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DISCUSSES COUNTER CURRENT REGENERATION FOR RESIDUE UPGRADE AS THE KEY TO LOW EMISSIONS AND CONTROLLED INVESTMENT COST.

Different regenerator designs are commercially available for resid fluid catalytic cracking (RFCC). Two of the more important variations are:

- Single stage or two stage catalyst regeneration.
- Operating the regenerator in total or partial CO combustion.

This article indicates some of the more important design and operating parameters associated with these design differences and discusses their potential impact on unit operations. Discussion of a new regeneration technology and its advantages is also included.

The success of any fluid catalytic cracking (FCC) unit is highly dependent on the continuous regeneration of spent catalyst from the reactor. In the reactor, coke formed during the reaction is deposited on the catalyst. The regenerator must reactivate the catalyst by burning the coke off the catalyst while minimising catalyst degradation which results in loss of both catalyst activity and the most economic yield selectivity.

With the recent increases in crude prices, the use of resid as feed to the FCC unit is receiving more attention. Regenerator operation is even more important for RFCC unit operation. Processing resid streams increases the coke yield

HOLDING THE KEY

- **Minimize catalyst deactivation**
- **Uniform regeneration to low carbon levels**
- **Uniform temperatures in bed and dilute phase**
- **Flexibility for feedstocks and catalysts**
- **Robust and reliable mechanical design**

Figure 1. Regenerator design requirements.

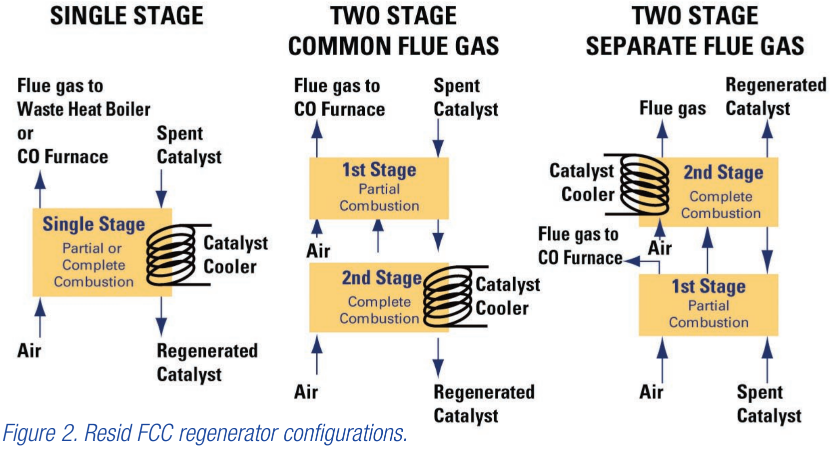

Figure 2. Resid FCC regenerator configurations.

and requires more combustion air to burn it. The resulting increase in the size of the regenerator causes its investment to rise to approximately 60% of the RFCC converter investment. In order to preserve operating economics, the regenerator design needs to minimise size and mechanical complexity while maintaining the catalyst activity and selectivity associated with the optimum yield slate. A list of ideal regenerator features is summarised in Figure 1. In the discussion that follows, key regenerator design considerations are described and related to commercially available technologies for single and two stage catalyst regeneration. A new regeneration technology is also outlined and its advantages described.

Commercial RFCC regenerator technologies

RFCC units must process feeds with higher concentrations of feed components that can have adverse affects on yields and unit operations. These components include metals (nickel, vanadium, sodium, iron, calcium), sulfur, nitrogen (particularly basic nitrogen), and heavy hydrocarbons that increase the coke yield which are typically indicated by high Conradson carbon residue (CCR). The increased coke yield has the greatest effect on regenerator design. The increased heat release can raise the regenerator temperature to an unacceptable level for equipment design as well as catalyst activity maintenance. Methods must be considered that will remove heat from the regenerator. The main options are operation in partial CO combustion (followed by a CO boiler) and/or the use of a catalyst cooler.

Commercially available RFCC technologies provide different approaches for processing the heavier, contaminant laden feeds. A schematic representation of the regenerator concepts is provided in Figure 2.

- The KBR Orthoflow™ Resid FCC employs a countercurrent single stage dense bed regenerator and can operate in either full or partial CO combustion. Feeds with CCR levels as high as 9 wt% have been processed. Regenerator temperature can be controlled with a variable duty dense phase catalyst cooler when required.
- The two stages, common flue gas system features a two stage counter flow regeneration system. The first stage of catalyst regeneration operates in partial CO combustion and burns 60 - 80% of the coke including much of the hydrogen. The remaining coke is then burned in the second stage that can include a catalyst cooler when required to limit regenerator temperature to a reasonable value. Flue gas from the second catalyst stage is combined with additional air and the combined flow is used to burn coke in the first catalyst stage.
- The two stages, separate flue gas system also features a two stage regeneration scheme, but the catalyst and gas flows are cocurrent. The first stage operates in partial CO combustion. The flue gas from this first catalyst stage is routed to further processing and fresh combustion air is used to lift the partially regenerated catalyst to the second catalyst stage. This second stage is operated in total CO combustion and produces a separate flue gas stream. The second catalyst stage can include a catalyst cooler when required.

Other RFCC technologies are in use. These employ a single catalyst regeneration stage and catalyst coolers are typically required whenever CCR exceeds 3 - 4 wt%.

Regenerator design considerations

Maintaining catalyst activity and selectivity is influenced by many considerations, some of which are discussed in more detail below. In many cases reducing the adverse effects of one of these considerations serves to increase the adverse affects of another. As a result, an optimised regenerator design must address all these considerations simultaneously in order to maintain the highest achievable catalyst activity and selectivity.

Catalyst particle temperature control

The combustion of coke on the spent catalyst entering the regenerator is a kinetic reaction. The rate of reaction increases with increasing carbon content in the regenerator bed and on the individual catalyst particle. The rate of reaction also increases with increasing bed temperature and increasing oxygen concentration in the combustion gases. Excessive local reaction rates can raise individual catalyst particle temperatures to higher than desired levels, leading to loss of surface area due to sintering of the catalyst. Catalyst activity is further reduced by increased hydrothermal deactivation by the water vapours present in the flue gas, which is discussed in further detail below. Processing resid in the FCC increases the potential for high particle temperatures because of the higher amounts of coke deposited on each particle of catalyst.

Table 1. Commercial catalyst activity improvement from countercurrent regeneration

Catalyst data	Base case side entry	Revamp counter current	Delta
Surface area, m^2/g	143	162	+18
Average bulk density, g/cc	0.90	0.88	-0.02
Pore volume, cc/g	0.34	0.39	+0.05
Microactivity, wt%	68.5	73	+4.5

The most effective method for optimising the coke combustion kinetics is to use countercurrent flow of spent catalyst and air to the maximum extent permitted by economics. The catalyst with the highest coke content is exposed to the combustion gas with the lowest oxygen content. The low oxygen content controls the burning rate. The combustion gas with the highest oxygen content is exposed to the catalyst with the lowest coke content. In this case, the low coke content controls the burning rate. Thus, the rate of combustion is more uniform throughout the combustion process, which minimises the potential for localised high particle temperatures. By contrast, co-current regenerators contact the highest coke content catalyst with the highest oxygen content combustion gases which maximises the potential for localised high particle temperature.

The overall kinetics for countercurrent and co-current regenerators are the same. This occurs because operating economics force all regeneration systems to produce nearly the same results, essentially the same carbon on regenerated catalyst and oxygen content in the flue gas leaving the regenerator. These overall results do not give cocurrent regeneration schemes any advantages for the initially high burning rates, which are, then offset by lower burning rates at low concentrations of both coke and oxygen. Countercurrent regeneration averages out the burning rates, avoiding the high particle temperatures associated with initial high burning rates. Equipment sizing and operations are essentially the same for both systems.

Figure 3 is a schematic drawing of a system KBR uses successfully to promote countercurrent regeneration of catalyst. Spent catalyst is distributed evenly at the top of the bed and combustion air is distributed evenly at the bottom of the bed. The catalyst flows downward and the air flows upward giving a countercurrent system. While vertical mixing in a fluid bed is fast, it is not instantaneous. The next two paragraphs quantify some of the benefits for this countercurrent system.

In one unit, KBR replaced a cocurrent regeneration scheme with the countercurrent technology shown in Figure 3 but adapted to a configuration that introduces the

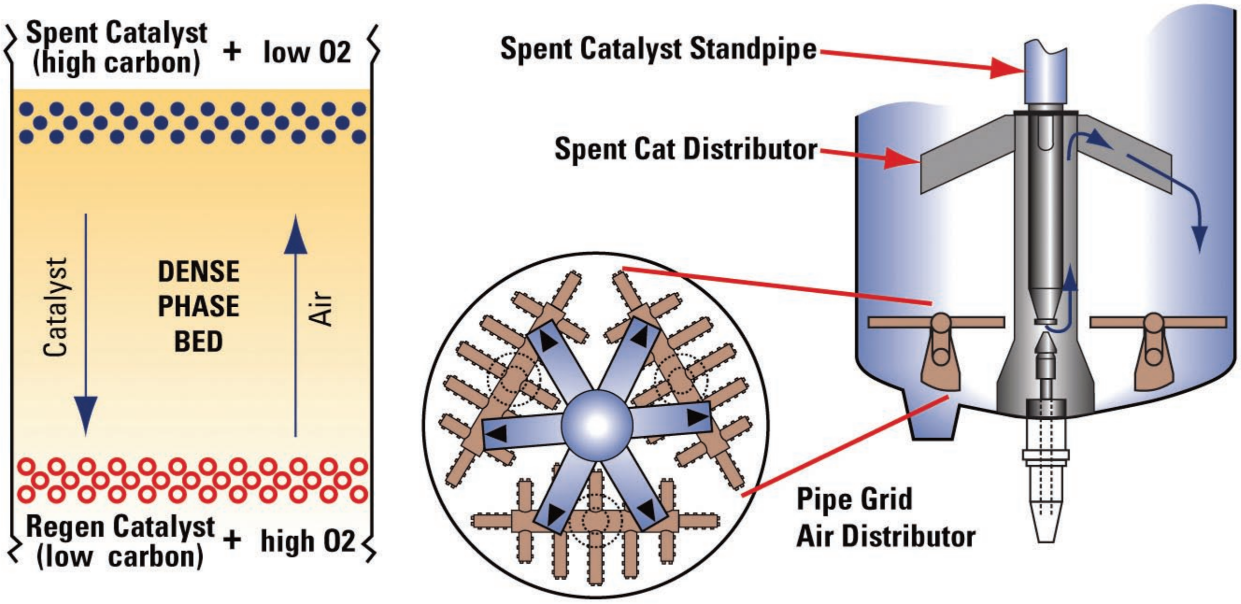

Figure 3. Countercurrent regeneration.

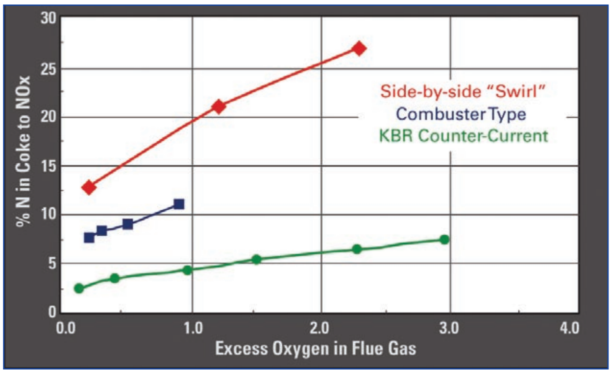

Figure 4. NOx emissions from commercial FCCUs.

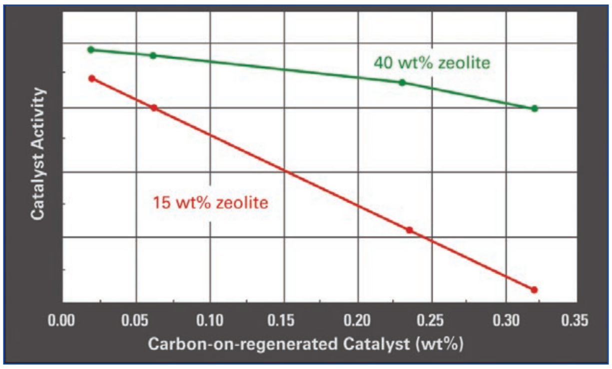

Figure 5. Modern high zeolite catalysts lose less activity in the presence of moderate CRC levels.

spent catalyst from the side of the regenerator. Table 1 shows the results on catalyst properties and activity maintenance. The equilibrium catalyst activity increased by nearly five points at the same makeup rate. The primary reason for this is the relatively lower particle temperatures created by the switch to countercurrent regeneration. A further gain was obtained by reducing the water partial pressure as discussed below.

Countercurrent regeneration also emits less NOx than other regeneration technologies, as shown in Figure 4. The countercurrent regeneration scheme produces a high concentration of carbon at the top of the bed. As a result, the following reaction reduces much of the NOx produced lower in the bed:[1]

$$2\,C + 2NO \rightarrow 2\,CO + N_2$$

For a given nitrogen content in the coke, countercurrent regeneration produces 60 - 80% less NOx than other regenerator designs.

Water partial pressure

Steam is always present in the regenerator. The major sources include the combustion of hydrogen in the coke, water vapour in the combustion air, and steam entrainment from the catalyst stripper included in the reactor. Hydrothermal deactivation occurs when the steam attacks the crystalline structure in the zeolitic structure of FCC catalysts. The resulting collapse of the crystalline structure causes a loss of activity due to loss of surface area and pore volume.

Countercurrent regeneration also reduces the average partial pressure of water in the regenerator bed. Most of the hydrogen in the coke is combusted at the top of the bed and is swept out with the combustion gases.

The two stage system with separate flue gas does achieve a lower water vapour pressure in the second catalyst stage by removing the water generated by hydrogen combustion in the first stage before the catalyst reaches the second stage. This helps to reduce, but not eliminate, hydrothermal deactivation in the second stage. Water vapour is present in the combustion air and not all of the hydrogen is combusted in the second catalyst stage.

The two stage system exposes the spent catalyst to all the water generated by burning coke as well as all the water entering with the air and spent catalyst. Hydrothermal deactivation would be expected to be the highest for this system.

Carbon on regenerated catalyst

The amount of carbon left on the regenerated catalyst, typically expressed as a weight per cent, is almost universally used as the best measure of how well the regenerator is performing. While a lower carbon on regenerated catalyst (CORC) is an indication of a higher activity, much of the emphasis on minimising CORC began with older catalyst formulations that contained substantially less zeolite than more modern formulations. As shown in Figure 5, increasing the CORC has a less dramatic effect on catalyst activity with the higher zeolite content. Loss of activity is relatively low up to about 0.2 wt% CORC.

The concern about CORC typically surfaces when comparing partial combustion operation with total combustion. Regenerator flue gas from partial combustion operations contains significant amounts of CO, typically in the range of 5 - 7 vol%. CORC is typically lower for total combustion units; the typical number being 0.05 wt% compared to 0.10 - 0.15 wt% for partial combustion units. But as indicated above, this difference is less significant than it used to be.

Contaminant metals in the feed

Resid feeds contain higher levels of contaminant levels that can degrade catalyst activity. Nickel, vanadium, sodium, iron, and calcium are the metals and alkali metals that cause the most concern. However, when considering regenerator design, vanadium is more important than the others because it is mobile and can move from one catalyst particle to another, thus contaminating the newer and more active makeup catalyst as well as the aged catalyst remaining in the system. Vanadium promotes dehydrogenation reactions, which lead to an increase in hydrogen (dry gas) as well as coke. In addition, vanadium actively attacks the zeolite crystalline structure, resulting in the loss of surface area due to collapse of the pores.

The mechanism for vanadium mobility is generally attributed to a two stage reaction. First, vanadium reacts with oxygen, forming V_2O_5, which then reacts with steam to form vanadic acid, $VO\,(OH)_3$, a strong acid:

$$4\,V + 5\,O_2 \rightarrow 2\,V_2O_5$$
$$V_2O_5 + 3\,H_2O \rightarrow 2\,VO\,(OH)_{3(g)}$$

In the presence of steam, the volatility of vanadium pentoxide is increased tenfold over that in dry air.[2]

Regenerator designs typically focus on minimising one or both of these reactions. One method is to design for partial CO combustion. Commercial data shown in Figure 6 indicate that partial combustion units maintain activity better than complete combustion units, especially at vanadium concentrations above 2000 wt ppm.[3] Part of the activity increase is due to the reduced availability of oxygen, which inhibits the first reaction. Another part of the activity increase is due to the lower particle temperatures as a result of the slower burning kinetics present at lower oxygen concentration.

Designing to prevent the reaction of vanadium pentoxide with steam is much more difficult. The combustion air must be dried because sufficient water is present to mobilise the vanadium. In addition, steam entrainment from the catalyst stripper must be minimised which typically requires the use of a much more expensive stripping gas. Finally, a way must be found to combust the hydrogen in the coke separately from the carbon. In general, designing a catalyst regeneration system to prevent the reaction of vanadium pentoxide with steam is not economical.

Catalyst residence time

Increasing catalyst residence time provides the opportunity to reduce the CORC. However, increased residence time increases catalyst deactivation due to the steam in the regenerator. As a result, the regenerator bed volume must be set to provide the optimum point that provides good catalyst regeneration without incurring excessive deactivation at the same time. As noted above, economic factors push regenerator designs to roughly the same kinetic point, which produces roughly the same total catalyst residence time for all technologies. The two stage systems divide the catalyst residence time between two different vessels.

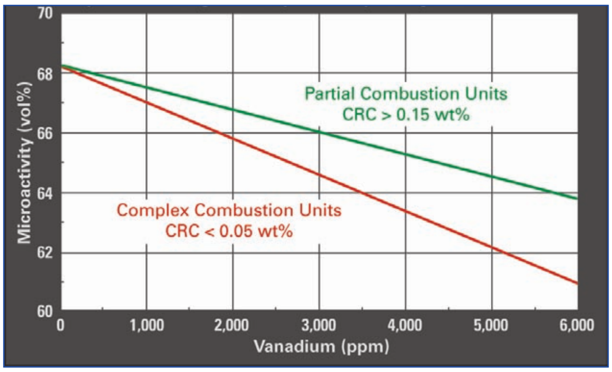

Figure 6. FCCUs operating in partial combustion equilibrate at higher catalyst activity for a given metals level.

Afterburn

Afterburn is the term used for the tendency of FCC regenerators to operate with an ever increasing temperature from the bed to the flue gas outlet of the regenerator. Severe cases of afterburn can cause equipment damage or excessive catalyst deactivation.

One type of afterburn is a gradual and relatively small increase in temperature (less than approximately 30 ˚F) but relatively even radial temperatures at any given level in the regenerator. This type of afterburn occurs because the combustion of carbon monoxide to carbon dioxide is slower than the combustion of carbon to a mixture of the two oxides. Providing sufficient residence time to eliminate all this type of afterburn is not economic due to the large regenerator volumes required and the excessive catalyst deactivation that would occur at the longer residence times required.

Another type of afterburn occurs when uneven distribution of spent catalyst produces a low amount of coke in one part of the bed and a high amount of coke in another. This maldistribution can produce an oxygen rich flue gas from the low coke portion and a carbon monoxide rich flue gas from the high coke portion. When these two gases mix in the regenerator dilute phase or the regenerator cyclones, a very high temperature can be produced. Afterburns as high as 200 ˚F have been noted. This type of afterburn is typically diagnosed when the radial temperature differences are very large or if large temperature differences are seen between the cyclone inlets and the flue gas outlet.

The countercurrent regeneration system shown in Figure 3 has been used on several occasions to eliminate this second type of afterburn. The even distribution of spent catalyst across the entire regenerator bed evens out the carbon distribution and minimises the potential generator the oxygen rich and carbon monoxide rich flue gases that cause it.

Table 2. Comparison of single and two stage regenerations systems for RFCC operation

	Single stage	Two stage common flue gas	Two stage separate flue gas
Combustion mode	Partial	Partial/total	Partial/total
Particulate temperature	Lowest	Reasonable	Reasonable
Water partial pressure	Moderate	Highest	Lowest
CORC	Moderate	Low	Low
Catalyst makeup (contaminant metals)	Lowest	Low	Moderate
Catalyst residence time	Equivalent	Equivalent	Equivalent
Afterburning	Low	Moderate	Moderate
Investment	Lowest	Higher	Higher
Ease of operation	Easiest	Complex	Complex

Investment

The two stage regeneration systems obviously require more investment than the single stage system. The additional regenerator vessel along with the associated catalyst control and handling systems increase the investment by 15 - 20% compared to the single regenerator system, based on the total investment required for the converter section (air blower, reaction/regeneration system, flue gas system(s), and catalyst storage/handling). In order to justify this investment, the catalyst makeup must be reduced by one third to one half. The results of regenerator simulations previously published by KBR indicate that catalyst makeup is actually lowest for the single stage system operated in partial CO combustion, thus minimising the possibility that catalyst advances can ever produce the makeup reduction required to justify the added investment.[4]

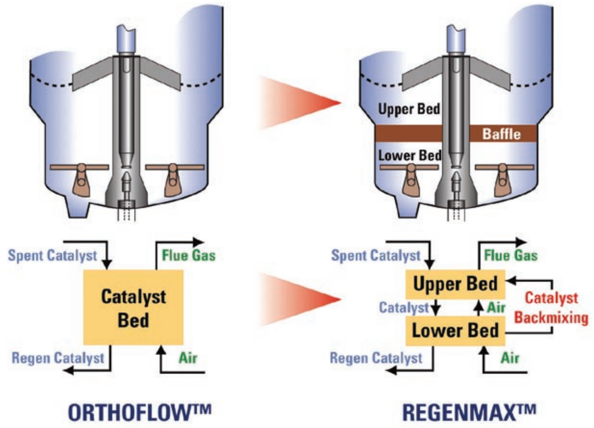

Figure 7. RegenMax™ technology baffle provides staging in single vessel.

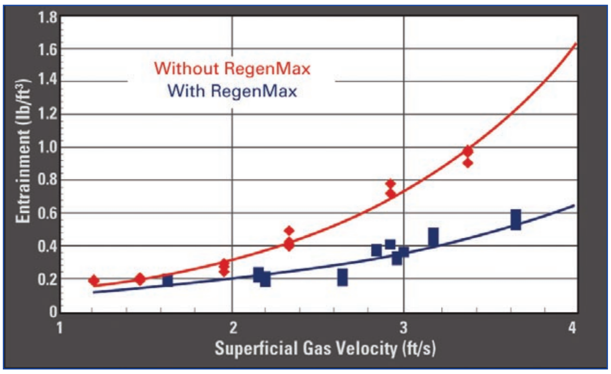

Figure 8. Baffle reduces entrainment.

Trying to justify the additional investment with increased gasoline make is also difficult (based on higher catalyst activity due to the lower CORC). In this case, the gasoline yield must increase by 3 - 4 vol% of the feed to justify the investment. Part of the reason for this difficulty is that much of the increase in gasoline yield comes at the expense of products such as LPG and LCO that also have some value.

Ease of operation

The two stage regeneration systems are also more difficult to operate. Obviously the extra equipment requires extra operator attention. The distribution of airflow further complicates unit operations. For every change in feed properties or operating conditions that changes the coke yield, not only must the total air rate be adjusted but also the split between the two regenerators must be adjusted to ensure effective and efficient unit operation. For a single stage system, only the total air rate needs adjustment.

Summary comparison

Table 2 summarises the discussion above comparing the single and two stage regeneration systems for RFCC operation. The two stage systems appear to offer some advantages for minimising CORC, but the required investment does not seem to justify the increased investment and operating complexity.

The next generation

KBR has developed a new regeneration technology that provides all the advantages of a two stage regeneration system within a single vessel. The technology is marketed as RegenMax™.

As shown in Figure 7, this technology installs a baffle in the regenerator to divide the single regenerator into an upper and lower bed. Catalyst flows countercurrent to air. The baffle is very similar in construction to stripper packing now in widespread use throughout the industry. Cold flow modelling indicates that the back mixing between the upper and lower beds is reduced by 70 - 80%. Regenerator modelling indicates that this is sufficient to provide catalyst regeneration equivalent to total CO combustion.

The RegenMax™ technology is a good fit with KBR's countercurrent regeneration technology. Regenerator modelling and operating data confirm that the countercurrent arrangement provides sufficient staging to ensure low catalyst deactivation and low vanadium mobility, but not sufficient staging to produce a CORC equivalent to that of total combustion units. Adding RegenMax™ technology introduces staging in the bed to obtain the same CORC as two stage regeneration units but at a fraction of the cost.

Cold flow modelling also demonstrated an unexpected benefit for the RegenMax™ technology, a reduction in the entrainment of catalyst particles to the cyclones (Figure 8). The entrainment is more pronounced at higher superficial vapour velocity. The reduced entrainment reduces wear on the cyclones, thus extending their life. In addition, particulate emissions from the regenerator are reduced which can help reduce particulate emissions at the stack. Alternatively, the regenerator could be operated at higher superficial velocity without reducing current cyclone life or increasing regenerator particulate emissions.

Conclusion

The increased coke yield and feed contaminants represent challenges in the design of an RFCC regenerator. Care must be taken to ensure that the increased coke can be burned off the catalyst without excessive deactivation by excessive catalyst particle temperatures while minimising the potential for catalyst deactivation associated with the feed contaminants (especially vanadium). The following concepts have been demonstrated:

- Single stage regenerators with variable duty catalyst coolers can and have processed a broad range of feedstocks, including CCR contents up to 9 wt%.
- The two stage regenerator systems are more expensive and more difficult to operate than single stage designs.
- The extra costs associated with two stage regenerator systems do not appear to be economically justified.
- A new technology (RegenMax™) is available that combines the advantages of both the single and two stage regenerator designs.

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