Victor Scalco, General Atomics, USA, explains how fines control in the catalytic process can help to increase profits from the 'bottom of the barrel'.

THE CURE TO SEPARATION ANXIETY

The refining and petrochemical industries are facing a variety of challenges in the area of propylene production with heavier crude slates. Historically, fluidised catalytic cracking (FCC) and residual fluidised catalytic cracking (RFCC) have been the main processes to upgrade low value feedstocks to higher value products. In today's advanced refining industry, modern FCC/RFCC technologies are designed to drive higher propylene yields to increase profits and improve a refinery's bottom line. While increasing higher value yields throughout a refinery is beneficial to the refiner, managing fines control in a concentrated residual slurry has become a greater challenge.

The petroleum industry requires a new method for removing fine solids from refinery streams. Excessive catalyst fines in the catalytic cracking process' main column bottoms can make the solids material unsuitable for carbon-black feedstock or fuel oil. Just as important, solids in many streams cause plugging of fixed-bed reactors and fouling of heat transfer and other equipment, directly adding to maintenance, blending and other operating costs. Conventional membrane-type filters have been used to reduce these problems, but as stream-solids content increases, filter operating, maintenance, and replacement costs become more problematic and costly.

This article will outline the benefits of proper fines control in the catalytic processes of FCC, RFCC, and deep catalytic cracking (DCC) to increase profits from the 'bottom of the barrel.' Clarified slurry oil has great earning potential when applied to make speciality product feedstocks, higher value fuels and blend stocks. At the same time, reducing erosion and disposal concerns also has an immediate impact on the bottom line.[1] This article will illustrate how the application of an electrostatic separator at a Middle Eastern refinery helped to significantly reduce catalyst fines. When compared to

Table 1. Typical slurry oil properties ranges from a number of FCCs[8]

Property	Range (minimum to maximum)
API gravity	-6 to + 8
Sulfur (wt%)	0.3 to 5.0
Nitrogen (wt%)	0.1 to 0.5
Nickel (ppmw)	0 to 110
Vanadium (ppmw)	5 – 200
Asphaltenes (vol.%)	0 to -8
Solids (ppmw)	1000 – 6000

Table 2. Particle size distribution ranges from a variety of slurry oils[8]

Particle dia.	% in range
0 – 5	30 – 60
5 – 15	30 – 55
15 – 25	2 – 12
25+	1 – 5

other installed systems used for slurry oil clarification, including mechanical filtration and settling tanks, the refinery's selection of the more efficient electrostatic separation method proved paramount in helping to increase profits and reduce waste throughout the refinery.[2]

Slurry oil yields and properties

Slurry oil yields from FCC and RFCC are a function of the severity of the operation. Yields are generally inversely proportional to factors such as catalyst activity, temperature, catalyst to oil ratio, etc., and are directly proportional to the nitrogen, sulfur and asphaltenes (or alternatively vacuum bottoms) content of the FCC feed. Slurry oil yields ranging from approximately 1 to 2 vol.% for paraffinic feeds to as much as 15 vol.% on RFCC feeds have been observed.[3]

As might be expected, slurry oil quality is a function of such variables as the properties of the FCC feed, severity of the operation, type of catalyst, operating conditions in the fluidised catalytic cracking unit (FCCU), etc.[4]

The main concern with concentrated slurry is the presence of asphaltenes, which are large chemical structures with a high ratio of carbon to hydrogen. They contain nickel and vanadium, which promotes coke generation when deposited on FCC/RFCC catalysts. These are complex structures and are difficult to describe chemically. Instead, asphaltenes are defined by their solubility:

- Materials that are insoluble in an excess of n-heptane (or less often, n-pentane).
- Those materials that are soluble in benzene.

When cracking residual feedstocks, the FCC catalyst pore size is not large enough to allow the large asphaltenes structures to enter the pores of the catalyst. The level of conversion of asphaltenes in an RFCC unit is then a function of the activity of the matrix of the catalyst.[4] If the FCC feed contains significant levels of asphaltenes, as it would in RFCC, the slurry oil will likely contain higher concentrations of asphaltenes. When asphaltenes are present, nickel and vanadium will be present on the catalyst and initially deposited as part of the coke on catalyst and in the slurry as metalorganic compounds. Catalyst particles in the slurry, besides containing nickel and vanadium, also bring in sodium and trap iron. Antimony and tin, which are used as metal passivators, may be present on the catalyst or in the slurry oil as well. Other FCC additives are used to control carbon monoxide, sulfur oxide and nitrogen oxide emissions, and metals traps may reside in the slurry oil, all of which contain a variety of other elements that make removal extremely difficult.

Recycling smaller micron particles is crucial for RFCC and FCC fluidisation. BASF catalyst manufacture relies on a certain amount of fines that are 45 µm and smaller, for proper fluidisation of the catalyst within the reactor. Note that for these slurry oils, over 90% of the particles range in size from 0 to 25 µm dia. This means that very large holding tanks and long holding times are required to meet higher value product specifications. Some relief is obtained with the use of settling aids[5] in this service. Sludge from slurry oil holding tanks, however, is listed as hazardous waste by the US Environmental Protection Agency (EPA), requiring more frequent tank cleanings and the increased associated expense.[4]

Slurry oil particulate removal technologies

Historically, holding tanks have been used to allow solids to settle out of the slurry oil. The resultant decant oil solids content are a function of the sedimentation tank design, the physical characteristics of the slurry, the temperature of the storage tank, and whether or not settling aids are used. In addition to generating clarified oil, sludge results from the settling process. Slurry oil holding tank sludge is classified as hazardous waste. Depending on the tank size and rate of slurry oil production, treatment and disposal cost estimates are US$1 – 4 million per cleaning. In the absence of countermeasures, increasing resid feed to the FCCU will increase the rate of slurry oil production and sludge formation.[6]

Membrane filters were first put into slurry oil service around 1990. Mechanical filtration operates at temperatures up to 600°F and employs tubular porous metal elements. The solids collect on the inside of the elements, while the filtrate passes through to the outside. Some filters use porous sintered woven wire mesh metal filters and operate at 400 – 650°F, while others employ a 2 – 5 µm woven wire filter element, using light cycle oil (LCO) as a backwash at 350°F and claim 85 – 95% solids removal from the feed slurry. Use of these filters in the area of slurry fines removal, especially in the RFCC process, has become unreliable. In many cases, elements are completely clogged by asphaltenes and waxes, causing the unit to become inoperable. Upon inspection, many elements show high evidence of erosion during turnaround or unscheduled maintenance. In the case of replacement, over 300 elements are affected and maintenance costs are substantial.[6]

Electrostatic precipitators are routinely used to remove catalyst fines from the FCCU stack. An electrostatic

Table 3. Electrostatic separation vs mechanical filtration. Economics based on 49 tph - 8558 bpd slurry (design) Middle Eastern Refinery RFCC

	Electrostatic separation	Mechanical	~ ES economic value	Comments
HCO back flush medium impact	0 bpd (raw feedback flush)	8558 bpd (slurry) * 4% = 342 bpd	US$5 367 690/y savings	342 bpd * 365 days * US$43/bbl
RFCC overall production yield impact	0 bpd displacement of RFCC feed with HCO	(342 bpd) 4% HCO backflush will have -2% impact on overall production yield	US$6 865 650/y savings	171 bpd * US$110/bbl, conversion lost production
Market 'conversion' impact	Increased sub-micron removal: instantaneous	3 months off spec product to develop cake (initial commissioning and every time the filter has to be taken offline for repair – average one month per year)	US$4 621 320/y increased revenue from clarified slurry oil (CSO) market (numbers for first year and start up only)	US$6/bbl * 8558 bpd (slurry) * 90 days

separator uses a similar principle to remove solids from liquids. For over 30 years, electrostatic separation has evolved to be a robust, proven, automatic process to remove FCC catalyst fines from slurry oil or other hydrocarbon streams. Unaffected by the presence of asphaltenes, electrostatic separation can be used to remove solids not only from resid FCC derived slurry oil but also from gas oil crackers. Operating at 160°C – 220°C, electrostatic separators use depolarised glass beads to departiculate fines from the product stream. The fluidised glass bead allows for a low pressure drop and is not susceptible to blockage from asphaltenes or waxes. Even the presence of antimony does not cause issues within the system.[7]

Economics

Recently, a Middle Eastern refinery installed an electrostatic separator to replace a failed mechanical filtration unit. The refinery conducted an economic study to evaluate the impact of the change in separation and filtration technologies. Several advantages became evident once the electrostatic separator unit was put on line, including the following:

- The increased quality of clarified slurry oil and proper fines removal provided a fast return on investment (ROI), offering increased profit realisation within months.
- The use of raw FCC/RFCC feed enabled the refinery to realise all the LCO and heavy cycle oil (HCO) for production. The mechanical filtration unit was depriving the RFCC of valuable HCO for backflush and increased overtime due to the constant blockage of the system's cartridges. The new electrostatic separator utilises FCC/RFCC feed as the backflush medium, allowing the reactor to run at full production with the reduction of HCO recycle.
- The recycling of small fines showed a reduction in catalyst uptake due to longer reaction time and increased fluidisation within the reactor. As mentioned earlier, catalyst savings might vary depending upon residual units due to multiple factors, but still remain significant. Individual cases involving deep resid cracking benefits should be calculated based on a thorough knowledge of the RFCC feed, operating conditions, catalyst characteristics, etc. It is important to note that smaller catalyst particles returned to the unit have an inherently larger surface to volume ratio and could have a considerably higher resid cracking activity than the larger equilibrium catalyst held in the unit. This is an advantage when separating with electrostatic separation due to the ability to collect sub-micron particles, too small for mechanical filtration, during the separation stage.

Conclusion

The lack of new refinery construction, ongoing environmental enforcement concerns, and mandated product quality issues have increased capital addition and operating costs while reducing flexibility. The challenge for refineries is to process crude into quality oil products by removing the impurities as efficiently as possible, while considering the environment. Each refinery is limited by two main factors in this area: the products that the refinery is designed to create and the quality and characteristics of the crude oil used to create these products. From a filtration standpoint, slurry oil/FCC fractionator bottoms is one of the most challenging applications for a refinery. The electrostatic separator provides an economic and efficient solution to removing the catalytic fines that would otherwise devalue residual fuel oil (RFO) and feedstock products. Every refinery with an FCC/RFCC unit has this need to highly concentrate solids in the slurry oil into a small volume for easy recycling, while maximising the recovery of saleable clarified oil.

By decreasing the operating temperature and not having to use increased pressures for back washing, the electrostatic separation process reduces overall operational cost, maintenance and downtime. These factors provide valuable returns from the 'bottom of the barrel.'

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