

**FCCU OPERATION:
OVERCOMING OPACITY LIMITATIONS ON THE FLUID CATALYTIC CRACKING UNIT**

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ABSTRACT

Refiners are challenged to remain in environmental compliance as regulations tighten. A Fluid Catalytic Cracking unit operating at or near a stack opacity limitation has the potential to be the primary refinery limitation. This paper develops a strategy to troubleshoot an opacity limitation by reviewing the United States E. P. A. standard procedure for measuring opacity, optimizing operating conditions, modifying catalyst physical properties and considering downstream abatement hardware options.

Opacity is defined as the quality or state of a substance which renders that substance impervious to rays of light.¹ Identifying the variables which influence opacity provides refiners with several degrees of freedom to move the FCCU and possibly the refinery away from this limitation.

I INTRODUCTION

As the economies of the world move toward globalization, increased competition in the oil refining industry is forcing many refiners to seek higher levels of operating efficiency. In Fluid Catalytic Cracking, one of the eventual results of this operating philosophy is increased opacity. Learning to *accurately* measure and minimize stack opacity will assist refiners in achieving higher efficiencies while staying within compliance of environmental emissions regulations.

Particulate opacity emissions are a constant concern of all FCC unit operators. In the United States, flue gas particulate emissions is limited to 1 lb. of solids per 1000 lbs. of coke burned or $\sim 6.5 \times 10^{-6}$ (lb./SCF) of flue gas whereas in Europe this limit ranges from 100 - 500 (mg/N cu. meters).² Refiners are obligated to allow state authorized contractors to measure their stack opacity. This, however, does not relinquish the refiner's responsibility to ensure that the measurements are accurately taken in the prescribed technique defined in *Method 5 of the Federal Register written by the U. S. Environmental Protection Agency*.³ In fact, refiners should become familiar with all environmental regulations which effect his/her operation as these rules may vary widely from state to state.

Commercial models of EPA approved particulate sampling trains are available and look similar to the one described in the following figure.

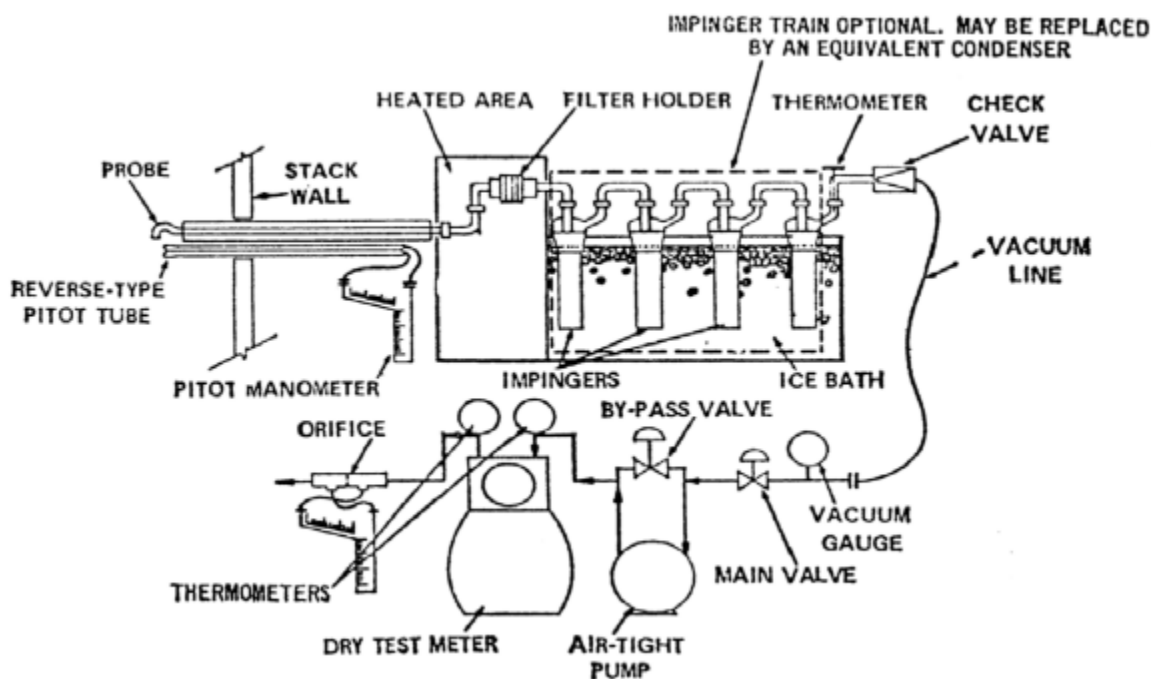


Figure 1: Particulate sampling train

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 minutes. The collected sample of gas from the stack must remain ideally slightly above 250 deg F to prevent some sulfur compounds and hydrocarbons from condensing on the filter paper. If this condensation occurs, the result will be an erroneously high particulate measurement due to the additional non-particulate weight. Placing the filter in a dessicator over night to remove moisture is suggested if maintaining a 250 deg 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 to standard conditions of 70 deg F and 29.92 inches of Hg using the following equation:

$$V_{mstd} = V_m * \left(\frac{T_{std}}{T_m} \right) * \frac{\left(P_{bar} + \frac{\Delta H}{13.6} \right)}{P_{std}}$$

Equation 1

where V_{mstd} = Volume of gas sample through the dry gas meter at STP, cu. feet.

V_m = Volume of gas sample through the gas meter, cu. feet.

T_{std} = Absolute temperature at STP, 530 deg Rankin.

T_m = Average dry gas meter temperature, deg Rankin.

P_{bar} = Barometric pressure at the orifice meter, inches of Hg.

ΔH = Average delta P across the orifice meter, inches of H₂O.

13.6 = Specific gravity of mercury (Hg).

P_{std} = Absolute pressure at STP, 29.92 inches of Hg.

The volume of water vapor is required to obtain the moisture content of the gas sample. This information is also useful to validate the accuracy of the heat balance as the calculated hydrogen in coke is consumed in the regenerator and converted to water vapor. The Ideal Gas Law is used for this determination as follows:

$$V_{wstd} = V_{lc} * \left(\frac{\rho_{H_2O}}{M_{H_2O}} \right) * \left(\frac{R T_{std}}{P_{std}} \right)$$

Equation 2

where V_{wstd} = Volume of water vapor in the gas sample at STP, cu. feet.

V_{lc} = Total volume of liquid collected in the impingers and silica gel, ml.

ρ_{H_2O} = Density of water, 1 g/ml.

M_{H_2O} = Molecular weight of water, 18 g/lb-mole.

R = Ideal Gas constant, 21.83 $\frac{in. Hg \times cu. ft.}{lb - mol \times ^\circ R}$

T_{std} = Absolute temperature at STP, 530 deg R.

P_{std} = Absolute pressure at STP, 29.92 inches of Hg.

The moisture content is then determined using the following equation:

$$B_{wo} = \frac{V_{wstd}}{V_{mstd} + V_{wstd}}$$

Equation 3

where B_{wo} = Volumetric proportion of water vapor in the gas stream, dimensionless.

V_{wstd} = Volume of water in the gas sample, cu. feet.

V =

The concentration of particulate matter in the stack gas is then calculated using the following formula:

$$c_s = \frac{\left(\frac{1 \text{ lb}}{453.6 \text{ gr}}\right) * \left(0.0154 \frac{\text{gr}}{\text{mg}}\right) * M_n}{V_{mstd}} = 2.205 * 10^{-6} \frac{M_n}{V_{mstd}}$$

Equation 4

where c_s = Concentration of particulate matter in stack gas, lb./scf, dry gas.

M_n = Total amount of particulate matter collected, mg.

V_{mstd} = Volume of gas sample through dry gas meter at STP, std. cu. feet.

To complete the exercise, calculate the sampling accuracy and determine that the percentage of isokinetic sampling (I) falls inside the range of $90\% \leq I \leq 110\%$. If the accuracy falls outside this range, complete the tests again.

$$I = \frac{T_s \left[\frac{V_{lc}(r_{H_2O})R}{M_{H_2O}} + \frac{V_m}{T_m} \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{qV_s P_s A_n} * 100$$

Equation 5

where I = Percent of isokinetic sampling, %.

V_{lc} = Total volume of liquid collected in the impingers and silica gel, ml.

r_{H_2O} = Density of water, 1 gr./ml.

R = Ideal Gas constant, $21.83 \frac{\text{in. Hg} - \text{cu. ft.}}{\text{lb. mole} - ^\circ R}$

M_{H_2O} = Molecular weight of water, $18 \frac{\text{lb}}{\text{lb} - \text{mole}}$.

V_m = Volume of gas sample measured through the dry gas meter, cu. feet.

T_m = Average absolute dry gas meter temperature, deg R.

P_{bar} = Barometric pressure at sampling site, inches Hg.

ΔH = Average delta P across the orifice, inches H₂O.

T_s = Average absolute stack gas temperature, deg R.

q = Total sampling time, minutes.

V_s = Stack gas velocity, ft./sec.

P_s = Absolute stack gas pressure, inches Hg.

A_n = Cross sectional are of sampling nozzle, sq. ft.

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.

II OPERATIONAL VARIABLES

Each FCC unit operation is unique primarily due to differences in feedstock quality, hardware, refining objectives and limitations. When a catalyst loss problem develops, the operating variables of percent throughput over design, transport disengaging height and turnaround frequency have an impact on stack opacity. Each variable will offer opacity relief at some economic cost. The goal is to use a combination of all the degrees of operational freedom to gain the maximum opacity reduction at 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. The following figure illustrates this relationship.

The decision to operate above design throughput is limited by many factors including opacity. For the above example, the optimum charge rate is above 110% but less than 115% design throughput. At this elevated charge rate, a refiner forfeits all remaining margin which could keep the unit away from an opacity excursion if an upset is experienced. This consideration may force operators to place a self-imposed maximum below 110% of design throughput.

The Transport Disengaging Height (TDH) in the regenerator is defined as 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.⁴ Operating an FCC regenerator catalyst bed level above the minimum transport disengaging height will increase head pressure when catalyst circulation increases and additional slide valve dP is needed. This is a common scenario when operating at maximum charge rate. Some units may operate without incident under this condition but others may experience a step change increase in catalyst losses resulting in higher stack opacity.

The relation between TDH versus bubbling gas flux through the fluidized bed reveals that a larger TDH is required for higher fluxes.⁵ As the vessel diameter at the bed surface increases at constant gas flux, the TDH requirement also increases.

Throughput vs. Relative Opacity

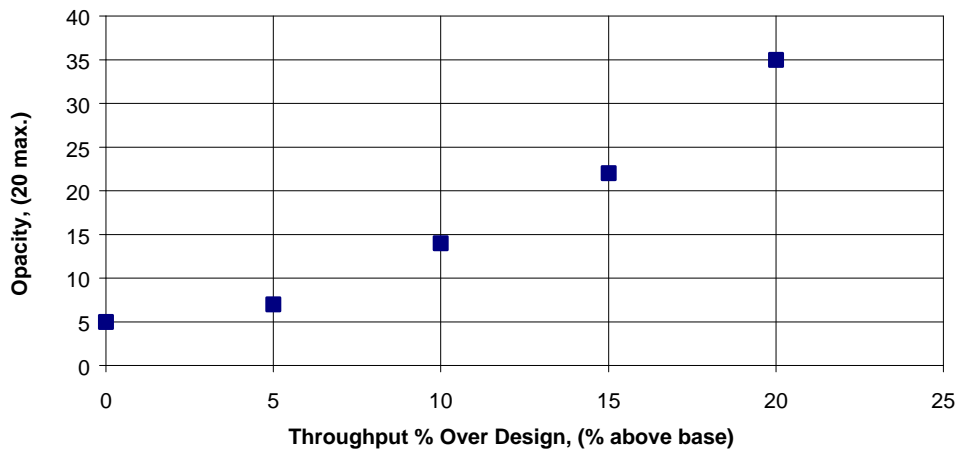


Figure 2: Effect of throughput on opacity

TDH versus Bubbling Gas Flux

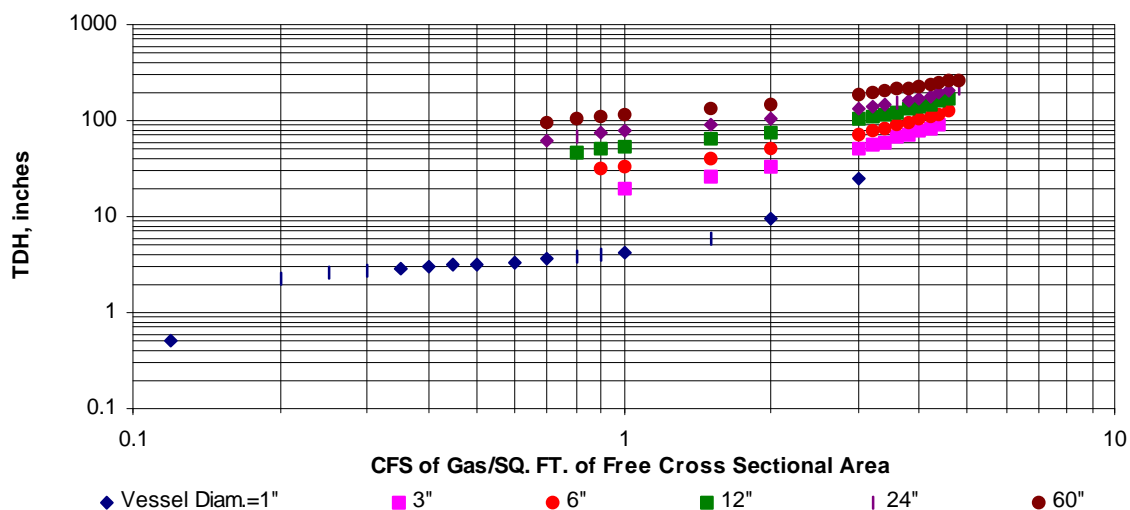


Figure 3: TDH versus bubbling gas flux

A refiner must discover his/her optimal operating range for TDH. The following figure proves there is no advantage in providing excessive TDH; however, 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 will increase exponentially when the minimum TDH is violated. Some refiners successfully operate below the minimum TDH relying on other factors (higher regenerator pressure, higher pressure drop cyclones, multistage cyclones, WGS, ESP) but this is not a recommended practice. The exponential increase in solids loading will accelerate the mechanical wear down of the cyclones and diplegs. Holes in cyclones and diplegs grow larger in size and will eventually force the shutdown of the FCC unit. This event will negatively impact the refinery.

Catalyst Entrainment vs. Transport Disengaging Height

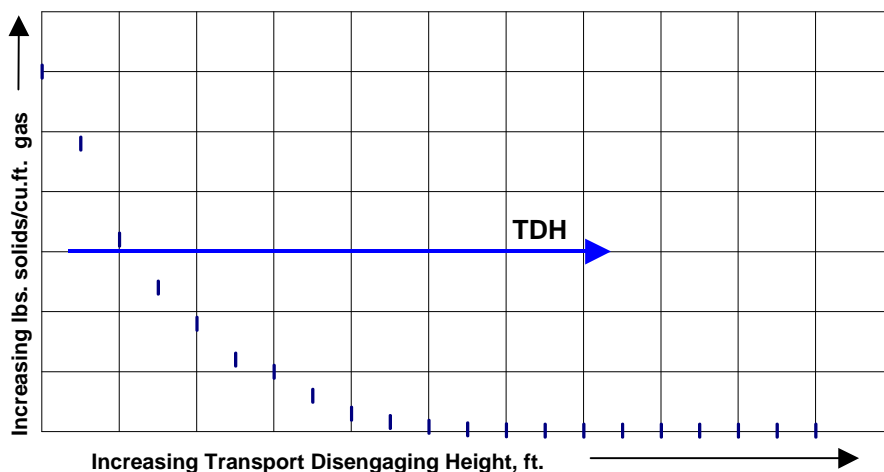


Figure 4: Effect of transport disengaging height on catalyst entrainment

Fluid catalytic cracking qualifies as a major engineering achievement on the basis that tons of hot (~1300 deg F), tiny (~70 μ APS) catalyst particles are circulating continuously in the unit for several years between scheduled maintenance shutdowns. The shortest scheduled FCC unit run length is 24 months and the longest approached 60 months. While extending a run is a commendable undertaking, one of the inevitable side effects in FCC is the gradual deterioration of cyclone separation efficiency. Day after day, the cyclone's abrasion resistant lining continues to get 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 loss problem develops. The difference between SOR and EOR particle size distribution is graphically described in the Figure 5.

Stack opacity will increase as the FCC unit turnaround frequency is spaced farther apart. While the economics are favorable to keep the FCC unit 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 independent of the lost production time, can easily result in a more expensive turnaround if the unit has to come down before the new turnaround date. This is especially true if major hardware components (cyclones, air distributor) need replacement.

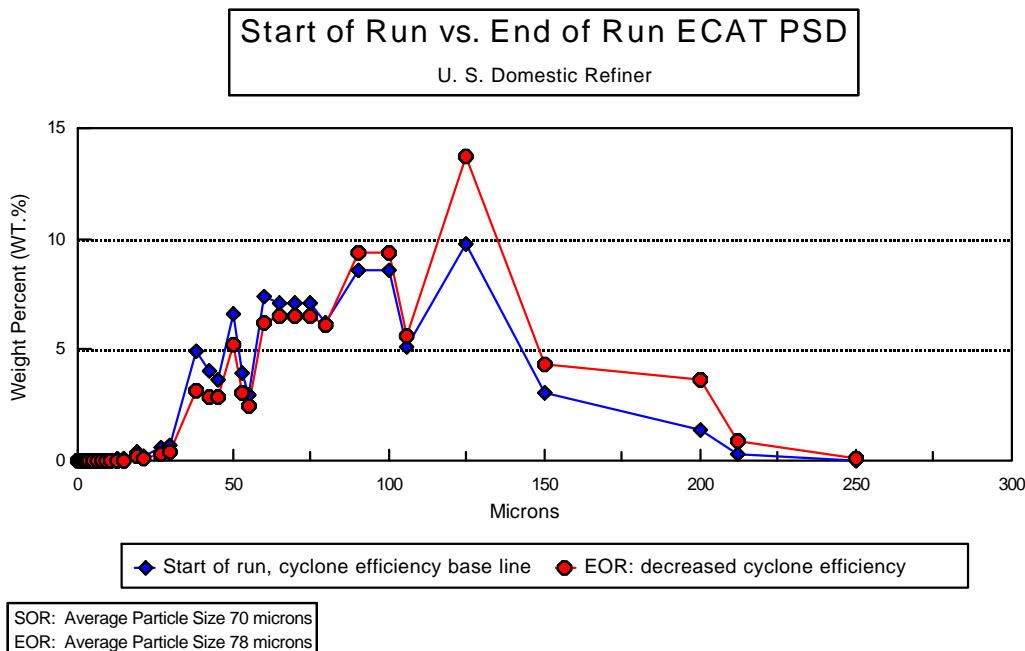


Figure 5: Example of SOR and EOR particle size distribution

Each FCC unit presents its own distinct operating challenges and opportunities. Judicious balancing of the key operating variables such as charge rate, regenerator bed level (TDH) and maintenance turnaround frequency through an understanding of their effects on hardware and thus stack opacity can insure the unit's mechanical integrity and still allow the refiner to remain competitive. Once the operational variables are deemed optimized, the catalyst system is reviewed for possible gains in opacity relief.

III CATALYST PHYSICAL PROPERTIES

The performance requirements made on fluid catalytic cracking catalysts are confined to a physical size measured in microns and include the ability to selectively crack oil to higher value products while exhibiting excellent fluidization, metals tolerance, hydrothermal stability and attrition resistance. This section will focus on how particle size, apparent bulk density and the attrition index of FCC catalyst are tailored to control stack opacity.

All FCC catalyst suppliers offer multiple coarseness grades of FCC catalyst to the market. Multiple coarseness grades are needed to satisfy fluidization requirements primarily on pressure - balanced units and units with long vertical standpipes. This variable can assist refiners who are experiencing higher catalyst losses by switching 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 as most of the particles measuring 40 microns and smaller will eventually be lost through normal attrition. A stack opacity problem is controllable by lowering the 0 - 40 micron fraction of the fresh catalyst. This effective proven practice is called scalping. However, the FCC unit requires some percentage of 0 - 40 microns 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). Apparent bulk density (ABD) measures the mass per unit volume of many catalyst particles examined in a bulk quantity and includes the void space. Apparent bulk density is measured whereas particle and skeletal densities are calculated using the following formulas.

$$\text{Particle Density } (\rho_p): \quad r_p = \frac{\text{SkeletalDensity}}{(\text{SkeletalDensity} + \text{PoreVolume}) + 1}$$

Equation 6

$$\text{Skeletal Density } (\rho_{SD}): \quad r_{SD} = \frac{100}{\frac{Al_2O_3}{3.4} + \frac{SiO_2}{2.1}}$$

Equation 7

Particle density and particle diameter are the catalyst physical properties used in the design of cyclones. The diameter of the smallest particle that would theoretically be collected in a cyclone is calculated using Stokes Law modified for a particle falling due to centrifugal acceleration.⁶

$$\text{Stokes Law:} \quad D_{ph} = \sqrt{9m_G w / \pi N_s u_i (r_P - r_G)}$$

Equation 8

where D_{ph} = theoretical particle diameter, microns.

m_G = gas viscosity, centipoise.

w = inlet width of cyclone, feet.

π = pi, 3.14159

N_s = number of spiral turns in the barrel of a cyclone

u_i = velocity at cyclone inlet, feet/second

r_P = catalyst particle density, pounds/ft³

r_G = gas density, pounds/ft³

Stokes Law was used to determine the comparative difference in cyclone collection efficiency between three catalysts with different densities. A three cyclone system was considered and the following graph was constructed. Observe that all three curves are essentially overlapping and the absolute size difference between the 0.95 ABD catalyst and the 0.80 ABD catalyst is within ± 2 microns. Thus, a major improvement in cyclone collection efficiency needs to be created from the other process and catalyst variables. Note 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 transport disengaging height. TDH has a major impact on cyclone efficiency.

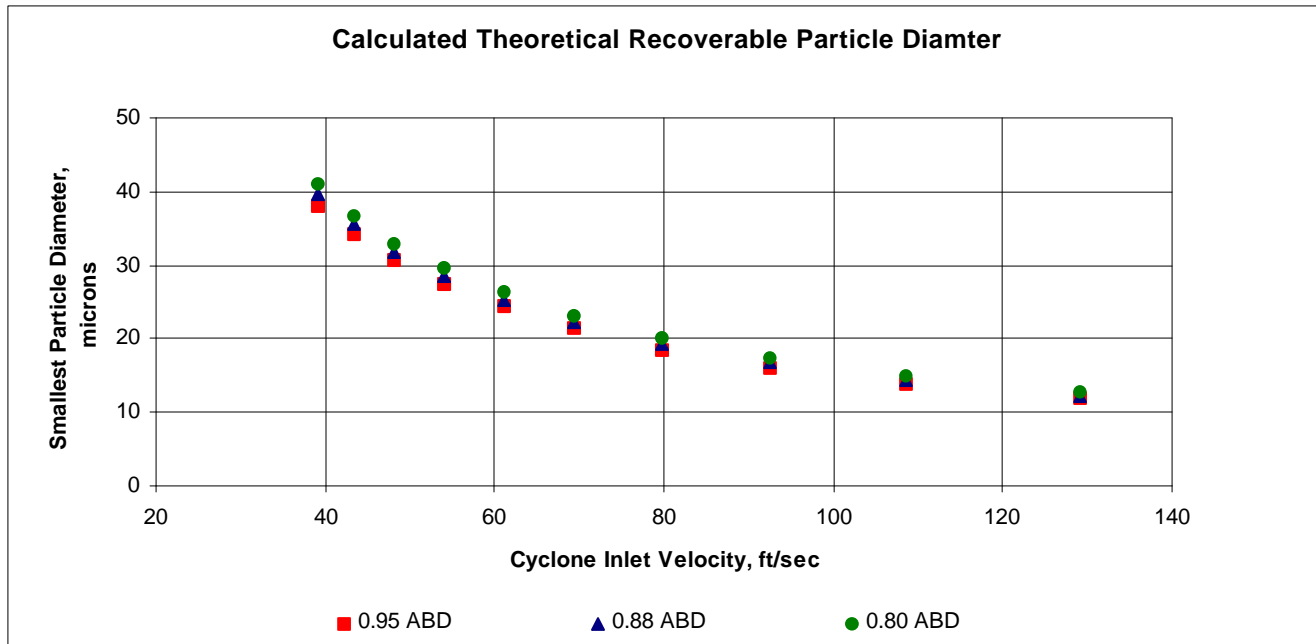


Table 1: Cyclone efficiency

CSA of Cyclones (ft ²)	Inlet Velocity (ft/s)	Number of Swirls	0.95 ABD theoretical Diameter (microns)	0.88 ABD theoretical Diameter (microns)	0.80 ABD theoretical Diameter (microns)
9.98	129.09	5.5	11.9	12.3	12.8
11.88	108.47	5.2	13.9	14.4	15.0
13.94	92.43	4.9	16.1	16.8	17.4
16.17	79.69	4.6	18.6	19.3	20.0
18.56	69.42	4.3	21.4	22.2	23.0
21.12	61.02	4.0	24.4	25.3	26.3
23.84	54.05	3.8	27.4	28.5	29.5
26.73	48.21	3.6	30.7	31.9	33.0
29.78	43.27	3.4	34.2	35.6	36.8
33.00	39.05	3.2	38.1	39.6	41.0

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 an index (relative number) where lower numbers are better. Neither a standard attrition test or a standard equation for calculating attrition index exist. As a result, catalyst companies and some oil companies have developed their own test 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 ~20 hours whereas the jet cup test is completed in ~1 hour. 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 attrition index from the air jet test uses the following equation.

$$AI = \frac{\text{wt\% fines collected during 20 hr test}}{\text{initial mass of sample}}$$

Equation 9

The attrition index of the jet cup test is more sophisticated.

$$AI = \left\{ \left[\frac{\left(\frac{c}{m} \times 100 \right) + H - G}{100} \right] - G \right\} \times 100$$

Equation 10

- where
- c = weight percent of fines collected, %.
 - m = weight of the initial sample, grams.
 - G = weight of particles less than 20 μ in the sample before the test, grams.
 - H = weight percent of particles less than 20 μ remaining in the sample after testing, %.

The air jet test categorizes fines in the fresh catalyst equal to fines produced through attrition. The air jet attrition index 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 Davison Index makes this distinction. Attrition tests exhibit a bias towards the type of catalyst sample being tested. Fresh catalyst has a much higher attrition index than calcined fresh catalyst, steamed fresh catalyst and equilibrium catalyst.⁷

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

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 by calcination offers refiners several relief opportunities. 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.

IV HARDWARE OPTIONS

Refiners have many options when they consider adding new hardware to improve stack opacity especially when price is not an issue. These options include high pressure drop cyclones, third stage cyclones, third stage separators, wet gas scrubbers and electrostatic precipitators. Each will offer different degrees of collection efficiency and the choices are primarily dependent on how much money a refiner is willing to spend. A review of the functional basics of a third stage separator, wet gas scrubber and electrostatic precipitator is presented. This information is intended to serve as a foundation for future consideration of these technologies.

Shell Oil company is credited with introducing the first successful commercial design of a third stage separator in 1957.⁸ It was invented out of necessity to remove catalyst fines measuring 10 μ and larger 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, illustrated as follows and is limited to applications where the majority of the catalyst fines are bigger than 10 microns.

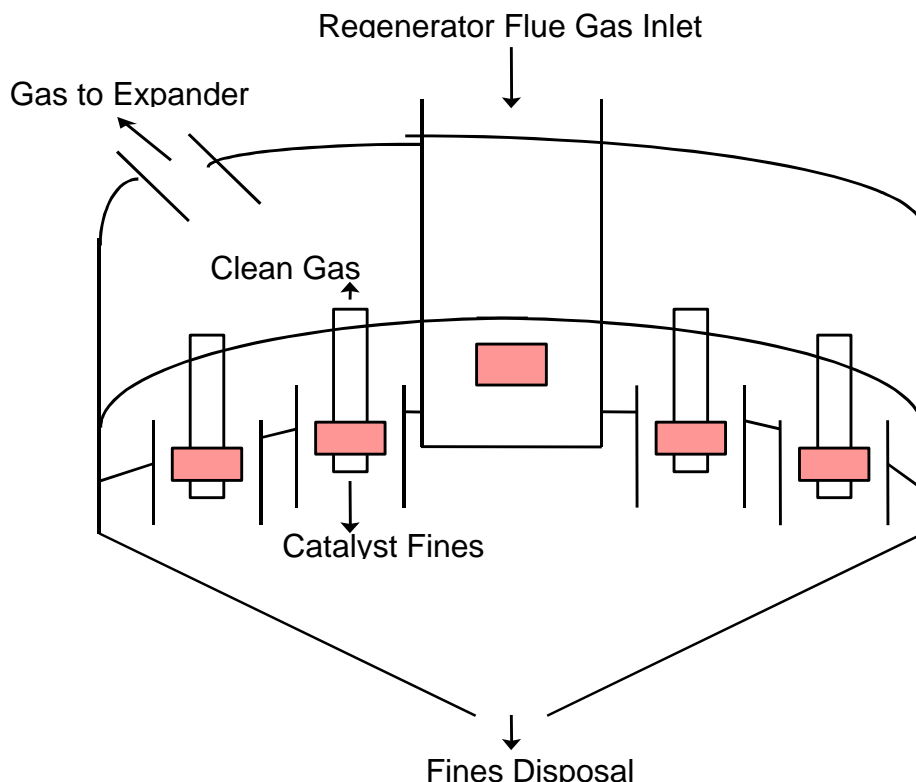


Figure 6: Third Stage Separator

Electrostatic precipitation technology for controlling the particulate emissions from an FCC unit is as old as FCC itself.⁹ This technology is more sophisticated than the third stage cyclone due to the high voltage electricity requirement and higher maintenance associated with the controls and moving parts. The metallated 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 and “cleaning” the plates.

Precipitators employ Ohm’s Law, $V = I \times R$. 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.¹⁰ Be aware that an ESP is designed to handle a certain gas stream volume with a certain solids content. When the gas volume or percent solids increase, the ESP may not be able to handle the additional load. This event is mostly likely to occur at higher feed rates and when units approach end of run.

Wet gas scrubbers 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 wet gas scrubber would be unfortunate if upgrading the cyclones and installing a third stage separator would have met the requirement.

V CONCLUSIONS

Refiners are increasingly challenged to find new ways to remain competitive and still protect the environment against harmful emissions. Becoming familiar with the procedure to measure stack opacity will create an awareness of the variables which effect opacity. This knowledge coupled to operating and catalyst data defining a unit's base line conditions is helpful when troubleshooting an opacity problem. As a last resort, several technologies exist for controlling or eliminating stack opacity losses. These optional degrees of freedom require capital and add another level of complexity to the overall operation.

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