RACING TO FIND THE RIGHT SEPARATION TECHNOLOGY

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Vic Scalco, General Atomics Electromagnetic Systems, USA, details the importance of selecting the correct separation technology in order to support growing petrochemical demand.

The global pandemic, economic slowdown, and instability caused by regional conflicts have significantly impacted the approximately 735 petroleum refineries worldwide. Today's highly complex and competitive refining environment, coupled with eroding profits and difficulty maintaining a positive bottom line, is forcing over half of these refineries to seek new market opportunities from the bottom of the barrel in order to remain competitive. In addition to this, compliance with tougher climate regulations is further taxing refineries' ability to invest in technology innovations to help keep pace with changing market demands, while maintaining profitability.[1]

Refining management's balancing act between new technology investment and increasing revenue potential is driving a trend toward utilising severe catalytic cracking technology to increase profits while taking advantage of the existing crack spreads. Over 18 million bbl of crude oil are processed daily through a fluidised catalytic cracking (FCC) system, along with three-quarters of worldwide gasoline. FCC systems have become the refinery's most versatile operating units to improve the bottom line. With the increase in crude prices, environmental compliance cost, and current International Maritime Organization (IMO) 2020 regulation enforcement, the spread between lighter, less severe crudes and heavier, opportunistic crudes will become a bigger part of the refining sector's economics. The FCC's capability to convert heavy atmospheric gas oils, vacuum gas oils, and atmospheric resids into more valuable gasoline and middle distillates can be exploited to support more positive profit margins.[2]

Heavier, opportunity crudes are pushing the limits of catalytic cracking. Refiners are increasingly considering the utilisation of more complex technologies for deeper conversion of challenging feedstocks arising from the processing of opportunity crudes. There are a range of technologies tailored for processing heavier crudes and producing high-quality final products. As the future of refining has the industry moving towards the use of higher severity conversion units and synthetic crudes, the FCC will remain the workhorse of the refinery.

Asia joins the race

In Japan, approximately 30 petroleum refining companies are utilising FCC or resid fluid catalytic cracking (RFCC) units to produce propylene, LPG, gasoline and light oil. S-Oil Korea installed its first high severity FCC, and PERTAMINA Indonesia is investing in new RFCC units to increase overall international market supply. India is expanding its ability to produce polypropylene through RFCC units, as petrochemical feedstock production is in high demand. New products generated from these RFCC units can be consumed in the global market for transportation, power generation, and petrochemical supply, or shipped as a product blended for marine fuel. With years of operation in the RFCC market, Asia is now faced with a need to generate increased profits in a competitive environment, and will have to address applications for the bottom of the barrel streams from these units ladened with concentrated catalyst.[1]

The challenge

Creating greater profits from an FCC unit comes with a cost. Driving the FCC technology into higher severity for increased propylene demand for petrochemical feedstocks is a growing trend. Along with fuel gas, C3S and C4S, FCC units also produce a 650+°F heavy aromatic oil, known as slurry oil, as a byproduct. Slurry oil nomenclature refers to the catalyst fines carried over from the FCC reactor which end up in these bottoms. Because catalyst fines must be separated or be allowed to settle out of the oil, the product is more correctly referred to as main column bottoms (MCB), decant clarified oil (DCO), clarified oil (CO), or clarified slurry oil (CSO).[3]

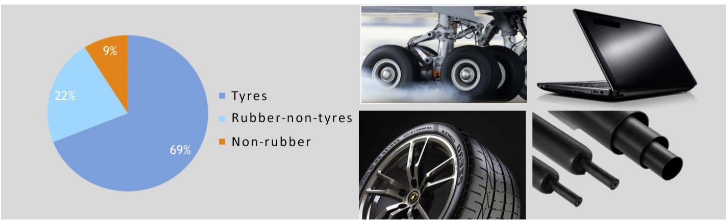

Figure 1. Carbon black industry supply.[3]

Table 1. Typical slurry market feedstock properties[4]

CSO market/opportunity	CSO clarity (ppm)
Carbon fibre feedstock	5 – 10
Carbon black feedstock (specialty)	10 – 20
Hydrotreater feedstock	10 – 50
IMO 2020 marine fuel	50 – 60
Pitch feedstock	25 – 100
Needle coke feedstock	25 – 100
Refinery fuel	50 – 100
Carbon black feestock (tyre)	100 – 500
Hydrocracker feedstock	200 – 300

Slurry oil is the lowest-value stream produced by an FCC unit (FCCU), representing only 3 – 7 vol% of the total products. A typical 50 000 bpd FCCU would produce 2000 bpd or 125 000 tpy of slurry oil as a byproduct. The quality varies according to numerous factors including crude oil origin, FCC design, and fractionation equipment. The two most important factors affecting quality are catalyst type and conversion level. Quality may also vary for marketing reasons by dilution in the FCC fractionator with heavy cycle gas oil. Table 1 shows the typical concentration range of catalyst in marketable slurries.[3]

Meeting market demands

Severe FCC feed hydrodesulfurisation can reduce the sulfur content of slurry oil to less than 0.5 wt%, however the hydrotreating would result in decreased slurry aromaticity unless conversion is greatly increased. Currently, approximately 40% of the US FCC feed is hydrotreated primarily at mild conditions so that slurries contain 0.5 – 1.5% sulfur. Refiners do not desulfurise FCC feed just to lower the slurry oil's sulfur content; they have other objectives such as lowering gasoline sulfur, reducing sulfur emissions from catalyst regeneration, improving product yields and quality, or meeting new market requirements. Efforts to meet the IMO 2020 marine fuel regulation entail a joint process of hydrodesulfurisation to less than 0.5%, and fines removal to comply with less than 50 ppm catalyst fines required by MARPOL IV.[2, 5]

Sediments are composed of large particles that are greater than 20 μm, while filterable solids are composed of smaller particles typically in the range of 20 μm to submicron level. The sources of the solids are iron sulfide, silica, clays, scales, ash, coke, and catalyst fines. Feedstock contamination starts upstream after the desalter, reaching downstream of the catalytic cracking unit. While new catalysts, co-catalysts and additives benefit the process, they simultaneously add more sediments, solids, and poisoning metals to the bottom of the barrel, creating more challenges facing the removal of these contaminants. Severe catalytic cracking activities come with the challenge of producing a higher concentration of these sediments and filterable solids within the slurry oil stream.[6]

Ash, or catalyst fines, are a particular problem for slurry, especially for heavy and viscous oils that require long residence time to allow for catalyst settling. Obtaining low ash (less than 0.05 wt%) requires dedicated techniques, such as specialised catalyst selection, heating, chemical additives, separation technology, electrostatic precipitators, centrifuges and cyclones. The selection of an attrition-resistant catalyst helps to a great extent, and a few refiners buy higher-priced hard catalysts to alleviate ash problems in slurry oil. If a higher-priced catalyst or the idea of a new upper cyclone system is not an option, the challenge of catalyst fines separation and the recovery of lost profits can be efficiently addressed by adopting the right (MCB) separation technology.[7]

The race for profits

Higher severity FCC units operate at critical conditions and concentrations in the production of higher ends for petrochemical feedstock supply. This makes the process more challenging, especially at the bottom of the barrel where high concentrations of solids, contaminants and catalysts are undermining the possibility of upgrading the slurry oil stream. Upgrading catalytic cracking technology must coincide with increasing efficiency, reducing maintenance cost, and improving the catalyst equilibrium cycle. Removing solids and ultimately increasing the lifespan of the FCC system is part of this equation, and is directly related to incrementing the bottom line in refining.

The success of higher severity production relies on providing clarified slurry oil at < 50 ppm to maintain a marketable DCO. Several different filtration and separation technologies have been reviewed to find the most suitable solution capable of upgrading the challenging DCO stream. Many refiners 'de-ash' with chemical aids to accelerate ash settling in storage. These chemicals are polymeric compounds that adhere to the catalyst surface, causing agglomeration of the fine particles to accelerate separation.[8] For some time, refiners have found it economical to cat crack increasing quantities of 1000+°F boiling material. Current analysis shows that approximately 40% of the industry is cracking some resid. Cracking an unhydrotreated resid might result in a heavier, more viscous slurry oil with low aromaticity and high metals content. When resid is added to an existing FCC, ash separation might be more difficult because the catalyst removal system must handle a greater volume of more viscous slurry.[9]

Settling tanks for decanting slurry oil have been in use for more than 40 years, and this remains the most popular separation process for removing catalyst in slurry oil. Today, over 61% of refineries use settling tanks to separate catalyst and other contaminates from slurry oil. The settling process is very lengthy and creates a larger challenge once the tank is full of sediment. Refineries must resort to using settling agents to assist in speeding up the process. This creates sludge, hazardous waste, and increased cost over time for the refinery. One tank per year can cost a refinery US$40 000 in settling agent, US$500 000 in cleaning and maintenance, and US$150 000 in landfill and waste disposal fees. This represents approximately US$690 000 in increased costs to accomplish a bunker fuel at 500 ppm. DCO resulting from the settling tank process will continue to experience rising costs as environmental laws direct the handling of hazardous waste, and as the decline in construction causes stockpiles of dried catalyst to collect at concrete kilns.[8]

Figure 2. Slurry oil settling tanks.

In addition to recovering profits eroded by tank settling, by installing catalyst fines separation technology at the outlet of the FCC slurry oil rundown, most of the fines can be collected and sent back to the riser. With this technology in place, the returned catalyst fines would support fresh catalyst reactivity while finding more acceptable avenues of escape via gas scrubbers, electrostatic precipitators, and spent catalyst collection hoppers, ultimately leaving through the flue stack. Additional profit recovery occurs by removing fines from escaping through the bottoms circuit and rundown to tank settling. By keeping the fines out of this process, the refiner can realise additional profit by adding the now-retired settling tank to a refinery's marketable inventory tank list. This is an added benefit to any refinery, and could be worth as much as US$1 million in annual revenue.[9]

World demand for refined products is unique to the domestic market and international demand for each region. North American FCCs operate at high severity to maximise gasoline and polypropylene. The result is a very heavy, aromatic decant oil. Due to low fuel oil production and specific-gravity limits, US refineries are only able to blend low quantities of decant oil in resid, allowing the excess to be sold for other uses such as carbon black feedstock.[10]

The quality of CSO for carbon black feedstock can generate as much as US$18.00/bbl of increased revenue, and increase middle distillate inventory. With separation technology in place, a refiner can increase annual revenue by not having to use heavy cycle oil (HCO) or light cycle oil (LCO) as cutter stock with the CSO to meet lower concentration specifications, and more middle distillate can be used to produce lighter products such as diesel. Regarding the use of LCO, mechanical filtration is limited in backwash mediums, and costly HCO/LCO is required for back washing the filters. Electrostatic separation, however, provides an economic advantage over other processes. This technology uses raw feed from the FCC/RFCC for back flushing and does not decrease the overall production of the reactor or rob valuable lighter products. Middle distillate production is therefore increased, along with profitability.[3]

CSO used as carbon black feedstock carries the best value in lower conversion markets. When sourcing markets for MCB production, whether it is marine fuel or highly-profitable specialty carbon black feedstock, a refiner must decide to increase the quality of the CSO to meet the unique specification for each market. The efficiency and reliability of the fines removal technology is critical to realising increased profits from these markets. The properties of MCB make it difficult to find a solution without understanding the downsides of each technology. Centrifuges have been found to be unsafe and inefficient over time. Decanting or settling is only able to provide bunker-grade products with long residence time. With the heavy asphaltene and coke content in severe RFCC or FCC operation, mechanical filtration solutions become blocked or severely eroded, requiring complete disassembly or replacement of costly cartridges in order to continue operating. Other technologies are susceptible to plugging or blocking due to the inherent plugging properties.[6,7]

An electrostatic separator system, referred to as the 'Gulftronic® Electrostatic Slurry Separator', has been found to work in concentrated slurries without plugging or blockage. The electrostatic separator for slurry oil operates continuously without plugging or blockage from asphaltenes, with an efficiency at the outlet averaging < 10 ppm catalyst fines after separation. To successfully increase refinery profits from the bottom of the barrel, proven robust technologies such as electrostatic separator technologies are needed to handle the challenges accompanying high severity processing while driving the FCC to increase propylene yield.[2]

Active response

There are three factors that should be considered when determining the feasibility of separation applications to downstream refinery processes. The first is refinery economics. Not all refineries with the FCC or RFCC process have the economic parameters needed to justify the installation of a catalyst fines removal system. The second is the severity of the fines. Controlling the quality of the slurry oil produced can influence the refinery's marketable products and downstream maintenance. The third is the cost associated with the environmental impact of removing catalyst fines and particulates from the settling tank.

Not all refineries using FCC/RFCC have a market or economic requirement for producing CSO < 100 ppm. Slurry oil is typically 6% of the overall production of the FCC when the focus is on making transportation feedstock. If an FCC is smaller than 30 000 bpd, the economic driver to upgrade a small amount of slurry is not beneficial, and it becomes more economical to blend cutter stock to meet desired specifications. Larger complex refineries processing over 30 000 bpd are in the best economical position to increase profits from departiculating process streams such as slurry oil.[10]

Aside from the profitability of increased production and middle distillates, consideration should also be given to decreasing downstream maintenance and downtime. With over 60% of the fines in slurry oil's distribution being < 15 µm, it is very difficult for mechanical filtration or centrifuges to capture smaller fines. Instead, these processes allow them to pass through. The corrosive element of catalyst passing downstream erodes valves and other critical piping systems.

Taking control

A reactor running at 80 000 bpd can produce 5600 bpd of slurry. At this production level, over 16 t of new catalyst is added to the FCC. With constant unit operation, cyclones in the reactor release fines and, over time, larger catalyst can escape through this process. With the proper separation technology in place, lost catalyst, especially in older FCC units, can be recovered and sent back to the riser. This adds greater attrition to the life of the catalyst equilibrium cycle in the FCC, and assists in better production and operation of the unit. With the recovery of 1900 tpy, savings of over US$1.6 million could be claimed just in catalyst loss and environmental savings.

Conclusion

The evolution of the refining industry is racing toward more severe catalytic cracking technologies that are capable of processing heavier opportunistic crudes and meeting the profitable petrochemical demand. Refining improvements and petrochemical integrations are allowing for refineries to make increased profits from every barrel processed. Implementing more severe catalytic technologies is an important step toward improving refinery flexibility. However, as licensors begin to develop new innovative processes and the demand for new synthetic pyrolysis oil blended crudes becomes more of a reality, the need for selecting the right separation technology is critical.

Regardless of the separation path chosen, spent catalyst removal and waste management will remain one of the most difficult processes in the refinery. Settling is expensive in terms of lost time and profits. Mechanical separation processes are limited and come with costly downtime and maintenance schedules. The refining industry has evolved away from centrifuges, and filtration technology is becoming harder to operate in the more concentrated slurries. Electrostatic separation is a proven solution for trouble-free separation of high severity FCC and RFCC slurries. The solution exists with the technology of today to increase profits from new markets or recover profits from lost revenue for every refinery with an FCC or RFCC. It is now up to the refiner to take advantage of this solution.

References

1. Website data from http://abarrelfull.wikidot.com/
2. SCALCO, V. M., 'The plight of the modern refinery: racing to meet IMO 2020 regulations', *Hydrocarbon Processing*, (November 2019), pp. 69 - 73.
3. GUERICO, V. J., 'US Producing, exporting more slurry oil', *Oil & Gas Journal*, (4 October 2018).
4. 'Methodology and Specifications Guide, Petroleum Product & Gas Liquids: US Caribbean and Latin America', Platts, (January 2021).
5. SCALCO, V., 'AFPM '19: IMO 2020 and beyond', (19 March 2019), https://www.hydrocarbonprocessing.com/conference-news/2019/03/afpm-19-imo-2020-and-beyond
6. HOUSER, T., GIBSON, S., and SCALCO, V., 'Confronting unconventional oil', *Hydrocarbon Engineering*, (October 2018), pp. 57 - 62.
7. BAI, Z., WANG, H. L., and TU, S. T., 'Removal of Catalyst Particles from Oil Slurry by Hydrocyclone', *Separation Science and Technology*, (2009), pp. 2067 - 2077.
8. MINYARD, W. F., and WOODSON, T. S. 'Upgrade FCC Slurry Oil with Chemical Settling Aids', *World Refining*, (November/December 1999).
9. SILVERMAN, L. D., WINKLER, S.., TIETHOF, J. A., and WITOSHKIN, A., 'Matrix effects in catalytic cracking', presented at the 2018 AFPM Annual Meeting, (23 – 25 March 2018).
10. 'S&P Global Commodity Insights', S&P Global, https://www.platts.com/IM.Platts.Content/InsightAnalysis/IndustrySolutionPapers/SR-IMO-2020-Global-sulfur-cap-102016.pdf