Question 99: Have refineries experienced an increase in particulate emissions in the regenerator flue gas caused by oxygen enrichment of air to the regenerator?

BROOKS (BP Refining)

We have quite a few refineries that use oxygen enrichment. One of them uses it in very high concentration. None of the sites – and I spoke with them specifically about this – say that they have seen an increase in particulate emissions as a result of increasing their oxygen enrichment. As I mentioned earlier in response to a question, a lot of our units use oxygen enrichment to help reduce the superficial velocity in their regenerators in order to make their cyclones last longer and perhaps operate more efficiently. In essence, the oxygen enrichment is used to make the cyclones better and thus reduce losses.

LALL (UOP, A Honeywell Company)

Regarding Paul Diddams' earlier comment, if you are at a regenerator cyclone velocity limit, reducing the blower air rate, or shutting any portable blowers and supplementing oxygen, then particulate emissions will be reduced due to a significant reduction in nitrogen moles and decrease in air volume entering the regenerator.

AVERY (Albemarle Corporation)

Oxygen enrichment will reduce superficial velocity in the regenerator and increase the O_2 partial pressure. This alone would not favor SO_3 (sulfur trioxide) formation since the rate of SO_3 development, which is in equilibrium with SO_2, is not instantaneous. However, increased oxygen will also raise regenerator temperature, which will then lower the rate of SO_3 formation since SO_2 is favored at higher temperatures. These two rates move opposite of each other. Since each regenerator is different, it is difficult to say with certainty that the overall effect may be the rate of bulk SO_3 formulation in the regenerator. SO_3 formulation will be at its maximum in the region of the highest oxygen partial pressure, which is just above the air grid. Using supplemental oxygen will increase the oxygen partial pressure in this region and can directly result in increased SO_3.

Now downstream from the regenerator, oxygen concentration present in the flue gas is a key factor. Technically, this is unrelated to whether or not supplemental oxygen is used, but it depends on how the refinery chooses to operate the unit. Again, increased oxygen here increases SO_3 formation over SO_2. Lower temperature drives equilibrium towards SO_3 until about 1,110ºF. At this point, the kinetics of SO_3 formation are sufficiently hindered, so little SO_3 is formed at temperatures below 1,060°F.

If a refiner is having an issue with the emissions compliance due to condensable particulates, then it is recommended that they minimize the oxygen content of the flue gas and, if possible, operate the flue gas cooler in a manner that will reduce minimize the amount of time the flue gas is between 1,050°F and 1,200°F. This will help minimize the condensable particulate formation from SO_3. A scrubber, if present, will do a good job removing most of the SO_2 in the flue gas, but it may only remove a small to moderate amount of SO_3. SO_3 will be measured as a condensable particulate in stack testing.

SCHOEPE (Phillips 66)

I do not have any additional comments on this question.

JACK OLESEN (Praxair, Inc.)

Someone made a good point about oxygen in the flue gas line and how that impacts the SO_2 and SO_3. But if you are buying oxygen and running excess O_2 coming out the flue gas, then you are throwing away money. So, you need to keep the excess oxygen down to probably less than 2%.

MARTIN EVANS (Johnson Matthey Intercat)

I am being told that I am cutting into people's drinking time, so I will be fast. With regard to reducing condensable particulates, SOx additive is great to use. We have some refiners who add SOx additives in small amounts simply to reduce condensable particulates. It works very well.

BROOKS (BP Refining)

Oxygen enrichment is typically put in place to provide some relief in air blower limited operations. Additionally, most of our sites that employ this technology also use it to reduce superficial velocity in the regenerator. This can reduce wear on the cyclones and improve cyclone efficiency which may result in a net effect of lower losses.

AVERY (Albemarle Corporation)

Oxygen enrichment will reduce the superficial velocity in the regenerator and increase the O_2 partial pressure. This alone would favor SO_3 formation since the rate of SO_3 development (which is in equilibrium with SO_2) is not instantaneous. However, increased oxygen will also increase the regenerator temperature, which lowers the rate of SO_3 formation since SO_2 is favored at higher temperatures. These two rates move opposite of each other. Since each regenerator is different, it is difficult to say with certainty what the overall effect may be on the rate of bulk SO_3 formation in the regenerator.

SO_3 formation will be at its maximum in the region of highest oxygen partial pressure, which is just above the air grid. Using supplemental oxygen will increase the oxygen partial pressure in this region and can directly result in increased SO_3 formation.

Downstream of the regenerator, the oxygen concentration present in the flue gas is the key factor. Technically this is unrelated to whether or not supplemental oxygen is used, but it depends on how the refiner chooses to operate the unit. Again, increasing oxygen here will increase SO_3 formation over the SO_2. Lower temperature drives the equilibrium towards SO_3, until about 600°C. At that point, the kinetics of SO_3 formation are sufficiently hindered, so very little SO_3 is formed at temperatures below 570°C. If a refiner is having an issue with emissions compliance due to condensable particulates, then it is recommended that they minimize the oxygen content of the flue gas and, if possible, operate the flue gas cooler in a manner that will minimize the amount of time the flue gas is between 570°C and 640°C (1,050°F to 1,200°F). This will help minimize condensable particulate formation from SO_3.

A scrubber (if present) will do a good job of removing most of the SO_2 in the flue gas, but it may only remove a small to moderate amount of the SO_3. The SO_3 will be measured as a condensable particulate in stack testing.

LALL (UOP, A Honeywell Company)

Oxygen enrichment option is typically considered by refiners to achieve incremental feed processing. In general, oxygen enrichment marginally increases particulates due to a richer oxidizing environment; however, it is highly dependent upon whether regenerator net vapor and cyclone velocities increase or decrease. In cases where the air blower is limited and oxygen is added on the grounds of economics for additional feed processing, the regenerator vapor velocity increases, leading to marginal increases in catalyst entrainment to the regenerator cyclones and catalyst loss increases slightly. If, on the other hand, the regenerator is operating at a vapor velocity limit and the blower air rate is reduced or supplemental portable blowers are turned down, the particulate emissions reduce due to the significant reduction in the N_2 moles and decreasing air volume entering the regenerator. This results in lowering the overall regenerator vapor velocity and catalyst entrainment to the cyclones. Lower cyclone velocities reduce the particulate fines generation by reducing the force of catalyst particle collision with the cyclone wall.

ROBERTSON (AFPM)

That concludes this FCC session. I want to thank the panel for all the work they have done in the last four or five months. We really appreciate it. And, we ended 50 minutes earlier than last year. Also, I want to thank Cheryl Joyal who was the coach for this team; she did a really good job. This concludes the Q&A portion of the meeting. I appreciate all of you coming. I hope you have gained a lot of insight from this session and will take it back with you to your facilities. Thank you.

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