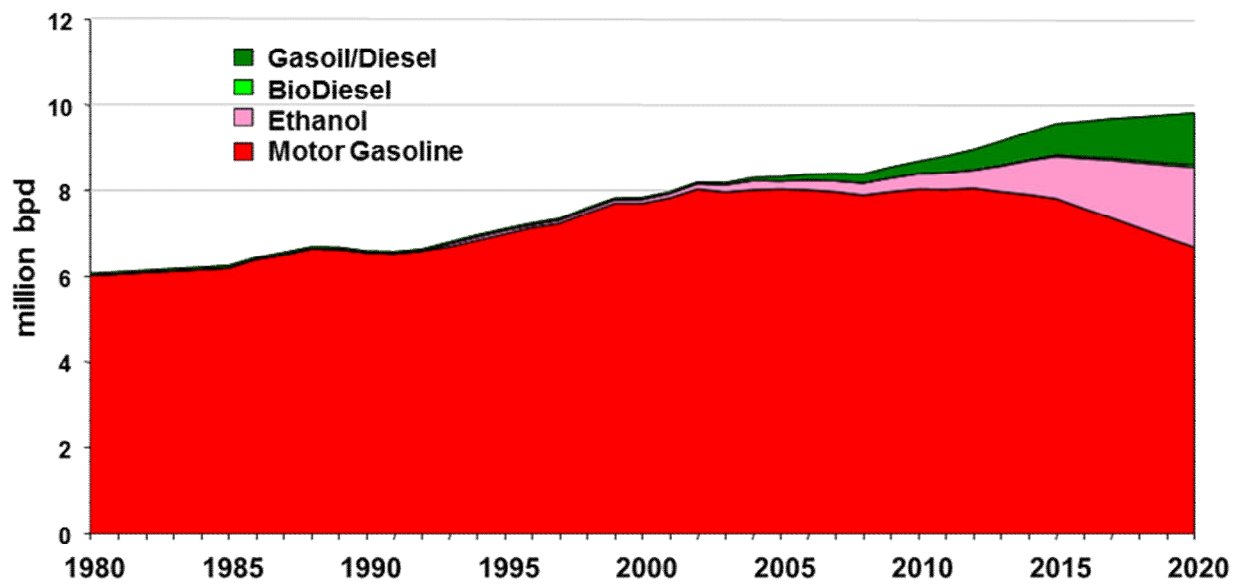


Figure 20: Road transport fuel demand trends in the United States

Given these demand shifts, the refining industry needs a redefinition of the FCC process to enable the following process objectives to be satisfied:

- Lower gasoline yield;
- Higher LCO yield, with better product quality characteristics (lower density and higher cetane number);
- Higher propylene yield;
- Flexibility to switch seamlessly between these different production modes and conventional FCC operation depending on the market demand.

There are several new FCC process technologies available that address these expected shifts in market demands. One of them is the Shell MILOS process [11, 12], or Middle Distillates and Lower Olefins Selective process.

A relative new direction of FCC is to co-process bio-liquid feedstock. The FCC unit is the single largest contributor, accounting for 30 to 50%, to the overall CO₂ footprint of a refinery. Beside the benefit of a potential, inexpensive, alternative feedstock, processing bio-liquid feedstock has the added benefit of a tax credit in a region where CO₂ emissions are regulated. Processing bio-feedstock presents totally different challenges, yet to come, in FCC operation such as extremely high oxygen content in the feedstock.

MILOS – Process Background

Recycling cat-cracked gasoline to the bottom of the riser (where the temperature is typically in the range of 1250-1320 °F) has been widely practiced in the refining industry with the objective of increasing propylene yields. This has the desired effect of producing more propylene, but with significant penalties of producing large amounts of coke, dry gas, butylenes, LCO+ and it would produce little iso-butane. To confirm this, experiments were conducted in which light and heavy cat cracked gasoline were recycled in the Shell Global Solutions large FCC riser pilot plant.

The most favorable condition for the production of propylene was found when light CC gasoline was injected below the VGO feed such that the residence time for cracking pure light CC gasoline was approximately 0.5 to 1 second prior to the VGO injection point. However, it had a large impact on VGO conversion, which dropped at constant coke rate. As a result the net LCO+ flow rate at riser exit increased significantly. Such large increases in LCO+ material were also observed in all other tests. Additionally, injecting light CC gasoline with or above the VGO feed yielded a net decrease in propylene yields due to quenching in that section of the riser reactor. For heavy gasoline, the results were even more disappointing in all cases. The flaw of this option is that it is impossible to achieve optimal conditions for both feeds (both the recycled gasoline and the VGO) in one single riser.

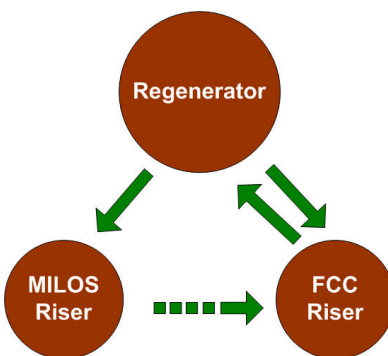


Figure 21: MILOS concept

MILOS Process Concept

The MILOS concept, shown in Figure 22, consists of adding a separate riser to the FCC unit, in which gasoline or other suitable streams are cracked under process conditions tailored specifically to maximize propylene yields, to maintain or increase the iso-butane yield (which is desirable for the alkylation unit) without producing excessive amounts of dry gas, coke and butylenes. The ideal temperature is relatively low (1050-1150 °F) in order to minimize thermal reactions. At temperatures lower than these, high gasoline conversions cannot be easily obtained. The catalyst used is the same as in a conventional cat cracker with ZSM-5 added to boost the propylene yield. Typical yields obtained by cracking catalyst cracked gasoline in a MILOS riser are 15.5 %wt propylene, 7.5 %wt dry gas and 5%wt iso-butane.

Case Study – Diesel Mode

A case study focusing on diesel-mode implementation is presented to demonstrate one aspect of implementing MILOS in existing FCC units.

The base-case is a Shell Global Solutions' designed long residue CCU, processing feed with a Conradson Carbon content of 3.2%wt. Shell's rigorous heat-balanced Catalytic Cracking Process model was used. This model was tuned to the actual operating conditions of the specific FCC unit, including realistic unit constraints and feed properties.

The base-case (Case #1) represents the average operating conditions and average feed properties of the unit over the recent years. Besides this case, the following cases were explored:

- Cases #2 and #3: the maximum diesel and the maximum propylene cases based on the conventional FCC-unit without the addition of a separate MILOS riser
- Case #4: a MILOS riser is added to the FCC unit to achieve maximum diesel and propylene
- Case #5: a sensitivity case with the same MILOS-FCC unit, maximizing propylene only.

The results of the case studies are presented in Table 4.

The comparison between the base case FCCU (Case #1) versus the diesel mode FCCU (Case #2) or propylene mode FCCU (Case #3) is straightforward. If we operate the unit in diesel mode (Case #2), the LCO yield is boosted by more than 3%wt (Table 4) and the cetane index is increased by 5 points. However, propylene yield suffers a reduction of 1.2%wt. Valuable LPG (total C3s and C4s) also suffers a reduction of 3.5%wt. On the other hand, if we operate the unit in propylene mode (Case #3), the propylene yield is boosted by 3%wt, and the LPG (total C3s and C4s) is also increased by 9%wt. (The increase in butylenes Cases #3, 4 and 5 is a direct result of ZSM-5 addition). However, the cetane index of LCO suffers a big hit of about 6 points reduction. LCO yield is slightly reduced by 1%wt.

The situation above is a typical dilemma faced by FCC that is supplying a diesel and propylene driven market. The diesel mode and propylene mode represent the opposite extreme ends of operation and depending on market forces, the operator swings from one mode to the other. Some operators might choose to operate in the middle of the two modes and not make either maximum propylene or maximum diesel in terms of quantity and quality. However, after revamp with MILOS, the operator can produce more propylene than the standalone FCC propylene mode and more LCO than the standalone FCC diesel mode, with even a higher cetane index, all achieved at the same time (Case 4 in Table 4).

Table 4: Diesel revamp case study results

Case number		#1	#2	#3	#4	#5
Case		Base	FCC only Diesel mode	FCC only Propylene mode	FCC Diesel mode + MILOS	FCC Propylene mode + MILOS
Case description		Typical operating conditions in recent years	Existing unit operated to produce maximum LCO	Existing unit operated to produce maximum propylene	Existing FCC revamp with a addition of MILOS technology. FCC is operating in diesel mode	Existing FCC revamp with a addition of MILOS technology. FCC is operating in propylene mode
Fresh feed rate to FCC riser	t/d	10000	10000	10000	10000	10000
Recycle of light cat crack gasoline to MILOS	t/d	N/A	N/A	N/A	2500	2500
FCC riser outlet temperature	°C	Base	-19	+5	-30	+5
ZSM-5 additive in catalyst inventory	%wt	0	0	10	10	10
LCO Cetane Index	-	25.9	31.0	24.9	33.3	24.8
Overall yield						
C2 minus	%wt	4.3	3.2	4.4	4.7	6.3
Ethylene	%wt	1.1	0.8	1.2	1.9	2.4
Total C3	%wt	8.2	6.3	12.2	13.7	17.1
Propylene	%wt	5.2	4.0	8.2	9.8	11.9
Propane	%wt	3.1	2.3	4.0	4.0	5.1
Total C4	%wt	10.2	8.6	13.7	16.0	17.8
i-Butane	%wt	3.2	2.8	3.8	5.5	5.6
n-Butane	%wt	1.2	0.9	1.5	1.7	2.0
Total C4 Olefins	%wt	5.8	4.9	8.4	8.9	10.2
i-Butylenes	%wt	1.3	1.1	2.9	2.9	3.5
Light cat crack gasoline (C5 - 142 degC)	%wt	34.7	32.8	30.3	14.4	16.1
Heavy cat crack gasoline (142 - 221 degC)	%wt	11.2	12.4	9.4	12.0	10.8
LCO (221 - 370 degC)	%wt	15.8	18.9	14.7	19.3	15.2
HCO (370 - 425 degC)	%wt	3.4	4.4	3.4	4.5	3.5
SO (425 degC+)	%wt	4.5	6.7	4.4	7.5	4.5
Coke	%wt	7.6	6.8	7.5	7.9	8.8
Gasoline/Cycle Oil ratio	wt	2.9	2.4	2.7	1.4	1.8

It is clear from the results above that a revamp with MILOS (Case #4) on a conventional FCC unit brings the benefits of maximising propylene make, maximising LCO make and increasing LCO Cetane quality, all at the same time. This is achieved by allowing the FCC to operate in diesel mode to achieve the desired high LCO yield and high LCO Cetane. Directing the cooler MILOS spent cat (cooler relative to regen temperature) to the FCC riser also plays an important role in improving the LCO yield and quality. On the other hand, the MILOS riser is focusing on maximising propylene by cracking recycled light cat-cracked gasoline.

With the same FCC and MILOS unit, we have studied a sensitivity case to see if the propylene make can be boosted further. In this study, the conventional FCCU is operated towards maximum propylene make instead of operated in the diesel mode (Table 4).

It is clear that with this MILOS-FCC configuration (Case #5), the propylene yield can be further boosted if the operator is ready to accept the same level of LCO yield and quality as they are getting during the conventional FCC propylene mode operation. The propylene yield can be increased to almost 1.5 times compared to the standalone FCC propylene mode operation.

MILOS vs. other process technologies

The MILOS process has significant advantages compared to technologies licensed by Shell's competitors (Tables 5 and 6). Most importantly, the operational flexibility offered by MILOS is a key advantage. As MILOS is integrated in an FCCU, it can even be reverted on the run to regular FCC operation if this is required. DCC and PetroFCC do not have this flexibility. A DCC/PetroFCC implementation requires many more significant changes to an existing FCC unit.

Overall, the revamp of a conventional FCC unit to a Diesel MILOS-FCC is a very attractive option to refiners, especially for those units located in Europe or other regions where both diesel and propylene demand are expected to grow rapidly. The operating flexibility provided by MILOS helps set a refinery up for long term success with changing market environments.

CONCLUSIONS

The FCC process is one of the most important circulating fluidized bed processes. Through a few examples, some current challenges of high temperature erosion, corrosion and NOx emission in operating a high temperature CFB process like FCC have been highlighted.

Although the FCC process has been in commercial operation for over 60 years, the technology continues to evolve. A new FCC technology, MILOS, for producing more light olefins and diesel in light of the market demand shift has been proposed and the new trend of co-processing bio-feedstock has been discussed. These new applications will present new challenges to the operation of FCC.

MILOS vs DCC

	MILOS	DCC
Yield selectivity	High C3= Low dry gas/coke	High C3= High in dry gas and coke
Flexibility	Very high can run in multiple modes	Low only max C3=
Main Product	C3=/C4=, gasoline Better quality LCO	C3=/C4= (sometimes C2=)
Feedstocks	Any FCC feedstocks, Raffinate, FCC Naphtha, Coker Naphtha, GIL wax, V-oils, Palm oil, ...	Resid with high H, VGO, Hydrowax
Capacity Limit	250 kb/day FCC feed	90 kb/d
Implementation	FCC revamp*, grass-root	FCC revamp*, grass-root
Commercial Experience	No (However, similar FCC configuration existed)	One in Thailand Several in China
Capex for 92 kbb/d unit	487 Mln\$	529 Mln\$
Margin	94.5 USD/tfeed	87.4 USD/tfeed

* If a FCC is revamped to a DCC it can no longer be operated as a conventional FCC and capacity is likely reduced significantly. MILOS can run as a Conventional FCC unit if desirable.

Table 5: Typical features of MILOS relative to Deep Catalytic Cracking technology

MILOS vs PetroFCC

	MILOS	PetroFCC
Yield selectivity	High C3= Low dry gas/coke	High C3= Low dry gas/coke
Flexibility	Very high can run in multiple modes	Low only max C3=
Main Product	C3=/C4=, gasoline Better quality LCO	C3=/C4=
Feedstocks	Any FCC feedstocks, Raffinate, FCC Naphtha, Coker Naphtha, GIL wax, V-oils, Palm oil, ...	Resid with high H, VGO, Hydrowax
Capacity Limit	250 kb/day FCC feed	50 kb/d
Implementation	FCC revamp*, grass-root	FCC revamp*, grass-root
Commercial Experience	No (However, similar FCC configuration existed)	One unit in construction
Capex for grassroots unit	Base	++ (HDT for feed)
Opex	Base	++ Steam
Margin	Base	-20%

*A PetroFCC can be operated as a conventional FCC but its capacity is reduced significantly. MILOS can run as a Conventional FCC unit with no capacity impact. The PetroFCC unit under construction is a revamp.

Table 6: Typical features of MILOS relative to PetroFCC technology

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