Take the heat off
Bart de Graaf, Eugenio Macaluso, Tom Ventham and Paul Diddams, Johnson Matthey Process Technologies
Explore how operators can increase profitability in delta coke constrained fluid catalytic cracking units.

The fluid catalytic cracking (FCC) unit is one of the most fascinating conversion units, and resides at the very heart of most complex refineries. It is an extremely versatile unit that processes many different types of feed, and is relatively easy to continuously adjust to maintain optimum product yield structure. Optimisation of the FCC unit is of key importance for overall refinery profitability; hence, the FCC performance weighs heavily in day to day considerations with refinery operations and process engineering personnel.

Fluid catalytic cracking unit (FCCU) profitability and operation depends on refinery configuration, feed availability and product demands. Regardless of the specific objectives, a well run FCCU should be run up against as many constraints as possible. This is clearly the most economic position for the refinery, but requires a careful and continuous balancing act by the operators and unit engineers. The main air blower, regenerator temperature and wet gas compressor are the most frequently occurring hard limits; however, cyclone velocities, hydraulic limitations in the main fractionator, or in different parts of the gas plant, and other variables, also deserve a place on the list. Each of these constraints requires a different approach. This article will examine effective catalytic solutions to increase the FCCU profitability when the unit is limited by one or all of the three main constraints listed above (main air blower, regenerator temperature and wet gas compressor).

**Challenges in residue operation**

Many FCC units process a feedstock comprising vacuum gas oil (VGO), plus some proportion of atmospheric residue. The key to increasing profitability in such FCC units is to maximise the amount of lower cost residue feed in the feed mixture. Residue feeds are low cost because processing them comes with a number of challenges, especially due to their higher contaminant metals (e.g., nickel and vanadium) and Conradson carbon residue (CCR or Concarbon) content, which lead to increased coke and gas make. Metals deposit can accumulate on the FCC catalyst, reducing its activity and selectivity, requiring increased catalyst addition rates to help compensate. The deposited metals also promote unwanted dehydrogenation reactions that produce additional coke, hydrogen and dry gas. Both the presence of feed metals and CCR have a major impact on the heat balance of the unit, catalyst activity and catalyst makeup requirements.

**Catalytic solutions**

Various catalytic solutions are available today to help cope with the different feed contaminant metals on the catalyst. Rare earths (e.g., lanthanum) are used, for instance, to stabilise the catalyst’s zeolite and reduce the deleterious effects of vanadium and sodium, while specialised low surface area alumina is often incorporated into the catalyst particle’s matrix to help handle high levels of nickel. High surface area alumina can also be utilised to improve the pre-cracking of very high molecular weight molecules, typically present in feeds containing high levels of CCR, to allow subsequent cracking on the zeolite part of the catalyst particles. Various other types of metal trap have also been incorporated into the catalyst particles, either integrally as part of the catalyst matrix, or as a separate particle to further mitigate the effects of contaminant metals that build up on the catalyst.

**Catalyst activity management**

Refiners processing high levels of residue in the feed have various options available for controlling catalyst activity, while aiming to minimise daily catalyst cost. Catalyst addition rate is used to compensate for a higher rate of deactivation in the unit, and also to control the level of contaminant metals building up on the catalyst particles via flushing. The level of contaminant metal a catalyst can tolerate depends on the catalyst design and how much coke and gas operators are prepared to accept. A unit running up against main air blower, regenerator temperature or wet gas compressor constraints will be forced to decrease percentage residue, and/or total feed rate, as metals levels increase on the catalyst.

Optimising the circulating catalyst’s equilibrium catalyst (ECat) activity level is a key factor in processing residue feeds, higher activity equilibrium catalyst leads to higher delta coke and lower catalyst circulation rates. Conversion is essentially determined by the number...
of active sites being circulated, i.e. is a function of catalyst circulation rate multiplied by catalyst activity. Finding the optimum trade-off between these two factors is very important. A lower activity fresh catalyst can be helpful when processing heavier feeds because increasing catalyst addition rate lowers the level of contaminant metals on the catalyst, thereby decreasing their negative effects.

Co-blending fresh catalyst with a purchased low metals equilibrium catalyst from another FCC unit is another option (flushing catalyst). Flushing catalyst effectively increases the overall catalyst addition rate and, therefore, decreases the level of contaminant metals on the circulating catalyst in the inventory. However, flushing catalysts inevitably come from FCC units that operate with light feeds and with limited amount of metals, hence these catalysts by design do not usually contain metals traps or other features to help protect them in a high metals environment, and are designed to target different product selectivities. This may be the lowest cost solution for coping with contaminant metals, but, in cases where high levels of flushing catalysts are used, yield penalties will usually outweigh the cost reduction.

Controlling delta coke
Coke formed on catalyst particles during the brief transit up the riser, together with unstripped products, is burnt in the regenerator to generate all the energy that is subsequently required to convert the raw feed into valuable products. The purest definition of delta coke is the mass of coke deposited on a mass of catalyst following a single pass through the riser/reactor. In other words, it is the mass difference between the coke on spent catalyst leaving the stripper (CSC) and the coke remaining on regenerated catalyst (CRC) after exiting the regenerator (delta coke = CSC - CRC). Delta coke is calculated as follows:
- Delta coke (wt%) = coke yield (wt%)/cat-to-oil ratio (w/w).

Mathematically simplifying the heat balance demonstrates that delta coke is directly proportional to the difference between the regenerator temperature (RgT) and reactor temperature (RxT):
- Delta coke = K x (RgT - RxT)

This means that for a constant reactor temperature, the regenerator temperature is directly proportional to the delta coke. Accordingly, everything affecting delta coke has a direct impact on regenerator temperature:
- RgT = 1/K x delta coke + RxT.

Where 1/K is typically about 250 when temperatures are in centigrade.

Delta coke components and determinants
There are four main contributors to delta coke: conversion, contaminants, Concarbon and cat/oil.
- ‘Conversion’ coke, also called ‘catalytic’ coke, is a consequence and byproduct of the main catalytic reactions that occur in the riser; its contribution to the total delta coke increases with increased conversion.
- ‘Contaminant’ coke is associated with the de-hydrogenation reactions catalysed by the feed contaminant metals; its contribution to total delta coke depends on ‘active’ metals types and levels accumulated on the catalyst (‘active’ because some of the metals may be passivated using effective metals traps).
- ‘Concarbon’ coke is associated with the heaviest part of the feed that is most difficult to crack, resulting in its deposition on the catalyst.
- ‘Cat/oil’ coke accounts for unstripped hydrocarbons remaining with the catalyst as it enters the regenerator; its contribution to the total delta coke increases with poorer stripping efficiency. Unstripped products have the highest hydrogen content, resulting in production of steam and local hot spots on catalyst particles when combusting in the regenerator.

Controlling regenerator temperature
Several options are available for the refiner to control regenerator temperature or manage operations at higher delta coke. Mechanical solutions usually require large capital investment, such as the installation of a catalyst cooler, feed pretreatment system, or operating the regenerator in partial combustion mode through the addition of a steam generating boiler (CO boiler).

A cat-cooler requires increased delta coke by increasing heat demand in the regenerator. The heat is utilised to produce high pressure steam as a byproduct, which has value to the refinery. The heat sink effect of increasing cat-cooler duty allows the FCC to run heavier feeds on a constant maximum regenerator temperature limit. This requires more coke combustion, which may relocate the unit constraint to the main air blower. Therefore, although the cost of a cat-cooler is substantial, it allows for the processing of lower cost heavier feeds, providing net benefits that may ultimately outweigh the outlay cost.

Switching the regenerator from full burn to partial burn mode also demands more delta coke at constant maximum regenerator temperature. However,
this assumes the availability of another expensive piece of equipment: a CO boiler. Running with a sub-stoichiometric oxygen to carbon ratio leads to the combustion of coke to a mixture of carbon dioxide (CO₂) and carbon monoxide (CO), rather than completely to carbon dioxide. The heat of combustion in the regenerator is thereby reduced (with excess energy being shifted to the CO boiler), resulting in an increased demand for delta coke in the regenerator at constant maximum regenerator temperature (the deeper into partial burn one goes, the higher the delta coke demand). With a lower oxygen to carbon ratio available in the regenerator, in partial burn the effectiveness of coke combustion suffers somewhat, leading to higher carbon on regenerated catalyst (CRC) going back to the riser. CRC needs to be carefully monitored to prevent a rapid decline in observed unit conversion. Many FCC units do not utilise all of the decrease in heat of combustion to run heavier feeds. Quite often, running with a lower regenerator temperature (below the unconstrained) is favoured – this is usually where the main air blower is the unit constraint. In such cases, the operator should look into additional options, such as additional air blowing capacity or oxygen enrichment. A side benefit of partial burn operation is that catalyst deactivation by vanadium is somewhat slower, because vanadium mobility is lower, leading to a lower rate of zeolite destruction.

Other options are available for FCC operators to accommodate running higher levels of residue at higher delta coke, without huge capital investments – the easiest one being to reduce conversion levels. This can happen via adjustments of combined feed temperature, riser temperature and/or catalyst make-up rate. In these cases, the contribution from catalytic coke is reduced, allowing higher contribution from the contaminant coke and Concarbon coke components. Sacrificing some conversion is often the most economical solution, leading to higher unit profitability due to increasing the proportion of lower cost incremental residue in the feed, but the optimum trade-off between increased residue rate and lower product values needs rigorous calculation. Good stripper design and operation will also help reduce regenerator temperature by minimising the amount of entrained hydrocarbons entering the regenerator, hence reducing ‘cat/oil’ coke.

FCC additive solutions to reduce delta coke

FCC additives can be effective in reducing delta coke via various mechanisms. One of the most obvious mechanisms is the use of a separate particle metal trap. By adding metal trap functionality, ‘contaminant’ metal activity is reduced, meaning less coke and hydrogen formation. Metal traps can also be incorporated into the base catalyst. However, the advantage of putting the

---

**Figure 1.** Coke yield for base catalyst with and without LO-COKER.

**Figure 2.** Delta coke for base catalyst with and without LO-COKER. The advantage in delta coke is obtained while maintaining conversion.

Reprinted from Hydrocarbon Engineering, September 2016
metal trap into a separate particle is that it allows more effective and diverse materials to be utilised; materials that could not be used in the base catalyst and are only useable in an independent separate particle.

The use of basic materials, such as earth alkaline metal oxides, has shown to exhibit a synergistic effect with active FCC catalyst matrices in converting the Conradson carbon residue part of feedstocks into useful products. Investigations into the exact mechanisms and why this synergy occurs is ongoing – the current description is based on empirical data collected from small scale test units (ACE), from pilot plant data, and from various commercial applications. A parallel theory suggests that the large amount of mesopores present in this type of additive gives the benefit of reducing ‘cat/oil’ or strippable coke.

The new Johnson Matthey LO-COKER® delta coke reducing additive incorporates all of the above functionalities (metal trapping, synergistic effect with an FCC matrix to enhance pre-cracking of CCR feeds and improved porosity for better strippability), plus a higher heat capacity, which will improve the rate of heat transfer from the regenerator to the riser more efficiently.

**Testing results: ACE pilot plant studies**

Extensive laboratory work has been carried out to optimise the formulation of this new and revolutionary FCC additive, not previously attempted by any other catalyst vendor. It is specifically designed to lower delta coke and reduce dry gas make.

The following data has been collected from ACE pilot plant studies using a fresh catalyst formulated for moderate residue operation as a base case. Both sets of fresh catalyst and the 90/10 blend of fresh catalyst and LO-COKER additive are deactivated following the standard deactivation procedure: metal deposition on 11 cracking/regeneration cycles targeting 2750 ppm of vanadium and 1650 ppm of nickel and steam deactivated at 788°C for 10 hours with 70% steam.

Testing results show significant reduction in both coke yield and delta coke on the one hand, and dry gas and hydrogen on the other (Figures 1 - 4). These results stem from various functions of the synergy of additive and base catalyst: mitigation of metal effects, increased mesoporosity and improved matrix activity.

The refinery can take advantage of this improvement in coke selectivity by increasing conversion, to increase feed rate or to increase the amount of residue in the feed. The FCC unit will continue to be operated against all of its constraints, but at a substantially higher profitability than the previous point.

This reduction in both dry gas and H₂ yield debottlenecks a wet gas constrained FCC unit, enabling processing of heavier
feeds, increased feed rate, operating the unit at higher severity, or providing the ability to target higher LPG yields.

**Comparing additive delta coke reduction with cat-cooler duty**

In order to get a better idea of the order of magnitude of what an additive can do for a delta coke constrained FCC unit, the way in which a 5% and 10% reduction of delta coke impacts the energy balance of an FCC unit has been calculated. Represented here are two real case studies, by applying a typical FCCU heat balance calculation.

On a 75000 bpd residual fluid catalytic cracking (RFCC) unit operating with a cat-cooler, a 5% delta coke drop results in a cat-cooler duty reduction of 45 GJ/hr (at a constant regenerator temperature, cat/oil, feed rate and feed quality). This is equivalent to about 70% of the duty of this cat-cooler.

On a 90000 bpd FCC unit operating without a cat-cooler, a 10% delta coke reduction is equivalent to operating the unit with a cat-cooler operating at a duty of 95 GJ/hr. This means a unit originally designed to process clean feed can now function with much heavier feeds, whilst avoiding the need to install a full size cat-cooler.

**Conclusion**

Use of additives can unlock additional options to maximise FCC unit profitability. This new and unusual additive concept is clearly highly effective in reducing delta coke, hydrogen and dry gas make in pilot plant testing. Use of the LO-COKER additive can offset the need for large Capex projects, such as feed pretreatment or a catalyst cooler, and allow for the processing of heavier, lower cost feedstocks, while staying within regenerator temperature, air blower and wet gas compressor constraints.

Information contained in this publication or as may be otherwise supplied by Johnson Matthey is believed to be accurate and correct at the time of publication and is given in good faith. JOHNSON MATTHEY GIVES NO WARRANTIES, EXPRESS OR IMPLIED, REGARDING MERCHANTABILITY OR FITNESS OF ANY PRODUCT FOR A PARTICULAR PURPOSE. Each User must determine independently for itself whether or not the Products will suitably meet its requirements. Johnson Matthey accepts no liability for loss or damage resulting from reliance on this information other than damage resulting from the death or personal injury caused by Johnson Matthey’s negligence or by a defective product. Freedom under Patent, Copyright and Designs cannot be assumed.