Less Fuel – Less Fire – Less Pollution
Using Low Temperature Tail Gas Catalysts and Catalytic Incineration in Sulfur Plants

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Introduction

Criterion Catalysts & Technologies LP continues to assess the needs for improved products and processes. Well-operated Claus tail gas units are required for today's refineries and gas plants to meet strict environmental regulations for sulfur emissions. While providing 99.8+ percent recovery of sulfur, these units are costly to build and to operate. In many circumstances, hydrogenation catalysts that can operate at lower reactor inlet temperatures would allow for substantial savings in capital and operating expenditures. The actual operating expenditures are site and fuel cost dependent. Usually, tail gas units operate at reactor inlet temperatures in the 540° F (280° C) range.

Criterion offers the proven Criterion 234 catalyst that can operate at reactor inlet temperatures in the 435°–460° F (225 –240° C) range. Criterion 234 is a low density (28 lbs/ft3, 450 kg/m3) 3.2 mm extruded catalyst. A catalyst in the development stage, Criterion 734, can be operated at reactor inlet temperatures in the 390° F (200° C) range.

Criterion has offered its Criterion 099 incineration catalyst to the industry for a number of years. This catalyst is selective for the oxidation of sulfur compounds to sulfur dioxide (SO_2) while minimizing the formation of sulfur trioxide (SO_3). This catalyst operates at much lower temperatures than does thermal incineration.

When the low temperature tail gas catalysts are coupled with catalytic incineration, substantial savings may be realized in fuel costs.

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The Tail Gas Treating Process

Tail gas units on Claus plants increase the sulfur recovery from about 96–97 percent to about 99.8–99.9 percent. The Claus reaction,

$SO_2 + 2\ H_2S \rightleftarrows 3\ S + 2\ H_2O$,

is equilibrium limited, so the tail gas exiting the process contains levels of SO_2 and H_2S dictated by that equilibrium. The tail gas also contains uncondensed sulfur because the sulfur is in equilibrium with the gas phase at the temperature of the sulfur condenser. In addition, any hydrocarbon that enters the Claus process is converted to carbonyl sulfide (COS) and carbon disulfide (CS_2).

Claus Tail Gas Units (TGUs) that utilize catalytic reduction and hydrolysis over Criterion 534 or Criterion 234 catalysts to provide for the optimum overall recovery of sulfur in refineries and gas plants. These units are characterized as "Best Available Control Technology" (BACT) because they recover 99.8–99.9+ percent or more of the sulfur that enters the Claus plant as hydrogen sulfide feed.

These tail gas units, when equipped with the proper catalysts, will successfully convert all of the sulfur compounds in the Claus tail gas to hydrogen sulfide. H_2S is efficiently picked up by the downstream amine systems so the H_2S can be recycled to the Claus process. To achieve 99.8+ recovery of the sulfur, the catalyst must be effective in facilitating a number of reactions.

Sulfur Dioxide must be reduced:

$SO_2 + 3\ H_2 \rightarrow H_2S + 2\ H_2O$
BTU/lb-mol S = -91,600

Sulfur vapor must be reduced:

$S + H_2 \rightarrow H_2S$
BTU/lb-mol S = -14,400

Because of its relatively high concentration and high heat of reaction, the reduction of sulfur dioxide is the primary source of the heat release seen in the tail gas reduction reactor catalyst bed. In general, this reaction, and the reduction of sulfur vapor are easy to catalyze.

Carbonyl sulfide and carbon disulfide are formed in the Claus process from unavoidable hydrocarbon impurities. These two compounds are neutral, and are not captured in downstream amine systems. These compounds must be hydrolyzed to H_2S; otherwise, they are converted to SO_2 in the incinerator and escape to the atmosphere:

$COS + H_2O \rightleftarrows CO_2 + H_2S$
BTU/lb-mol S = -14,400

$CS_2 + 2\ H_2O \rightleftarrows CO_2 + 2\ H_2S$
BTU/lb-mol S = -28,800

These conversions must be accomplished without the formation of unwanted sulfur – containing compounds such as methyl mercaptan. Methyl mercaptan is also neutral and will pass through the amine system and would too be oxidized in the incinerator to SO_2.

Catalysts for Lower Temperature Operation – Criterion 234

Commercial Operation

It has been standard practice to run the tail gas unit hydrogenation reactor inlet temperature at about 540° F (280°C). However, it has been shown in the two tail gas units of Motiva's Port Arthur, Texas refinery that the inlet temperature for reactors loaded with Criterion 234 cobalt – molybdenum catalyst operate well at about 464° F (240° C). These two units have run at this temperature range for over four years, and the emissions from these units remained in the 10–20 percent range of the strict New Source Performance Standards (NSPS) sulfur emissions limit. This excellent performance is achieved without the use of expensive carbonyl sulfide conversion catalysts in the Claus reactors and without mercaptan formation.

The catalyst was originally sulfided at a maximum temperature of about 464° F (240° C). Therefore, no special sulfiding procedures are required.

Laboratory Testing

Pilot plant studies had demonstrated that the inlet temperature on such reactors could even be reduced further to the 430° F (220° C) range. With this evidence that inlet temperatures even lower than 465° F (240° C) could be utilized for satisfactory performance of the catalyst, the technical staff at Motiva were in agreement to further testing of one of their refinery tail gas units at reduced temperatures. It was specified that the testing would not allow the SO_2 level in the incinerator stack to approach the regulated limit of 250 ppm.

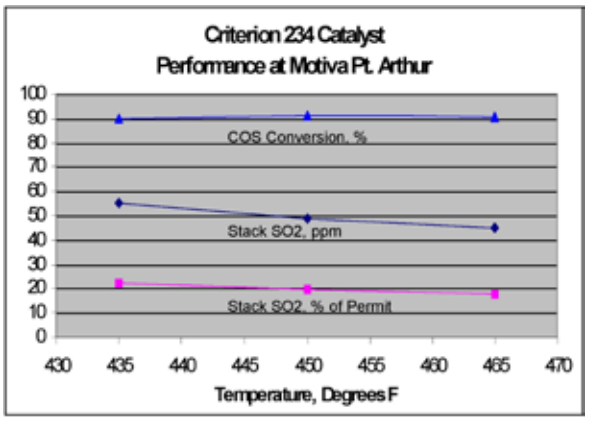
Testing on Refinery Unit

Testing was undertaken on the Motiva tail gas unit reactors when the catalyst's on-stream time was approaching five years. In the first series of tests, the inlet temperature to the tail gas reactor was systematically lowered from 465° F (240° C) to 450° F (232° C) and then to 435° F (224° C). During the entire test series, the stack SO_2 remained in the 22–28 ppm range, which is only about 10 percent of the permitted maximum.

In the second series of tests, greater detail was sought in the reactor inlet and outlet analyses. At that time the sour water stripper were upset with hydrocarbons, and the stack analyses was measuring at about 55 ppm of SO_2, approximately 20 percent of the allowable emissions. The reactor inlet temperature was 465° F (240° C) at the start of the testing. After samples for analysis were collected, the inlet temperature was decreased to 435° F (224° C) and then increased to 450° F (232° C). At no time did the stack SO_2 emissions increase to over 60 ppm, thereby demonstrating excellent COS hydrolysis and SO_2 conversion.

Catalysts for Lower Temperature Operation – The New Criterion 734

Recent investigations have led to the development of an entirely new tail gas catalyst, Criterion 734. This catalyst is so active that it has been shown to operate at reactor



inlet temperatures in the range of 390° F (200° C) or even lower. Again, COS hydrolysis activity is excellent, and no expensive COS hydrolysis catalyst is required in the Claus process reactors. No mercaptans are formed.

Opportunities for Improved Economics

Opportunities for Tail Gas Process Savings in Existing Fired Units

In existing tail gas units equipped with either in-line burners or indirect heaters, substantial fuel savings can be realized by merely operating at lower temperatures. The amount of savings is related directly to the cost of fuel. One European client with a reducing gas generator burner has calculated that he will save 3,500 Euro per year for each cubic meter of Criterion 234 that he has installed. This is accomplished by merely operating at 465° F, 240° C, instead of 536° F, 280° C reactor inlet temperature. For this customer, the entire cost of the catalyst is paid back in less than two years by merely operating at a lower temperature.

Of course, operating at even lower reactor inlet temperatures saves more fuel and cost.

Opportunities for Tail Gas Process Savings in New Units

The reductive tail gas processes usually include the following primary components:

- In-line Heater
- Catalytic Reactor
- Waste Heat Boiler/Product Cooler
- Quench Tower
- Amine System

In the TGU, the tail gas is typically heated in a gas-fired reducing gas generator (RGG) burner prior to entering the reactor.

With the success of this lower temperature catalyst, consideration could be given to the design of new units with less costly components. For example, a TGU could be designed with indirect heaters that use steam generated in the Claus reaction furnace boiler. In addition, reactor outlet temperatures are low enough to be handled easily by the quench tower. This, then, allows omission of the waste heat boiler.

In new designs and in existing units, the fuel savings must be balanced by the value of the steam that is generated by operating at higher temperatures with a waste heat boiler. If that steam has value, then it must be replaced. However, low temperature steam of this quality is usually in abundance in refineries and gas plants.

Opportunities for Tail Gas Process Savings in "Retrofit" Units

With the success that Criterion 234 catalyst has shown operating at lower reactor inlet temperatures, it is now possible to consider using existing heaters and reactors from other, less effective tail gas technologies as the basis of improved sulfur recovery. Consideration could also be given to converting the last stage Claus reactors and existing heaters to tail gas units. Adding an amine system to capture and recycle the hydrogen sulfide would be required.

Expectations of Sulfur Plant and Tail Gas Unit Operation

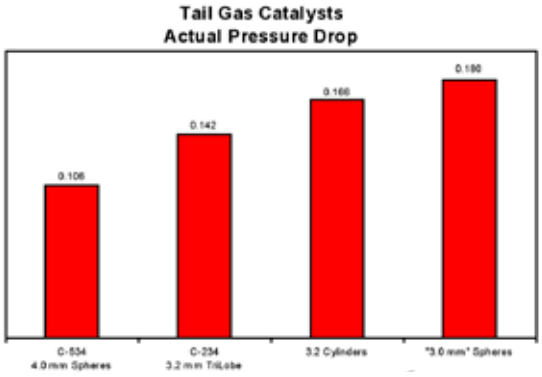
What are the attributes of a successful operation? Here are some:

1. Meets Environmental Permit!
2. Allows High Throughput
3. Trouble-free Operation
4. The Operation and Catalyst are Robust, not impacted by minor upsets.
5. The Process and Catalyst have a Long Cycle Length

Pressure Drop Considerations

Among tail gas unit catalysts in common use, Criterion 234 3.2 mm Trilobe™ tail gas catalyst is second only to Criterion 534 catalyst is giving the lowest pressure drop. Criterion 734 catalyst is a 4.0-millimeter sphere and enjoys the same low pressure drop as does Criterion 534. *(See Figure.)*

Catalyst pressure drop is extremely important in tail gas units. The sulfur plant and tail gas unit operate at atmospheric pressure, with only about five pounds of pressure drop across the entire system including three Claus catalyst beds, the tail gas catalyst bed, all piping, towers, and heat exchangers. Any increase in pressure drop across these processes carries severe penalties in lost capacity for sulfur handling. In the worse case, crude oil or natural gas must be backed out of the front of the refinery or gas plant, with substantial decrease in the amount of products available for sale.



Criterion 234 Catalyst Usage

Criterion 234 catalyst has found wide acceptance in the world. Over five million pounds of this catalyst have been installed throughout the world. It is in use in the largest tail gas unit in the United States, the largest SCOT unit in the United States, and in many refineries. It has been selected for use in the very large SCOT tail gas units to be built in a new refinery in the Middle East. It is also been delivered to a new large gas plant in the Caspian Sea area. This catalyst has also been operated in a large gas plant at reactor inlet temperatures as low as 470–475° F (243–246° C), and other refinery units in addition to the Motiva – Port Arthur work reported here.

Catalytic Incineration

Most refineries are equipped with incinerators as the final step to convert the traces of sulfur compounds that escape the tail gas treating process to sulfur dioxide prior to entering the atmosphere. Sulfur dioxide is less toxic and less odoriferous than hydrogen sulfide, carbonyl sulfide, and carbon disulfide. These incinerators are normally operated at about 1,300° F (700° C). Criterion 099 catalyst was developed to selectively oxidize hydrogen sulfide, carbonyl sulfide, and carbon disulfide to sulfur dioxide. It does not catalyze the formation of sulfur trioxide, so the incinerator stack does not fume. The catalyst is used for both Claus tail gas and the off-gas from the amine absorbers of tail gas units.

In a tail gas off-gas application where the off-gas contained 0.03 percent H_2S, 10 ppm COS and 1 ppm CS_2, the product gas contained less than 1 ppm SO_3 and less than 4 ppm H_2S.

Criterion 099 catalyst does not oxidize other tail gas components such as carbon monoxide, hydrocarbons, and hydrogen. This attribute keeps the catalyst from destroying itself from extremely high exotherms as other combustibles are carried into the reactor. This selectivity reduces the opportunity for thermal oxidation of sulfur compounds to sulfur trioxide that would occur if the catalyst bed did reach high temperatures.

In general, the use of Criterion 099 catalyst behind a tail gas unit allows the savings of 60 percent of the fuel that would be required for a similar installation of a thermal incinerator.

This incineration catalyst is quite robust – it has performed satisfactorily for over 10 years in a number of locations. The only caution that must be observed is to not operate the catalyst in a reductive environment. A minimum of five percent excess air, based on combustibles in the feed, is strongly recommended. Otherwise, the metal sulfates on the catalyst will reduce to the sulfide state, and then will re-oxidize when the air is reintroduced to the catalyst. This re-oxidation releases much heat that would promote and sustain the undesirable thermal reactions.

Conclusion

Energy costs money. If you must burn a fuel to increase the process temperature to where the reaction will proceed, then simply, it costs less money to heat to a lower temperature. Less fuel burned means less greenhouse gases generated. If it is possible to utilize energy for process heating that is recovered from elsewhere instead, then even greater savings are realized.

If Criterion tail gas catalysts are utilized, which require less heat, money is saved. It is also possible to make equipment changes in new tail gas plant installations so less capital is required. If a catalytic incinerator is added, then again, less fuel is required.

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