The history of residual oil processing in fluid catalytic cracking (FCC) units dates back prior to the 1970s, but it was not until the late 1970s that the concept became mainstream. The rapid increase in crude oil price during this decade and the desire to utilise more of the crude barrel drove the demand for residual oil processing in FCC units. Early efforts to process residual feeds consisted of means to manage the extra coke and control the high heat of combustion in regenerators. This typically involved steam generation in regenerator bed coils and other manipulations to the heat balance including water injection to the feed. In addition to managing the negative impact of higher asphaltenes in the feed, residual oil processing presents other concerns, including contamination from heavy metals, particularly nickel and vanadium. These metals can result in accelerated catalyst deactivation, higher operating costs and reduced product value. In the early days, the problems associated with processing residual oil in the FCC effectively limited such feedstocks to a minor blending component of the total gas oil feed.

Residual feeds are difficult to process due to their high Conradson carbon residue (CCR) and metals content, which pose several challenges in the design of the unit. In the late 1970s and early 1980s, UOP worked with Ashland Oil to develop the UOP Reduced Crude Conversion™ (RCC) process, which was the first of its kind residue fluid catalytic cracking (RFCC) specifically designed to process up to 100% heavy residual oil. This process pioneered the use of two stage catalyst regeneration and external dense phase catalyst cooling. With the two stage regenerator and catalyst cooler, the challenge of processing feedstocks up to 10 wt.% CCR could now be met. The first RCC unit was commissioned in 1983 by Ashland Oil (now Marathon Petroleum Company, LLC) at its Catlettsburg, Kentucky refinery. The unit was designed to process a mixture of raw reduced crude (atmospheric tower bottoms), sour vacuum gas oil, deasphalted oil (DAO) and vacuum tower bottoms.

Paolo Palmas, UOP, a Honeywell Company, USA, traces the history of RFCC and provides guidelines for choosing the appropriate regenerator style.
In the 25 years since the initial commissioning of the Ashland unit, UOP has continued to develop and improve the RFCC process. Today, residual oil processing in the FCC is a routine objective that many refiners can employ to help improve refinery margins. This article presents a summary of the learnings and unit design advancements over the past 25 years, as well as guidelines for when a two stage regenerator is preferred over the more conventional single stage combustor style regenerator.

RFCC regenerator

Regenerator selection

The three parameters that are typically considered in regenerator selection are the feed CCR, the feed metals content and the expected regenerator temperature. The regenerator temperature is primarily a function of delta coke ($\Delta C$), which is the difference in coke content between the spent and regenerated catalyst and the net heat of combustion.

$$T_{\text{Reogen}} = T_{\text{Rx}} + \frac{\Delta C}{C_p} \left[ \Delta H_{\text{comb}} - \Delta H_{\text{air}} - \Delta H_{\text{loss}} \right]$$

Where: $C_p =$ catalyst heat capacity  
$\Delta C = $ delta coke

The net heat of combustion is dependent on the $\text{CO}_2/\text{CO}$ molar ratio in the flue gas due to the relative heats of combustion of coke to $\text{CO}$ and $\text{CO}_2$.

$$\text{C} \rightarrow \text{CO} \approx 3960 \text{ BTU/lb}$$

$$\text{C} \rightarrow \text{CO}_2 \approx 14150 \text{ BTU/lb}$$

The coke yield from the unit can then be written as:

$$\text{Wt.} \% \text{ coke yield on feed} = \frac{100 \left( \Delta H_{\text{feed}} + \Delta H_{\text{diluent}} + \Delta H_{\text{recycle}} + \Delta H_{\text{Rx}} \right)}{\Delta H_{\text{comb}} - \Delta H_{\text{air}} - \Delta H_{\text{loss}} \text{ BTU/lb}}$$

Note that the coke yield depends on the energy balance of the unit and is essentially independent of feed quality. The only term that is directly due to feed quality is the heat of reaction. The conversion and the cat:oil ratio are the variables that change with varying feed quality. In essence, conversion coke from a quality feed is replaced by contaminant coke from a poor feed at a correspondingly lower conversion.

Thus as the heat of reaction changes, there will be a change in coke yield; otherwise, the coke yield is set by the operating conditions imposed by the operator. When processing residual feedstocks with higher CCR, the catalyst cooler enables the operator to increase the heat of reaction to maintain higher conversion of feedstock to more valuable products. As the desired feedstock CCR is pushed progressively higher, contaminant coke replaces conversion coke and additional flexibility is required to maintain product margins. Designing the unit for partial combustion operation reduces the amount of heat release ($\Delta H_{\text{comb}}$) in the regenerator to enable maintaining high conversion with more contaminated feedstocks.
A simplification of the selection process is shown in Figure 1.

The objective of the process is to ensure reasonable regenerator temperatures and catalyst life. Since combustion of C to CO\(_2\) generates approximately 3.8 times the heat compared to combustion of C to CO, partial combustion is one of the ways of achieving the desired regenerator temperature. The other enabler is catalyst cooling, which can be applied to both full and partial combustion operation. As shown in Figure 2, there is some overlap in regenerator selection as a function of CCR. Much of this overlap is due to design flexibility that the refiner may, or may not want in the process design.

For units with feed CCR below 2.0 wt.%, the preferred choice is full combustion operation. The need for catalyst cooling is determined based on maintaining a regenerator temperature below 1375 °F. An increase in regenerator temperature leads to:

- Lower catalyst:oil ratio and a consequent loss in conversion.
- Higher catalyst deactivation in the regenerator due to hydrothermal dealumination of the zeolite.
- Higher non-selective thermal reactions in the reactor yielding more dry gas (C\(_2\)-) at the expense of valuable liquid products.

The addition of catalyst cooling removes some of the heat of combustion of burning coke, thereby lowering the normal operating temperature in the regenerator. The subsequent increase in catalyst:oil ratio enables the operator to maintain optimum feed conversion with progressively higher contaminant coke bearing (CCR) feeds. While this does result in a higher total coke yield for the operation, this is required to maintain high conversion of feedstock to LCO and lighter products. The alternative would be to leave a greater percentage of the feedstock as low value fuel oil (slurry oil).

In units with feed CCR above 5.0 wt.%, the amount of metals, primarily vanadium, accumulated on the equilibrium catalyst inventory is most often the governing factor in unit design. In the presence of steam and high temperature (regenerator conditions), vanadium forms vanadic acid, a highly mobile compound that moves freely across the catalyst surface. It reacts with the aluminum in the zeolite structure which dealuminates the zeolite, causing the crystal structure to collapse, resulting in catalytic activity loss.

The increase in metals directly impacts catalyst deactivation and the need for higher fresh catalyst makeup rate. As metals contamination increases, maintaining a moderate regenerator temperature becomes essential to minimise the harmful effects on catalyst activity. This can best be achieved in a partial combustion two stage regenerator, and is typically required when feed vanadium contamination meets or exceeds approximately 10 wppm.

**Single stage regenerator**

The combustor style single stage regenerator is the most appropriate regenerator style for applications where the feed CCR is below 5 wt.%. This style of regenerator can achieve a low level of carbon on regenerated catalyst (typically less than 0.05 wt.%), which is uniform through the regenerated catalyst. Bypassing of spent catalyst to the regenerated catalyst standpipe is physically impossible with this regenerator style.

The combustor style regenerator consists of a lower burning chamber (combustor), an internal riser (combustor riser) and an upper section (regenerator) that is essentially a disengaging vessel containing two stages of cyclones (Figure 3). The upper section holds a dense phase surge inventory of regenerated catalyst.

Spent catalyst from the reactor enters the lower section of the combustor where it meets with hot recirculated catalyst from the upper regenerator. Air enters the bottom of the combustor through a distributor. The spent catalyst from the reactor mixes with blower air and recirculating catalyst at the bottom of the combustor.
Catalyst regeneration, as a carbon removal process, is widely accepted as being first order with respect to carbon concentration and oxygen partial pressure. The change in coke concentration on a catalyst particle with respect to time fits the following equation:

\[-dC/dt = K_c e^{-\frac{\Delta E}{RT}} CP_{O_2}\]

Where:
- \(K_c\) - Frequency constant, (h\(^{-1}\)atm\(^{-1}\))
- \(C\) - Carbon on catalyst, wt.fraction
- \(P_{O_2}\) - Oxygen partial pressure, (atm)
- \(\Delta E\) - Activation energy, BTU/lb-mol
- \(R\) - Gas constant, BTU/lb-mol-˚R
- \(T\) - Temperature, ˚R

The circulation of hot regenerated catalyst from the upper section to the combustor raises the spent catalyst temperature and increases the coke burning rate due to the increasing rate constant. This relationship for the rate of carbon burning in FCC catalysts holds over a wide range of temperatures with diffusional limitation not controlling. The coke burn kinetic rate doubles approximately every 40 °F increase in temperature, and the fast fluidised regime ensures a high degree of heat transfer and even temperature distribution in a medium density catalyst phase approaching plug flow.

Air is used to burn the coke off the catalyst as it travels up the combustor and riser and all the burning takes place in these sections. The combustion gases and catalyst from the riser are separated in the upper regenerator by a ‘tee’ disengager. Catalyst falls into the upper annulus to form a dense bed, while the combustion gases and entrained catalyst pass through two stages of cyclones. Catalyst recovered by the cyclones is returned to the bed through the cyclone diplegs and the combustion gases leave the regenerator through the plenum chamber.

The regenerated catalyst is transferred to the reactor riser where it is lifted and then contacted with the feed. A number of metals typically found in the FCC feed are deposited on the catalyst. These metals, including nickel, vanadium, copper and iron can catalyse unwanted dehydrogenation reactions to produce large quantities of coke and hydrogen. A frequent method for expressing the combined contaminant potential of these metals is through the use of an equivalent nickel value, where:

\[\text{EqNi} = \text{Ni} + \text{Cu} + \frac{\text{V}}{4} + \frac{\text{Fe}}{16}\]

The hydrogen:methane ratio is an indication of metals catalysed dehydrogenation reactions. A sponge absorber off gas \(H_2/CH_4\) for uncontaminated catalyst should be 0.1 - 0.3. A figure of 1.0 or greater would indicate metals contamination.

When it is anticipated that the refiner will operate the dehydrogenation function of the active metals. The change in coke concentration on a catalyst particle with respect to time fits the following equation:

\[-dC/dt = K_c e^{-\frac{\Delta E}{RT}} CP_{O_2}\]

Spent catalyst from the reactor stripper enters the first stage along with combustion air from the main air blower. Approximately 75% of the total combustion air is consumed in the first stage with the remainder consumed in the second stage. Flue gas from the second stage travels up into the first stage through vent tubes located on the second stage head and any excess oxygen in this stream is utilised in the first stage. The combined flue gas exits through two stages of cyclones located at the top of the first stage regenerator. The combined flue gas is oxygen deficient with a typical \(CO_2/CO\) ratio of approximately 3.0, resulting in partial combustion overall. The flow through catalyst cooler cools the catalyst as it is transferred from the first stage to the second stage. A circulating catalyst standpipe is provided to move the remaining catalyst from the first stage to the second stage. A back mix catalyst cooler can be utilised to provide supplemental cooling. Regenerated catalyst from the second stage containing less than 0.05 wt.% coke on catalyst is transferred to the reactor riser, where it is contacted with the feed.

As previously discussed, vanadium is a catalyst poison that is most harmful in the fully oxidised \(V_2O_5\) state and in the presence of water at high temperature. Since hydrogen is oxidised very readily in the combustion process, most of the hydrogen from coke is converted to water in the cooler first stage and leaves directly with the flue gas. Subsequently the remaining hydrogen deficient coke is burned in an excess oxygen environment in the second stage.

In the second stage, the catalyst is fully regenerated at relatively low temperature and low water partial pressure but with excess oxygen. The second stage fully restores the catalyst activity to the circulating equilibrium level. The vanadium is fully oxidised in the second stage, but as the temperature and water partial pressure are much lower, it is less harmful to the catalyst zeolite.

The specialised lift gas system is designed to preaccelerate the catalyst to a lower density and more uniform average slip velocity prior to feed injection. A benefit of the system is the ability to use a light hydrocarbon stream such as recycled tail gas \((C_2)\) from the gas concentration unit as the lift medium in a controlled residence time lift section to passivate the active metals prior to feed injection.

The more common RFCC regenerator is a two stage regenerator within one vessel and a single flue gas stream exiting at the top of the first stage (Figure 4). The first stage operates in partial combustion while the second stage operates in complete combustion.

\[\text{Figure 7. Two stage regenerator air distribution improvement.}\]
Advances in single stage combustor style regenerator

Combustor style regenerators were first commercialised 35 years ago and currently number over 50 in operation. Many of the older regenerators have been pushed far beyond their initial design capacity so advances in the combustor style regenerator have been focused on improving unit reliability and increasing coke burning capacity.

Some of the reliability and capacity focused improvements are:

- The combustor air distributor has been redesigned to eliminate cracking and erosion (Figure 5).
- Catalyst coolers have been added where needed to process higher residue feeds.
- The earlier combustors were designed to mix the recirculation and spent catalyst in a riser prior to the combustor and then air lift the combined catalyst to the combustor. Modern combustors are designed to directly introduce both the spent and recirculation catalyst directly into the lower combustor without an external riser.
- The regenerator internal combustor cone has undergone redesign to resolve some of the earlier deformation problems. A new cone detail was developed to dissipate stress by incorporating a flexible, soft packed ceramic lining and a flexible skirt section that connects to the regenerator wall.

In order to increase the coke burn capacity of existing regenerator, two stages of cyclones in the upper regenerator have been replaced with a single stage (Figure 6). This allows for additional cyclones in the regenerator thus allowing for higher flue gas rates. The single stage cyclones are of a special high efficiency design. The increased efficiency of the single stage cyclone coupled with the separation efficiency of the combustor riser disengager results in an equal or in some cases better system efficiency than that of the two stage cyclone system.

Advances in two stage regenerators

Advances to the two stage regenerator have been focused primarily on improving the catalyst/air distribution and unit reliability. Since the initial 1983 implementation, the second stage air distributor has been redesigned to eliminate cracking and erosion. Extrusions are used for the main headers to eliminate stress concentrations and are fully hex lined for both erosion protection and to act as a heat sink to minimise stress concentrations, especially during startup and shutdown. Additionally, the distributor nozzles are dual diameter with a lower outlet velocity to minimise catalyst attrition and distributor jet erosion.

The air distribution in the first stage has also changed significantly since the earlier designs. The initial dome air distributor has been replaced with a multiple pipe grid design similar to that of the second stage to improve the air coverage across the regenerator (Figure 7). The vent tubes between the stages that distribute flue gas from the lower stage have been redesigned. The new vents have a simplified design and provided for better distribution of the oxygen rich flue gas from the second stage to the first stage.

Catalyst coolers

The UOP catalyst cooler is an external cooler that uses a dense phase catalyst bed (Figure 8). Heat removal is a variable easily controlled by adjusting the fluidising air and regulating the catalyst flow.

Catalyst coolers are a common feature of many of the RFCC units currently in operation. Since its commercialisation, this piece of equipment has undergone continuous improvements to extend the cooler duty and increase its reliability. The technology has evolved to a point that tube leaks are rare.

Improvements to increase the mechanical reliability have been made to the aeration system to ensure uniform distribution of air to the bundle along with changes to the metallurgy to improve against corrosion. Safeguards against plugging of lances have been incorporated in the design for turndown and loss of fluffing air. The tube bundle support system has also undergone change to reduce the cooler maintenance needs. Measures have also been taken to protect the cooler from debris, which could potentially affect the performance.

Since the initial installation in 1983, the cooler design has continuously evolved to meet the increasing need for heat removal in the regenerator. The initial catalyst coolers consisted of a 7 ft diameter bundle to generate 450 psig steam. Today, a variety of cooler diameters ranging from 6 - 9 ft, producing anywhere from 100 - 650 psig steam are available. The larger coolers have a duty of 200 million BTU/h.

Summary

Processing of residue containing feeds in UOP FCC units has increased steadily over the last 25 years with demonstrable unit reliability. This has increased refiners’ confidence in the ability of the FCC unit to process heavier and more contaminated feeds.

To date, 47 UOP units are operating with residual oil at feed CCR levels of 2% and above. This consists of units with varying regenerator styles from single stage to two stages. The innovation and reliability of the catalyst cooler has enabled users to extend their ability to process residual feeds in units with either two stage or single stage regenerators, with as many as four catalyst coolers mounted on a single regenerator.

Much of the earlier experience with single stage regeneration came from revamping of older units. As a result of this experience, many new units processing residual oil are being designed not only with two stages of regenerator but also with single stage regeneration. Finally, regenerator selection is highly dependent on feed quality with profitability favouring a two stage design for heavier, more contaminated feeds. Selecting the optimal regeneration technology is a crucial part of the unit design and in meeting the specific needs of each refinery project.