MAKE MONEY IN A SLURRY

Steve Kalota, Expertech, USA, and Victor Scalco and Robert Buckingham, General Atomics, USA, explain how return from the bottom of the barrel can be maximised by improving the value of the slurry oil stream.

Fluid catalytic cracking is a process refiners use to convert heavy atmospheric gas oils, vacuum gas oils, and sometimes atmospheric resids, into more valuable gasoline and middle distillates. A refinery generally keeps its FCC units fully loaded because these units have a significant effect on refinery profitability.

Along with fuel gas, C_3s and C_4s, FCC units also produce a byproduct heavy aromatic oil called 'slurry oil' because catalyst fines carried over from the FCC reactor end up in the bottoms of the fractionator. The key to improving the value of this stream is to economically remove the solids to low levels. Historically, refiners have used heated holding tanks with very long residence times to allow the solids to settle. The decant oil is then removed from the upper part of the tank and the bottoms sludge, which is listed as a hazardous waste, is also periodically removed.

Other approaches to removing catalyst include hydroclones, filtration and in some cases centrifugation. Electrostatic separation, on the other hand, uses a charge that causes the catalyst particles to become trapped in beds of glass beads while maintaining flow without significant pressure drop. In this way electrostatic separators have been able to remove over 97% of the catalyst present in most slurry oils. As the concentration of vacuum tower bottoms in FCC feeds grows, modern techniques used for selection of catalyst removal from slurry oil will increasingly favour electrostatic separation, because it is inherently less likely to foul or coke due to increasing asphaltene levels in the slurry.

As refiners introduce more and more resid into the FCC, slurry oil yields will increase and the quality of the slurry oil will decrease, since a larger proportion of asphaltenes and heteroatoms will enter the unit. This is relevant because the level of asphaltenes in the slurry oil becomes a factor in deciding which technology is best for removing particulate solids. Asphaltenes are the most hydrogen deficient constituents of slurry oil. They become more active and react with one another at higher temperatures and especially in the presence of metal surfaces, to form coke.

Slurry oil yields and properties

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

Particle size distribution ranges from a variety of slurry oils are shown in Table 2. Note that for these slurry oils, over 90% of the particles range in size from 0 – 25 microns in particle diameter. 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 in this service.[4] However, sludge from slurry oil holding tanks has been listed as a hazardous waste by the EPA, so frequent cleaning of these tanks becomes expensive.

Clarified slurry oil

Applications and markets

Worldwide FCC slurry oil production is estimated to be approximately 750 000 bpd. North America represents approximately 45% of this, while Europe and the Asia Pacific regions constitute 42 % of the total production.[1] Possible applications for slurry oil include:

- Recycle it to extinction in the FCC.
- Charge it to a coker.
- Use it as fuel in the refinery.
- Market it as fuel oil blending stock.
- Market it as carbon black feedstock or as a component of anode grade or needle coke feedstock manufacture.
- Further refine it to higher value fuel products in hydroprocessing.

Slurry oil can be recycled to the FCC unit, but this route increases coke make, resulting in higher regenerator temperatures that can adversely affect selectivity to prime products and economics. In this application, however, it may not be necessary to remove the catalyst to low levels, as long as erosion of FCC injectors and fouling of heat exchange equipment do not become an issue. Some refiners charge their slurry oil to a coker to help avoid making shot coke. Use of slurry oil as fuel in the refinery is practiced routinely and is a good option as long as applications and equipment to be used are critically examined for processing a solids containing stream. Such equipment as piping, burner tips, nozzles, heat exchangers etc., needs to be evaluated for long term viability when charging solids containing streams. To minimise downstream processing difficulties, sufficient removal of the contained catalyst will keep solids diluted to below highest recommended concentration levels.

Unfiltered or untreated slurry oil is generally valued equal to no. 6 fuel oil. This typically receives US$ 80 – 100/bbl in recent markets. Beyond fuel use, clarified slurry oil is also sold to make carbon black which is used in automobile tires, belts, hoses and pigments. Typical carbon black feedstock properties[1] are given in Table 4. Worldwide consumption of carbon black feedstock is approximately 130 000 bpd. The required density for carbon black feedstock is high and special attention must be given to operating the FCC fractionator at a high enough temperature to obtain the desired density.

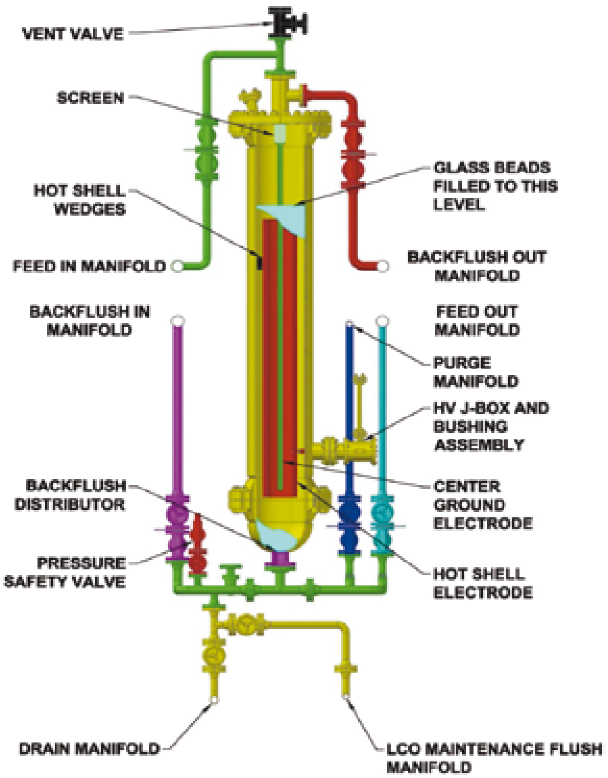

Figure 1. High capacity Gulftronic separator module.

Figure 2. Gulftronic separator, side view.

Typical needle and anode grade coke properties[6] are shown in Table 5. Globally, only approximately 22 000 bpd of slurry oil production is used for needle coke manufacture. Needle coke feedstock price can be considerably greater than that for residual fuel oil blending and fuel grade coke manufacture, and US$ 1 – 2/bbl higher than carbon black uses. Recent price differentials have been US$ 150 – 200/t.[1]

When feeding clarified slurry oil (CSO) to hydroprocessing (primarily hydrocracking or severe hydrotreating), slurry oil solids contents should be reduced to very low levels. Downflow packed bed reactors will accumulate particulates near the entrance of the reactor that will eventually bridge the hydroprocessing catalyst particles and cause plugging and premature shut down. Reactors operating in trickle flow do not have the velocity to carry FCC particles through the packed bed.

Particulate removal technologies

Ash is a particular problem for slurry oil, especially heavy, viscous oils that need long residence times to allow for catalyst settling. Obtaining low ash levels (less than 0.05 wt%) requires special techniques, including heating, chemical additives, filters, electrostatic precipitators, centrifuges and cyclones. Selection of an attrition resistant catalyst helps to reduce ash content, and a few refiners buy higher priced hard catalysts to alleviate ash problems in slurry oil.

The traditional practice has been to allow gravity settling of entrained solids within the product storage tank. The slurry oil contains practically all the catalyst fines not collected by the FCC unit reactor cyclones, plus

Table 1. Typical slurry oils: range of properties

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

Table 2. Typical particle size distribution in slurry oils

Particle diameter (microns)	% in range
0 – 5	30 – 60
5 – 15	30 – 55
15 – 25	2 – 12
25+	1 – 5

Table 3. Typical permissible solids content for various slurry oil product applications

Market	Clarified slurry oil solids (ppm)
Carbon black feedstock	50 – 500
Refinery use, fuel or coker feed	50 – 150
Marine fuel #6	50 – 150
Pitch feedstock	25 – 100
Needle/anode coke feedstock	25 – 100
Hydroprocessing feedstock	10 – 50
Carbon fibre feedstock	5 – 10

refractory and corrosion scale particles. The settling rates of these fines are influenced by many factors, including particle mass, particle diameter, differential density between the particles and the fluid, and the fluid viscosity. Flocculation of the particles increases their settling rate by increasing the effective particle diameter, and chemical additives are available for this purpose. Asphaltene precipitation can also act as a flocculent, increasing settling rates.

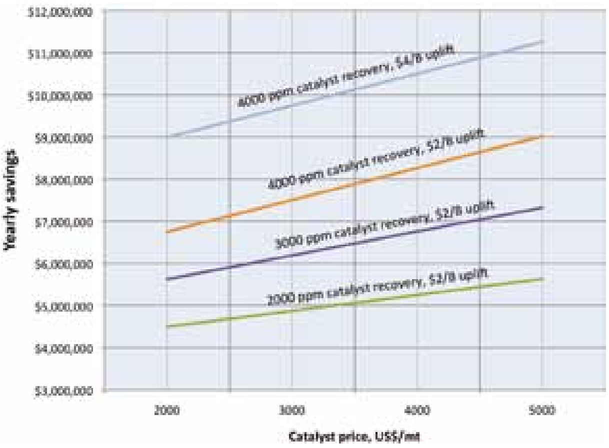

Figure 3. Estimated savings from using the separator.

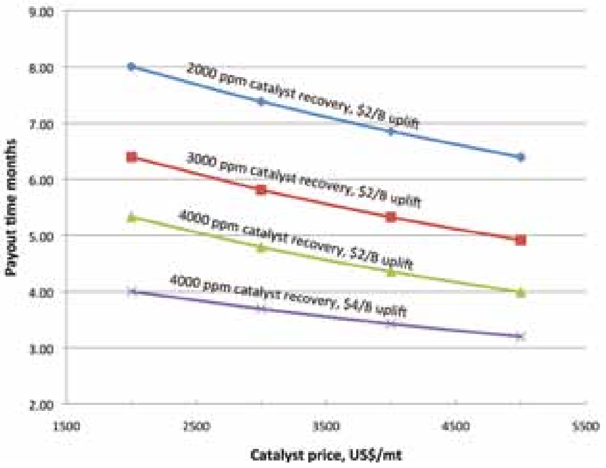

Figure 4. Payout times for the separator.

Table 4. Typical carbon black feedstock requirements on slurry oil [1]

Property	Value
BMCI, min	120
°API, max	2
Specific gravity, min	1.06
Sulfur (wt%), max	0.5 – 4.0
Ash (wt%), max	0.05 – 0.07
Sodium (ppmw), max	10
Potassium (ppmw), max	5 – 10
Pentane insolubles (wt%), max	7
Water (wt%), max	0.2
Viscosity, saybolt at 210 °F (sec), max	100
Flash (°F), min	180

In the following example, the electrostatic separator is applied in place of tank settling and remedial removal and disposal:

Refinery A operates a FCC unit with a throughput of 80 000 bpd. The FCC unit has a slurry oil product flow of 6.0 vol% of feed, or 4800 bpd at 0.0 API. The FCC unit uses an electrostatic separator to remove fines from 3000 – ‹500 ppmw (equivalent to 2.25 tpd of fines). Assuming 2 tpd of sludge for every tpd of fines, a total 4.5 tpd of sludge and fines would have accumulated in the storage tank. In one year, the accumulation would be approximately 1600 t.

The electrostatic separator adds value by upgrading the slurry oil quality for high grade coke production. Assuming a product value increase of US$ 2/bbl of slurry oil, the added value is:

4800 bpd slurry oil product x 365 days x US$ 2/bpd = US$ 3.5 million/y

The only meaningful process cost for the electrostatic separator is for recycle flow. For this scale, the recycle flow rate would be 2 vol% of the effluent, or 100 bpd. At US$ 1/bpd, the cost is:

100 bpd recycle x 365 days x US$ 1/bpd = US$ 36 500

Ignoring the labour and material costs of tank cleaning, consider the cost of land fill for the sludge removed. Assuming landfill is US$ 1/lb, the cost is:

1600 tpy x US$ 2000/t = US$ 3.2 million/year

The annual savings are:

US$ 3.5 million – US$ 0.04 million + US$ 3.2 million = US$ 6.7 million/y

Perhaps the least expensive (both capital and maintenance) cost method for removing solids from slurry oil is the liquid phase cyclone separator or hydroclone. Unfortunately, this method only allows solids levels to be reduced to 300 – 500 ppmw at best. The hydroclone does not give the refiner the product application flexibility provided by other methods that can remove solids to a greater extent. Because of the dynamics of the hydroclone, approximately 10% of the feed slurry is sent back to the riser. Although centrifuges have been used to remove solids from slurry oil, their use has been limited and it is difficult to make generalisations. The one refiner known to use centrifuges in this service has expressed satisfaction with their operation, but the ultimate disposition of that slurry oil is not known.

The first membrane filters were 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 filter systems use porous sintered woven wire mesh metal filters and operate at 400 – 650 °F. Others employ a 2 – 5 micron woven wire filter element, using light cycle oil as a backwash at 350 °F, and claim 85 – 95% solids removal from the feed slurry.

Electrostatic precipitators are routinely used to remove catalyst fines from the FCC unit stack, and a similar principle is used for the removal of solids from liquids in the electrostatic separator. Electrostatic separation of FCC catalyst fines from slurry oil has been in commercial operation for over 30 years. It has been improved continuously over this period. It is a robust, automatic

Table 5. Typical anode and needle coke properties [6]

Property	Anode grade coke		Needle grade coke	
	Green	Calcined	Green	Calcined
Sulfur (wt%)	4.0 max	3.5	0.5	0.5
Nitrogen (wt%)			0.7	0.5
Ash (wt%)	0.4 max	0.4 max	0.1 max	0.1 max
Nickel (ppmw)	250 max	200 max	5 – 7	
Vanadium (ppmw)	400 max	350 max		
Real density (g/cc)		2.05 min		2.1 – 2.14

Table 6. Basis of economics estimate

100 000 bpd refinery, using holding tanks
40 000 bpd FCC unit, 8% slurry yeild, 2° API
2050 – 4050 ppm catalyst in slurry cases considered
Catalyst prices US$ 2000 – 5000/mt
Tank cleaning: 2000 ppm catalyst once/y for US$ 1.5 million
Upgrade in slurry oil value US$ 2 and US$ 4/bbl
Recovered catalyst is sent back to the FCC unit
Catalyst fines removal by regenerator cyclones and ESPs
Fresh catalyst purchases are reduced by recovered catalyst
Tank cleaning savings included
Savings due to reduced chemical settling aid costs and holding tank heating costs are not included

process that removes catalyst fines from slurry oil or other hydrocarbon streams. Because this technology is not affected by the presence of asphaltenes, it is an excellent choice for removing solids not only from resid FCC derived slurry oil, but also from gas oil crackers.

Electrostatic separators

The electrostatic separator technology was developed more than 35 years ago to deliver the highest possible level of particle separation. It was specifically designed to avoid the pitfalls of other media filtration systems, including rapid cake and pressure build up, and deterioration of the recoverable pressure drop over time, while achieving the maximum rejection of small micron particles. The electrostatic separator is ideally suited for separation of particles sized 10 microns or less entrained in high viscosity, resinous oils such as FCC unit slurries or delayed coker feeds.

The electrostatic separator comes in a modular design. Each model is constructed of multiple separator modules. A 12 module electrostatic separator is pictured schematically in Figure 1. Each module is filled with glass beads. In this case, the module is 18 in. in diameter and 11.0 ft in length. Flow rates to each module can range from 600 – 1000 bpd and each module has a holding capacity of 40 lbs of catalyst fines. During the separation cycle, the beads are charged in an electrostatic field. Catalyst fines are attracted to and held back at the many points of contact between the glass beads while the particle free liquid flows though the module. During the backflush cycle, the electrostatic charge is removed and the catalyst particles are flushed from between the beads.

Economics

The value generated by using the separator to remove FCC catalyst fines from slurry oil is illustrated in the following example. In this case, an 80 000 bpd gas oil FCC unit has a slurry oil yield of 4 vol%, or 3200 bpd. Catalyst content of the slurry oil for three cases is 2000, 3000 or 4000 ppm. All cases are compared against the base case in which the refinery uses a holding tank to reduce solids. The slurry holding tank is assumed to require cleaning once per year with 2000 ppm slurry solids at a cost of US$ 1.5 million. Increased catalyst loads will incur higher frequency slurry holding tank cleaning and total costs.

A portion of the FCC feed is used to backwash the electrostatic separator after which it and the associated catalyst are fed back to the FCC unit, thus reducing fresh FCC catalyst costs. FCC catalyst costs are assumed to range from US$ 2000 – 5000/metric t. It is estimated that average product upgrade value for this clarified slurry oil can be between US$ 2 – 4/bbl. Benefits from not having to purchase chemical settling aids were not considered even though such costs are estimated to be in the order of 6 – 20 ¢/bbl treated.[4] Heating costs for maintaining the holding tank at temperature are also not included. Other assumptions underlying this analysis are shown in Table 6.

Figure 3 shows the graphical results of this analysis. The three cases with slurry oil catalyst concentrations of 2000, 3000 and 4000 ppm and slurry uplift of US$ 2/bbl are presented along with one case for recovering 4000 ppm of catalyst with US$ 4/bbl uplift. Savings made due to use of the electrostatic separator range from US$ 4.5 – 11 million.

Figure 4 shows the estimated payout times for the various cases, which range from 3 – 8 months. Catalyst savings may not be as high for a resid unit, but would nonetheless still be significant. Individual cases involving deep resid cracking benefits would have to be calculated based on a thorough knowledge of the RFCC unit 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.

Conclusion

Removal of FCC slurry oil solids to low levels presents an opportunity for improved profitability for refiners in many ways:

- Permits clarified oil to be used in higher value applications, yielding US$ 2 – 4/bbl net.
- Reduces or eliminates the need for the disposal of hazardous waste from slurry oil holding tank sludge.
- FCC catalyst recycling reduces fresh catalyst make up costs.
- Additive costs are reduced because need for chemical settling aids is eliminated.
- Payout times less than a year are estimated for an electrostatic separator.

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