Refiners have several options to overcome FCCU opacity limitations

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A fluid-catalytic cracking unit (FCCU) operating at or near a stack-opacity limitation potentially can be the primary refinery-run limitation.

Refiners can overcome opacity (that is, flue-gas particulate emissions) limitations in several ways:

- Identifying variables that affect opacity measurements
- Optimizing operating conditions
- Modifying catalyst physical properties
- Considering abatement-hardware options

Familiarity with the procedure to measure stack opacity allows refiners to identify the variables which affect opacity. This knowledge, coupled with operating and catalyst data, can help to troubleshoot an opacity problem. As a last resort, several hardware options exist for controlling or eliminating stack opacity losses.

In the U.S., flue-gas particulate emissions are limited to 1 lb of solids per 1,000 lb of coke burned, or about $5 \times 10^{-6}$ lb/scf of flue gas. In Europe, this limit ranges from 100 to 500 mg/normal cu m. Typically, opacity is measured as a relative index based on a base number that varies among states. Usually, the maximum opacity limit is 20; measurements of 10-12 are desirable.

Measuring opacity

U.S. refiners are obligated to allow state-authorized contractors to measure their stack opacities.

It is still the refiner’s responsibility to ensure that the measurements are accurately taken in the prescribed technique defined in U.S. Environmental Protection Agency (EPA) regulations. In fact, refiners should become familiar with all environmental regulations which effect his/her operation because these rules may vary widely from state to state.

Commercial models of EPA-approved particulate-sampling trains look similar to the one in Fig. 1.

Quantification of the stack opacity involves determining the weight of mass collected on a filter after isokinetic sampling of the stack for at least 5 min.

The collected sample of gas from the stack must remain slightly above 250°F, to prevent certain sulfur compounds and hydrocarbons from condensing on the filter paper. If condensation occurs,
the particulate measurement will be erroneously high.

Placing the filter in a dessicator overnight to remove moisture is suggested if maintaining a 250°F sample gas temperature is unattainable.

Once the weight of mass collected on the filter paper is calculated, the volume of sample gas measured by the dry-gas meter needs to be corrected for standard conditions of 70°F and 29.92 in. of Hg using Equation 1.

The volume of water vapor is required to calculate the moisture content of the gas sample. This value, calculated by the ideal gas law in Equation 2, can also be used to validate the accuracy of the heat balance. The calculated hydrogen in coke is consumed in the regenerator and converted to water vapor.

The moisture content is then determined by Equation 3.

The concentration of particulate matter in the stack gas is then calculated using Equation 4.

Equation 5 is used to calculate the sampling accuracy. It determines the percentage of isokinetic sampling (I) that falls inside the range of 90% and 110%. If the accuracy falls outside this range, the tests must be redone.

Becoming knowledgeable with the standard method for measuring stack opacity is the first step in monitoring and correcting an opacity problem. Once the integrity of the test is verified, then troubleshooting focuses upon the unit operation for potential opacity source contributors.

Operational variables

Each FCCU operation is unique as a result of differences in feedstock quality, hardware, refining objective, and limitations.

When a catalyst-loss problem develops, the operating variables of percent throughput over design, transport-disengaging height (TDH), and turnaround frequency have an impact on stack opacity. Each variable will offer opacity relief at some cost. The goal is to combine these variables to gain the maximum opacity reduction at a minimum economic impact to unit profitability.

Most units try to maximize throughput to take advantage of economies of scale. While profitability is the ultimate motivation, charge rates above unit design typically increase stack opacity. Fig. 2 illustrates this relationship.

The decision to operate above design throughput is limited by many factors, including opacity. For those refiners who maximize throughput, the optimum charge rate is above 110% but less than 115% design throughput. At elevated charge rates, a refiner consumes the remaining opacity margin. This margin, if preserved, could keep the unit away from an opacity excursion during an upset. This consideration may force operators to place a self-imposed maximum below 110% of design throughput.

The TDH in the regenerator is the level above the fluidized bed at which pulsations from bursting bubbles have been dissipated and the gas velocity has stabilized to a reasonably constant profile. Operating an FCCU regenerator catalyst bed level above the minimum TDH increases the head pressure when catalyst circulation increases. Thus, additional slide valve differential pressure is required.

This is a common scenario when operating at maximum charge rate. Some units operate without incident under this condition; others experience a step change increase in catalyst losses resulting in higher stack opacity.

The relation between TDH and bubbling gas flux through the fluidized bed reveals that a larger TDH is required for higher fluxes. As the vessel diameter at the bed surface increases at constant gas flux, the TDH requirement also increases (Fig. 3).

A refiner must discover his/her optimal operating range for TDH. Fig. 4 proves there is no advantage in providing excessive TDH. Most refiners today do not have the luxury of excess TDH when they are in maximum charge-rate mode. At the other extreme, catalyst entrainment increases exponentially when the minimum TDH is violated.

Some refiners successfully operate
below the minimum TDH by relying on other factors (higher pressure drop cyclones, multistage cyclones, the WGS, the ESP). This, however, is not a recommended practice. The exponential increase in solids loading will accelerate the mechanical wear down of the cyclones and diaphragm. Holes in cyclones and diaphragms eventually grow larger in size and force the shutdown of the FCCU.

In an FCCU, tons of hot (about 1,300°F), tiny (average particle size of about 70 μ catalyst particles circulate continuously for several years between scheduled maintenance shutdowns. While extending an FCCU run beyond 60 months is commendable, one of the inevitable side effects is the gradual deterioration of cyclone-separation efficiency. Day after day, the cyclone’s abrasion-resistant lining gets thinner until bare metal is exposed. When this occurs, it is only a matter of time until a hole is formed and a serious catalyst-less problem develops. For one U.S. refiner, start of run (SOR) particle sizes averaged about 70 μ and end of run (EOR) particle sizes averaged 78 μ.

Stack opacity increases as the FCCU turnaround frequency is spaced farther apart. While economics may be favorable to keep the FCCU on stream, decisions to postpone a scheduled maintenance turnaround should be weighed against the potential consequences of experiencing mechanical problems with critical hardware.

A decision to defer turnaround costs, which are measured in millions of dollars independently of the lost production time, can easily result in a more expensive turnaround if the unit has to come down before the next turnaround date. This is especially true if major hardware components (cyclones, air distributor) need replacement.

Judicious balancing of the key FCCU operating variables, such as charge rate, regenerator bed level, and maintenance turnaround frequency (considering their effects on hardware and thus stack opacity), can ensure the unit’s mechanical integrity and still allow the refiner to remain competitive. Once the operational variables are optimized, the catalyst system is reviewed for possible gains in opacity relief.

**Catalyst properties**

Fresh catalyst physical properties can be tailored to improve opacity. Switching to a coarser grade, increasing the density via reformulation, and lowering the fresh-catalyst attrition index (AI) by calcination offers refiners several relief opportunities.

FCCU catalysts are confined to a physical size measured in microns. They are expected to be able to selectively
crack oil to higher-value products while exhibiting excellent fluidization, metals tolerance, hydrothermal stability, and attrition resistance.

Particle size, apparent bulk density (ABD), and the AI of FCCU catalysts can be tailored to control stack opacity.

All FCCU catalyst suppliers offer multiple coarseness grades of FCC catalyst. Multiple coarseness grades satisfy fluidization requirements primarily on pressure-balanced units and units with long vertical standpipes. Refiners who experience higher catalyst losses can switch to a coarser grade of fresh catalyst.

Regenerator stack opacity is primarily caused by a discharge of fresh and equilibrated catalyst microparticles along with condensable sulfur compounds and hydrocarbons. Approximately 80-85% of the fresh catalyst sent into the unit is retained; most particles measuring 40 μ and smaller are eventually lost through normal attrition.

A stack opacity problem is controllable by lowering the 0-40 μ fraction of the fresh catalyst via a proven practice called scalping. The FCCU requires, however, some percentage of 0-40 μ in the inventory to maintain adequate fluidization. Thus, there is a low end limit to scalping fresh catalyst.

An FCC catalyst has three distinct densities: particle, skeletal, and apparent bulk. Particle density is a function of pore volume and measures mass per unit volume of a single catalyst particle with its porous voids. Skeletal density is a function of the alumina and silica content and only takes into account the solid components of the catalyst (no contribution from the pore volume). ABD measures the mass per unit volume of many catalyst particles examined in a bulk quantity and includes the void space. ABD is measured, whereas particle and skeletal densities are calculated using Equations 6 and 7.

Particle density and particle diameter are catalyst physical properties used to design cyclones. The diameter of the smallest particle that would be theoretically collected in a cyclone is calculated using Stokes Law (Equation 8), modified for a particle falling due to centrifugal acceleration.

Stokes Law was used to determine the comparative difference in cyclone collection efficiency between three catalysts with different densities. For a three-cyclone system, Fig. 5 was constructed.

All three curves in Fig. 5 essentially overlap, and the absolute size difference between the 0.95 ABD catalyst and the 0.80 ABD catalyst is within ±2 μ. Thus, a major improvement in cyclone-collection efficiency needs to be created from the other process and catalyst variables.

An important operational difference between catalysts of differing densities is that each catalyst will create different bed levels in the regenerator at the same delta pressure. Depending on the density difference between catalysts, this bed level difference could measure several feet of TDH, which has a major impact on cyclone efficiency.

When a stack opacity problem develops, one of the first variables reviewed is fresh catalyst attrition. The attrition resistance of a catalyst is expressed as a relative index, where lower numbers are better.

Neither a standard attrition test nor a standard equation for calculating the AI exists. As a result, catalyst companies and some oil companies have developed their own tests for measuring attrition. Becoming familiar with the conditions and calculations of the two most widely used attrition tests will enable refiners in their troubleshooting efforts.

The air-jet test and the jet-cup test are the two most widely used attrition tests. Both tests use air at high velocity to create fines from a catalyst sample. The air-jet test requires about 20 hr, whereas the jet-cup test is completed in about 1 hr.

Each test creates fines through a different mechanism. The air-jet test produces fines through particle-to-particle collisions. The jet-cup test generates fines by impacting catalyst against the wall of the jet cup.

Calculation of the AI from the air-jet test can be done with Equation 9.

The AI of the jet-cup test is known as the Davison Index (DI), and its calcula-
tion is more sophisticated (Equation 10).

The air-jet test categorizes fines in the fresh catalyst equal to fines produced through attrition. Its AI should be normalized to account for the ~20 μ fraction already present in the fresh catalyst because these fines are created in the catalyst-manufacturing process, not through attrition.

The DI makes this distinction. Attrition tests exhibit a bias towards the type of catalyst sample being tested. Fresh catalyst has a much higher AI than calcined fresh catalyst, steamed fresh catalyst, and equilibrium catalyst.

Thus, it is important to know the ~20 μ fraction of the fresh catalyst, as an increase in the fines content of the fresh catalyst could contribute to a stack-opacity problem.

If troubleshooting efforts still do not produce acceptable opacity reductions, then a refiner is left to consider installing hardware downstream specifically designed to reduce stack-opacity emissions.

**Hardware options**

Refiners have many options when they consider adding new hardware to improve stack opacity. These options include high-pressure drop cyclones, third-stage cyclones, third-stage separators, electrostatic precipitators (ESPs), and wet-gas scrubbers (WGSs). Each option offers different degrees of collection efficiency, and the choices are primarily dependent on cost.

Third-stage separators are installed on the flue-gas line leaving the regenerator, upstream of a WGS or ESP. Shell Oil Co. designed the first successful commercial design of a third-stage separator in 1957. It was invented out of necessity to remove catalyst fines measuring 10 μ during the development of power-recovery turbines. Third-stage separators are inexpensive and require low maintenance (no moving parts, support equipment, or utilities). This hardware option is limited to applications where ~20% of the catalyst fines are bigger than 10 μ (Fig. 6).

Electrostatic precipitation technology for controlling the particulate emissions from an FCCU is as old as fluid-catalytic cracking itself. This technology is more sophisticated than the third-stage cyclone. It requires high-voltage electricity, and its controls and moving parts require higher maintenance.

The metal-containing catalyst particles are attracted to charged plates and form a layer over time. Rappers operate on a timed sequence to strike the plates, thus knocking off the precipitated catalyst.

Pricipitators employ Ohm’s Law, \( V = kR \). Collection efficiency is improved if the induced current (I) is maximized via increasing voltage (V) or lowering resistance (R). Optimal performance is directly related to collection plate cleanliness, higher operating temperatures, and the use of resistance-conditioning agents such as ammonia.

Refiners should be aware that an ESP is designed to handle a certain gas stream volume with a certain solids content. When the gas volume or solids percentage increases, the ESP may not be able to handle the additional load. This event mostly likely occurs at higher feed rates and when units approach the end of a run.

WGSs offer the greatest protection against opacity excursions by eliminating catalyst losses to the atmosphere. The flue gas is spray washed with copious amounts of water. Entrained catalyst particles are weighed down by the water and never go out the stack. Eventually, the catalyst is separated out in a clarifying pond for further processing.

Scrubbers, like precipitators, cost more than third-stage separators. Scrubbers require large expensive pumps, lots of water, and a clarifying pond. Scrubbers, unlike precipitators, can handle a large increase in catalyst lost out the regenerator, and they also reduce sulfur emissions.

Many factors must seriously be considered regarding the purchase of these technologies. Their associated costs are significant, and these capital-intensive projects do not yield a tangible return on investment. Purchasing a precipitator or a WGS would be unfortunate if upgrading the cyclones and installing a third-stage separator would have met the opacity requirement.

**References**